

CALIBRATING ARCHEAN AND MIOCENE  
LARGE IGNEOUS PROVINCE EMPLACEMENT  
AND GEOLOGIC TIMESCALES  
WITH HIGH-PRECISION U-Pb ZIRCON GEOCHRONOLOGY

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## Abstract

In the past decade, methodological advances in the precision and accuracy of geochronology have improved estimates of the timing and duration of large igneous province (LIP) emplacement, mass extinction events, and global climate perturbations, and in general have supported a temporal link between them. In this thesis, I use high-precision U-Pb ID-TIMS zircon geochronology to present new temporal constraints on Earth's oldest and youngest LIPs.

By integrating paleomagnetism and geochronology into a detailed stratigraphic study of two intervals of flood basalt volcanism in the Neoarchean Fortescue Group (Western Australia), I provide temporal constraints on rapid plate motion at 2.7 Ga, and the timing of Earth's oldest documented magnetic field reversal. I then apply U-Pb zircon geochronology to the Miocene Columbia River Basalt Group (Northwest USA), Earth's youngest LIP, and show that it erupted in  $\sim 750$  ka, 2.4 times faster than previously thought, with its largest formation emplaced in  $\sim 500$  ka. The new age model provides estimates for a constant eruptive flux through the main phase of volcanism, the timing of Miocene magnetic field reversals during a poorly calibrated interval of the Geomagnetic Polarity Timescale, and stronger temporal evidence for a correlation between the beginning of LIP volcanism and the onset of the Miocene Climate Optimum (MCO), an interval of global warming and elevated atmospheric carbon dioxide.

Age models for the MCO and other paleoclimate events in the sedimentary record are often calibrated by biostratigraphy and magnetostratigraphy rather than absolute geochronology, which may hinder their correlation to high-precision eruptive timelines for LIPs. I present a case study from the Early Miocene Bisciaro Formation (Italy) to

show the importance of radiometric calibration of sedimentary records where astronomical tuning is not possible, to address inadequacies in traditional methods of age calibration.

Finally, I review existing high-precision geochronology from 12 LIPs and their corresponding extinction or climate events, to begin to assess if advances in geochronology support a causal relationship between them. Despite much progress, higher precision geochronology of both LIPs and environmental records will be required to further understand how these catastrophic volcanic events have changed the course of our planet's surface evolution.

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## Conference Presentations

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*In memory of my grandfathers,  
Anthony P. Blose & Martin L. Kasbohm –  
I hope I make you proud*

## Table of Contents

Abstract.....	iii
Acknowledgments.....	iv
Conference Presentations.....	viii
Dedication.....	ix
<b>Chapter 1: Introduction and Methods.....</b>	<b>1</b>
<b>Chapter 2: Paleogeography and high-precision geochronology of the Fortescue Group, Pilbara, Western Australia.....</b>	<b>18</b>
<b>Chapter 3: Rapid eruption of the Columbia River flood basalt and correlation with the mid-Miocene climate optimum.....</b>	<b>65</b>
<b>Chapter 4: Eruption history of the Columbia River Basalt Group constrained by U-Pb geochronology.....</b>	<b>109</b>
<b>Chapter 5: High-precision U-Pb zircon geochronology of the Miocene Bisciaro Formation, Contessa Section, Italy: A case study for requisite radiometric calibration of bio- and magnetostratigraphy .....</b>	<b>151</b>
<b>Chapter 6: Radiometric constraints on the timing, tempo, and effects of large igneous province emplacement.....</b>	<b>180</b>

# Chapter 1

## Introduction and Methods

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*This chapter is taken from*

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The observation that Large Igneous Province (LIP) magmatism has in some cases occurred concurrently with mass extinctions (Courtilot & Renne, 2003; Ernst & Youbi, 2017) leads to the question of whether there is a cause-and-effect relationship between them. While various hypotheses exist as to how LIPs lead to catastrophic climate change that can lead to ecosystem collapse and mass extinctions, they generally focus on volatile release from either magma-derived gases or indirectly through heating of organic-, carbonate-, or evaporite-rich sediments (Self et al., 2006; Svensen et al., 2004; Thordarson & Self, 1996). Determining whether any of these mechanisms are important contributors to climate change requires understanding the relative rate of both extrusive and intrusive magmatism, and correlating these with paleoenvironmental records. The

only way to directly date the rates of LIP emplacement is through radioisotope geochronology. Furthermore, as LIP lava flows and biological evidence for mass extinctions rarely occur in the same stratigraphic sections, making direct stratigraphic temporal correlation impossible, geochronology is also essential to test the plausibility of causality.

Although a wide range of geochronologic techniques have been applied to dating LIPs, uranium-lead (U-Pb) and argon-argon ( $^{40}\text{Ar}/^{39}\text{Ar}$ ) geochronometers are the most widely used geochronometers for this application because their parent isotopes are characterized by long half-lives and relatively high concentrations in a variety of mineral phases (Reiners et al., 2017; Renne et al., 1998a). Temporal correlation between some LIPs and mass extinctions were suggested over 30 years ago (McLean, 1985), and this was rapidly tested using  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology on basalts (Courtilot et al., 1986; Duncan & Pyle, 1988). However, not until the 1990s were  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb geochronology used to demonstrate a temporal coincidence between the Siberian Traps LIP and the end-Permian mass extinction to within  $\sim 1$  Ma (Campbell et al., 1992; Dalrymple et al., 1995; Renne & Basu, 1991; Kamo et al., 2003; Reichow et al., 2002). Attempts to further correlate LIPs and mass extinctions have both capitalized on, and pushed the development of, higher precision geochronology. Because the duration of the hypothesized individual environmental effects of LIPs can vary in timescale from years (cooling associated with sulfate aerosols, acid rain, ozone depletion) to 100 ka (warming associated with  $\text{CO}_2$ ) (Black & Manga, 2017; Wignall, 2001), greater and greater precision is required to test hypotheses relating LIPs to paleoclimate and paleontological records. Geochronological

uncertainties > 1 Ma, which were commonplace in datasets from the early efforts to date these events, obscure the relative timing of LIP eruptions versus global change on relevant climatic timescales, and limit assessment of the plausibility of a causal connection. However, the last decade has seen dramatic improvement in the precision and accuracy of dates generated by radiogenic geochronology, such that recently published datasets can begin to compare and resolve relative timing differences between the onset and duration of LIP magmatism and potential downstream environmental effects, such as biotic decline, ecosystem deterioration, global warming and carbon cycling, and sea level change. With methodological advances in U-Pb geochronology, it is now possible to discern a coincidence of events with precision of 10-100 ka, allowing testing of a potential causal connections at the sub-100 kyr level. However, further increases in analytical precision of dates for LIPs and of age models for stratigraphic sections that contain paleoenvironmental records will be required in order to resolve the timing of environmental effects operating on shorter timescales, such as cooling due to SO<sub>2</sub>.

### ***Dating methods for Large Igneous Provinces***

Most dates for LIPs and their corresponding environmental perturbations are derived from the <sup>40</sup>Ar/<sup>39</sup>Ar or U-Pb techniques. Historically, <sup>40</sup>Ar/<sup>39</sup>Ar studies have yielded a temporal framework of LIP emplacement at ~1% resolution (e.g., Barry et al., 2013; Kerr et al., 2003; Marzoli et al., 2018; Renne et al., 1995), sufficient to establish a broad correlation, but in excess of that required to resolve the relative timing of LIP emplacement relative to environmental change. This relatively coarse resolution is due to small concentrations of the parent isotope, <sup>40</sup>K, found in whole-rock basalt samples or

plagioclase separates. U-Pb geochronology can yield higher-precision dates (to better than  $\pm 0.1\%$ ), but amenable minerals (e.g., zircon, baddeleyite) are not ubiquitous in LIPs. With their particular strengths and shortcomings, both techniques have been crucial to improving understanding of the connection between LIPs and environmental change, and working to better understand that connection has produced methodological breakthroughs in both geochronometers. In this section, we will briefly describe the methodological advances leading to improved accuracy and precision for both techniques, with a stronger focus on U-Pb methods as these have provided the majority of high-precision ages discussed in this review. We follow the definitions of accuracy and precision summarized in Schoene et al. (2013): an accurate date agrees with the actual age of an event within uncertainty, while precision is defined as the reported uncertainties, which may include both random and systematic uncertainties (Renne et al., 1998b; Schoene, 2014).

The accuracy of  $^{40}\text{Ar}/^{39}\text{Ar}$  dates has increased as methodology evolved from analyzing primarily LIP whole-rock/groundmass samples, to more recent efforts focused on analysis of aliquots of plagioclase or biotite separated from basalts, or sanidines separated from intercalated silicic ashes. These recent studies have also used more careful means to hand-pick plagioclase grains to avoid the effects of weathering, and choosing grains of sufficient size to mitigate effects from  $^{39}\text{Ar}$  recoil (Renne et al., 2015). New procedures also treat translucent, inclusion-free grains with an HF solution in an ultrasonic bath to lessen the effect of surface alteration (Sprain et al., 2019). While these efforts aid in improving the accuracy of  $^{40}\text{Ar}/^{39}\text{Ar}$  dates, increases in analytical precision have resulted from increasing the number of different aliquots from the same sample used to derive a

weighted mean plateau age, densely bracketing samples with standards during irradiation (Sprain et al., 2019), and advances in mass spectrometry, including the use of multi-collector mass spectrometers (Jicha et al., 2016). As will be discussed further below, the decades-long effort to reduce uncertainties resulting from neutron fluence monitors that act as age standards in  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology (Kuiper et al., 2008; Renne et al., 1998b, 2010, 2011), as well as efforts to better quantify decay constants (Min et al., 2000; Renne et al., 2010, 2011), have also helped to advance the accuracy and precision of dates.

U-Pb geochronology has been applied to three different U-bearing accessory minerals in pursuit of dating LIPs: baddeleyite, perovskite, and zircon. Baddeleyite has proven useful for dating diabase dikes and gabbros as well as hydrothermal contact aureoles (Fraser et al., 2004; Heaman & LeCheminant, 1993; Kamo et al., 1989; Söderland et al., 2103), but can be prone to Pb-loss (e.g., Rioux et al., 2010). Perovskite has also been utilized to date LIPs, but >50% of the Pb in the mineral can be “common” Pb, not derived from radioactive decay, making the accuracy of perovskite dates accordingly sensitive to the chosen isotopic composition of common Pb (Burgess & Bowring, 2015; Kamo et al., 2003). Zircon lacks common Pb, but is rarely saturated and crystallized in LIP basalts. However, it has been dated from coarse-grained intrusions (sills and/or dikes) and thick lava flows (Blackburn et al., 2013; Burgess & Bowring, 2015; Davies et al., 2017; Dunning & Hodych, 1990; Kamo et al., 1996; Krogh et al., 1987; Schoene et al., 2010; Svensen et al., 2009, 2010), and from silicic ashes intercalated with LIP lava stratigraphy (Kasbohm & Schoene, 2018; Schoene et al., 2015a, 2019). U-Pb dates are obtained through secondary ion mass spectrometry (SIMS), laser ablation inductively coupled

plasma mass spectrometry (LA-ICPMS), and isotope dilution – thermal ionization mass spectrometry (ID-TIMS). While SIMS and LA-ICPMS techniques are rapid and well-suited to studies requiring high spatial resolution, both of these techniques yield dates with analytical precision on the order of 2-3% (Schoene, 2014). Because LIP emplacement and potentially associated environmental effects occur on timescales between 10-100 ka, here we focus only on U-Pb datasets generated via ID-TIMS, which commonly yields precision on the order of 0.1%.

ID-TIMS has seen a number of methodological advancements that have improved the accuracy and precision of analyses while reducing sample size. Reduction of laboratory blank and improvements in mass spectrometry over decades has enabled routine dating of single zircon grains and even fractions of single grains (e.g., Davis et al., 2003; Krogh, 1973; Michard-Vitrac et al., 1977; Parrish, 1987; Schoene, 2014). A key development allowing for substantial improvement to the accuracy of zircon ages came with the introduction of the chemical abrasion (CA) protocol, which preferentially dissolves portions of zircon grains that have been affected by radiation damage, and thus are more prone to Pb-loss (Mattinson, 2005). The EARTHTIME initiative has pushed for enhanced interlaboratory calibration through the use of the  $(^{202}\text{Pb})^{205}\text{Pb}\text{-}^{233}\text{U}\text{-}^{235}\text{U}$  tracer solutions (Condon et al., 2015; McLean et al., 2015), as well as a detailed account of uncertainties that factor into each date generated, allowing for comparison with dates derived from other methods (Bowring et al., 2011; McLean et al., 2011; Schmitz & Schoene, 2007).

While improvements in accuracy and precision have allowed geochronologists to better assess the correlation between LIPs and environmental perturbations, these breakthroughs have illuminated further complications inherent in interpreting the accuracy of an unknown quantity: the age of the rock being dated. Once a *date* is obtained, by using mass spectrometry to solve radioactive decay equations for time, geological uncertainty must be addressed at every stage of data interpretation, ultimately yielding an *age*, an interpretation of that date in terms of geological processes (Schoene, 2014). Geological uncertainty may be reflected in macroscopic questions, such as how well the timing of an intrusive unit aligns with its corresponding extrusive unit, or in essential smaller-scale questions of how to deal with complex age populations, when high-precision techniques yield individual dates that do not overlap within analytical uncertainty (Davydov et al., 2010; Keller et al., 2018; Mundil et al., 2004; Ramezani et al., 2007; Schoene et al., 2010).

Interpreting pre-eruptive zircon growth in volcanic ashes provides an instructive example of addressing complex age populations and geological uncertainty in geochronological data. This interpretation is an important consideration, as zircon geochronology of volcanic ashes has yielded most of the age constraints for the environmental perturbations described in this paper, and for some of the constraints on the timing of LIP eruptions (e.g., Burgess et al., 2014; Clyde et al., 2016; Kasbohm & Schoene, 2018; MacLennan et al., 2018). Zircon dates obtained for dikes and sills are understandably more reproducible because zircon saturates very late during crystallization of mafic magmas. However, detecting age dispersion among single crystals is not unique to U-Pb zircon

geochronology; high-precision  $^{40}\text{Ar}/^{39}\text{Ar}$  studies utilizing multi-collector mass spectrometry are beginning to resolve complex age populations of single sanidine crystals (Andersen et al., 2017), and the ramifications of these new datasets have yet to be teased out. Below, we discuss how this geological uncertainty has been addressed in zircon geochronology in the past decade, as it has not yet been routinely dealt with in the  $^{40}\text{Ar}/^{39}\text{Ar}$  community.

Many of the studies presented here use weighted means of several individual zircon dates to provide an age for an ashbed, yielding lower uncertainty than that obtained for individual measurements. Calculating a mean square of weighted deviates (MSWD), with an expected value of 1, can assess how well analytical uncertainty explains the observed dispersion of dates about the mean (Wendt & Carl, 1991). However, a weighted mean should be used when the analytical uncertainty of the data corresponds to the actual error. Given evidence for protracted zircon crystallization and incorporation of xenocrysts and antecrysts in magma chambers, ~100 ka or even 1 Ma before an ash is deposited (Charlier & Zellmer, 2000; Ramezani et al., 2007; Schmitt, 2011; Schoene et al., 2010), a weighted mean age may under-represent the geologic uncertainty in the age of an ash. An alternative approach using the youngest zircon dated in a population as the age of the rock may be more tenable, as one may assume this youngest crystal most closely approximates the timing of eruption (Kasbohm & Schoene, 2018; Schoene et al., 2010). This approach minimizes age bias from pre-eruptive crystallization, though it assumes the youngest zircon in the rock was sampled, and yields a lower-precision age than a weighted mean approach. Its accuracy may be assessed by observing whether or not the

youngest zircon ages young upward in a comprehensively dated stratigraphic section. Some U-Pb studies utilize a combination of these approaches, by presenting the weighted mean age of the youngest few grains of the sample, which overlap within analytical uncertainty (Day et al., 2015; Kasbohm & Schoene, 2018; Meyers et al., 2012; Du Vivier et al., 2015). Importantly, unless high-precision single analyses are obtained by the method, either U-Pb or  $^{40}\text{Ar}/^{39}\text{Ar}$ , geologic scatter cannot be recognized and accuracy cannot be assessed to better than the approximate precision of a single analysis.

While geological uncertainty can complicate interpretation of geochronological data, geological or stratigraphic constraints have been used to improve the accuracy and precision of geochronology through statistical modeling. Bayesian statistical models have been used in combination with high-precision data to evaluate eruptive ages for samples based on the timing of crystallization of individual zircon grains leading up to eruption (Keller et al., 2018; Schoene et al., 2019). Additionally, several studies incorporate Markov Chain Monte Carlo sampling of numerous samples taken from a single stratigraphic sequence, inspired by the practices of the radiocarbon community (Buck et al., 1991; Haslett & Parnell, 2008). Stratigraphic position has been leveraged to refine the precision of groups of zircon ages using this technique (Guex et al., 2012; Keller et al., 2018; Meyers et al., 2012; Schoene et al., 2015, 2019; De Vleeschouwer & Parnell, 2014). The combination of using high-precision dates and robust statistical models can test for whether age interpretations of individual ashbeds themselves are permissible.

Although accuracy and precision have improved in recent decades for U-Pb and  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology, systematic uncertainties remain in radioactive decay constants, isotope tracer composition for U-Pb analysis, and ages of fluence monitors used in  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology. Indeed, an early observation that U-Pb and  $^{40}\text{Ar}/^{39}\text{Ar}$  ages for the Siberian Traps were offset at the  $\sim 1\%$  level considering analytical uncertainty alone led to greater efforts to report and propagate systematic uncertainties for both methods (Renne et al., 1998b; Schoene et al., 2006). This offset has largely been attributed to inaccuracy in the  $^{40}\text{K}$  decay constants (Renne et al., 2010). Although the  $^{238}\text{U}$  and  $^{235}\text{U}$  decay constants are among the best characterized in geochronology, with 0.11% and 0.14% uncertainty, respectively (Jaffey et al., 1971), these estimates derive from a single set of measurements, leaving open the possibility that inaccuracies in one or both U decay constants may exist (Parsons-Davis et al., 2018; Schoene et al., 2006).

Perhaps the most important remaining source of systematic uncertainty for Cenozoic samples is the adopted age of neutron fluence monitors used in  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology. These monitors, also known as reference materials or standards, are natural minerals whose prescribed ages directly influence the calculated ages of samples. A typical monitor used is the Fish Canyon Sanidine, for which most  $^{40}\text{Ar}/^{39}\text{Ar}$  labs have adopted the age of either 28.201 or 28.294 Ma (Kuiper et al., 2008; Renne et al., 2010, 2011). However, the U-Pb date for zircons from the Fish Canyon tuff from which the sanidine is derived is  $28.196 \pm 0.038$  Ma (youngest zircon from (Wotzlaw et al., 2013)), agreeing better with the younger Fish Canyon sanidine age estimate of Kuiper et al. (2008). Studies working to intercalibrate U-Pb, astrochronology, and  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology

have shown improved concordance of U-Pb with  $^{40}\text{Ar}/^{39}\text{Ar}$  ages when using the 28.201 Ma age for the Fish Canyon Sanidine (Kuiper et al., 2008; Meyers et al., 2012). This source of uncertainty affects the ability to compare U-Pb to  $^{40}\text{Ar}/^{39}\text{Ar}$  dates as well as discern the existence of pre-eruptive zircon crystallization, but is irrelevant for comparing dates within the  $^{40}\text{Ar}/^{39}\text{Ar}$  system, if the same age, standard, and decay constants are used.

The following studies were undertaken to better understand the timing and tempo of LIP emplacement in the Archean (Chapter 2) and Miocene (Chapters 3 & 4), and to recalibrate the timescales that provide age models for their corresponding climate events (Chapters 3-5). In Chapter 6, I provide a review of high-precision geochronology of 12 pairs of LIPs and environmental events, which reveals new insights into the temporal dynamics of LIP emplacement, while highlighting future challenges for the field that must be resolved to better understand the effects of LIPs on the Earth system.

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## Chapter 2

# Paleogeography and high-precision geochronology of the Fortescue Group, Pilbara, Western Australia

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*This chapter will be submitted to a journal with the following authors:*

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### ABSTRACT

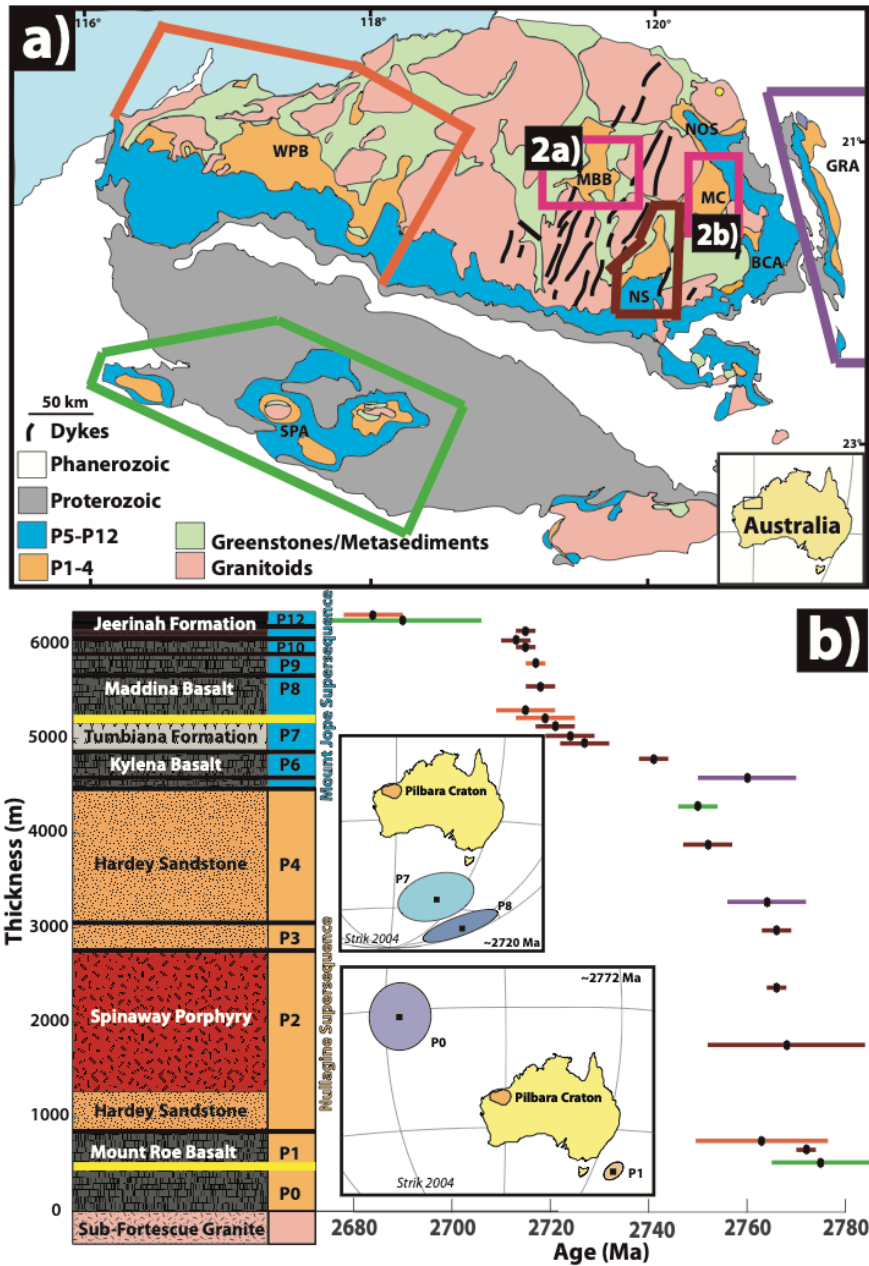
While rates of Phanerozoic plate movements and magnetic field reversals have been well studied, little is known about such phenomena on early Earth. The 2.7 Ga Fortescue Group on the Pilbara craton in Western Australia has been recognized as a well-preserved sequence of Archean rift volcanics thought to derive from a flood basalt, and may have been moving rapidly at two different intervals in its depositional history. We present the results of a magnetostratigraphic study integrated with high-precision U-Pb ID-TIMS geochronology to quantify rates of plate motion and provide a continuous time series for changes in Pilbara paleogeography during these two rapid intervals. We resolve a minimum continental drift rate of  $68 \pm 24$  cm/a during the craton's largest geographic displacement, which exceeds both background and modern rates of plate motion. We provide a new high-precision U-Pb zircon age of  $2721.23 \pm 0.88$  Ma for the Tumbiana

Formation stromatolite colony, which developed as the Pilbara craton drifted from  $48\pm 9.1^\circ$  to  $31\pm 9.5^\circ$  paleolatitude. Although the Fortescue Group has been considered an early prototype of large igneous provinces, it presents significant differences from its Phanerozoic counterparts and would not fit the definition of a large igneous province.

## **INTRODUCTION**

The acceptance of plate tectonics irreversibly changed the way geoscientists understand Earth's mantle dynamics and lithospheric movements. However, a point of contention in the study of Earth history is whether tectonic processes were operating during the Archean (Hamilton, 1998; De Wit, 1998), and if so, whether they were fundamentally different from those of the present. Did a hotter Earth allow for more vigorous convection and rapid plate motion (Davies, 1992), or were tectonics slowed by dehydration and thickening of the mantle lithosphere (Korenaga, 2003)?

A paleomagnetic study integrated with high-precision geochronological data has the potential to quantify rates of plate motion during the Archean. Collecting both paleomagnetic and geochronological samples within a detailed stratigraphic context may provide a continuous time series for changes in paleogeography, and removes the need for regional correlation. Continental flood basalts are ideal targets for this type of study because basalt is a faithful paleomagnetic recorder that retains a record of paleohorizontal, and is erupted in a layered stratigraphic manner. The 2.7 Ga Fortescue Group of the Pilbara craton in Western Australia (Figure 1a) has been recognized as one



**Figure 1. Geologic Context of the Fortescue Group.** The areal extent of the Fortescue Group is shown in part (a) (after Blake et al., 2004), with different abbreviations for different regions: WPB – West Pilbara Basin; MBB – Marble Bar Basin; NS – Nullagine Syncline; MC – Meentheena Centrocline; GRA – Gregory Range Area; SPA – Southwest Pilbara Area. Prior work on the stratigraphy (Thorne & Trendall, 2001), paleomagnetism (Strik, 2004), and geochronology (Blake et al., 2004, and references therein) is summarized in part (b). The colored error bars for geochronology data correspond to outcrop areas outlined in part (a). Yellow lines indicate the two intervals of Fortescue stratigraphy discussed in this paper, between Packages 0 and 1 and Packages 7 and 8.

of the oldest and best-preserved Archean flood basalt successions from a continental rift (Blake, 1993), with an estimated basaltic volume of 250,000 km<sup>3</sup> (Thorne & Trendall, 2001). The Fortescue has the potential to not only yield insights into the rate of continental drift occurring in the Archean, but also into how these processes may have affected evolving life on Earth on the eve of the Great Oxidation Event.

The Fortescue Group has been subject to prior lithological (Thorne & Trendall, 2001), geochronological, and paleomagnetic study that suggest its suitability for a detailed stratigraphic approach (Figure 1b). Blake (2001) divided the Fortescue into 12 unconformity-bounded packages, which were later dated with SHRIMP U-Pb zircon geochronology (Blake et al., 2004). Guided by Blake's stratigraphic framework, Strik et al. (2003) published the first paleomagnetic study of the Fortescue Group, which yielded an apparent polar wander path for the ca. 60 Myr depositional history of the group, and the earliest known reversal in Earth's geomagnetic field. There are two intervals in the Fortescue Group where the Pilbara craton appears to have been moving rapidly (Strik et al., 2003; Strik, 2004). Analytical errors on the order of millions of years for the current ages for the Fortescue inhibit the calculation of Pilbara drift rates in the short time span of these potentially rapid intervals. Additionally, the difficulty in correlating rocks from distant regions of the Fortescue (Figure 1a) precludes the possibility of integrating the current paleomagnetic and geochronological datasets.

Presented here are the results of an integrated stratigraphic, paleomagnetic, and geochronological study aiming to quantify the plate velocity of the Pilbara during these

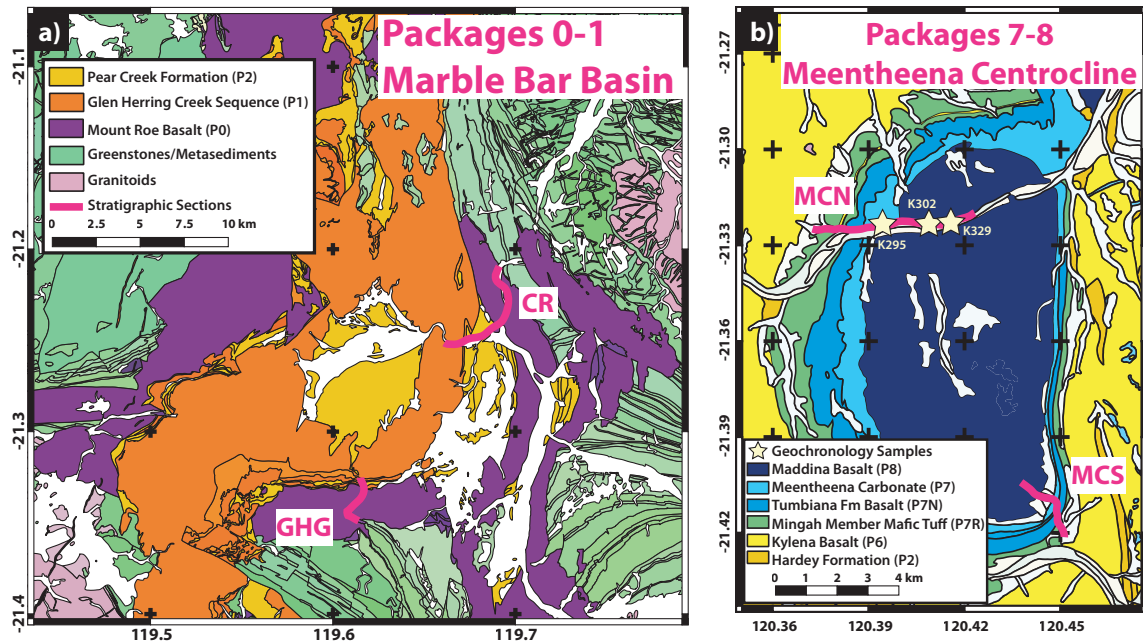
two intervals of potentially rapid motion. With four new high-precision U-Pb CA-ID-TIMS ages, we are able to provide improved velocity constraints that exceed both modern and Mesoarchean drift rates. We revisit the classification of the Fortescue Group as a large igneous province, and comment on its potential for calibrating the Precambrian Geologic Time Scale. Whether or not the Fortescue meets the criteria for classification as a large igneous province, it can provide numerous insights into tectonics, magmatism, and the geodynamo of the Archean Earth system.

## **GEOLOGIC CONTEXT**

The Fortescue Group is an ~6 km thick succession comprising flood basalts, mafic tuffs, felsic volcanics, and clastic sediments currently exposed over 40,000 km<sup>2</sup> of the Pilbara craton. It unconformably overlies the 3.5-2.9 Ga granite-greenstone terrane of northwestern Australia (Thorne & Trendall, 2001). The Fortescue Group is mostly undeformed, and at most was metamorphosed to the prehnite-pumpellyite-epidote phase (Blake et al., 2004). The Fortescue is divided into the lower Nullagine Supersequence, and the Upper Mount Jope Supersequence, each thought to represent a phase of continental rifting (Blake, 1993). Blake (2001) later divided these supersequences into 12 unconformity-bound packages. Even though unconformities are decreasingly obvious higher in the Fortescue stratigraphy (lacking obvious changes in bedding or lithology, or signs of erosion), significant time gaps are thought to have occurred between each package (Blake, 2001).

The onset of Fortescue Group deposition, beginning with the Nullagine Supersequence, occurred in geographically disconnected fault-bounded basins (Blake, 1993). The earliest Fortescue Group unit, the braided fluvial sedimentary succession of the Bellary Formation, is found only in the Marble Bar Basin. It is overlain by the subaerial Mount Roe Basalt (Packages 0–1, as classified by Blake (2001) and Strik (2004)), which marks the base of the Fortescue in the rest of the Pilbara. These basalts are followed by the mostly sedimentary Hardey Formation, which also consists of a felsic porphyry and minor mafic components (Packages 2–4; Blake, 2001). By the time the Mount Jope Supersequence began, the Fortescue Group had coalesced across the craton. The Mount Jope Supersequence begins with the subaerial Kylena Basalt (Packages 5–6), which gives way to the volcanoclastics and carbonates of the Tumbiana Formation (Package 7), followed by emplacement of the Maddina Basalt (Packages 8–10), and ultimately, marine sediments of the Jeerinah Formation (Packages 11–12). While the entire Fortescue Group underwent regional subsidence, increased normal faulting in the southern part of the craton led to coastal depositional environments and subaqueous volcanism, in contrast to continued subaerial conditions in the northern Pilbara (Thorne & Trendall, 2001). Four mafic dyke suites (Black Range, Mount Maggie, Five Mile Creek, and Castle Creek) have been geochemically and paleomagnetically correlated to the Fortescue Group (Strik et al., 2003). While the Fortescue Group is suggested to be one of Earth's oldest continental flood basalts, with an estimated volume of 250,000 km<sup>3</sup> (Thorne & Trendall, 2001) its long duration of emplacement and varied geologic record may complicate that assessment, despite the physical resemblance of its basaltic packages to other Phanerozoic large igneous provinces (Thorne & Trendall, 2001).

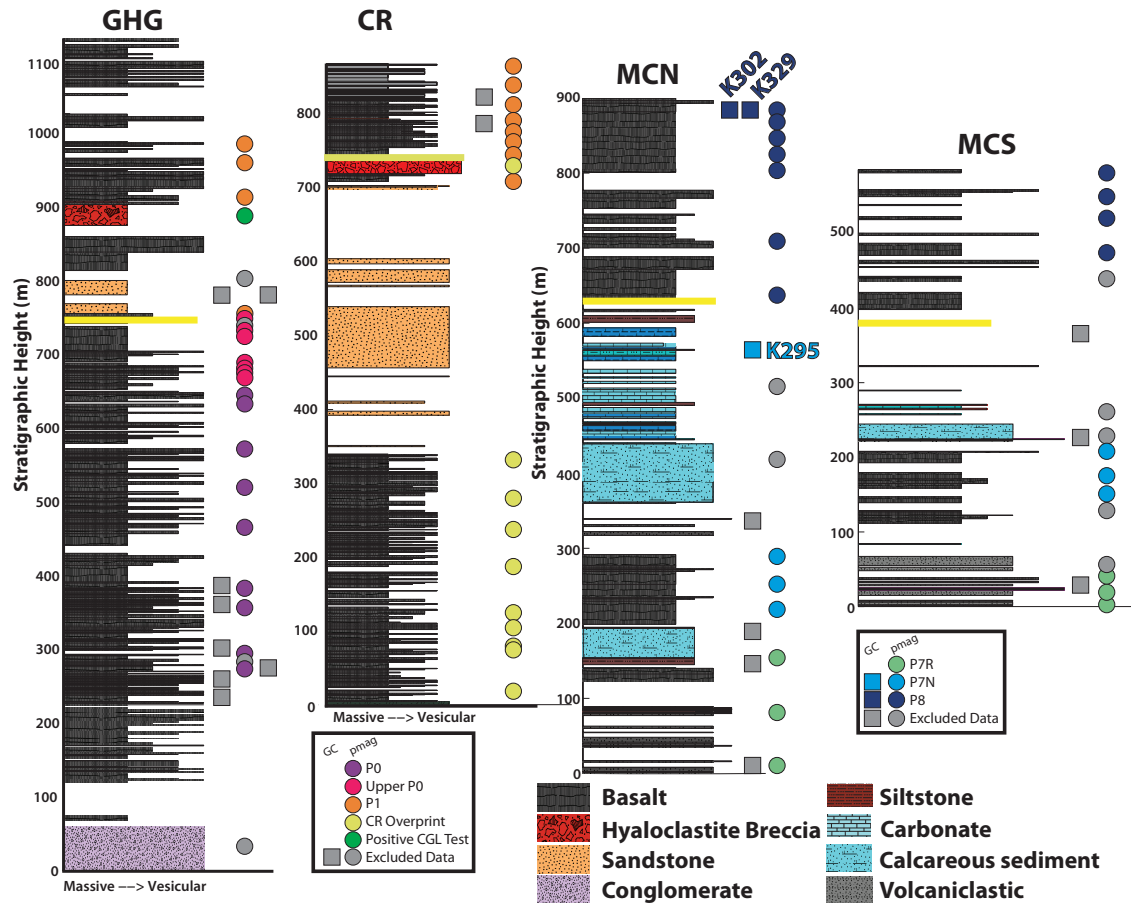
Determining a rate of plate motion for the Archean Pilbara craton has been dependent on findings from geochronology and paleomagnetism. When first described, the Fortescue Group was identified as Proterozoic, since it lacked the greenstones characteristic of Archean sequences (Blake, 2001). The first attempt to date the group with a Rb-Sr whole rock isochron yielded an age of  $2124 \pm 195$  Ma (Trendall, 1975). The first conventional zircon age for the Fortescue Group was  $2768 \pm 13$  Ma (upper intercept), for the Package 2 Spinaway Porphyry (Pidgeon, 1984), Arndt et al. (1991) produced the first suite of sensitive high-resolution ion microprobe (SHRIMP) zircon U-Pb ages for the Fortescue Group, which ranged from  $2775 \pm 10$  for a felsic volcanic rock from the base of the Mount Roe Basalt to  $2684 \pm 6$  for an ignimbrite member of the Jeerinah Formation. Blake et al. (2004) produced 11 high precision SHRIMP ages for the Fortescue, and ranging from  $2766 \pm 2$  for the Spinaway Porphyry, to  $2715 \pm 2$  for a reworked felsic tuff in Package 11, yet dates obtained for a number of packages overlapped within analytical uncertainty. There are no age constraints on Package 0 because it has been defined only on the basis of its paleomagnetic direction. Without precise age constraints, the observation of Strik (2004) that there was  $70^\circ$  of movement of the virtual geomagnetic pole (VGP) between Package 0 and 1, and  $14.4^\circ$  of movement across the Package 7–8 boundary could not allow for the calculation of the rate of motion for the Pilbara craton during these most notable changes in paleogeography.



**Figure 2. Regional maps with stratigraphic sections.** The Glen Herring Gorge (GHG) and Coongan River (CR) Package 0-1 stratigraphic sections were measured in the Marble Bar Basin, as seen on the geologic map in part (a). Sections of Packages 7-8 were measured in the Meentheena Centrocline, both North (MCN) and South (MCS) sections seen in part (b).

## METHODS

Two field seasons in summers 2013 and 2014 were undertaken in the Fortescue Group, in which stratigraphic sections were measured and sampled at four different localities. Two sections were measured at dm-scale across the Package 0–1 boundary at Glen Herring Gorge (GHG; 900 m) and Coongan River (CR; 900 m) (Figure 2a). For Packages 7–8, two sections were measured on opposite sides of the Meentheena Centrocline (Figure 2b); the Meentheena Centrocline North (MCN) section was 900 m thick, while the Meentheena Centrocline South (MCS) section had a thickness of 600 m. Unit thicknesses and lithologies, as well as the stratigraphic positions of paleomagnetism sample sites and geochronology samples, were recorded in each section (Figure 3).



**Figure 3. Measured stratigraphic sections.** The four sections measured for this study are shown here, with lithological legend and positions of paleomagnetic sample sites (circles) and geochronology samples (squares), color-coded by directional group. Grey circles indicate paleomagnetic sites not included in site means due to present day field overprints or scattered directions; grey squares indicate interbeds sampled that either didn't yield zircons or yielded inherited zircons. Yellow lines indicate proposed package boundaries.

### *Paleomagnetism*

Eight hundred forty-six paleomagnetic cores were drilled from 75 sites, and oriented by magnetic and solar compasses. Most sites were single stratigraphic horizons (lava flows) with 5–10 samples collected, but JK1319, JK1321, JK1328, and JK1417 consist of multiple stratigraphic heights with 1–2 samples per horizon. Three sites, JK1315 (GHG Package 1 hyaloclastite breccia), JK1407 (GHG Package 0 basal conglomerate), and

JK1435 (CR Package 1 hyaloclastite breccia), each consist of 20 clasts sampled for conglomerate tests on the age of paleomagnetic remanence (Watson, 1956). No significant deviation of magnetic declination from the regional average ( $1.7^\circ$ ) was observed in any of the sites sampled.

Samples were trimmed to  $\sim 10 \text{ cm}^3$  specimens and analyzed at the MIT Paleomagnetism Laboratory using a cryogenic DC-SQUID magnetometer (sensitivity with sample holder  $\sim 10^{-9} \text{ Am}^2$ ) with automated sample changer (Kirschvink et al., 2008). NRM measurements were followed by a liquid nitrogen, low-temperature demagnetization step, and underwent Alternating Field (AF) demagnetization at steps of 0, 2.5, 5, 7.5, and 10 mT. Samples then were subject to  $\sim 20$  successive high-temperature demagnetization steps of decreasing intervals up to  $600^\circ\text{C}$ , when measurements' intensity decreased by two orders of magnitude. Typical demagnetization steps were  $100^\circ\text{C}$ ,  $200^\circ\text{C}$ ,  $250^\circ\text{C}$ ,  $300^\circ\text{C}$ ,  $350^\circ\text{C}$ ,  $400^\circ\text{C}$ ,  $450^\circ\text{C}$ ,  $480^\circ\text{C}$ ,  $500^\circ\text{C}$ ,  $520^\circ\text{C}$ ,  $530^\circ\text{C}$ ,  $540^\circ\text{C}$ ,  $550^\circ\text{C}$ ,  $560^\circ\text{C}$ ,  $568^\circ\text{C}$ ,  $575^\circ\text{C}$ ,  $580^\circ\text{C}$ ,  $585^\circ\text{C}$ ,  $590^\circ\text{C}$ ,  $595^\circ\text{C}$ ,  $600^\circ\text{C}$ . Each sample's magnetic components were resolved with Principal Component Analysis (Kirschvink, 1980), using software created by Jones (2002) — least-squares fits were applied to successive demagnetization steps that represented the characteristic remanence magnetization (ChRM) of each sample. All samples with mean angular deviation (MAD) greater than  $10^\circ$  were omitted from locality means. Mean declination (D), inclination (I), precision parameters (k), and 95% confidence limits ( $\alpha_{95}$ ) were calculated to find the average ChRM of each sampling site using Fisher (1953) statistics.

Since almost all sandstone and all but ~20 basalt samples lost remanence at or below 580°C, the primary magnetic mineral is inferred to be magnetite. The remaining 20 basalt samples, which lost signal between 600 and 675°C, are interpreted to contain hematite, which likely formed during initial cooling, since the hematite component gives the same direction as the magnetite component for each sample. Carbonate samples lost remanence at or below 340°C, suggesting titanomagnetite or pyrrhotite as the primary magnetic mineral.

### ***Geochronology***

Twenty-one interflow units were logged and collected as potential geochronology samples in all Package 0-1 and 7-8 stratigraphic sections, and from the Package 2 Spinaway Porphyry. Four samples yielded zircons of Neoproterozoic age (~2.7 Ga). Sample photographs can be found in Supplemental Figure 1. Geochronology methods are as described in Kasbohm & Schoene (2018).

### ***Zircon separation and preparation***

Zircons were separated from their host rock through standard methods of crushing, gravimetric-, and magnetic-separation techniques using a Bico Braun “Chipmunk” Jawcrusher, disc mill, hand pan, hand magnet, Frantz isodynamic separator, and methylene iodide. Zircons from the least magnetic and most dense mineral separate were transferred in bulk to quartz crucibles and annealed in a muffle furnace at 900°C for 48 hours after Mattinson (2005). After annealing, 20-40 zircon grains from each sample were photographed and picked in reagent-grade ethanol for analysis. Euhedral grains with

a range of morphologies were selected, while those with visible cracks, inclusions, and cores were avoided. Individual grains were transferred using stainless steel picking tools to separate 3-mL Savillex Hex beakers containing distilled acetone and taken to the clean lab for analysis.

#### *U-Pb zircon ID-TIMS analysis*

Single zircon grains were loaded into 200  $\mu\text{L}$  Savillex “micro”-capsules with 100  $\mu\text{L}$  29 M HF + 15  $\mu\text{L}$  3N HNO<sub>3</sub> for a single leaching step in high-pressure Parr bombs at 185°C for 12 h to remove crystal domains affected by Pb-loss (Mattinson, 2005). Grains were rinsed post-leaching in 6 N HCl, MQ H<sub>2</sub>O, 3N HNO<sub>3</sub>, and 29 M HF prior to spiking with EARTHTIME <sup>205</sup>Pb-<sup>233</sup>U-<sup>235</sup>U tracer and addition of 100 $\mu\text{L}$  29 M HF + 15  $\mu\text{L}$  3N HNO<sub>3</sub> (Condon et al., 2015; McLean et al., 2015). Zircons were then dissolved to completion in Parr bombs at 210°C for 48 h. Dissolved zircon solutions were subsequently dried down, dissolved in 100  $\mu\text{L}$  6N HCl, and converted to chlorides in Parr bombs at 185°C for 12 h, after which solutions were dried again and brought up in 50  $\mu\text{L}$  3N HCl. The U-Pb and trace element aliquots were then separated by anion exchange chromatography using 50  $\mu\text{L}$  columns and AG-1 X8 resin (200-400 mesh, chloride from Eichrom) (Krogh, 1973), and dried down with a microdrop of 0.015 M H<sub>3</sub>PO<sub>4</sub>. The dried U and Pb aliquot was loaded in a silica gel emitter (Gerstenberger & Haase, 1997) to an outgassed zone-refined Re filament.

Isotopic determinations were performed using an Isotopx Phoenix62 thermal ionization mass spectrometer (TIMS) at Princeton University, with Pb analysis performed in peak-

hopping mode on a Daly-photomultiplier ion-counting detector. A correction for mass-dependent Pb fractionation was applied using a Pb fractionation of  $0.182 \pm 0.041\%$ /amu, as determined by repeat measurements of NBS982 at Princeton. Daly-photomultiplier deadtime was monitored, as determined by repeat measurements of the NBS 982 standard. Corrections for interfering isotopes under masses 202, 204, and 205 were made cycle-by-cycle by measuring masses 201 and 203 and assuming they represent  $^{201}\text{BaPO}_4$  and  $^{203}\text{Tl}$  and using natural isotopic abundances to correct for  $^{202}\text{BaPO}_4$ ,  $^{204}\text{BaPO}_4$ ,  $^{205}\text{BaPO}_4$ , and  $^{205}\text{Tl}$ .

$\text{UO}_2$  measurements were performed in static mode on Faraday cups with a bulk U fractionation correction calculated from the deviation of measured  $^{233}\text{U}/^{235}\text{U}$  from the known tracer  $^{233}\text{U}/^{235}\text{U}$  ( $0.995062 \pm 0.000054$  ( $1\sigma$ )), and an oxide composition of  $^{18}\text{O}/^{16}\text{O}$  of 0.00205 was used (Nier, 1950). Data reduction was performed using the programs Tripoli and U-Pb Redux (Bowring et al., 2011; McLean et al., 2011) and the decay constants of Jaffey et al. (1971). All Pb was attributed to laboratory blank with a mean isotopic composition determined by total procedural blank measurements (see Supplemental Table 1 for values). Two different blank corrections are applied; Pre-Side Filaments (PSF) was used for measurements made prior to January 2018, when the lab began routinely heating side filaments prior to analyses, and Side Filaments (SF) for measurements made after. Uncertainties in reported U-Pb zircon dates are at the 95% confidence level and exclude tracer calibration and decay constant uncertainties. Correction for initial  $^{230}\text{Th}$  disequilibrium in the  $^{206}\text{Pb}/^{238}\text{U}$  system was made on a fraction-by-fraction basis by estimating  $(\text{Th}/\text{U})_{\text{magma}}$  using  $(\text{Th}/\text{U})_{\text{zircon}}$  determined by

TIMS and a mean  $(\text{Th}/\text{U})_{\text{zircon-magma}}$  partition coefficient ratio of  $0.19 \pm 0.11$ , which encompasses the range of values for  $(\text{Th}/\text{U})_{\text{zircon-magma}}$  partition coefficients obtained from glasses from a variety of volcanic settings (Claiborne et al., 2018). Uncertainties for the resulting  $(\text{Th}/\text{U})_{\text{magma}}$  were also calculated on a fraction-by-fraction basis, propagating the uncertainty in the  $(\text{Th}/\text{U})_{\text{zircon-magma}}$  partition coefficient.

## RESULTS

### *Volcanostratigraphy*

#### *1. Packages 0-1: Mount Roe Basalt*

The lowermost part of the Fortescue stratigraphy has an unconformable boundary with the underlying granite-greenstone terrain. At GHG, the Fortescue overlies the Duffer Formation, and at CR, it overlies the Apex Basalt; these are members of the greenstone Warrawoona Group, with ages ranging from 3525–3426 Ma (Van Kranendonk et al., 2007). The earliest unit in the Fortescue stratigraphy was recognized by Blake (1984) as the clastic sedimentary Bellary Formation, which outcrops discontinuously only in the Marble Bar Basin; it is the base of the section at GHG (Figure 3). Regionally, the Bellary Formation consists of up to 700 m of silicified, coarse-grained quartzofeldspathic sandstone and conglomerate, with cm–dm scale clasts of banded iron formation and sediments. The mode of deposition for the formation is interpreted as a braided fluvial environment (Blake, 1993). The next stratigraphic unit at GHG, and the base of the section at CR, is comprised of hundreds of meters of subaerial lavas of the Mount Roe Basalt. The 76 lava flows measured at GHG and the 51 lava flows measured at CR displayed similar internal textures. Most lava flows began with pipe vesicles at the base

of the flow. This is followed by a massive interval, which typically constitutes the majority of flow thickness, and frequently contains isolated bands of vesicles or pods of vesicles, interpreted as representing paths of volatile escape from a cooling flow (Thorne & Trendall, 2001). Above the massive interior of the flow, the lava flow becomes increasingly vesicular until the most vesicular flow top, in which vesicles are either scattered randomly or aligned in bedding-parallel sheets. In each measured section, three categories of vesicularity were identified ( $1V \leq 25\%$ ,  $2V = 25\text{--}50\%$ ,  $3V \geq 50\%$ ), corresponding to the width of stratigraphic intervals in Figure 3. Some lava flows were overlain by thin glassy interbeds, sampled as potential ash beds. Near the boundary between Packages 0 and 1, aphyric lavas were replaced with those containing mm-cm scale plagioclase phenocrysts seen singularly or in a glomeroporphyritic array. In the Marble Bar Basin, Package 1 of Strik (2004) corresponds to the Glen Herring Creek Sequence of Blake (1984). The basal unit of the sequence is ~100 m of coarse-grained sand to gritstone, with cross beds occasionally present and showing north-to-south flow directions. Above the sandstone, a 10 m flow of a distinctive basalt with much larger plagioclase phenocrysts (few cm-scale) was observed at GHG and CR, followed by 30 m of a hyaloclastite breccia and a few meters of pillow basalts, indicating a brief interval of subaqueous eruption. Subaerial basaltic lava flows return after these basal units; 18 lava flows were measured at GHG, through the end of available basalt outcrop, and 17 lava flows were measured at CR, though basalt flows continued above the end of the measured section.

## *2. Packages 7-8: Tumbiana Formation & Maddina Basalt*

Stratigraphic sections were measured across the Package 7–8 transition at MCN and MCS (Figure 3). Package 7 lithostratigraphically corresponds to the Tumbiana Formation, comprised of the basal Mingah Member volcanoclastic sequence overlain by the Meentheena Member carbonates and stromatolites. MCN is the Pelican Pool type section where Lipple (1975) first described the members of the Tumbiana. The first unit observed in the field was 150 m of a fine- to medium-grained basaltic sandstone, recognized as a mafic tuff (Blake, 2001). Weathered units of this sediment were marked by mm-scale vugs, while more coherent beds exhibited cross beds, teepee structures, and desiccation cracks. Accretionary lapilli of 2–10 mm diameter were prominently interbedded in the mafic tuff, either in layers of cm–dm scale thickness or filling hollows such as desiccation cracks. Lapilli showed an internally concentric structure, and are interpreted as primary pyroclastic fall deposits from subaerial hydroclastic eruptions (Thorne & Trendall, 2001). Grain size sorting of the lapilli varied from well- to poorly-sorted, and lapilli layers were sometimes observed to be reverse-graded.

Above the mafic tuff, at MCN, minor microbialite layers were observed (possibly under cover at MCS), followed by three coherent subaerial basalt flows observed at both sections. As in Package 0, the flows exhibited a massive base and vesicular top, but were substantially thicker than the Mount Roe Basalt flows (~30 m each in Package 7, rather than <10 m). The flows were aphryic and sometimes had pipe vesicles at the base of the flow. The basalts were followed by cover (with a coherent bed of lapilli observed in both sections), and then by the Meentheena Member calcareous sediments (mostly under cover

at MCS). This unit began with spheroidally-weathering calcareous sandstone, which became cross-bedded with a north-to-south flow direction at the meter scale up-section. The sandstone was overlain by carbonate with laminated or ripple bedding. Climbing ripples and minor interbedded silt layers were observed in the carbonate. Stromatolites ranged from cm–m scale and were observed with both columnar and domal morphologies. A layer of well-sorted mm-scale lapilli was found near the top of the carbonate succession in both sections, and may serve as a stratigraphic tie-point; it was sampled for geochronology at MCN (K295). After a small amount of cover, the Package 8 Maddina Basalt began to outcrop.

The 200–300 m of Maddina Basalt outcropping at MCN and MCS consists of subaerial flows ranging from massive to vesicular textures, as with the other basalts described above. The massive portion of the flows commonly contain vesicle cylinders. At both MCN and MCS, the first Maddina Basalt flows are coarse-grained with visible sub-mm pyroxene phenocrysts (identified as augite in petrographic studies (Thorne & Trendall, 2001)). An interbedded accretionary lapilli unit overlies the uppermost measured flow at MCN and was sampled for geochronology (K302 and K329, described below); no lapilli tuffs were found interbedded with Package 8 lava flows at MCS.

### ***Paleomagnetism***

The stratigraphic positions of each sample site are shown with circles on Figure 3. Colored circles indicate sample sites that are included in mean directions and discussed below; greyed-out circles represent sites not discussed due to scattered ChRM directions

or present local field overprints. All Site mean directions and directional groups are provided in Supplemental Table 2, with equal area plots of paleomagnetic data for each

Paleomagnetic Pole	Code	Age	Method	Pole lat	Pole long	A95	1	2	3	4	5	6	7	Total	Test
Package 0	P0	>2772±2		4.7	92.2	9.4	0	1	1	1	1	0	1	5	cgl
Upper Package 0	Upper P0	2772±2 Ma	SHRIMP-b	-8.3	115.6	13.7	1	1	1	1	1	0	1	6	cgl
Package 1	P1	>2762.111±0.68 Ma	ID-TIMS-z	-44.4	169	8.3	1	1	1	1	1	0	0	5	cgl
CR Overprint	CR Overprint			-54.7	142.6	7.7	0	1	1	0	1	0	0	3	
Package 7 Reversed	P7R			-34.1	175	10.7	0	1	1	1	1	1	0	5	fold
Package 7 Normal	P7N	>2718.69±0.99 Ma	ID-TIMS-z	-61.4	135.6	9.1	0	1	1	1	1	1	0	5	fold
Package 8	P8	2718.06±0.90 Ma	ID-TIMS-z	-68.4	175.3	9.5	1	1	1	1	1	0	0	5	fold

**Table 1. Summary data for virtual geomagnetic poles.** This table summarizes the paleomagnetic poles calculated for this study, compared with data from existing poles, along with ages and quality criteria of Van der Voo (1990).

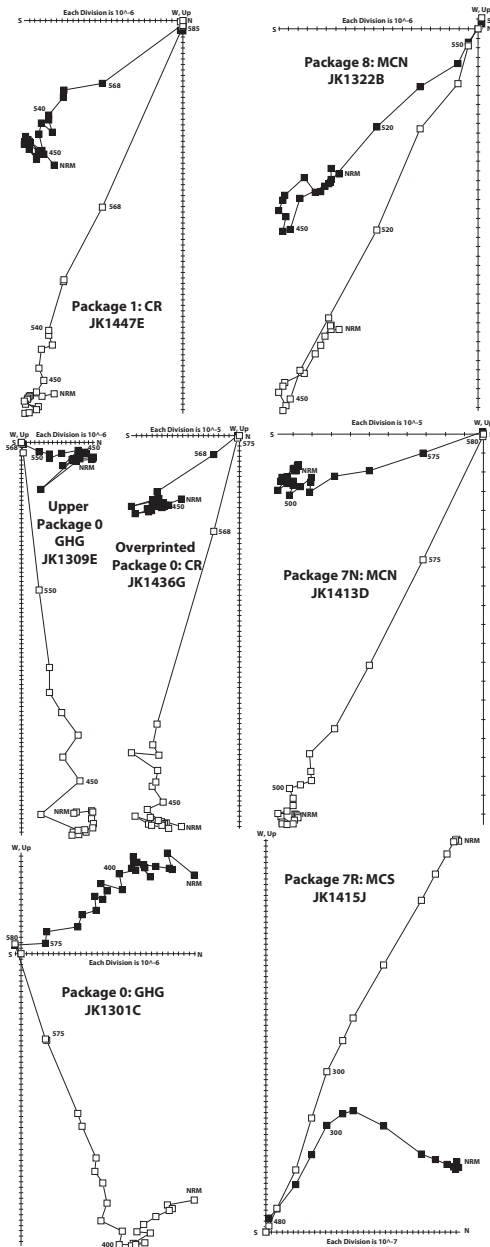
directional group in Supplemental Figure 2. Table 1 summarizes VGPs calculated for this study, evaluating them against the quality criteria of Van der Voo (1990).

### *1. Packages 0-1: Mount Roe Basalt*

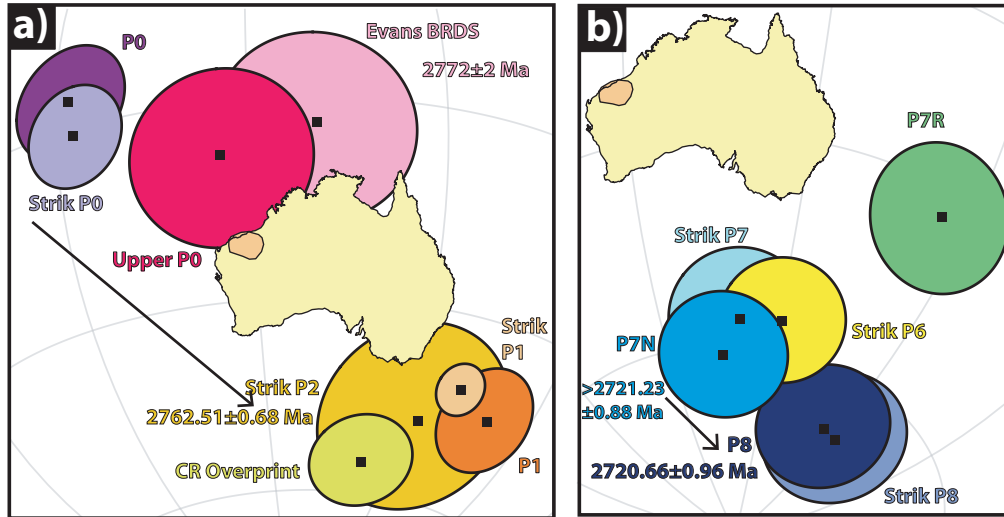
For the most part, samples from Packages 0 and 1 exhibited excellent stability to thermal demagnetization, with single component behavior (Figure 4). Unblocking temperatures were most consistently high, mostly between 550 and 580°C. Samples were generally well-clustered within each locality, and four different directional groups emerged from the two sections sampled.

The lowermost basalts at GHG (0-650 m in stratigraphic height) yielded a mean ChRM direction (northwest and moderately down) that broadly agreed with the Package 0 of Strik (2004). A pole is calculated at 4.7°N, 092.2°E, A95 = 9.4° (9 sites, 57 samples). Samples collected between 650 and 752 m were found to exhibit a different direction,

with declination now north and east, and steep downward inclination. These are clustered into an “Upper Package 0” direction, with a pole calculated at 8.3°S, 115.6°E,  $A_{95} = 13.7^\circ$  (7 sites, 65 samples; Figure 5a). Package 1 directions are obtained at GHG



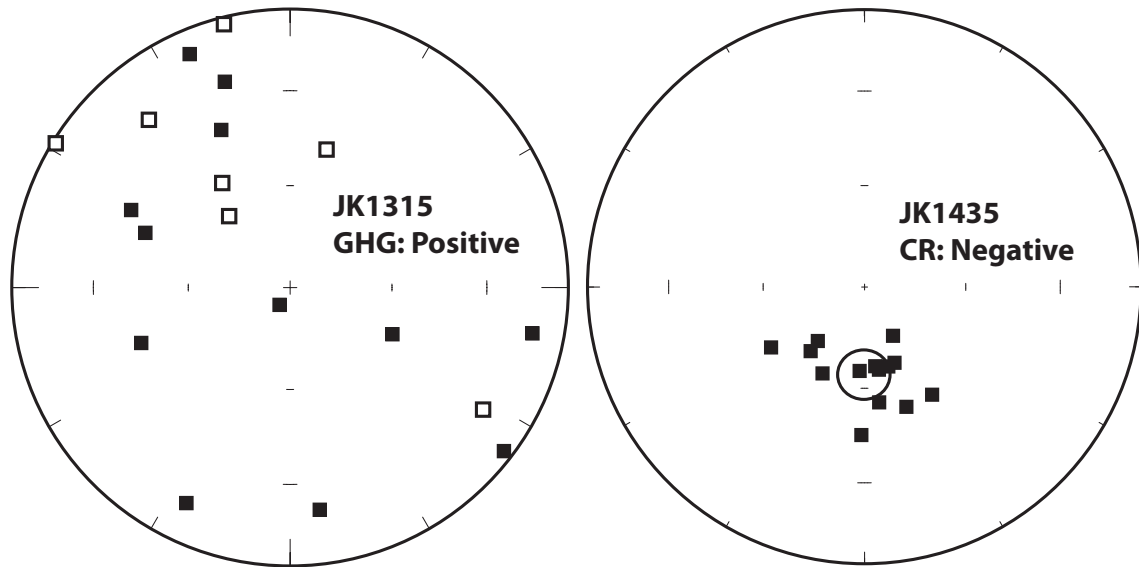
**Figure 4. Orthogonal projection diagrams of paleomagnetic samples.** These plots show the demagnetization behavior of representative samples from each of the directional groups in this study; numbers indicate temperature steps.



**Figure 5. Virtual geomagnetic poles.** The virtual geomagnetic poles calculated in this study for the Pilbara craton (highlighted in orange, in its current position) are shown in part (a) for Packages 0-1, and part (b) for Packages 7-8, compared to prior directions obtained by Strik (2004) and Evans et al. (2017). VGP ages are from this study except for that of the BRDS, which is from Wingate (1999).

beginning at 756 m, prior to the outcrop of sandstone, and continued through the top of the section. A conglomerate test on clasts of a hyaloclastite breccia at 904 m was found to be positive, following Watson (1956), with an R value of 4.8 less than the accepted cutoff of 6.98 for the 19 samples included (Figure 6), indicating that the magnetization at GHG is primary. This test also meets the criteria for positive support of uniformly random directions in the Bayesian conglomerate test of Heslop & Roberts (2018).

While only ~15 km away from GHG, CR yielded a markedly different set of paleomagnetic results in the lower half of the section. Basalt flows that were thought to represent Package 0 yielded a south and moderately dipping down ChRM direction, distinct from Package 0 at GHG; a VGP is calculated at 54.7°S, 142.6°E, A95=7.7° (9 sites, 71 samples). Strik (2004) also found that the lower basaltic unit on the east side of the Marble Bar Basin gave directions more similar to Package 1 than the expected



**Figure 6. Conglomerate test results.** These plots show the result of conglomerate tests performed on the Package 1 hyaloclastite breccia at GHG and CR. Scattered ChRM directions at GHG indicate a positive conglomerate test, and clustered directions at CR indicate a failed test.

Package 0, and grouped these eastern sites with Package 1. However, the lower CR basalts exhibited a different direction from the southeast and steeply down direction of Package 1 lava flows at both GHG and CR, which when combined yield a VGP of  $44.4^{\circ}\text{S}$ ,  $169^{\circ}\text{E}$ ,  $A05 = 8.3$  (12 sites, 87 samples).

One complicating factor in interpreting the results from CR is that the hyaloclastite breccia in this section, occurring just above the base of Package 1, yielded a negative conglomerate test (Figure 6). It failed the Watson (1956) conglomerate test, with an R value of 13.6 exceeding the allowed 5% significance level of 5.98, and exhibits very strong support for unimodal directions, failing the Bayesian conglomerate test of Heslop & Roberts. In fact, these clasts broadly show the same ChRM direction as the lower CR basalt flows. For this reason, we interpret the lower CR flow direction to represent an

overprint of Package 0, which was perhaps imparted during subsequent deposition of Package 2 of the Fortescue Group (Figure 5a). Because the directions obtained for Package 1 at CR cluster well with those obtained from GHG, as well as directions obtained by Strik (2004), we interpret these directions as primary, despite the failed test on the breccia in this section. The paleolatitudes obtained for the Package 0, Upper Package 0, and Package 1 poles are  $51.9 \pm 9.4^\circ$ ,  $76.3 \pm 7.7^\circ$ , and  $43 \pm 8.3^\circ$ , respectively.

## *2. Packages 7-8: Tumbiana Formation & Maddina Basalt*

Samples from almost all of the volcanoclastic and basalt paleomagnetic sites at the Package 7–8 transition showed excellent stability to thermal demagnetization, primarily with single-component behavior and unblocking temperatures of 480°C for the volcanoclastics in the lower part of the sections and 568-580°C for the basalts in the upper part of the sections (Figure 4). There was mostly good clustering of characteristic remanent magnetization (ChRM) directions from each locality. Sites with samples exhibiting inconsistent ChRM directions are excluded from the calculated mean directions presented here (JK1320, JK1423, with unblocking temperatures  $<300^\circ$ ), as are the calcareous sandstones and carbonates of JK1321, JK1328, and JK1424. These sedimentary units have unblocking temperatures of  $<340^\circ$  and show a wide scatter of ChRM directions around the present local field. A low temperature overprinting event is inferred.

The Package 7 volcanoclastic sediments at the base of the MCN and MCS sections yield northwest directions dipping moderately upward, in contrast to the overlying Package 7

basalt flows, which dip steeply south and down. This directional change either results from some overprint of the volcanoclastic units, given their relatively lower unblocking temperatures, or from a magnetic field reversal. If a reversal occurred, its stratigraphic height would be 140 m at MCN, or ~30 m at MCS, as samples collected from sites at these positions yielded dual polarity. The Package 8 basalts sampled yielded a moderate south to southeast, moderately downward dipping direction of ChRM. Mean directional groups and calculated VGPs are provided in Supplemental Table 2.

In light of our field stability tests, and directional agreements from normally magnetized Package 7 and 8 with results from Strik (2004), we suggest that our sampling at MCS and MCN reflects primary magnetization from Packages 7 and 8. Some uncertainty remains regarding the reversely magnetized Package 7 volcanoclastics. Strik (2004) observed sites with reversed polarity in Package 7 (from one basalt flow in the Boodalyeri Creek Area and a correlated sill in the West Pilbara Basin), suggesting that the reversed polarity described here is a reliable result. However, there is a 20-40° offset in declination between these units and our 7R sediments. An alternative interpretation, possibly bolstered by the lower unblocking temperatures of the 7R units, is that these represent and overprinted direction. Strik (2004) described a “Medium Temperature” direction that is northwest and moderately inclined upward, but our results show a steeper inclination. The VGP we calculate for Package 7R is distant from Package 7N, as well as the results of Strik (2004) for Package 6-8 and “Medium Temperature” components (Figure 5b). If this result is trustworthy, it could be interpreted as actual plate motion occurring as Pilbara oscillated between latitudes of  $48 \pm 8.9^\circ$  during Package 6 (Strik 2004),  $39 \pm 10.7^\circ$

during Package 7R,  $48 \pm 9.1^\circ$  during Package 7N and then  $31 \pm 9.5^\circ$  during Package 8 emplacement.

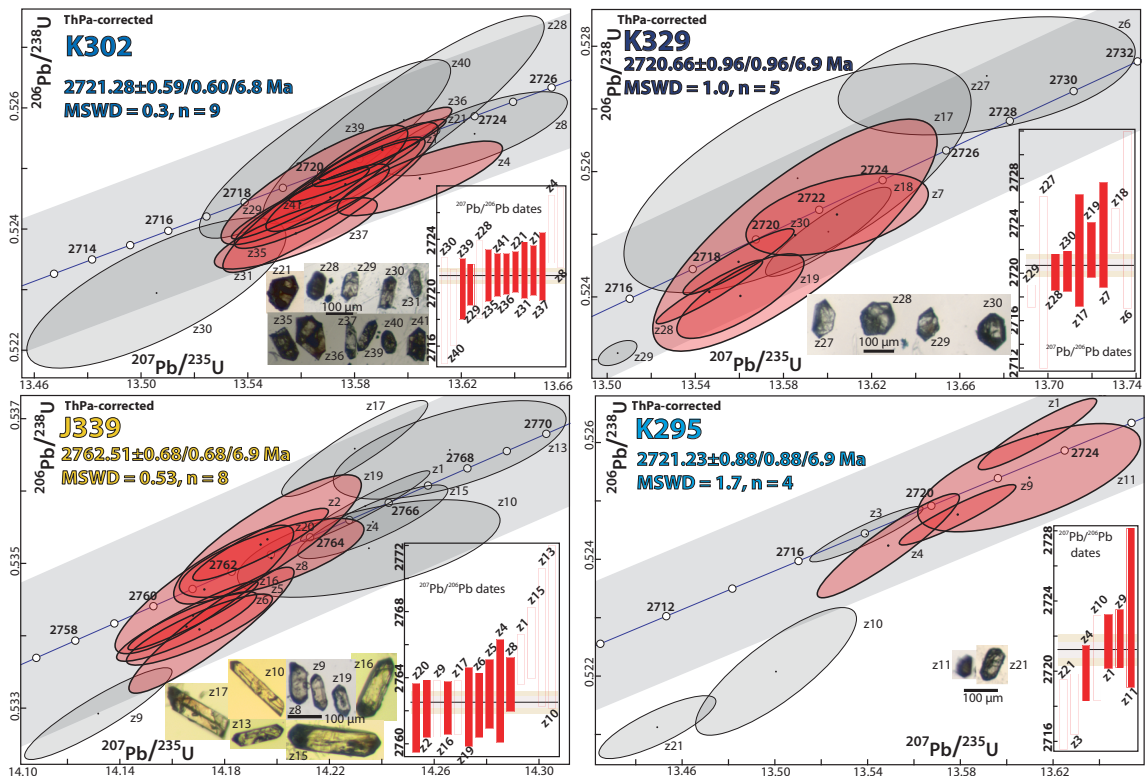
### ***Geochronology***

The stratigraphic positions of each sample are shown with squares on Figure 3. Colored squares represent samples that yielded zircon ages and are discussed below; greyed-out squares represent samples that either did not yield zircon or yielded only detrital or inherited grains. All geochronology samples collected in the Package 0-1 sections suffered from inheritance, yielding ages  $\sim 3.3$  Ga; the distribution of zircon dates from GHG are shown in Supplemental Figure 3. Concordia plots with some zircon images from each sample are given in Figure 7. Weighted mean ages were calculated from a number of overlapping individual zircon dates that overlapped with the Concordia line. A small number of grains with younger ages were excluded from weighted means because they may have been affected by Pb-loss; some older grains were excluded from weighted means when they were resolvably offset in age from the weighted mean population.

#### *1. Package 2: Spinaway Porphyry*

Sample J339 (21.76549°S, 129.091807°E) of massive quartz-feldspar porphyry was collected on Route 138 (Marble Bar Road) in the Nullagine Syncline, to serve as a minimum age for Package 0-1. Thousands of zircons were separated from this sample, and they are semi-translucent, with some colorless and others orange. Zircons range in morphology from equant and small ( $< 100 \mu\text{m}$ ) to long ( $> 200 \mu\text{m}$ ) with pronounced termination points. Twenty-one were selected for analysis, and 14 were successfully

dated. For this sample and others, a number of zircons were lost due to dissolution during chemical abrasion or zircon loss during chemistry; other analyses were unsuccessful due to discordance, high Pb blank relative to radiogenic Pb, or inheritance. Zircons range in age from  $2767.1 \pm 4.9$  Ma to  $2761.5 \pm 2.1$  Ma; all dates and ages reported in this paper are  $^{207}\text{Pb}/^{206}\text{Pb}$  ages. The weighted mean age of the sample is  $2762.51 \pm 0.68/0.68/6.9$  Ma (MSWD = 0.53, n = 8). This age is somewhat offset and more precise than the prior radiometric age of  $2766 \pm 2$  Ma obtained for the Spinaway Porphyry (Blake et al., 2004).



**Figure 7. Geochronology data.** These Concordia plots show new geochronology results from the Fortescue Group, with weighted mean ages and zircon images. Interception with the Concordia line indicates closed-system behavior.

## *2. Packages 7-8: Tumbiana Formation & Maddina Basalt*

Sample K295 (21.323106°S, 120.394508°E) was collected in the MCN section, and is comprised of an accretionary lapilli tuff interbedded with the upper carbonates of the Meentheena Member, providing an age for uppermost Package 7. Lapilli were ~1 mm scale (Supplemental Figure 1). Approximately 50 zircons were separated from this sample, and they were ~50  $\mu\text{m}$  in size, opaque, equant, and slightly rounded. Twenty-seven were selected for analysis, and 8 were successfully dated. Zircons range in age from  $2747.6 \pm 2.0$  Ma to  $2717.5 \pm 2.0$  Ma. The weighted mean age of the sample is  $2721.23 \pm 0.88/0.88/6.9$  Ma (MSWD = 1.7, n = 4). This age improves precision yet agrees with a SHRIMP age of  $2721 \pm 4$  for a tuff 300 m into the volcanoclastic section of Package 7 in the Nullagine Syncline (Blake et al., 2004).

Samples K302 and K329 were collected from two different outcrops of 1 cm-scale accretionary lapilli tuff, that were along strike from each other at the same stratigraphic height and immediately overlying the uppermost Package 8 lava flow at MCN. For sample K302 (21.323551°S, 120.409556°E), which had a lower density of lapilli, approximately 100 zircons were separated from this sample, and they were euhedral, prismatic, blocky and opaque in appearance. Forty-one zircons were selected for analysis, and 14 were successfully dated. Zircons range in age from  $2724.9 \pm 3.0$  Ma to  $2718.7 \pm 4.0$  Ma. The weighted mean age is as  $2721.28 \pm 0.59/0.60/6.8$  Ma (MSWD = 0.3, n = 9).

For sample K329 (21.323073°S, 120.413734°E), approximately 100 zircons were separated from this sample, and they are glassy, prismatic, and mostly euhedral in

appearance, with half equant and half tabular morphologies. Thirty zircons were selected for analysis, and nine were successfully dated. Zircons range in age from  $2724.5 \pm 7.4$  Ma to  $2718.06 \pm 0.90$  Ma. The weighted mean age of the sample is  $2720.66 \pm 0.96/0.96/6.9$  (MSWD = 1.0, n = 5). Our ages for K302 and K329 agrees well with each other, and with the SHRIMP age of  $2718 \pm 3$  Ma obtained in an accretionary lapilli tuff interbedded with Package 8 lava flows in the Nullagine Syncline (Blake et al., 2004).

Because the ages obtained for these 3 samples collected from Packages 7 and 8 overlap within  $2\sigma$  uncertainty, the ages were incorporated into a Markov Chain Monte Carlo simulation using a Gibbs sampler to refine their ages, based on the stratigraphic height of each sample (Schoene et al., 2019). The results of this model yield ages of  $2721.57 \pm 0.64$  Ma for K295,  $2721.18 \pm 0.51$  Ma for K302, and  $2720.52 \pm 0.80$  Ma for K329. These model ages overlap with our weighted mean ages, but improve precision for each age.

## **DISCUSSION**

Our stratigraphically-constrained paleomagnetic and geochronological analyses of the Fortescue Group yield a number of insights, with implications for Pilbara plate motion during the Archean, Fortescue magmatism, and calibration of the Precambrian Geologic Timescale. These are detailed in the following sections.

### *1. Neoproterozoic Pilbara plate motion*

There is a significant change in the paleogeography of the Pilbara craton during emplacement of the Package 0-1 Mount Roe Basalt flows. Between the lower and upper

Package 0 directions, there is  $2970 \pm 1844$  km of displacement between the VGPs, and between Upper Package 0 and Package 1, there is  $6505 \pm 1778$  km of displacement between the VGPs (Figure 5a). Since all zircons dated from GHG and CR were inherited, a plate velocity across these two transitions cannot be calculated at this time with our data.

However, the direction we obtain from Upper Package 0 agrees well with a new pole for the Black Range Dolerite Suite (BRDS) of dykes (Evans et al., 2017), which have been previously correlated to the Mount Roe Basalt based on geochronology. A SHRIMP zircon study yielded  $2763 \pm 13$  Ma and  $2775 \pm 10$  Ma ages for the Mount Roe Basalt (Arndt et al., 1991), a TIMS study on air-abraded zircons produced an age of  $2767 \pm 3$  Ma for the Mount Roe Basalt, and a SHRIMP baddeleyite study of the BRDS provided an age of  $2772 \pm 2$  Ma (Wingate, 1999). The age of  $2772 \pm 2$  Ma (Wingate, 1999) is still accepted as the best age estimate of the BRDS following additional ID-TIMS baddeleyite work on the suite (Evans et al., 2017). Given the overlapping position of the VGPs for the BRDS and Upper Package 0, the age of  $2772 \pm 2$  Ma can therefore be applied to this portion of the Mount Roe Basalt; the other Mount Roe Basalt ages cannot be correlated with our results, as it is unclear whether they constrain the paleogeography of Package 0 or Package 1.

We agree with the interpretation of Evans et al. (2017) that the most parsimonious explanation of the plate motion evidenced by VGPs from Package 0, Upper Package 0/BRDS, and Package 1 result from horizontal plate motion of the Pilbara craton, rather

than a block rotation, the preferred interpretation of Strik (2004). In this way, as described by Evans et al. (2017), the craton crossed the polar circle during emplacement of these basalt packages. We can attempt to constrain a minimum rate of the second portion of this motion, between Upper Package 0 and Package 1, using our new high-precision Package 2 age of the Spinaway Porphyry of  $2762.51 \pm 0.68$  Ma as a minimum age for Package 1. We calculate a minimum rate of  $68.5 \pm 24.2$  cm/a, which far exceeds the fastest plate motion observed on Earth today, of  $\sim 15$  cm/a.

Higher in the Fortescue Stratigraphy, during the emplacement of the Tumbiana Formation and Maddina Basalts of Packages 7 and 8, our new results also suggest significant cratonic motion to account for the  $4115 \pm 1559$  km of distance of the VGP from Package 7R from the poles for the underlying Package 6 and the overlying Package 7N, which overlap geographically. As Strik (2004) described, plate motion across the boundary between Packages 7 and 8 may not have been significant, as the VGPs for each unit overlap; we calculate a distance of  $1984 \pm 1460$  km between the VGPs of these packages (Figure 5b), with overlapping paleolatitudes within uncertainty. Our new high-precision ages from these units allow for the calculation of a maximum plate velocity. Geochronology sample J295 was collected from a lapilli tuff in the uppermost carbonates of the Tumbiana Formation, which overlies the basalt that yielded the Package 7N direction, and so its age of  $2718.69 \pm 0.99$  Ma serves as a minimum age for Package 7N. Combined with the Package 8 age of  $2718.06 \pm 0.90$  from K329, a maximum velocity could be hundreds of cm/a, though the high geological uncertainty of this estimate renders it of little utility.

Our calculated minimum plate velocity of  $68.5 \pm 24.2$  cm/a for the Pilbara as it drifted across the pole from the Upper Package 0 to Package 1 position is noteworthy not only because it exceeds modern rates, but also because it is far greater than the plate velocity calculated for the Pilbara craton during the Mesoarchean. A new paleomagnetic pole from the  $\sim 3180$  Ma Honeyeater Basalt sampled in the Eastern Pilbara allows for a calculated minimum plate velocity of 2.5 cm/a in the 170 Ma prior to 3180 Ma, and  $\geq 0.37 \pm 0.47$  cm/a between 3180 Ma and Package 0 emplacement (Brenner et al., in press). While a hotter Archean Earth with more rapid mantle convection or true polar wander have been invoked previously as possible explanations for rapid drift rates, these results show that Archean plate velocities were not uniformly fast or decreasing monotonically.

## *2. Timing of Fortescue Magmatism*

With an estimated basaltic volume of  $250,000 \text{ km}^3$  (Thorne & Trendall, 2001), the Fortescue Group invites comparison to other continental flood basalt provinces, such as the Columbia River Basalt Group or the Deccan Traps. Indeed, the basaltic volume of the Fortescue is 20% greater than that of the Columbia River Basalt Group (Reidel, 2015). However, Thorne & Trendall (2001) offer three primary objections to the classification of the Fortescue Group as a continental flood basalt. While the northern exposures of the Fortescue suggest predominantly subaerial, ‘continental’ emplacement, the basalts of the southern Fortescue are predominantly subaqueous, as if they erupted in a passive continental margin. Second, the Fortescue ‘basalts’ are geochemically basaltic andesites, while other continental flood basalts are more tholeiitic. Third, while most continental

flood basalts are deposited over less than 1 Ma, the depositional history of the Fortescue covers up to 60 Ma (Thorne & Trendall, 2001).

In recent decades, large igneous provinces (LIPs) have been defined more broadly to be more inclusive of a wider array of geologic expressions of voluminous magmatism, such as oceanic LIPs and silicic LIPs. While ‘continental flood basalt’ is generally used to describe a LIP on land, the subaqueous emplacement and more felsic geochemistry of the Fortescue basalts would not preclude the classification of the Fortescue as a large igneous province. However, the 60 Ma duration of Fortescue emplacement would be its most notable disqualifying factor, as LIPs should occur over a short duration (<5 Ma), or with multiple short pulses over a maximum of a few 10s of Ma (Ernst & Youbi, 2017). A recent review of high-precision geochronology of large igneous provinces suggests that all well-dated LIPs were emplaced in <1 Ma (Kasbohm et al., 2020).

Since the Fortescue Group contains three distinct basaltic formations (Mount Roe, Kylena, and Maddina Basalts), perhaps each of these could be considered as individual LIPs. Volume estimates for each of these units are 72,000 km<sup>3</sup>, 68,000 km<sup>3</sup>, and 110,000 km<sup>3</sup> ((Thorne & Trendall, 2001), though these may be hampered by limited geologic preservation. While the Mount Roe and Kylena Basalts no longer satisfy the >100,000 km<sup>3</sup> volume cutoff for LIP classification, the Maddina Basalt (Packages 8-10 could still qualify as a continental flood basalt with its larger volume. Our geochronology shows a minimum duration of 1.05±1.02 Ma for the emplacement of Package 8 at MCN,

suggesting that the rest of the Maddina Basalt could have been emplaced in a few Ma or less.

While the Fortescue Group may or may not meet specific criteria for LIP classification, assessing its emplacement dynamics may yield insights for an early prototype of LIP magmatism. One aspect of more recent LIP emplacement that is not always well-known is the relative timing of intrusive and extrusive magmatism (Kasbohm et al., 2020). By contrast, our paleomagnetic correlation showing the temporal coincidence of the Mount Roe Basalt flows of Upper Package 0 and the intrusive activity of the BRDS conclusively places the widespread BRDS within the temporal and stratigraphic context of the Fortescue Group, and allows for a temporal correlation between dikes and lava flows.

Another crucial aspect of LIP emplacement to consider is the duration of hiatuses. The Fortescue Group, with its prolonged sedimentary or felsic-intrusive dominated intervals, is more complicated than a typical LIP. The Package 1-10 subdivisions of Blake (2001) were initially envisioned to be bounded by significant time breaks in the Fortescue stratigraphy. Our geochronology sampling at the boundary between Packages 7 and 8 yield the first high-precision temporal constraints on one of these hiatuses, since J295 is in the uppermost Package 7, and K302 overlies the Maddina Basalts in Package 8. While Blake (2001) noted the Package 7–8 boundary was likely relatively short (1-5 Ma), and subsequent geochronology produced a duration of ~3 Ma (Blake et al., 2004), we show that the time elapsed between these two samples (whose dates overlap within uncertainty) is  $1.05 \pm 1.02$  Ma, suggesting that the actual amount of time elapsed before Package 8

volcanism started is much less. Therefore, it seems that time breaks between these packages may be less significant than previously thought.

### *3. Calibrating the Precambrian Geologic Timescale*

The integrated magnetostratigraphy and high-precision geochronology of the Fortescue presented here offers a detailed look at two different intervals of basalt eruptions during the emplacement of one of Earth's oldest continental flood basalts. Indeed, the base of the Mount Roe Basalts has been suggested as a Precambrian Global Boundary Stratotype Section and Point (GSSP) for the lower boundary of the Neoproterozoic Era (and proposed 'Methanian' Period) at ~2780 Ma, because the Fortescue Group, as potentially one of the first continental flood basalts, exemplifies the widespread crustal formation, global magmatism, and microbial life speculated to be characteristic of this time in Earth history (Van Kranendonk et al., 2012). Similarly, Ernst et al. (2020) suggest that LIPs provide natural boundaries for the Geologic Timescale based on their useful frequency of 20-30 Ma and their suggested connections to environmental change. Apart from its lack of a high-precision age constraint, the base of the Mount Roe Basalt (Package 0) seems like a suitable Precambrian GSSP, and future work is required to obtain a date for this interval, with two-fold goals of timescale calibration and velocity calculations.

Another aspect of the Geologic Timescale to which the Fortescue may contribute is the global magnetostratigraphy recorded in the Geomagnetic Polarity Timescale (GPTS). Strik (2003) documented Earth's oldest known magnetic field reversal between Packages 1 and 2, which we now constrain with a minimum age of  $2762.11 \pm 0.66$  Ma on the

Spinaway Porphyry, and the previously existing maximum age of  $2772 \pm 2$  Ma from the BRDS (Evans et al., 2017; Wingate, 1999). While polarity reverts to normal after Package 2, our data and analyses described in Strik (2004) suggest that a second reversed polarity interval occurs at the base of Package 7, in the Tumbiana Formation, at  $\sim 2720$  Ma. Normal polarity returns at or before  $2718.69 \pm 0.99$ , based on our zircon age from the Tumbiana stromatolites overlaying the normally magnetized basalts. Thus, we find that Earth's polarity reversed four times between 2772 and 2718 Ma, reflecting past observations that magnetic field reversals were more infrequent in the Precambrian (Dunlop & Yu, 2004). The durations of each polarity chron defined would potentially be  $\sim 10$  Ma during the Package 2 reversed interval,  $\sim 35$  Ma during the normal chron when Packages 3-6 were deposited, and  $\sim 1$  Ma for the reversed interval in Package 7. The pattern of the long normal chron (during the deposition of Packages 3-6) followed by the brief reversed interval in Package 7 reflects patterns in other Precambrian successions, where long intervals (30-40 Ma) of uniform polarity are juxtaposed with intervals of rapid reversals (Elston et al., 2002; Gallet et al., 2012; Pavlov & Gallet, 2010). This alternation between reversing and non-reversing regimes may reflect the sensitivity of the geodynamo to changing heat flux patterns at the core-mantle boundary, in a time prior to the crystallization of the inner core (Gallet et al., 2012).

## **CONCLUSIONS**

By using a stratigraphic approach to integrate paleomagnetic and high-precision geochronological data from the Fortescue Group, we provide crucial new constraints on plate velocities, large igneous province magmatism, and magnetic field reversals in the

Archean. We show that the Pilbara craton drifted at a minimum rate of  $68.5 \pm 24.2$  cm/a over an interval of 10 Ma in the Neoproterozoic, a rate far exceeding both background drift rates for the craton, and modern rates of plate motion. Our new age of  $2721.23 \pm 0.88$  Ma for the Tumbiana Formation provides the first high-precision U-Pb zircon age constraint on Archean stromatolites. The new constraints described here on plate tectonic rates, timing of magmatism, and magnetic field reversals show how one of Earth's oldest large igneous provinces may enlighten future investigations of its successors.

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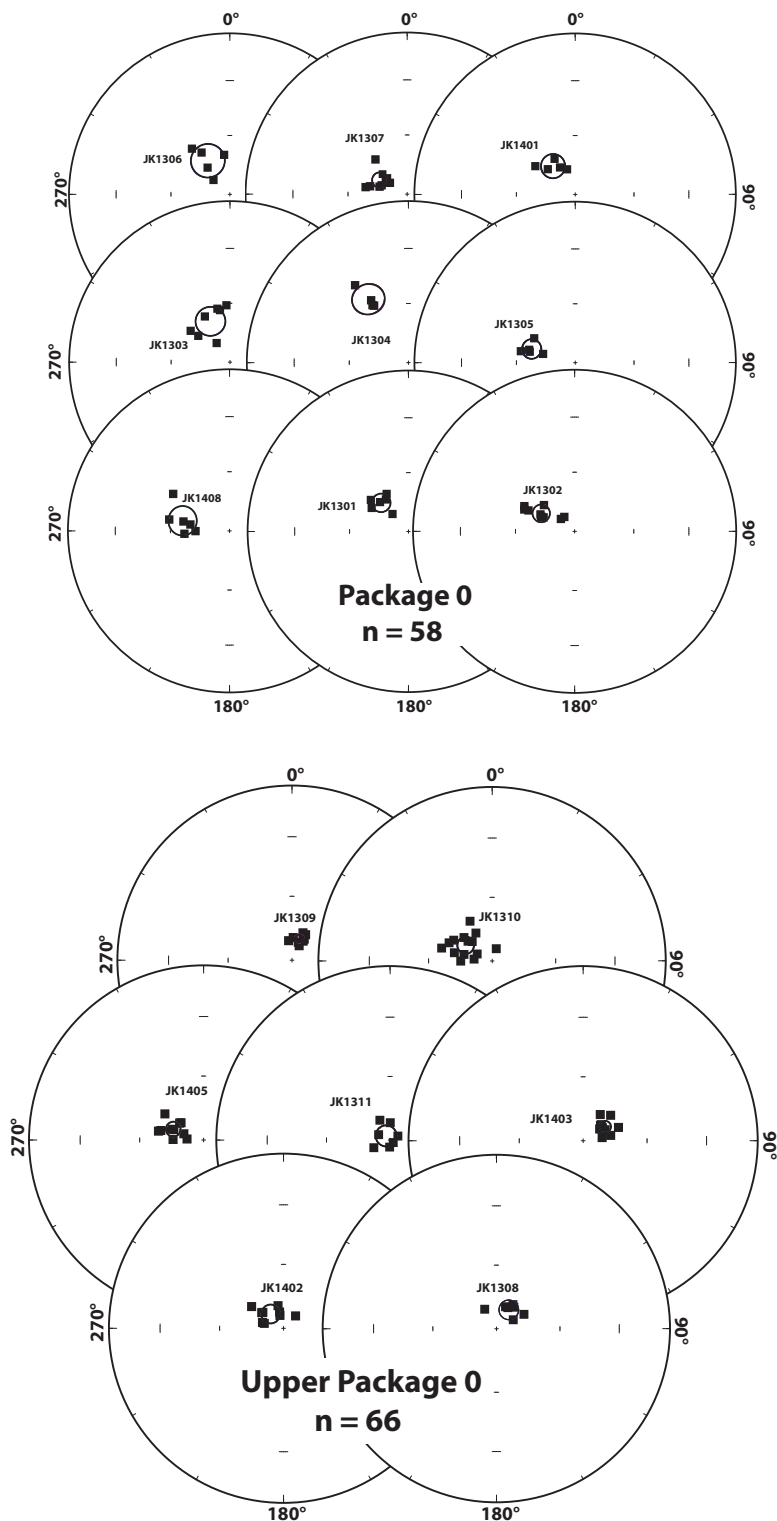
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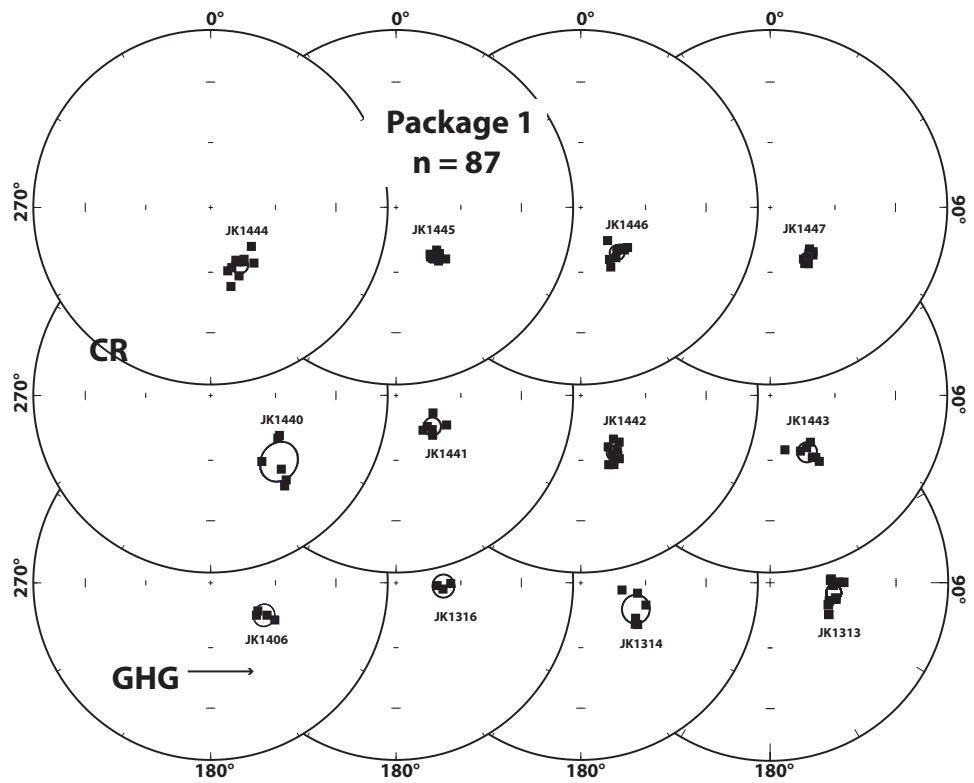
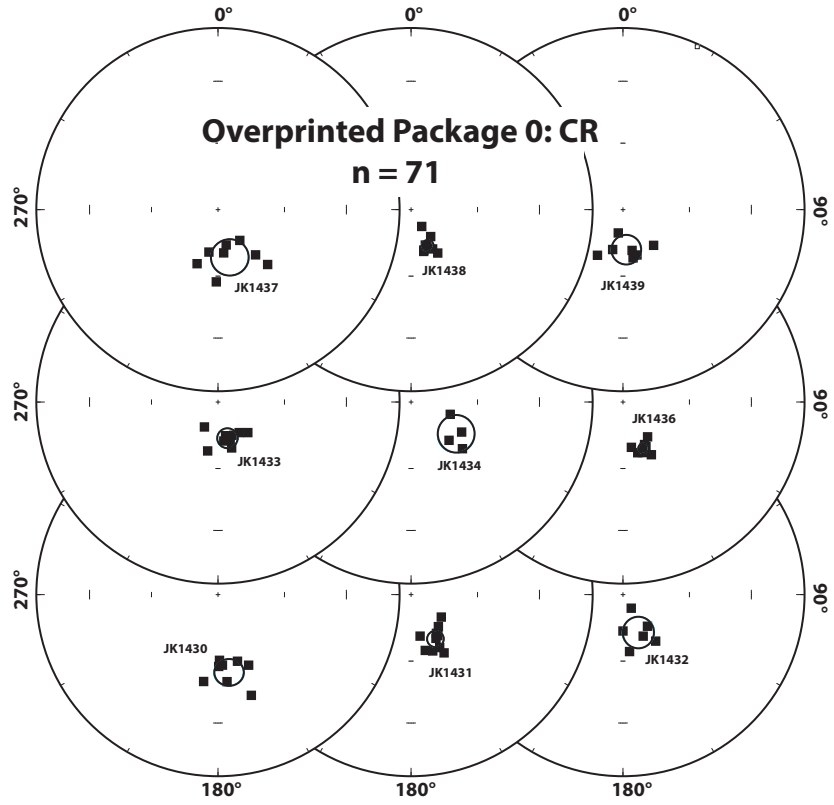
## SUPPLEMENTAL MATERIALS



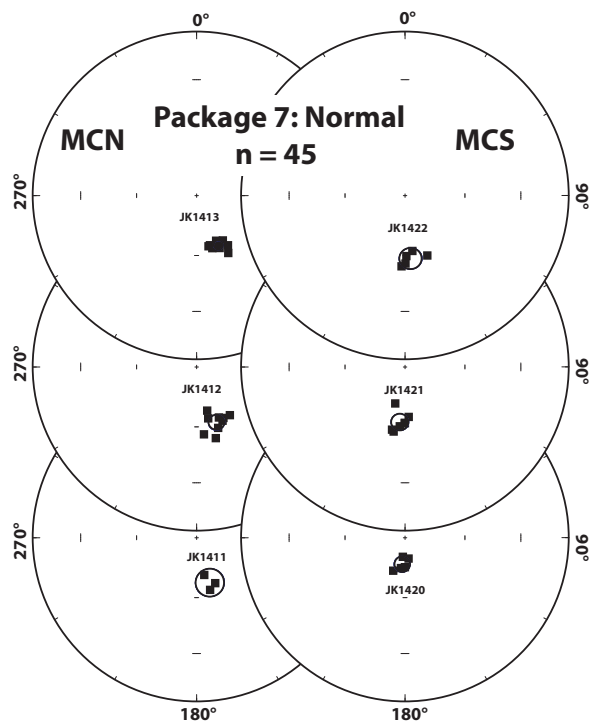
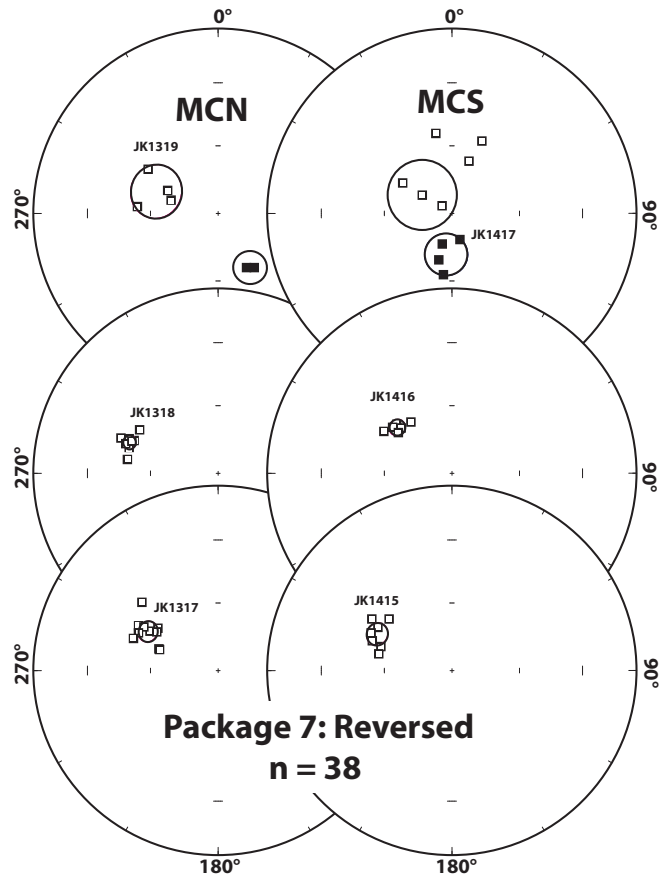
**Supplemental Figure 1. Geochronology sample photos.** Outcrop photos from geochronology samples K295, K302, and K329 are provided here, with pencil for scale (Photo credit: Jennifer Kasbohm, Princeton University).



**Supplemental Figure 2. Equal area plots of paleomagnetic sites.** ChRM directions for each paleomagnetic sample included in all sample site means used to calculate virtual geomagnetic poles are shown in these plots. Plots are arranged in stratigraphic order, from bottom left to right, to top left to right.

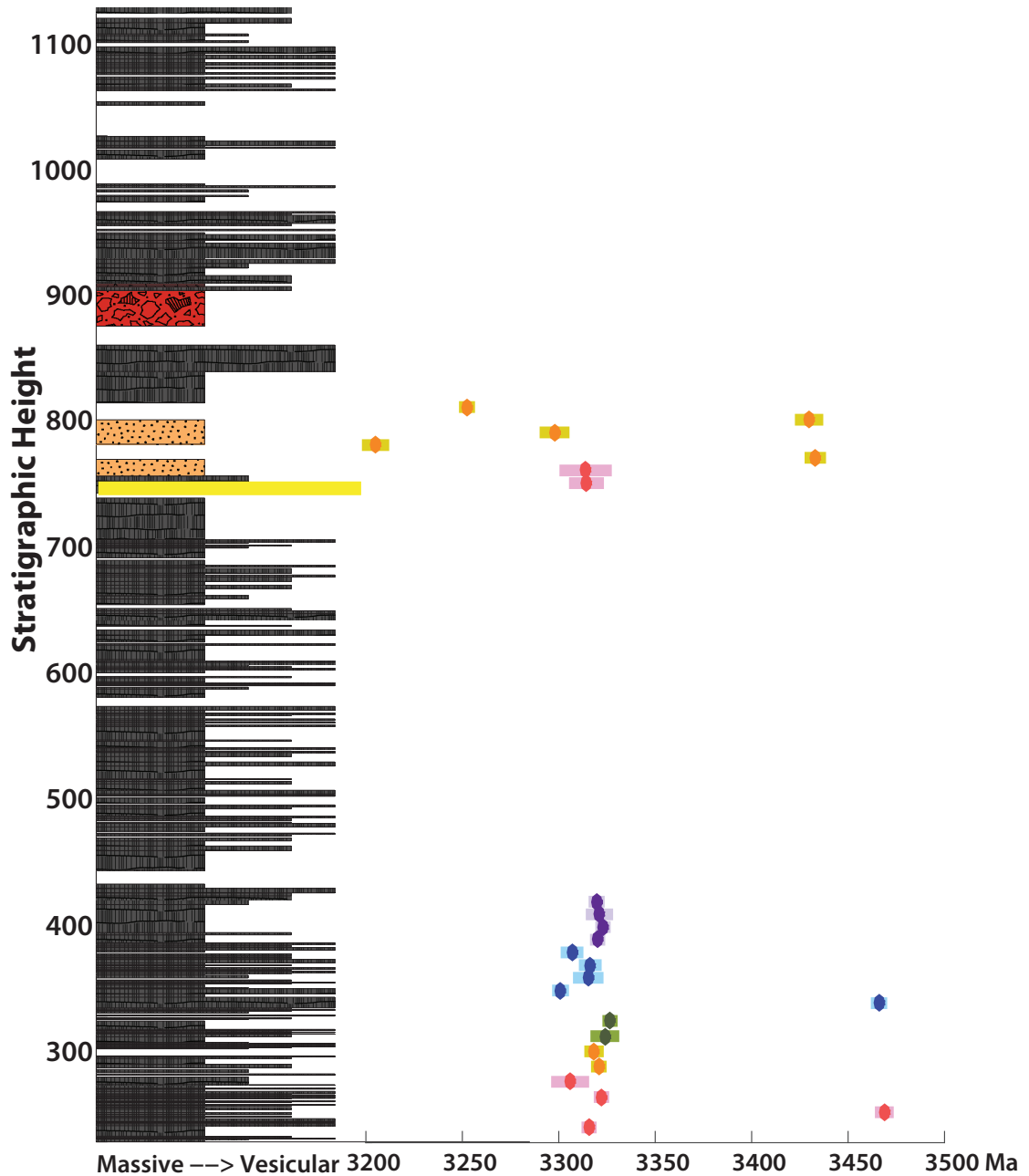


Supplemental Figure 2 (cont)



Supplemental Figure 2 (cont)





**Supplemental Figure 3. Glen Herring Gorge zircon dates.** This figure shows the distribution of zircon dates obtained for geochronology samples collected from the Glen Herring Gorge section. These dates are similar to ages reported for the Duffer ( $3465 \pm 3$  Ma) and Wyman Formations ( $3325 \pm 4$  Ma), which outcrop near the basalt unconformity at GHG, as well as the Corunna Downs Granitoid Complex (3313-3300 Ma), located immediately southeast of the Marble Bar Basin (Australian Stratigraphic Units Database).

**Supplemental Table 1. U-Pb geochronology data.** Data acquired by CA-ID-TIMS is presented in a separate file, with various corrections as specified in the notes beneath the table.

**Supplemental Table 2. Paleomagnetic site mean directions and calculated poles.** Directional and statistical data for each paleomagnetic sample site are provided in this table, with virtual geomagnetic pole data calculated for each directional group.

Supplemental Table 1: U-Pb geochronology data

Sample zircon	Dates (Ma)							Composition					Isotopic Ratios							Blank model			
	206Pb/ <sup>a</sup> ±2σ		207Pb/ <sup>a</sup> ±2σ		207Pb/ <sup>a</sup> ±2σ		% disc	Pb* (pg)	Pbc (pg)	Pb'/Pbc	Th/U	Th/U(magma)	206Pb/204Pb		207Pb/204Pb		207Pb/206Pb		Corr. coef.				
	absolute	±2σ	absolute	±2σ	absolute	±2σ							±2σ %	±2σ %	±2σ %	±2σ %							
<b>K329</b>	<b>21.323073°S, 120.413734°E</b>																						
z6	2731.0	4.0	2727.3	4.7	2724.5	7.4	-0.2	16.63	1.31	12.74	0.66	3.47	685	0.18	0.5275145	0.179	13.6722127	0.493	0.1880609	0.450	0.404	PSF	
z7	2721.7	2.8	2722.6	2.9	2723.2	4.4	0.1	82.83	3.82	21.70	0.58	3.05	1173	0.16	0.5253020	0.124	13.6043639	0.304	0.1879158	0.263	0.495	PSF	
z17	2720.3	7.8	2721.2	4.5	2721.9	4.7	0.1	10.07	0.55	18.18	0.51	2.68	1035	0.14	0.5249721	0.353	13.5852023	0.475	0.1877690	0.282	0.804	SF	
z18	2720.5	3.0	2722.3	2.0	2723.6	1.8	0.1	41.10	0.36	114.59	0.61	3.21	6298	0.17	0.5250250	0.135	13.6003421	0.210	0.1879593	0.103	0.892	SF	
z19	2716.2	2.9	2719.5	2.0	2722.0	2.3	0.2	103.13	1.39	74.29	0.64	3.37	4067	0.18	0.5239994	0.129	13.5604725	0.213	0.1877751	0.135	0.777	SF	
z27	2724.1	7.7	2721.3	5.5	2719.2	7.2	-0.2	5.33	0.52	10.21	0.52	2.74	589	0.14	0.5258810	0.347	13.5863766	0.580	0.1874607	0.436	0.659	SF	
z28	2716.5	2.1	2718.5	1.7	2720.1	1.5	0.1	208.36	0.59	354.67	0.58	3.05	19553	0.16	0.5240655	0.097	13.5463741	0.178	0.1875563	0.085	0.950	SF	
z29	2712.33	0.85	2715.62	0.61	2718.06	0.90	0.2	127.62	1.10	116.45	0.54	2.84	6485	0.15	0.5230906	0.038	13.5047621	0.065	0.1873286	0.043	0.547	SF	
z30	2718.5	2.2	2719.5	1.8	2720.2	1.7	0.1	58.42	0.49	118.44	0.63	3.32	6481	0.17	0.5245495	0.100	13.5596269	0.186	0.1875665	0.095	0.924	SF	
<b>K302</b>	<b>21.323551°S, 120.409556°E</b>																						
z1	2719.2	3.3	2720.6	2.1	2721.7	1.8	0.1	184.51	2.03	91.06	0.59	3.11	4858	0.16	0.5247258	0.148	13.5766179	0.220	0.1877385	0.105	0.892	PSF	
z4	2719.7	2.6	2722.6	2.2	2724.7	2.5	0.2	409.29	8.60	47.57	0.54	2.84	2571	0.15	0.5248226	0.117	13.6045048	0.227	0.1880894	0.147	0.800	PSF	
z8	2722.8	2.9	2724.0	2.4	2724.9	3.0	0.1	77.88	2.07	37.59	0.53	2.79	2040	0.15	0.5255590	0.132	13.6249888	0.255	0.1881086	0.177	0.744	PSF	
z21	2721.7	2.1	2721.6	1.7	2721.6	1.5	0.0	87.38	0.28	316.04	0.42	2.21	18038	0.12	0.5252971	0.095	13.5904512	0.175	0.1877253	0.085	0.943	SF	
z28	2723.7	7.3	2722.2	3.7	2721.0	2.9	-0.1	30.77	0.56	54.70	0.59	3.11	3029	0.16	0.5257884	0.327	13.5983896	0.387	0.1876595	0.171	0.894	SF	
z29	2717.9	2.5	2719.5	1.8	2720.6	1.5	0.1	126.15	0.36	346.07	0.60	3.16	19010	0.17	0.5244133	0.113	13.5596829	0.190	0.1876160	0.086	0.942	SF	
z30	2711.7	5.3	2715.7	3.4	2718.7	4.0	0.3	13.86	0.67	20.64	0.65	3.42	1140	0.18	0.5229312	0.237	13.5057615	0.359	0.1873996	0.238	0.750	SF	
z31	2718.3	5.2	2720.2	2.8	2721.7	2.1	0.1	22.61	0.37	61.72	0.62	3.26	3392	0.17	0.5245091	0.236	13.5709971	0.297	0.1877383	0.123	0.911	SF	
z35	2717.7	2.9	2719.8	2.0	2721.3	1.9	0.1	26.63	0.39	67.76	0.58	3.05	3751	0.16	0.5243631	0.133	13.5639913	0.214	0.1876936	0.112	0.878	SF	
z36	2721.9	2.8	2721.6	1.8	2721.4	1.5	0.0	248.99	0.26	972.27	0.60	3.16	53410	0.16	0.5253434	0.124	13.5903370	0.192	0.1877072	0.085	0.924	SF	
z37	2715.8	2.5	2719.3	2.1	2722.0	2.5	0.2	79.10	2.08	38.10	0.59	3.11	2114	0.16	0.5239152	0.112	13.5579967	0.225	0.1877710	0.148	0.794	SF	
z39	2719.2	4.2	2719.8	2.4	2720.3	2.2	0.0	23.50	0.24	98.32	0.60	3.16	5415	0.17	0.5247148	0.188	13.5649605	0.258	0.1875812	0.131	0.862	SF	
z40	2721.7	6.2	2720.1	3.3	2718.9	2.8	-0.1	14.84	0.41	36.60	0.50	2.63	2068	0.14	0.5253099	0.281	13.5689399	0.347	0.1874236	0.166	0.875	SF	
z41	2720.2	2.2	2720.9	1.7	2721.3	1.6	0.0	77.81	0.50	154.49	0.58	3.05	8528	0.16	0.5249513	0.098	13.5798147	0.180	0.1877020	0.090	0.933	SF	
<b>K295</b>	<b>21.323106°S, 120.394508°E</b>																						
z1	2725.2	2.6	2723.2	1.8	2721.7	1.5	-0.1	275.65	0.72	382.68	0.53	2.79	20589	0.15	0.5261311	0.116	13.6132588	0.188	0.1877423	0.085	0.928	PSF	
z3	2717.9	2.0	2718.0	1.7	2718.1	1.7	0.0	98.39	0.71	138.97	0.60	3.16	7386	0.17	0.5244172	0.091	13.5394932	0.180	0.1873353	0.097	0.926	PSF	
z4	2717.1	3.8	2718.7	2.1	2719.9	1.6	0.1	223.11	0.53	421.40	0.59	3.11	22398	0.16	0.5242186	0.170	13.5489470	0.226	0.1875371	0.088	0.926	PSF	
z5	2738.6	9.3	2743.8	4.2	2747.6	2.0	0.3	64.29	0.60	107.36	0.63	3.32	5664	0.17	0.5292980	0.418	13.9128115	0.449	0.1907255	0.114	0.965	PSF	
z9	2719.3	2.2	2720.8	1.8	2721.9	1.6	0.1	135.37	1.02	132.16	0.53	2.79	7122	0.15	0.5247485	0.098	13.5788138	0.185	0.1877607	0.094	0.934	PSF	
z10	2708.0	4.6	2715.3	2.4	2720.8	2.4	0.5	42.94	0.91	47.06	0.60	3.16	2515	0.16	0.5220666	0.209	13.5005206	0.257	0.1876371	0.142	0.824	PSF	
z11	2722.0	3.9	2722.9	3.3	2723.6	4.5	0.1	31.48	1.40	22.55	0.56	2.95	1224	0.15	0.5253843	0.176	13.6096672	0.353	0.1879596	0.272	0.647	PSF	
z21	2704.0	2.3	2711.7	1.8	2717.5	2.0	0.5	70.43	0.75	93.94	0.57	3.00	5203	0.16	0.5211117	0.103	13.4493482	0.188	0.1872684	0.114	0.819	SF	
<b>J339</b>	<b>21.76549°S, 129.091807°E</b>																						
z1	2765.8	2.0	2765.4	1.6	2765.1	1.5	0.0	1587.30	4.50	352.37	0.80	4.21	17928	0.22	0.5357784	0.091	14.2336593	0.173	0.1927638	0.084	0.957	PSF	
z2	2763.6	2.1	2762.7	1.7	2762.1	1.7	0.0	340.21	2.91	116.83	0.83	4.37	5921	0.23	0.5352477	0.093	14.1937418	0.182	0.1924138	0.098	0.918	PSF	
z4	2762.8	2.3	2763.0	2.4	2763.2	3.1	0.0	84.33	2.43	34.70	0.66	3.47	1831	0.18	0.5350625	0.102	14.1979635	0.248	0.1925376	0.185	0.723	PSF	
z5	2758.6	2.1	2761.2	1.9	2763.0	2.1	0.2	183.56	2.71	67.67	0.77	4.05	3478	0.21	0.5340717	0.092	14.1703840	0.197	0.1925201	0.121	0.867	PSF	
z6	2758.8	2.0	2760.8	1.8	2762.3	1.9	0.1	145.65	1.81	80.27	0.81	4.26	4087	0.22	0.5341147	0.090	14.1654748	0.188	0.1924379	0.112	0.883	PSF	
z8	2758.6	3.7	2761.5	2.1	2763.6	1.6	0.2	63.32	0.25	253.63	0.79	4.16	13363	0.22	0.5340628	0.163	14.1749861	0.222	0.1925858	0.091	0.919	SF	
z9	2753.8	2.7	2758.6	1.9	2762.1	1.7	0.3	73.64	0.71	103.21	0.78	4.11	5469	0.21	0.5329104	0.119	14.1317861	0.199	0.1924141	0.097	0.912	SF	
z10	2763.3	2.8	2765.5	3.3	2767.1	4.9	0.1	63.93	2.88	22.19	1.14	6.00	1073	0.31	0.5351921	0.126	14.2350070	0.352	0.1929932	0.296	0.577	PSF	
z13	2769.1	2.9	2767.6	3.0	2766.4	4.1	-0.1	34.80	1.42	24.43	0.68	3.58	1287	0.19	0.5365545	0.127	14.2659096	0.311	0.1929211	0.250	0.624	PSF	
z15	2764.9	2.1	2765.6	1.9	2766.1	2.1	0.0	555.03	8.75	63.44	0.80	4.21	3239	0.22	0.5355611	0.095	14.2365746	0.201	0.1928815	0.126	0.854	PSF	
z16	2759.5	2.0	2761.0	1.7	2762.2	1.6	0.1	123.19	0.63	195.58	0.76	4.00	10031	0.21	0.5342642	0.089	14.1679383	0.175	0.1924175	0.090	0.947	PSF	
z17	2769.1	2.8	2765.1	1.9	2762.2	1.6	-0.2	202.62	1.18	171.70	0.74	3.89	8844	0.20	0.5365741	0.124	14.2296542	0.196	0.1924238	0.091	0.914	PSF	
z19	2763.9	3.7	2762.9	2.4	2762.2	2.4	-0.1	31.02	0.64	48.34	0.71	3.74	2608	0.19	0.5353180	0.167	14.1963751	0.252	0.1924242	0.140	0.842	SF	
z20	2761.0	3.7	2761.3	2.3	2761.5</																		

**Supplemental Table 2: Paleomagnetic site mean directions and calculated poles**

Site	Section	Strat Height	Lat	Long	n	*	N	D	I	k	a95	VGP	VGP	plat
										K	A95	lat	long	
<i>Package 0</i>														
JK1407 C	GHG	56.7	-21.35	119.61	20	X	23.7	-68.4	48.02	4.8				
JK1408	GHG	284.9	-21.34	119.62	6	*	282.1	65.7	71.5	7.3	-8.0	78.3		
JK1409	GHG	289.1	-21.34	119.62	2	X	307.4	71.8	46.7	26.1				
JK1301	GHG	293.7	-21.34	119.62	6	*	316.5	70.0	170.9	4.7	5.9	95.6		
JK1302	GHG	359.9	-21.34	119.62	10	*	298.4	70.9	108.7	4.4	-2.7	89.5		
JK1303	GHG	372.4	-21.34	119.62	7	*	334.4	67.0	57.5	7.4	15.4	102.8		
JK1304	GHG	458.9	-21.34	119.62	4	*	327.7	51.5	101.9	7.9	28.2	88.7		
JK1305	GHG	513.9	-21.34	119.62	5	*	287.3	66.7	195.2	4.9	-5.4	80.9		
JK1306	GHG	570.6	-21.34	119.62	5	*	326.7	69.6	64.9	8.5	10.0	100.2		
JK1307	GHG	630.4	-21.20	119.70	9	*	297.1	74.5	161.6	3.8	-6.4	93.9		
JK1401	GHG	644.7	-21.20	119.70	6	*	321.8	71.8	24.7	6.2	5.6	99.7		
					<b>57</b>	<b>9</b>	<b>311.5</b>	<b>68.6</b>	<b>66.8</b>	<b>6.3</b>	<b>4.7</b>	<b>92.2</b>	<b>51.9</b>	
									<b>30.8</b>	<b>9.4</b>				
<i>CR Package 0 Overprint</i>														
JK1430	CR	14.8	-21.34	119.62	8	*	172.2	54.3	68.7	6.3	-74.7	144.7		
JK1431	CR	79.3	-21.34	119.62	10	*	151.4	67.3	155.7	3.7	-53.4	150.7		
JK1432	CR	80.5	-21.34	119.62	6	*	157.8	71.7	74.0	7.2	-51.1	139.1		
JK1433	CR	103.8	-21.34	119.62	9	*	165.8	73.3	117.5	4.5	-50.8	131.2		
JK1434	CR	123.9	-21.34	119.62	4	*	125.3	65.2	92.0	8.3	-39.1	165.3		
JK1437	CR	186.1	-21.20	119.70	8	*	166.5	67.9	40.1	8.3	-58.5	136.0		
JK1438	CR	235.8	-21.20	119.70	10	*	155.2	72.3	325.9	2.5	-49.5	140.0		
JK1439	CR	279.1	-21.20	119.70	7	*	175.2	72.0	70.4	6.7	-54.0	124.2		
JK1436	CR	332.6	-21.33	119.62	9	*	156.4	67.3	463.2	2.3	-55.6	146.8		
JK1435 C	CR	724.7	-21.30	119.70	14	X	180.6	64.1	27.2	7.5				
					<b>71</b>	<b>9</b>	<b>158.6</b>	<b>68.6</b>	<b>98.3</b>	<b>5.2</b>	<b>-54.7</b>	<b>142.6</b>	<b>51.9</b>	
									<b>45.7</b>	<b>7.7</b>				
<i>Upper Package 0</i>														
JK1402	GHG	661	-21.20	119.70	9	*	317.9	81.1	123.8	4.4	-8.1	107.9		
JK1308	GHG	667.4	-21.33	119.62	7	*	033.6	79.4	148.9	4.6	-4.8	114.7		
JK1405	GHG	682.9	-21.20	119.70	10	*	289.6	75.0	176.6	3.5	-10.0	92.8		
JK1311	GHG	699.6	-21.33	119.62	7	*	317.4	87.3	129.5	4.9	-17.3	115.8		
JK1403	GHG	725.8	-21.30	119.70	10	*	057.4	77.9	294.8	2.7	-7.8	139.2		
JK1309	GHG	739.3	-21.33	119.62	8	*	019.5	79.7	512.5	2.3	-2.4	126.2		
JK1404	GHG	743.8	-21.20	119.70	10	X	294.3	-02.0	01.2	77.5				
JK1310	GHG	752.8	-21.33	119.63	14	*	300.5	75.6	91.5	4.0	-6.2	96.3		
					<b>65</b>	<b>7</b>	<b>342.2</b>	<b>83.0</b>	<b>72.1</b>	<b>7.2</b>	<b>-8.3</b>	<b>115.6</b>	<b>76.3</b>	
									<b>20.3</b>	<b>13.7</b>				
<i>Package 1</i>														
JK1406	GHG	756.8	-21.33	119.62	4	*	121.3	61.1	255.1	5.0	-37.1	172.2		
JK1312	GHG	801.5	-21.33	119.62	9	X	007.6	-66.6	119.7	4.5				
JK1315 C	GHG	904.5	-21.32	119.62	17	X								
JK1316	GHG	907.5	-21.33	119.62	3	*	093.9	68.1	377.2	5.2	-18.9	161.0		
JK1314	GHG	948.9	-21.32	119.62	6	*	115.6	61.7	89.6	6.5	-32.8	171.5		
JK1313	GHG	957.7	-21.32	119.62	10	*	098.9	60.3	170.4	3.5	-20.4	172.0		
JK1440	CR	712.7	-21.30	119.70	6	*	134.1	45.2	48.3	8.9	-47.9	192.9		
JK1441	CR	744.7	-21.30	119.70	6	*	130.5	67.9	219.4	4.1	-41.6	159.5		
JK1442	CR	764.5	-21.30	119.70	8	*	149.7	59.4	237.8	3.4	-58.1	166.5		
JK1443	CR	782.4	-21.30	119.70	7	*	147.0	58.5	151.4	4.6	-56.6	169.8		
JK1444	CR	794.8	-21.30	119.70	10	*	153.4	59.9	151.1	3.7	-60.2	162.8		
JK1445	CR	814.2	-21.30	119.70	10	*	141.0	60.8	841.6	1.6	-51.4	168.5		

**Supplemental Table 2: Paleomagnetic site mean directions and calculated poles**

JK1446	CR	839.7	-21.30	119.70	8	*	141.3	63.2	223.7	3.5	-50.6	164.1	
JK1447	CR	862.6	-21.30	119.70	9	*	142.2	61.2	787.2	1.7	-52.1	167.3	
					<b>87</b>	<b>12</b>	<b>132.0</b>	<b>61.8</b>	<b>57.4</b>	<b>5.8</b>	<b>-44.4</b>	<b>169.0</b>	<b>43</b>
									<b>28.3</b>	<b>8.3</b>			

*Package 7: Mingah Member, Tumbiana Formation volcaniclastics*

JK1317	MCN	1.6	-21.3	120.4	10	*	299.0	-54.1	108.7	4.4	-35.3	182.3	
JK1318	MCN	79.8	-21.3	120.4	8	*	289.3	-48.0	303.8	3.0	-26.5	187.6	
JK1319r	MCN	140	-21.3	120.4	4	*	289.4	-60.7	48.5	11.5	-28.2	173.4	
JK1415	MCS	1.3	-21.4	120.5	7	*	296.0	-52.9	137.3	4.8	-32.8	183.6	
JK1416	MCS	20.6	-21.4	120.5	6	*	309.9	-58.3	299.3	3.5	-43.9	176.4	
		20.7-											
JK1417r	MCS	29.8	-21.4	120.4	3	*	302.4	-74.5	43.2	15.4	-34.1	150.1	
					<b>38</b>	<b>6</b>	<b>297.0</b>	<b>-58.3</b>	<b>64.9</b>	<b>8.4</b>	<b>-34.1</b>	<b>175.0</b>	<b>39.0</b>
									<b>40.2</b>	<b>10.7</b>			

*Package 7: Mingah Member, Tumbiana Formation basalts*

JK1319n	MCN	140	-21.3	120.4	2	*	149.2	62.0	588.3	7.3	-56.3	162.6	
JK1411	MCN	229.4	-21.3	120.4	3	*	163.5	66.6	204.4	7.1	-59.3	141.7	
JK1412	MCN	251.9	-21.3	120.4	9	*	160.2	60.5	152.7	3.9	-63.8	155.5	
JK1413	MCN	276.8	-21.3	120.4	10	*	156.3	62.9	392.9	2.3	-59.8	155.2	
JK1320	MCN	361.4	-21.3	120.4	0	X	scattered						
		33-											
JK1417n	MCS	38.5	-21.4	120.4	4	*	188.0	71.7	72.6	9.4	-54.4	112.8	
JK1418	MCS	52	-21.4	120.5	7	X	270.8	14.0	25.1	11.3			
JK1419	MCS	125.6	-21.4	120.4	3	X	200.7	53.8	50.7	14.2			
JK1420	MCS	146.9	-21.4	120.4	5	*	186.2	76.7	301.4	4.0	-46.5	116.6	
JK1421	MCS	169.4	-21.4	120.4	8	*	185.3	62.3	172.0	4.3	-67.4	110.4	
JK1422	MCS	206.6	-21.4	120.4	5	*	174.9	58.3	157.8	5.5	-71.9	133.2	
JK1423	MCS	224.6	-21.4	120.5	0	X	scattered						
					<b>45</b>	<b>8</b>	<b>168.7</b>	<b>65.7</b>	<b>86.8</b>	<b>6.0</b>	<b>-61.4</b>	<b>135.6</b>	<b>48.0</b>
									<b>38.1</b>	<b>9.1</b>			

*Package 7: Meentheena Member, Tumbiana Formation carbonates and sediments*

JK1321	MCN	400.4	-21.3	120.4	37	X	304.1	-50.4	08.2	8.8			
JK1328	MCN	439.2	-21.3	120.4	31	X	341.2	-69.4	20.2	5.9			
JK1424	MCS	258.3	-21.4	120.4	7	X	083.3	-40.4	07.8	21.1			

*Package 8: Maddina Basalts*

JK1322	MCN	637.5	-21.3	120.4	10	*	130.4	54.4	372.6	2.4	44.7	361.8	
JK1323	MCN	709.3	-21.3	120.4	10	*	161.6	63.1	277.9	2.8	62.2	329.2	
JK1324	MCN	805.7	-21.3	120.4	7	*	143.2	39.3	122.8	5.1	55.9	381.8	
JK1327	MCN	830	-21.3	120.4	7	*	145.5	46.4	76.8	9.1	58.1	371.9	
JK1325	MCN	830	-21.3	120.4	2	*	154.2	48.5	1185.7	5.1	65.4	365.8	
JK1414	MCN	893.2	-21.3	120.4	5	*	161.8	51.6	156.8	5.5	70.5	352.6	
JK1326	MCN	896.6	-21.3	120.4	7	*	158.3	41.5	222.1	3.8	69.8	379.1	
JK1425	MCS	441	-21.4	120.4	4	X	260.6	-77.6	35.2	13.6			
		471.6-											
JK1426	MCS	476.6	-21.4	120.4	3	*	169.4	49.3	64.9	12.6	77.1	345.6	
JK1427	MCS	522.3	-21.4	120.4	4	*	177.8	55.5	214.7	5.4	75.2	307.4	
JK1428	MCS	555.3	-21.4	120.4	8	*	173.1	49.5	219.1	3.5	79.1	333.7	
JK1429	MCS	585.6	-21.4	120.4	6	*	176.5	55.5	85.3	6.7	75.0	311.4	
					<b>66</b>	<b>11</b>	<b>158.7</b>	<b>51.3</b>	<b>49.7</b>	<b>6.5</b>	<b>-68.4</b>	<b>175.3</b>	<b>31</b>
									<b>31.9</b>	<b>9.5</b>			

## Chapter 3

### **Rapid eruption of the Columbia River flood basalt and correlation with the mid-Miocene climate optimum**

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*This chapter is taken from*

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#### **ABSTRACT**

Flood basalts, the largest volcanic events in Earth history, are thought to drive global environmental change because they can emit large volumes of CO<sub>2</sub> and SO<sub>2</sub> over short geologic timescales. Eruption of the Columbia River Basalt Group (CRBG) has been linked to elevated atmospheric CO<sub>2</sub> and global warming during the Mid-Miocene Climate Optimum (MMCO) ~16 million years ago. However, a causative relationship between volcanism and warming remains speculative as the timing and tempo of CRBG eruptions is not well known. Here, we use U-Pb geochronology on zircon-bearing volcanic ash beds intercalated within the basalt stratigraphy to build a high-resolution CRBG eruption record. Our dataset shows that more than 95% of the CRBG erupted between 16.7 and

15.9 Ma, twice as fast as previous estimates. By suggesting a recalibration of the geomagnetic polarity timescale, these data support that the onset of flood volcanism is nearly contemporaneous with that of the MMCO.

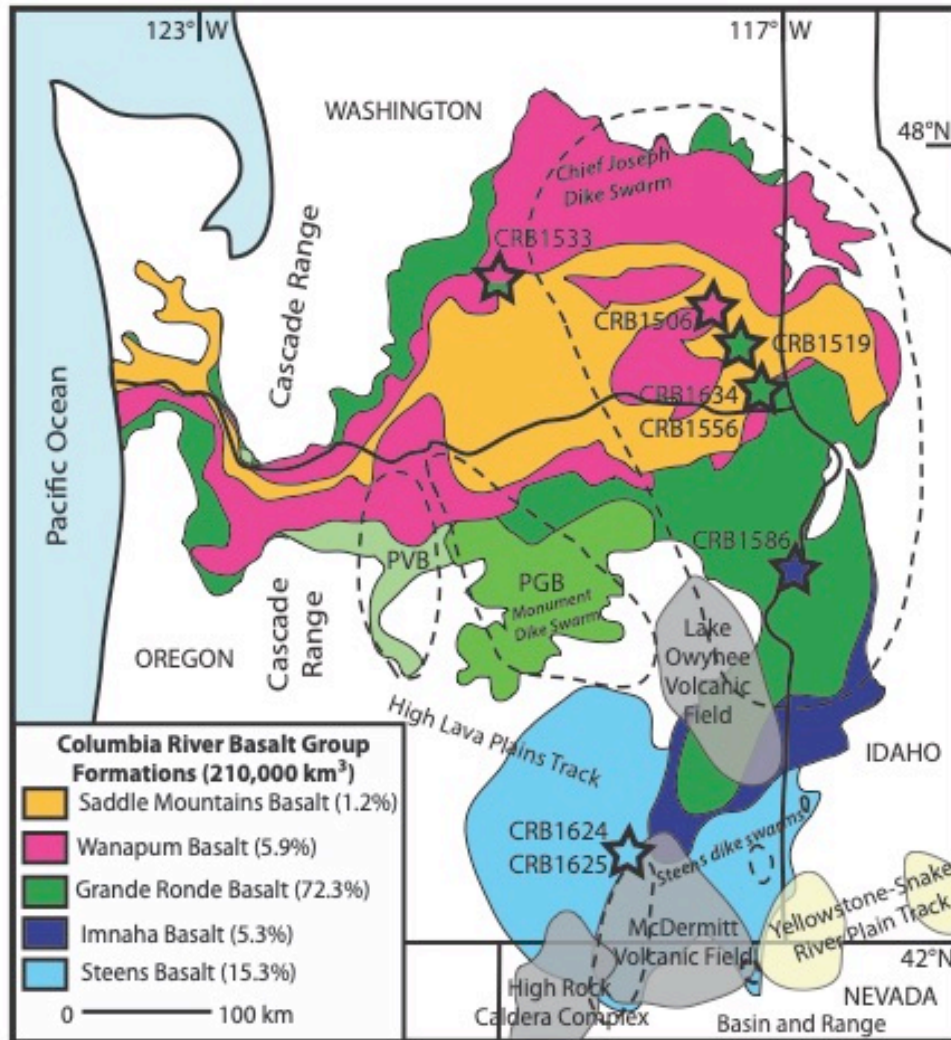
## **INTRODUCTION**

The Columbia River Basalt Group (CRBG) is the youngest, smallest, and best-preserved continental flood basalt. It erupted  $\sim 210,000 \text{ km}^3$  of lava in the Pacific Northwest, USA between  $\sim 17$  and 5 Ma. Forty-three distinct stratigraphic members with volume estimates have been defined using regional correlations based on detailed mapping, geochemistry, and paleomagnetic data (1). While many flood basalts have been implicated in mass extinction events (2), the CRBG is not associated with a mass extinction event and its total volume is up to an order of magnitude smaller than other flood basalts. However, single members yielded comparable volumes of lava (thousands of  $\text{km}^3$ ) to single formations of large igneous provinces implicated in mass extinctions (e.g., Deccan Traps (3)), and therefore may have had comparable short-term climate impacts (4). The  $\sim 17$ -15 Ma Mid-Miocene Climate Optimum (MMCO) is marked by high latitude sea surface temperatures  $4$ - $6^\circ\text{C}$  above background temperature (5) and is associated with vertebrate migrations and increased species originations (6). In paleoclimate records, the MMCO is marked by a benthic  $\delta^{18}\text{O}$  minimum, a benthic  $\delta^{13}\text{C}$  maximum, an ice sheet extent minimum (7), and a variety of  $\text{pCO}_2$  proxies which indicate a possible doubling of atmospheric  $\text{CO}_2$  levels to greater than 400 ppm (8–10). Given the apparent timing of both events, many studies have suggested that the environmental perturbations of the

MMCO are connected to CRBG eruptions (1, 8, 11), but high-precision geochronologic data that link the two events are lacking (7).

While most flood basalt provinces are thought to relate to mantle plume-driven processes, models for the origin of the CRBG include a mantle plume source (12), but also subduction-related processes such as slab tear (13) or slab rollback (14). Central to this debate is that the CRBG was erupted during a period of active regional volcanism, including subduction volcanism of the Cascade arc, rhyolitic volcanism of the Yellowstone-Snake River Plain hotspot track, the High Lava Plains of Central Oregon, and bimodal volcanism related to Basin and Range extension in Northern Nevada (Fig. 1). The CRBG began erupting from a north-trending linear fissure system in eastern Washington, eastern Oregon, western Idaho, and northern Nevada, in a back-arc setting between the Cascades and Rocky Mountains. Volcanism progressed from south to north, and the regional tectonic and geomorphic setting guided flows hundreds of km from east to west (1). An improved understanding of the timing of CRBG eruptions, the volumetric rates at which they were emplaced, and the rate at which they propagated geographically through the province are essential constraints on geodynamic models for the CRBG origin.

In this paper, we aim to test the hypothesis that there is a temporal relationship between CRBG eruptions and the MMCO by establishing an accurate and precise age model for the eruption of the CRBG. Decades of study have produced a high-resolution stratigraphic framework for the CRBG. The 350 tholeiitic basalt to basaltic andesite



**Fig. 1. Map of Columbia River Basalt Group and Regional Volcanism.** The map shows the areal extent of each formation of the CRBG, and the legend provides the volume contribution of each formation. Stars represent geochronology sample collection sites; dashed lines enclose areal extent of source dike swarms. The Prineville Basalt (PVB) and Picture Gorge Basalt (PGB) are coeval with the Grande Ronde Basalt, and represent 1.4% of total CRB volume, and are grouped with the Grande Ronde Basalt for all volume estimates presented here (1).

flows of the CRBG are divided into five formations: the Steens (31,800 km<sup>3</sup>; 15.3% of total volume), Imnaha (11,000 km<sup>3</sup>; 5.3%), Grande Ronde (150,100 km<sup>3</sup>; 72.3%), Wanapum (12,175 km<sup>3</sup>; 5.9%), and Saddle Mountains Basalts (2,424 km<sup>3</sup>; 1.2%), which are comprised by a total of 43 stratigraphic members, containing 1-20 lava flows each

(1). Magnetic field reversals were ongoing during the eruption of the CRBG. While the magnetic stratigraphy first was developed in the field using a portable fluxgate magnetometer during mapping efforts (1), some detailed modern paleomagnetic data have since been published (15, 16). The Steens Basalt erupts during a reversal from reversed to a normal polarity interval (sometimes referred to as  $R_0$  and  $N_0$  (17)), which continues through the Imnaha Basalt. The Grande Ronde Basalt is marked by two couplets of magnetic field reversals (locally defined magnetostratigraphic units are known as R1, N1, R2, N2). The N2 normal magnetozone continues through the majority of the Wanapum Basalt, which exhibits a final reversed interval (1, 18, 19).

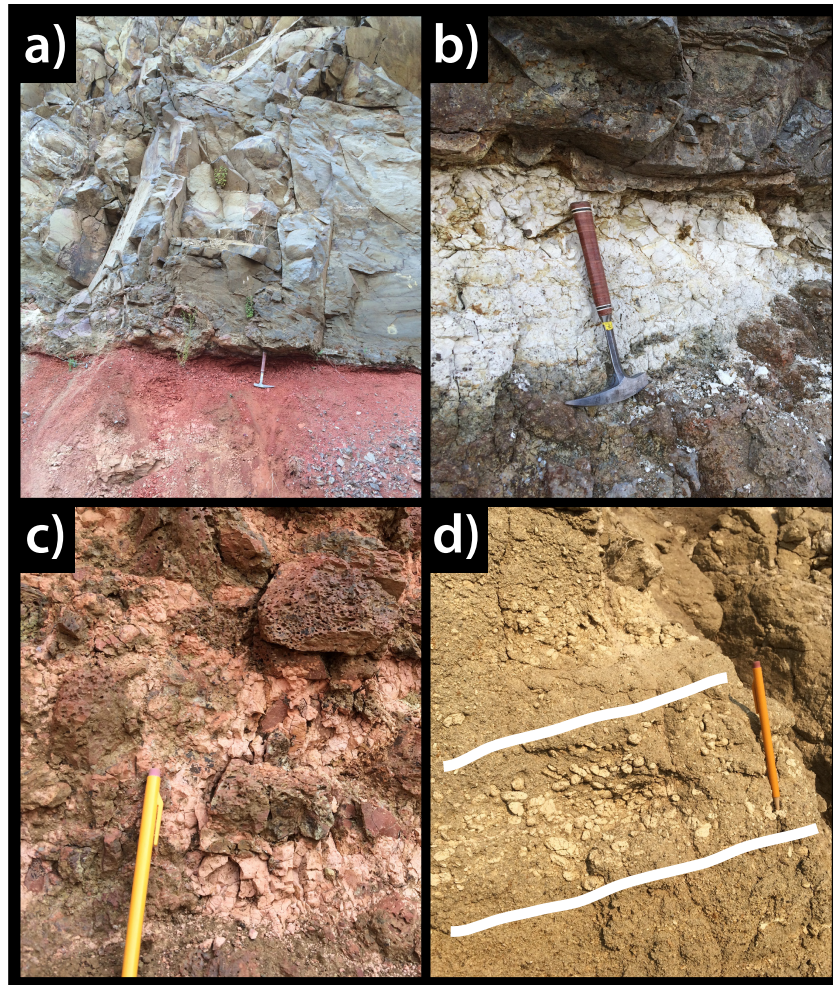
The majority of ages published on the CRBG have uncertainties that preclude the development of an unambiguous chronology for the timing and duration of CRBG volcanism. For example, in a review of K-Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology for the CRBG, a preferred chronology was developed with eruption of the Steens Basalt at 16.9–16.7 Ma, the Imnaha Basalt at 16.7–16.0 Ma, the Grande Ronde Basalt at 16.0–15.6 Ma, the Wanapum Basalt at 15.6–15.0 Ma, and the Saddle Mountains Basalt in several distinct events between 15–6 Ma (4). This eruptive age model is based on geochronologic analyses with large uncertainties (>1 Ma) that make adherence to stratigraphic order difficult to address, and the result is that it is inconsistent with the Geomagnetic Polarity Timescale (GPTS) (4, 20). For instance, this age model suggests a normally magnetized interval lasting ~600 ka through the Imnaha Basalt, which exceeds the duration of any normal chrons occurring around 16 Ma in different calibrations of the GPTS (20). Other inconsistencies are discussed in greater detail in the Results section. New high-precision

$^{40}\text{Ar}/^{39}\text{Ar}$  dates derived from feldspar phenocrysts in silicic tuffs interbedded in the Steens Basalt have revised its eruptive duration to ~16.75-16.54 Ma, and propose that the Steens magnetic field reversal occurred at  $16.603 \pm 0.028$  Ma (21) (dates recalculated with Fish Canyon sanidine age of Kuiper *et al.* (22); see Supplement). These new data highlight the potential that additional precise geochronology has to resolve the timing and duration of CRBG volcanism and its correlation to the GPTS and MMCO.

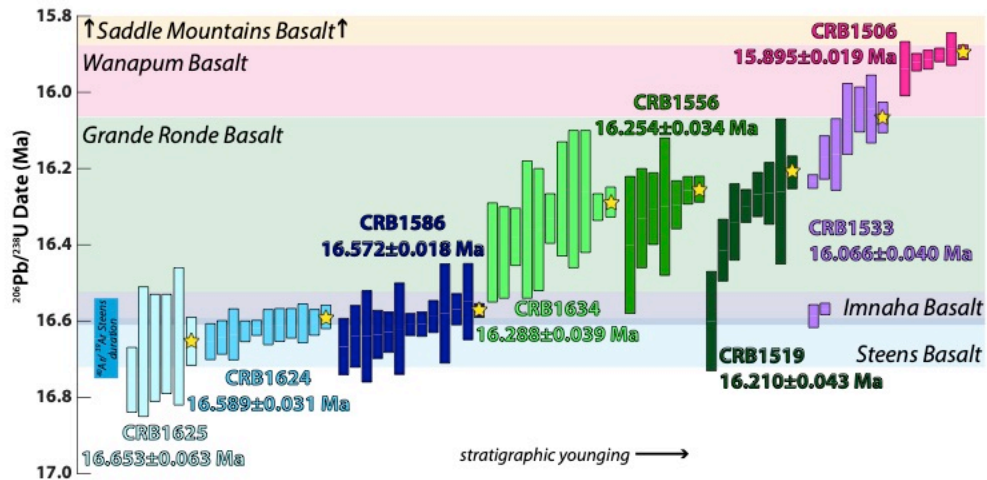
## RESULTS

In this study we use U-Pb zircon geochronology by chemical abrasion-isotope dilution-thermal ionization mass spectrometry (CA-ID-TIMS), which can achieve the precision (~0.1%) and accuracy required to address the issues with prior age models outlined above. Because basalts are generally too low in Si and Zr to saturate zircon, we follow the sampling strategy of Schoene *et al.* (23) by collecting silicic volcanic ash from between basalt flows and dating them by U-Pb geochronology on single zircon crystals. These ash beds were sourced from contemporaneous regional silicic volcanism, and deposits include ash-bearing paleosols (referred to as “redboles” in the remainder of this paper), interflow volcanoclastic sediments, and pumice-bearing airfall tuff (Fig. 2, Fig. S1). Zircons separated from these samples (Fig. S2) were dated by CA-ID-TIMS at Princeton University.

Data from eight horizons within the CRBG, reported as  $^{206}\text{Pb}/^{238}\text{U}$  dates from single zircons taken from a population of dated grains with 95% confidence intervals, are shown in Fig. 3. Dates on single crystals within each sample spread beyond analytical



**Fig. 2. Columbia River Basalt Group Geochronology Samples.** Certain interflow lithologies were targeted for sampling and found to contain magmatic zircons, allowing for high-precision dating techniques to be applied: **(A)** redboles, analogous to those found in the Deccan Traps (similar to CRB1519, CRB1556, CRB1624, CRB1625, and CRB1634); **(B)** ashes deposited from Cascade subduction volcanism or other silicic centers (CRB1506, CRB1586); **(C)** ash-bearing sediments trapped in brecciated basalt flow tops; and **(D)** pumice clasts in the Vantage sedimentary interbed (CRB1533); the horizon with these cm-scale clasts is outlined in white.



**Fig. 3. U-Pb Zircon CA-ID-TIMS Geochronological Data.** Rank order plot of geochronological data presented in this study, with sample names and the youngest, most precise zircon age starred and labeled. Error bars represent  $2\sigma$  uncertainty, and stratigraphic younging is from left to right. We present a timeline, shown with background shading and labels, for the eruption of each formation based on the stratigraphic position of these samples and consistent with our geochronology results. Steens Basalt geochronology is compared to the most recent  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology results (21), and is found to overlap U-Pb data when recalculated with the Fish Canyon Sanidine age of Kuiper *et al.* (22).

uncertainty, a common observation in volcanic ashbeds, because zircon can retain radiogenic Pb at temperatures of  $>900^\circ\text{C}$ . A spread in crystallization dates beyond analytical uncertainty can reflect growth of zircon in the magmatic system prior to eruption, incorporation of pre-eruptive zircon from the volcanic edifice during eruption, or inheritance from the rock hosting the magmatic system (24, 25). In light of these potential sources for complex zircon populations deposited within the CRBG ashes, we use the youngest single concordant analysis, excluding low precision analyses, as an estimate for the age of the ash (26) (Fig. 3). This approach is tested by dating a large number of zircons from each sample to obtain multiple analyses that overlap with the youngest grain, and further requiring that samples from stratigraphically higher positions in the CRBG are in chronological order. A growing database of zircon geochronology

from a variety of tectonic settings, using a variety of U-Pb analytical methods, shows that the youngest zircon analysis from continuous age population (excluding outliers that can be explained by residual Pb loss) overlaps with independent eruptive ages (27, 28). We also show in the Supplement that our use of single youngest zircon ages overlaps with weighted mean ages calculated from multiple grains for each sample, though we prefer the youngest zircon age as the more conservative interpretation. Our dates from the Steens Basalt show excellent agreement with ages derived from high-precision  $^{40}\text{Ar}/^{39}\text{Ar}$  sanidine geochronology (21) (Fig. 3).

Our zircon ages improve estimates for the timing and duration of each formation of the CRBG stratigraphy (Fig. 3), and indicate that 95% of its total volume erupted in  $758\pm 66$  ka (Fig. S3). The upper 72% of the Steens Basalt volume erupted between  $16.653\pm 0.063$  and  $16.589\pm 0.031$  Ma. The latest Steens eruptions occurred concurrently with Imnaha Basalt eruptions, which we have dated at  $16.572\pm 0.018$  Ma. While we currently do not have an estimate for the onset of the overlying Grande Ronde Basalt, four samples from the upper half fall in stratigraphic order and show its termination by  $16.066\pm 0.040$  Ma. Two samples from the bottom and top of the Wapshilla Ridge Member of the Grande Ronde Basalt, which comprises 20% of the total CRBG volume, gave dates overlapping within uncertainty of  $16.288\pm 0.039$  and  $16.254\pm 0.034$  Ma. These ages come from a single stratigraphic section, and the age of the upper bound is indistinguishable at the 95% confidence interval from the age from a redbole that is in the same stratigraphic position but is found 44 km away ( $16.210\pm 0.043$  Ma). Finally, the lower 77% of the Wanapum Basalt finished erupting before  $15.895\pm 0.019$  Ma (Fig. 3). Our dated samples

bracket 95% of the eruptive history of the CRBG, and these data show that the CRBG erupted 2.4 times faster than the previous estimates (4). Our ages agree with the relative chronology of the existing stratigraphic framework (1), and bolster regional correlation through geochemical and paleomagnetic data.

Combined with detailed volume estimates for each member of the CRBG (1), our new zircon ages yield effusion rates throughout the eruptive history of the CRB and provide a timeline for the release of CO<sub>2</sub>, SO<sub>2</sub>, and other gases into the atmosphere. For the main phase of eruption (Steens, Imnaha, and Grande Ronde Basalts), we calculate an average effusion rate of  $0.334 \pm 0.042$  km<sup>3</sup>/yr, which is double the prior estimate of 0.178 km<sup>3</sup>/yr for the same interval (12). During the eruption of the Wanapum Basalt, the rate slows to  $0.055 \pm 0.014$  km<sup>3</sup>/yr, whereas during the Wapshilla Ridge Member, the average rate calculated is 1.18 km<sup>3</sup>/yr, with a minimum rate of 0.376 km<sup>3</sup>/yr. However, because our ages for the top and bottom of this voluminous member in a single stratigraphic section overlap, effusion rates were likely far greater than the average values. A potential constraint for the maximum rate can be derived from prior estimates for the minimum duration of the 1,300 km<sup>3</sup> Roza Member to be 14 years (29), and the ca. 100 years or more needed to develop thin redbole horizons (30). Because there are at least 18 (and as many as 28) lava flow units in the Wapshilla Ridge Member (31) and 8 more redboles between the samples we dated, we estimate that peak eruption rates could be as high as 20-40 km<sup>3</sup>/yr for a duration of thousands of years.

The eruptive pulse for the Wapshilla Ridge Member is an order of magnitude higher than *average* effusion rates calculated for other large igneous provinces associated with mass extinction events: 1-2 km<sup>3</sup>/yr for the Deccan Traps (23), 3-5 km<sup>3</sup>/yr for the Central Atlantic Magmatic Province (32), and 1-4 km<sup>3</sup>/yr for the Siberian Traps (33). However, records from other flood basalts do not have the stratigraphic resolution to calculate effusive rates during high flux pulses compared to long-term average rates. More generalized models for the total climatic impact during flood basalt eruption will be dependent on delineating the timing of eruption pulses, such as the Wapshilla Ridge Member, from background fluxes.

## **DISCUSSION**

Our age model provides quantitative constraints that must be satisfied by any geologic or geodynamic model for CRBG volcanism. In particular, the mechanism must be consistent with: (1) eruption duration of ~750 ka from 16.65-15.90 Ma; (2) an average effusion rate of  $0.334 \pm 0.042$  km<sup>3</sup>/yr, with pulses of  $\gg 1$  km<sup>3</sup>/yr; (3) simultaneous eruptions at Steens Mountain and in the Imnaha Basalt vents 300 km away; and (4) an average linear geographic propagation rate of eruption of  $0.37 \pm 0.08$  m/yr to the north, given distances between the vents sourcing Imnaha through Wanapum eruptions. These criteria alone may be currently insufficient to fingerprint a mantle plume or subduction-related origin of the CRBG, both of which allow for eruptions to occur in this time frame (13, 34). The geographic propagation rate of  $0.37 \pm 0.08$  m/yr for CRB volcanism is also compatible with either model: a small plume head has been modeled to spread at 0.2-0.3 m/yr (35), while the proposed slab tear is modeled to propagate at 0.45 m/yr (13). This northward

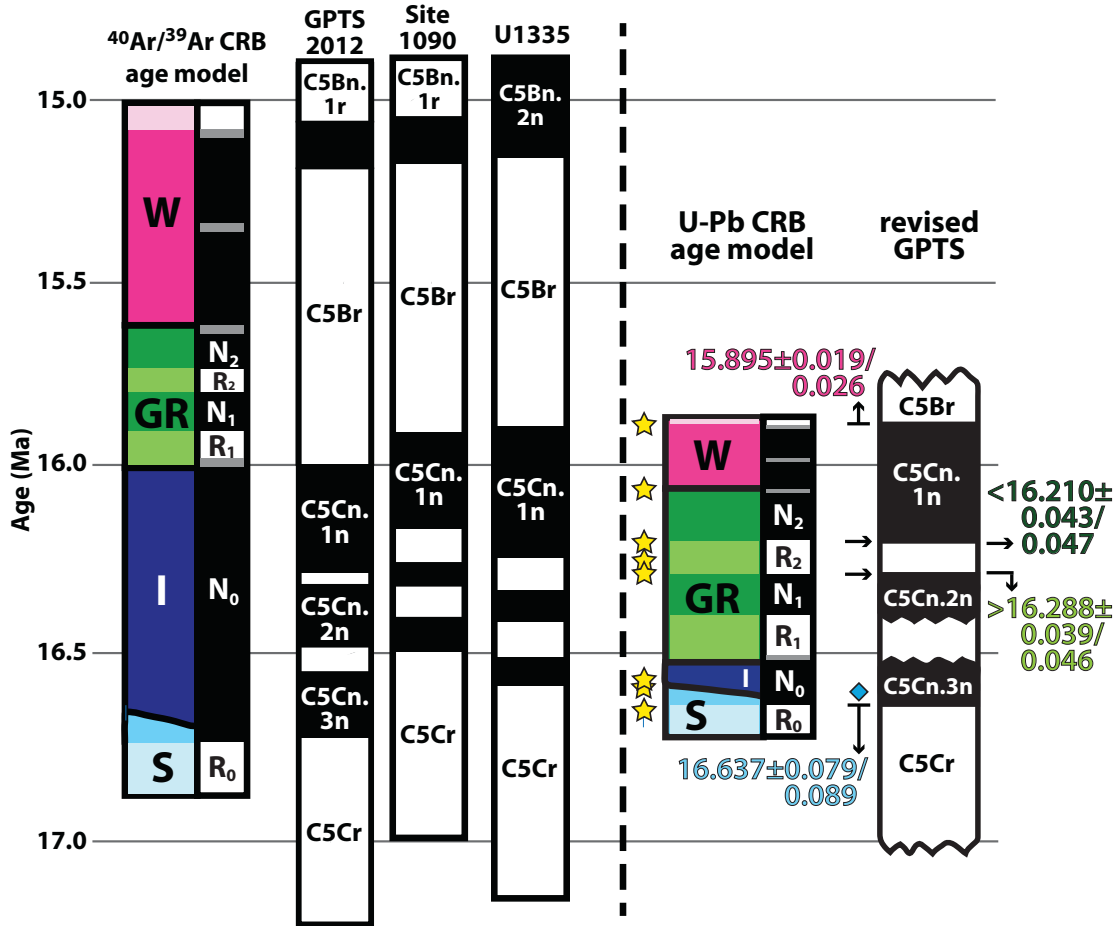
propagation rate is about three times faster than those calculated for the McDermitt and High Rock dike swarms that propagate to the south of Steens Mountain (0.12 m/yr and 0.14 m/yr, respectively) (36), showing that the potential radial propagation from Steens Mountain did not occur at the same velocity radially. Further modeling with our new quantitative constraints is required to better understand the process that allowed for CRBG eruption.

Determining the relative timing of CRBG volcanism and the MMCO requires independent chronologies that are equally precise. However, the early- and middle-Miocene is one of the most problematic periods in the Neogene for establishing precise independent chronologies in marine sediments due to the difficulty in obtaining undisturbed stratigraphic sections that yield reliable magnetostratigraphy, biostratigraphy, astronomical tuning, and radiometric ages (20). All timescales proposed for the middle-Miocene depend directly or indirectly on correlation with the GPTS, for which there are currently several proposals, the most recent being the Geologic Time Scale (GTS) 2012 (20). GTS 2012 was derived from the seafloor anomaly profiles of the Antarctic and Australian plates and assuming a relatively constant spreading rate tuned to give a 23.03 Ma age for the Oligocene-Miocene boundary (20). GTS 2012 rejected an astronomically-tuned record of Mid-Miocene  $\delta^{18}\text{O}$  and magnetostratigraphy from ODP Site 1090 in the subantarctic south Atlantic, whose record extends from the Oligocene-Miocene boundary to ~15.9 Ma, because the tuned record yields ages for chron boundaries that do not meet the assumption of constant seafloor spreading rates in the Pacific (20). The most recent age model for the CRBG (4) attempts to reconcile  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology with GTS

2012. However, the resulting age model is inconsistent with the existing GPTS and is clearly in need of refinement (Fig. 4).

Our new age model for the CRBG permits a more robust correlation of CRBG magnetostratigraphy with existing proposals for the GPTS (Fig. 4). However, this exercise also indicates that some prior proposals for the GPTS, including GTS 2012, are in error. For example, the most recent age model for the CRBG has the Imnaha Basalt, which is entirely normally polarized, erupting through several magnetic reversals and thus is not permissible. Similarly, the existing age model places the Grande Ronde Basalt, which records two reversed and two normal intervals, within a single normal chron. By comparison, in our proposed correlation illustrated in Fig. 4, the Imnaha Basalt erupted entirely during chron C5Cn.3n, while the Grand Ronde Basalt erupted during C5Cn.2r-C5Cn.1n – consistent with observed magnetostratigraphy in the basalts.

Using this baseline correlation with the GPTS, we can refine four proposed reversal ages (Fig. 4). Our ages in the Upper and Lower Steens bracket the “Steens Reversal” (between magnetozones R<sub>0</sub> and N<sub>0</sub>, and chrons C5Cr and C5Cn.3n) which can be conservatively constrained to 16.637±0.079/0.089 Ma (95% confidence intervals given for internal uncertainty/decay constant uncertainty). This estimate compares favorably with the estimate of 16.603±0.028/0.36 Ma obtained through recent <sup>40</sup>Ar/<sup>39</sup>Ar sanidine geochronology (21). Our samples from the base and top of the Wapshilla Ridge Member constrain the timing and provide a minimum duration for C5Cn.1r, to begin no later than 16.288±0.039/0.046, and to end no earlier than 16.210±0.043/0.047 Ma, because the



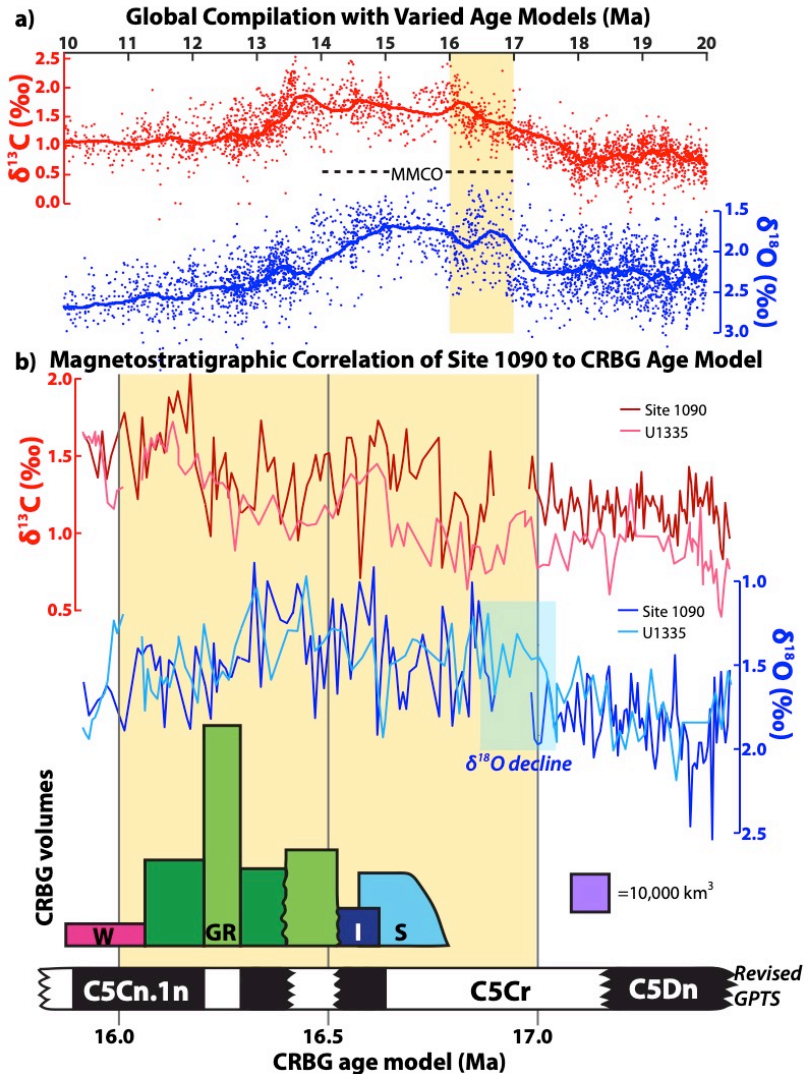
**Fig. 4. Revised CRBG Eruptive Timeline, Magnetostratigraphy, and GPTS Correlation.** U-Pb geochronology suggests a timeline of the eruption for each formation (from Fig. 3) as well as a revised GPTS consistent with CRBG magnetostratigraphy ((1) and references therein). These are compared to the eruptive chronology derived from  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology (4) and different GPTS calibrations (20, 37, 46). Given the magnetic polarity of different stratigraphic members, U-Pb geochronology constrains the age of four different chron boundaries (straight lines), identified with arrows and ages with internal and decay constant uncertainties. Estimated chron boundaries are shown with zigzag lines, and are not yet constrained by geochronology. Lighter shades of color in the stratigraphic column represent reversed polarity intervals in CRBG magnetostratigraphy, also shown by adjacent reversal stratigraphy to the right of each CRBG age model. Stars indicate the youngest zircon ages obtained for each sample in the study, and letters label each formation (S – Steens Basalt; I – Imnaha Basalt; GR – Grande Ronde Basalt; W – Wanapum Basalt). The blue diamond represents the age of the Steens reversal obtained in Mahood & Benson (21), recalculated with the Fish Canyon Sanidine age of Kuiper *et al.* (22), to be  $16.603 \pm 0.028 / 0.36$  Ma, which is consistent with our results.

Wapshilla Ridge Member comprises the majority of volume of the second reversed magnetostratigraphic unit of the Grande Ronde Basalt (R2) (31). The end of C5Cn.1n (N2) is well-constrained by our age of  $15.895 \pm 0.019/0.026$  Ma for the top of the transitionally magnetized Roza Member, which immediately overlies the normally magnetized Frenchman Springs Member, especially given prior estimates that the Roza Member erupted in as little as 14 years (29). Our initial data do not identify any significant hiatuses in eruptions – no more than  $\sim 200$  ka elapse between any two of our samples, during which volcanism is known to be ongoing even though we do not present zircon data from these intervals (Fig. S3). Therefore, high-precision geochronology can be used to bound the ages of magnetically-characterized CRB flows and to further refine the record of middle-Miocene magnetic field reversals. Our proposed GPTS is also consistent with the astronomically-derived age model for the magnetic reversal stratigraphy at Site U1335 in the equatorial Pacific (Fig. 4) (37), indicating an independent verification for our proposed age model for the GPTS.

Given the inconsistencies described above for the GPTS, demonstrating a link between the eruption of the CRBG and the MMCO requires a careful assessment of the age models used to develop proxy records across the MMCO. For example, the  $\delta^{11}\text{B}$  proxy record for  $\text{pCO}_2$  at ODP Site 761 indicates that atmospheric  $\text{CO}_2$  increases at 16.5 Ma (8), which agrees well for our suggested timing of the onset of voluminous Grande Ronde Basalt volcanism. However, the age model for Site 761 (38) depends on biostratigraphic (39) or isotopic events (40) tied to calibrations of the GPTS (41) that we have shown to be inaccurate. Recent work describing the  $\delta^{13}\text{C}$  and  $\delta^{18}\text{O}$  records from IODP Site U1337

identifies the onset of the MMCO at 16.9 Ma (42), which precedes our timing for all CRBG eruptions. This site has an age model derived from an astronomical solution (43) without radiometric age control or a magnetostratigraphy, thus adding subjectivity to the chosen isotopic tie points used to calibrate the tuning (44) and making correlation with our eruptive record difficult.

One way forward is to use proxy records from sites that contain reliable magnetostratigraphy (37, 45). Benthic  $\delta^{18}\text{O}$  values – a proxy for deep-ocean temperature - from Sites 1090 (46) and U1335 (37) (Fig. 5) indicate that the decline in  $\delta^{18}\text{O}$  values began during what is interpreted as C5Cr, reaching a nadir (the MMCO) during C5Cn.3n-C5Cn.1r. While it is currently difficult to validate the identification of C5Cr from site 1090 given potential for hiatuses in the record, it is corroborated by the astronomical model of U1335 and is interpreted to be the same chron in which CRB eruptions began with the Lower Steens Basalt. Although the absolute timing of the onset of the MMCO cannot be confirmed by our data, the astronomically tuned record from U1335 compared to our geochronology show that the decrease in  $\delta^{18}\text{O}$  preceded the eruption of Steens Basalt lava flows by 100-200 ka. CRBG volcanism may have played a role in eliciting global warming through cryptic degassing of  $\text{CO}_2$  as magma migrated through dike swarms prior to surface eruptions (7). Alternatively, the apparent mismatch between the onset of the CRBG and the MMCO may indicate that the two events are unrelated. Regardless, the  $\delta^{18}\text{O}$  minimum appears coeval with the eruption of the Grande Ronde Basalt, suggesting that a link may exist. Further work that refines age models for climate proxy records across the MMCO and investigates rates of eruptions for the CRBG is



**Fig. 5. Correlation of the Columbia River Basalt Group with the Mid-Miocene Climate Optimum.** (A) A compilation of proxy records exhibiting the MMCO (47), with age constraints as reported in each study. Although ages are susceptible to uncertainties in the Mid-Miocene timescale, the magnitude of the isotopic signals are not. (B) In order to compare zircon geochronology results for CRBG eruptions to paleoclimate proxy records of the MMCO, it is necessary to bypass age models tied to outdated calibrations of the GPTS. The robust magnetostratigraphy of Sites 1090 (45, 46) and U1335 (37) allows for correlation of these isotopic records to our CRBG eruption chronology and refined GPTS. The area of each colored rectangle corresponds to the volume of each formation (*I*) (*S* – Steens Basalt; *I* – Imnaha Basalt; *GR* – Grande Ronde Basalt; *W* – Wanapum Basalt), with width constrained by zircon ages (slanted boundary indicates that the onset of Steens Basalt volcanism is not yet constrained); polarity of the basalt flows is taken from Reidel (*I*) and references therein. Yellow shading compares global proxy data at 17-16 Ma (lacking an age model based on absolute geochronology) with volcanic events occurring 17-16 Ma, while the light blue shading highlights the onset of the MMCO in both records with the drop in  $\delta^{18}\text{O}$ .

required before it can be determined if the CRBG caused the MMCO. While our work constrains the age of the top of chron C5Cr, there are not yet absolute age constraints for either the bottom of C5Cr, or for the onset of the MMCO. Because the record for U1335 has an astronomical age model constrained by isotopic correlations with Site U1337 (37, 42), and does not have an absolute age defining the base of chron C5Cr, a tighter correlation of the CRBG and MMCO could be observed, particularly if the chron began later in time than is currently proposed. These uncertainties in the timing of this magnetic field reversal and the beginning of the MMCO must be resolved to better assess if the CRBG played a causative role in the MMCO.

Despite uncertainties present in Mid-Miocene age models, global proxy data (47) indicate that the MMCO continued for >1 Ma after the cessation of the majority of CRBG volcanism (Fig. 5). The time lag between the cessation of volcanism and a return to cooler climatic conditions could be understood as a consequence of the long response time of negative feedbacks within the global carbon cycle that regulate atmospheric CO<sub>2</sub> and Earth's temperature on geologic timescales. These feedbacks include interactions between temperature, the chemical weathering of continental silicate minerals, and the burial of CO<sub>2</sub> in marine carbonate sediments (48). While the sensitivity of the silicate weathering feedback remains poorly understood, recent estimates for response times vary from ~200-500 ka (49) and are consistent with the stabilization of atmospheric CO<sub>2</sub> (i.e. return to baseline conditions) on ~1 Ma timescales.

Our age model of CRBG emplacement shortens the duration of volcanism from 1.9 Ma (4) to 750 ka and correlates the onset of CRBG volcanism and the onset of the MMCO to within ~100 ka. A shorter duration of CRBG volcanism implies higher average CO<sub>2</sub> emissions and higher peak CO<sub>2</sub> concentrations during volcanism, to be compared with marine proxy records. However, current proxy records for atmospheric CO<sub>2</sub> during the MMCO are too coarse for a close comparison to the eruptive history of the CRBG, further inhibiting the ability to assess whether or not the CRBG caused the MMCO. Furthermore, establishing a quantitative link between CRBG volcanism and changes in the global carbon cycle and atmospheric CO<sub>2</sub> is hampered by uncertainties in the amount of CO<sub>2</sub> emitted by flood basalts from dissolved mantle carbon in addition to ‘cryptic’ sources, such as organic or inorganic sediments volatilized through contact with basaltic flows or sills (7). Armstrong McKay *et al.* (7), using a main phase CRBG eruptive duration of 900 ka, model that 4090-5670 Pg of emitted carbon can yield the observed changes in benthic  $\delta^{13}\text{C}$  and atmospheric CO<sub>2</sub>, although this amount includes a substantial component of cryptic degassing beyond the expected volatile release of subaerial basalt flows. Future studies should focus on further revision of the Mid-Miocene timescale and a high-resolution climate proxy record spanning the 700 ka duration of CRBG volcanism to explore the extent to which the timing of CRBG volcanism agrees with changes in atmospheric CO<sub>2</sub>. Such studies will lead to an improved understanding of the MMCO, more general models linking volcanism to climate change, and could be crucial for understanding why some flood basalts apparently result in mass extinctions and others do not.

## **MATERIALS AND METHODS**

Methods are as described in Schoene *et al.* (23) and Samperton *et al.* (50).

### **Zircon separation and preparation**

Zircons were separated from their host rock through standard methods of crushing, gravimetric-, and magnetic-separation techniques using a Bico Braun “Chipmunk” Jawcrusher, disc mill, hand pan, hand magnet, Frantz isodynamic separator, and methylene iodide. Zircons from the least magnetic and most dense mineral separate were transferred in bulk to quartz crucibles and annealed in a muffle furnace at 900°C for 48 hours after Mattinson (51). After annealing, 20-40 zircon grains from each sample were photographed (Fig. S2) and picked in reagent-grade ethanol for analysis. Given the low radiogenic Pb content of the samples, cathodoluminescence images were not obtained. Euhedral grains with a range of morphologies were selected, while those with visible cracks, inclusions, and cores were avoided. Individual grains were transferred using stainless steel picking tools to separate 3-mL Savillex Hex beakers containing distilled acetone and taken to the clean lab for analysis.

### **U-Pb zircon ID-TIMS analysis**

Single zircon grains were loaded into 200 uL Savillex “micro”-capsules with 100  $\mu$ L 29 M HF + 15  $\mu$ L 3N HNO<sub>3</sub> for a single leaching step in high-pressure Parr bombs at 185°C for 12 h to remove crystal domains affected by Pb loss (51). Grains were rinsed post-leaching in 6 N HCl, MQ H<sub>2</sub>O, 3N HNO<sub>3</sub>, and 29 M HF prior to spiking with

EARTHTIME ( $^{202}\text{Pb}$ - $^{205}\text{Pb}$ - $^{233}\text{U}$ - $^{235}\text{U}$  tracer and addition of 100  $\mu\text{L}$  29 M HF + 15  $\mu\text{L}$  3N  $\text{HNO}_3$  (52, 53). Zircons were then dissolved to completion in Parr bombs at 210°C for 48 h. Dissolved zircon solutions were subsequently dried down, dissolved in 100  $\mu\text{L}$  6N HCl, and converted to chlorides in Parr bombs at 185°C for 12 h, after which solutions were dried again and brought up in 50  $\mu\text{L}$  3N HCl. The U-Pb and trace element aliquots were then separated by anion exchange chromatography using 50  $\mu\text{L}$  columns and AG-1 X8 resin (200-400 mesh, chloride from Eichrom) (54), and dried down with a microdrop of 0.015 M  $\text{H}_3\text{PO}_4$ . The dried U and Pb aliquot was loaded in a silica gel emitter (55) to an outgassed zone-refined Re filament.

Isotopic determinations were performed using an IsotopX PhoeniX-62 thermal ionization mass spectrometer (TIMS) at Princeton University, with Pb analysis performed in peak-hopping mode on a Daly-photomultiplier ion-counting detector. A correction for mass-dependent Pb fractionation was applied in one of two ways. For double-Pb spiked analyses ( $^{202}\text{Pb}$ - $^{205}\text{Pb}$ , ET2535), a cycle-by-cycle fractionation correction was calculated from the deviation of measured  $^{202}\text{Pb}/^{205}\text{Pb}$  from the known tracer  $^{202}\text{Pb}/^{205}\text{Pb}$  ( $0.99924 \pm 0.00027$  ( $1\sigma$ )). For single-Pb spiked analyses ( $^{205}\text{Pb}$ , ET535), a Pb fractionation of  $0.182 \pm 0.041\%$ /amu was used, as determined by repeat measurements of NBS982 at Princeton. A Daly-photomultiplier deadtime of 28.8 ns was used, as determined by repeat measurements of NBS standards. Corrections for interfering isotopes under masses 202, 204, and 205 were made cycle-by-cycle by measuring masses 201 and 203 and assuming they represent  $^{201}\text{BaPO}_4$  and  $^{203}\text{Tl}$  and using natural isotopic abundances to correct for  $^{202}\text{BaPO}_4$ ,  $^{204}\text{BaPO}_4$ ,  $^{205}\text{BaPO}_4$ , and  $^{205}\text{Tl}$ .

UO<sub>2</sub> measurements were performed in static mode on Faraday cups with a bulk U fractionation correction calculated from the deviation of measured <sup>233</sup>U/<sup>235</sup>U from the known tracer <sup>233</sup>U/<sup>235</sup>U (0.995062±0.000054 (1σ)), and an oxide composition of <sup>18</sup>O/<sup>16</sup>O of 0.00205 was used (56). Data reduction was performed using the programs Tripoli and U-Pb Redux (57, 58) and the decay constants of Jaffey *et al.* (59). All Pbc was attributed to laboratory blank with a mean isotopic composition determined by total procedural blank measurements (see Table S1 for values). Two different blank models were generated to assess data collected before (OC) and after (SF) January 2017, when the laboratory began heating side filaments before collecting data on the mass spectrometer, which was found to reduce interferences. Uncertainties in reported U-Pb zircon dates are at the 95% confidence level and exclude tracer calibration and decay constant uncertainties. Correction for initial <sup>230</sup>Th disequilibrium in the <sup>206</sup>Pb/<sup>238</sup>U system was made on a fraction-by-fraction basis by estimating (Th/U)<sub>magma</sub> using (Th/U)<sub>zircon</sub> determined by TIMS and a mean (Th/U)<sub>zircon-magma</sub> partition coefficient ratio of 0.19±0.11, which encompasses the range of values for (Th/U)<sub>zircon-magma</sub> partition coefficients obtained from glasses from a variety of volcanic settings (60). Uncertainties for the resulting (Th/U)<sub>magma</sub> were also calculated on a fraction-by-fraction basis, propagating the uncertainty in the (Th/U)<sub>zircon-magma</sub> partition coefficient. Overall, these corrections for <sup>230</sup>Th disequilibrium affect our results by no more than ±10 ka, compared to an alternative approach using a constant (Th/U)<sub>magma</sub> of 3.5±1.0 (see Supplement).

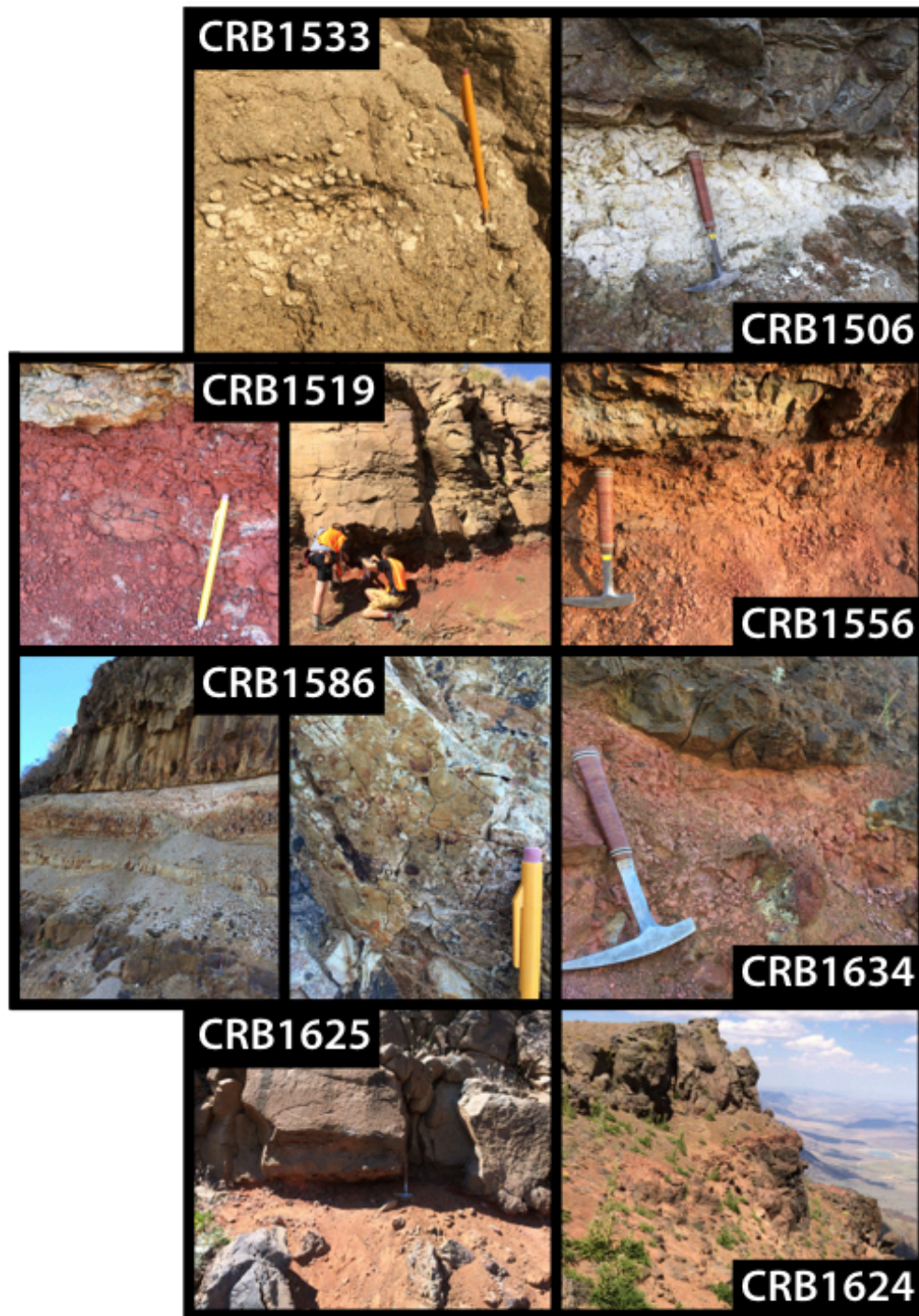
## ACKNOWLEDGMENTS

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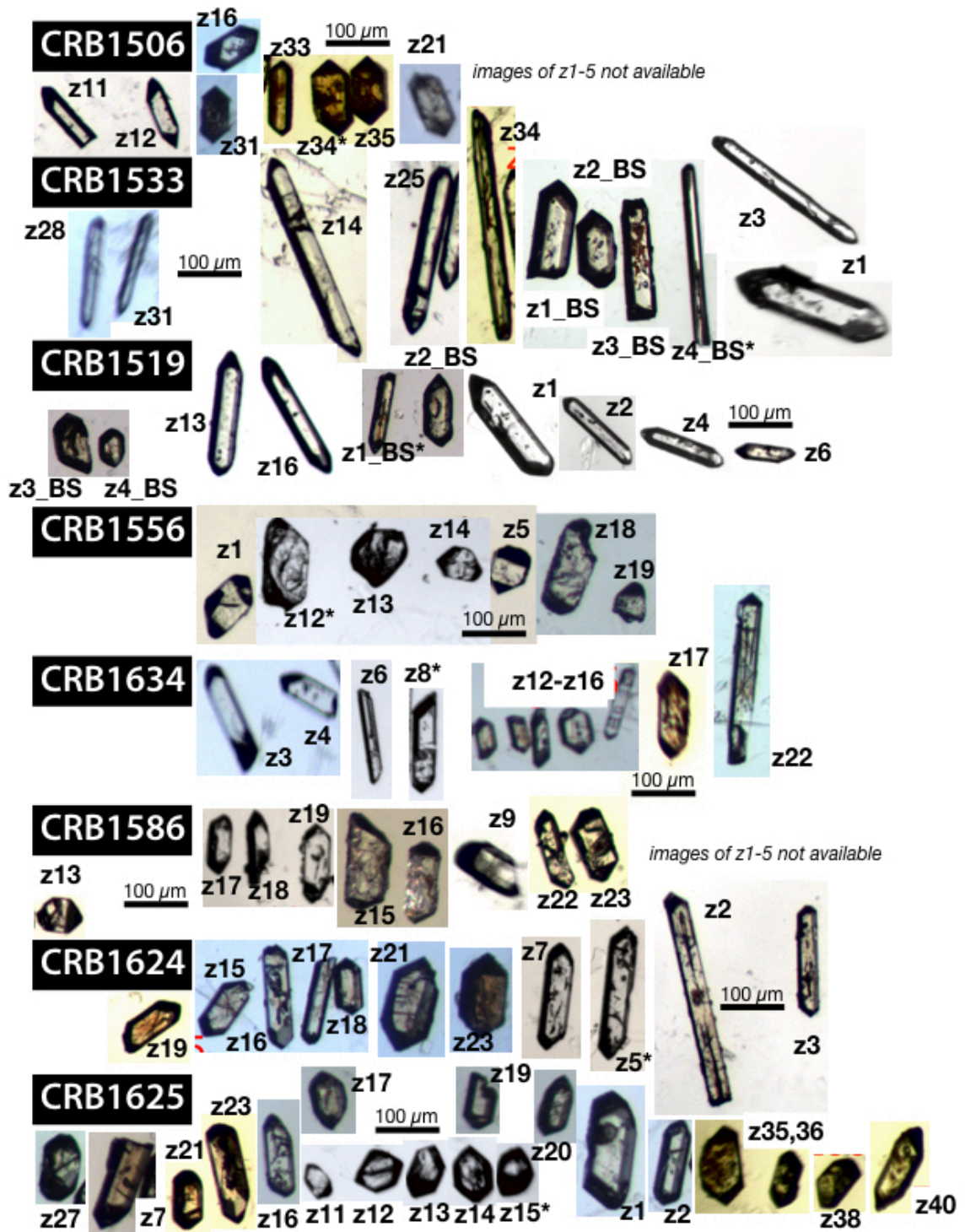
## SUPPLEMENTAL INFORMATION

### **Sample Descriptions**

Samples dated in this study were collected from roadcuts or natural exposures in Washington, Oregon, and Idaho in summers 2015 and 2016. Detailed sample descriptions are provided here, in stratigraphic order from oldest to youngest. Outcrop photographs are provided in Fig. S1, and zircon photographs are provided in Fig. S2.



**Fig. S1. Geochronology Sample Photos.** Outcrop-scale and/or hand-sample scale photos of each geochronology sample are provided here, with stratigraphic younging from bottom to top (Photo credit: Jennifer Kasbohm, Princeton University).



**Fig. S2. Zircon Photos.** Optical images of zircons under transmitted light are presented here, with stratigraphic younging from bottom to top. Zircons present a range of morphologies, but the majority are euhedral with sharp crystal terminations, indicating an igneous rather than detrital origin. The zircon yielding the youngest, most precise analysis for each sample is starred.

**CRB1625** (42.67542°N, 118.68724°W, elevation 2255 m)

This sample was collected from a ~0.5 m thick redbole between two Lower Steens Basalt flows, (based on the stratigraphy of Johnson *et al.* (60)) on the western side of Steens Mountain. The fine red sediment overlay a brecciated flow top and contained abundant vitreous microphenocrysts, black round lithic fragments, and subangular fragments of basaltic pumice up to 1 mm in size.

Fewer than 100 zircons were separated from this sample, and many of these grains are rounded and appear detrital. Some grains are euhedral, and ranged from equant to a high aspect ratio. Many grains are tinted orange, while some are clear. Forty grains were selected for analysis, and 19 were successfully dated. For this sample and the other samples described below, grains that were not successfully dated were lost at some stage of zircon chemistry prior to dating, or were dated and either did not fall on the Concordia line or exhibited a ratio of radiogenic Pb to common Pb that was  $\leq 1$ . Six of these grains were ca. 16.7 Ma, with a dispersion of 120 ka, while the other 13 are inherited. Both the Mid-Miocene and inherited grains exhibited a range of morphologies. The youngest grains were often euhedral, and ranged from equant to an aspect ratio of at least 4:1. While some of the young grains were glassy and transparent, others were opaque. While a few of the analyses exhibited elevated common Pb content ( $>1$  pg), others had low common Pb ( $<0.3$  pg) but also low radiogenic Pb content ( $<1$  pg), yielding generally less precise zircon ages for this sample than for the others in this study.

**CRB1624** (42.66626°N, 118.56479°W, elevation 2966 m)

This sample was collected from a ~0.5 m thick redbole interbedded between Upper Steens Basalt flows (60) at the East Rim Lookout on Steens Mountain. The sampled horizon was a fine pink sediment infilling a brecciated flow top, and contained abundant vitreous microphenocrysts with few dark round lithic fragments.

Hundreds of zircons were obtained from this sample, with a range of morphologies.

Generally, grains were angular to subangular, with fewer round detrital grains. The grains ranged from equant to higher aspect ratios, though few were acicular. Most of the grains are orange, while a few are clear and glassy. Twenty-three grains were selected for analysis, and 11 were successfully dated. The youngest grains appear to be the most euhedral, and range in size from <100 to over 300  $\mu\text{m}$ . All of the grains were found to be ca. 16.6 Ma, with a dispersion of <70 ka. The precision of these analyses is attributed to high radiogenic Pb content (up to 34 pg) of the grains and low common Pb content (often <0.3 pg) in the analyses.

**CRB1586** (44.83067°N, 116.90138°W, elevation 641 m)

This sample was collected from a ~0.5 m thick bed of lapilli tuff interbedded between columnar Imnaha Basalt flows on route 71 south of Brownlee Dam in Idaho.

Accretionary lapilli are mm-cm scale and exhibit concentric banding around lithic nuclei.

Fewer than 50 zircons were separated from this sample, and are found to be glassy, somewhat blocky, and ranging in morphology from equant to tabular. Most of the grains are around 100  $\mu\text{m}$  in length. Twenty-three grains were selected for analysis, and of these, 14 were successfully dated. One grain was found to be inherited, while the other 13 are dated to  $\sim 16.6$  Ma, with a dispersion of 120 ka. The youngest and most precise grains are among the largest analyzed, and have a high radiogenic Pb content (1-6 pg).

**CRB1634** (46.05072°N, 117.23906°W, elevation 538 m)

This sample was collected from a redbole in the lower flows of the Wapshilla Ridge Member of the Grande Ronde Basalt, on Rattlesnake Grade in southeastern Washington. The redbole infills topography on the underlying brecciated flow top, with a maximum thickness of 0.3 m, but pinches out over a few meters width. The redbole contains a few mm-scale light and dark lithic fragments, with some vitreous phenocrysts.

Hundreds of zircons were obtained from this sample, ranging in size from 50-250  $\mu\text{m}$ . Most are orange in color but a few are clear. Half of the zircons presented an acicular morphology, 20% appeared equant, and the rest have a medium aspect ratio. Twenty-four zircons were selected for analysis, and eleven were successfully dated. All zircons were found to be ca. 16.3 Ma, with a dispersion of 160 ka. The youngest grains appear somewhat wide, clear, and euhedral, and the most precise analyses came from zircons with the greatest amount of radiogenic Pb (1-2 pg).

**CRB1556** (46.08543°N, 117.17870°W, elevation 1145 m)

This sample was collected from the same stratigraphic section as CRB1634, from a 0.6 m thick redbole between lava flows of the Meyer Ridge Member, immediately overlying the Wapshilla Ridge Member. The horizon was most coherent in its upper half, and displayed few vitreous phenocrysts and rare lithics.

The sample yielded 19 zircons, and all were picked for analysis; 7 were successfully dated. The zircons were either <100  $\mu\text{m}$  and equant or larger and more tabular. A few were euhedral with pointy edges, while others appeared fragmented at the edges. The youngest, most precise analyses came from the largest grains. Even though these grains were not euhedral, they possessed the greatest amount of radiogenic Pb (1-2 pg). The grains exhibit a dispersion of 150 ka around ca. 16.3 Ma.

**CRB1519** (46.44171°N, 117.39066°W, elevation 701 m)

This sample was collected from a redbole found under a lava flow of the Meyer Ridge Member and overlying a lava flow Wapshilla Ridge Member, representing the same stratigraphic interval as CRB1556 but found 44 km away on US-12 east of Pomeroy, WA. The sample is fine-grained, with abundant vitreous microphenocrysts and few angular lithic fragments.

Hundreds of zircons were separated from this sample, and they appear mostly clear and glassy, with a few orange grains. Most present typical aspect ratio, while 10% are acicular and a few grains are equant. Many grains are subangular, with pointy tips slightly worn down. Twenty-one grains were selected for analysis, and 10 were

successfully dated. Two of the zircons analyzed were inherited, and appear somewhat opaque; five zircons were ca. 16.2 Ma but an age dispersion of 400 ka, outside the range of analytical uncertainty. The youngest grains each have one euhedral tip, are longer than 100  $\mu\text{m}$ , and the most precise analyses were for zircons with a higher radiogenic Pb content (2-4 pg).

**CRB1533** (46.95243°N, 119.99783°W, elevation 227 m)

This sample was collected from 2 kg of 1-10 cm-scale pumice clasts embedded in the volcanoclastic sediments of the Vantage Interbed type locality in Vantage, WA (Stop 7 in Tolan *et al.* (61)). Phenocrysts in the pumice contained quartz and sanidine, and the sampled horizon consisted of 1.4 m of the total 5.6 m of the Vantage Interbed exposed at the outcrop. The Vantage Interbed lies over the Basalt of Museum of the Sentinel Bluffs Member of N2 of the Grande Ronde Basalt, and under the Basalt of Ginkgo of the Frenchman Springs Member of the Wanapum Basalt.

Several thousand zircons were obtained from this sample, and all are clear, prismatic, and euhedral. The zircons range in size from 50-300  $\mu\text{m}$ , and about 10% are equant grains, while 10% of the grains are acicular. Forty zircons were selected for analysis, and 11 of these were successfully dated, with 9 grains found younger than 17 Ma. The age dispersion of these samples is greater than 500 ka, well beyond analytical uncertainty, suggesting pre-eruptive crystallization. The youngest grains appear to be the most acicular in morphology, and the most precise analyses are due to high radiogenic Pb content of 5-15 pg.

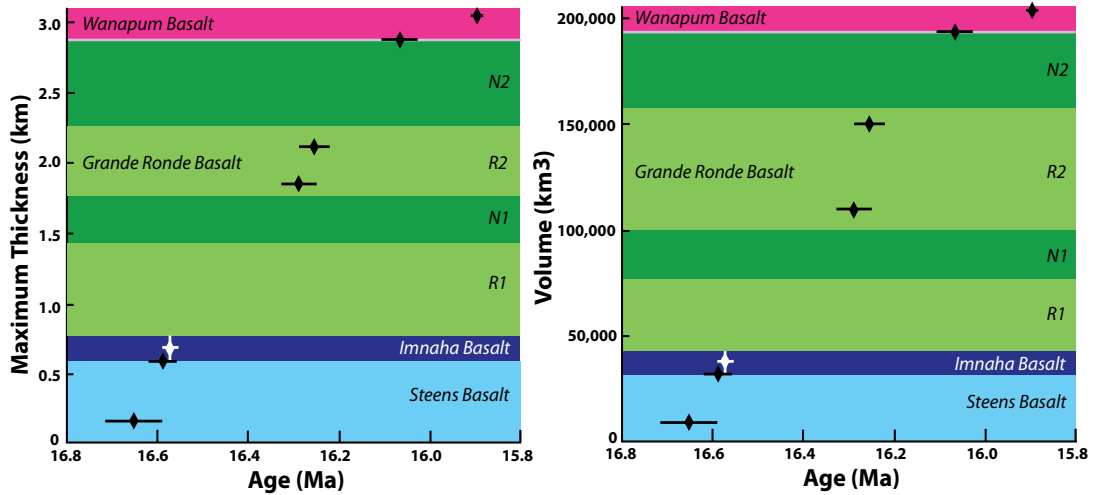
**CRB1506** (46.73914°N, 117.75500°W, elevation 470 m)

This sample was collected from 0.3 m of a fine white crumbly ash, with few round lithic fragments and glassy phenocrysts, interbedded between the overlying Basalt of Lolo and the underlying Basalt of Rosalia of the Priest Rapids Member of the Wanapum Basalt, on WA-127 southeast of Endicott, WA.

Hundreds of zircons were obtained from this sample, most of which are clear and subangular to subrounded. While a few zircons were angular, none were acicular. Thirty-five grains were selected for analysis, and 10 were successfully dated. Four of these were inherited, and the remaining six grains have a uniform age distribution within  $2\sigma$  uncertainty, of ca. 15.9 Ma. The youngest and most precise dates were obtained from somewhat opaque, orange-tinted zircons that were euhedral, and had high radiogenic Pb content of 11-40 pg.

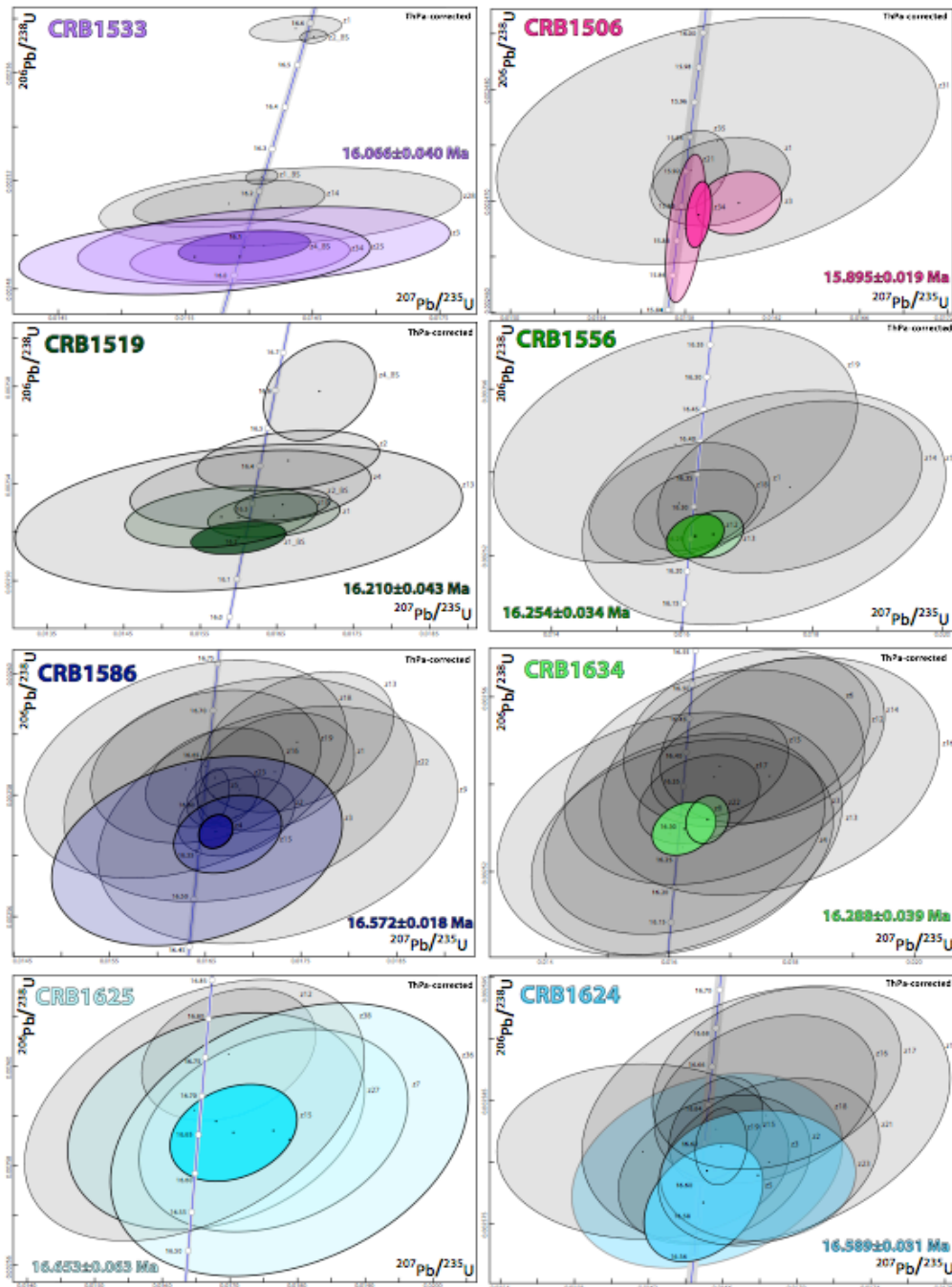
### **S2 U-Pb Age Interpretations**

Given the physical characteristics of both rock samples and zircons, the geochronology samples for this study are interpreted to be volcanic in origin, and deposited by unrelated regional silicic volcanism during cessations in CRBG volcanism. The presence of phenocrysts, lithic fragments, and fragments of basaltic pumice found at the hand sample scale are consistent with ash deposits, and the euhedral and prismatic appearance of the zircons are consistent with magmatic textures, with little evidence for rounding seen in alluvial or eolian grains.



**Fig. S3. Thickness and Volume versus Age Plots.** Detailed area and volume estimates for each member of the CRBG stratigraphy allows for plots of cumulative maximum thickness and volume versus age. Youngest zircon ages with  $2\sigma$  uncertainty for the samples dated in this study are plotted here. Cumulative thickness and volume are color-coded by CRBG formation as labeled on the plots.

Full U-Pb isotope results are given in Table S1, maximum thickness and volume versus age plots are given in Fig. S3, and Concordia plots for each sample are given in Fig. S4. All dates are presented with  $2\sigma$  uncertainty, which represents internal errors only. In Table S2, alternative age interpretations are also given with  $2\sigma$  uncertainties of  $\pm X/Y/Z$ . X is used for most of the geochronological uncertainty described in this paper, and indicates internal uncertainties only for comparison with U-Pb dates from labs using ET-(2)535 tracer solution. Y also incorporates tracer calibration uncertainties for comparison with other U-Pb dates determined with different tracer solution. Z includes full systematic uncertainties, including decay constants, to allow for comparison with other radioisotopic dates or astrochronologically-determined timescales that may be tied to other radioisotopic dates that are not derived from the U-Pb system (62, 63).



**Fig. S4. Concordia Plots for U-Pb ID-TIMS Geochronological Data.** U-Pb isotopic data for each analysis is available in Table S1. Each ellipse is labelled and represents a zircon analysis, with the width of the ellipse representing  $2\sigma$  uncertainty. The red ellipses are those analyses that are included in the “Youngest Few Zircons” weighted means described in Table S2, while the gray ellipses are not included in those weighted means. The shading around the Concordia line represents uncertainties in the U decay constants. Almost all ellipses overlap with Concordia, indicating closed-system behavior.

The ages we present in this study are influenced by how we dealt with the issue of Th/U disequilibrium in zircon, and our decision to present the single youngest, most-precise analysis as the age of each ashbed, rather than weighted means. Both of these decisions are discussed below, and ultimately, neither interpretation substantially affects our major conclusions about the timing and duration of CRBG eruptions.

### **Th/U disequilibrium correction in zircon**

During zircon crystallization,  $^{238}\text{U}$  is preferentially incorporated into the crystal lattice over  $^{230}\text{Th}$ , an intermediate daughter product, causing the system to depart from secular equilibrium and ages to be underestimated. Often, a minimal correction is made to address this fractionation. Either zircons are assumed to crystallize from a magma with a uniform (Th/U), or a uniform partition coefficient between Th and U from the liquid is assumed, and then the (Th/U) of the magma is calculated on a fraction by fraction basis, using the model (Th/U) of each zircon determined from the  $^{208}\text{Pb}/^{206}\text{Pb}$  ratios (64). Given the likelihood that the zircons in this study were crystallized from a variety of different magmatic systems, we prefer the constant partition coefficient approach for correcting Th/U disequilibrium. A recently published, comprehensive study (59) measures partition coefficients in zircon-glass pairs from a range of volcanic settings; volcanic glasses are assumed to display the same partitioning as the magma from which they crystallize. All measurements of Th/U partitioning in the study fell in the range of 0.06-0.3, so we use a conservative estimate of  $0.19 \pm 0.11$  ( $2\sigma$ ) to calculate  $(\text{Th}/\text{U})_{\text{magma}}$  for each zircon, using the  $^{208}\text{Pb}/^{206}\text{Pb}$  obtained for each zircon during mass spectrometry. To assess the impact of this correction, we also reduce our youngest zircon ages (upon which our

interpretations depend) with a constant  $(\text{Th}/\text{U})_{\text{magma}}$  of  $3.5 \pm 1.0$  ( $2\sigma$ ), which encompasses the majority of igneous liquids (Table S2). We find that our preferred interpretation with a constant Th/U partition coefficient adjusts our dates by no more than 10 ka, and adds no more than 5 ka of uncertainty to each age.

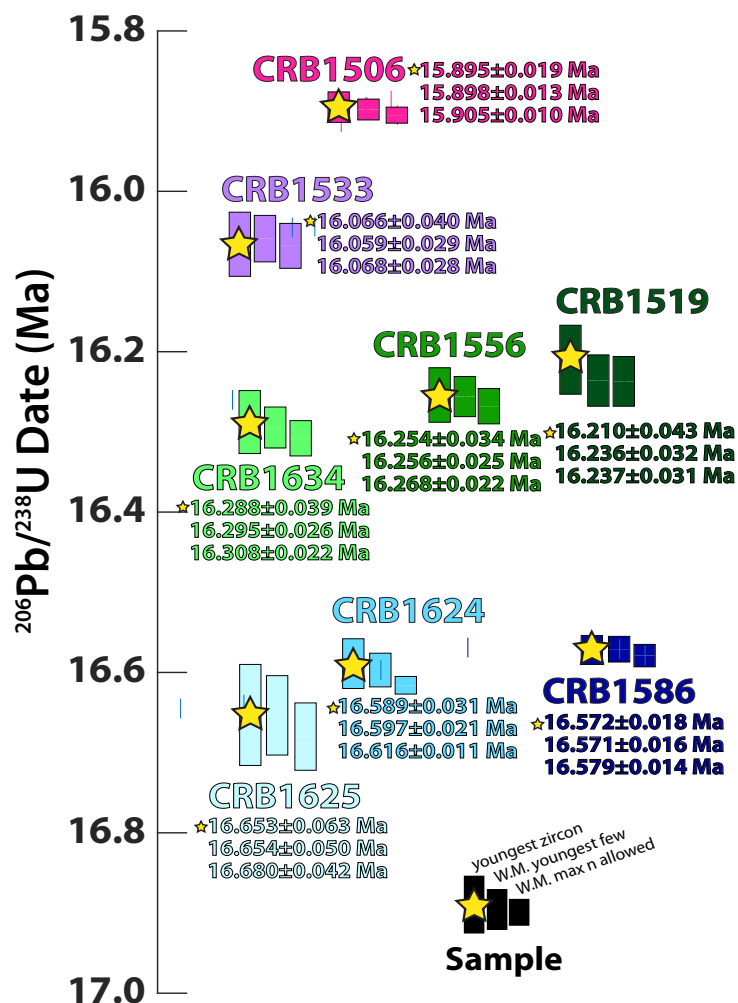
### **Interpretation of zircon crystallization age spectra**

The zircons dated from each geochronology sample displayed a dispersion in ages ranging from 40-500 ka (apart from inherited grains). We interpret this as geological scatter caused by pre-eruptive zircon crystallization or incorporation of zircons from older material in the same volcanic system (23), because the dispersion in most cases goes beyond analytical uncertainty. Therefore, the zircon that crystallized most recently should best time the eruption of the volcanic ash, and for this reason we interpret the youngest, most precise zircon dates as representing the age of the horizons in this study. Although Pb loss in zircons may sometimes cause U-Pb dates to be biased too young, chemical abrasion on young zircons nearly eliminates this effect. We find the pattern in our dataset of younging ages with increasing height in the CRB stratigraphy as further evidence that Pb loss does not affect our conclusions, as its effects would vary with grain size and U-content, and not systematically with age.

Other geochronological studies often use a weighted mean of several zircon dates to constrain the age of a sample. This approach yields dates with lower uncertainty than the single crystal approach as well as greater assurance that the resulting age is not biased by a young outlier, but should only be used for homogeneous age populations where the

only source of scatter is analytical uncertainty, which is not the case for all of our samples, and difficult to justify in most U-Pb datasets even if they overlap within analytical uncertainty. Additionally, including zircons beyond the youngest grain in the final age of the sample may bias the resulting age too old as a result of pre-eruptive crystallization. To assess how well the analytical uncertainty can explain the observed dispersion of crystallization ages, the mean square of weighted deviates (MSWD) may be calculated, and should be  $\sim 1$ , with deviance from 1 varying with the number of analyses included in the weighted mean (65). However, a dataset may still be subject to subtle geologic dispersion, even with an MSWD near 1 (64), resulting in weighted means that are biased too old.

We compare the single crystal ages presented in this study to weighted mean ages calculated for each sample in Table S2 and Fig. S5. First, we calculate the weighted mean for the youngest few zircons, whose dates overlap with the youngest date, where slight offsets may be caused by analytical uncertainty. We also calculate weighted mean ages using the maximum number of grains allowed to produce an acceptable MSWD near 1. We find that the more grains that are included in the weighted mean, the ages are biased older, though are more precise. Ultimately, as seen in Table S2 and Fig. S5, the decision to use the age of single crystals rather than weighted means ages does not substantially offset our ages, and does not have a major bearing on any of the conclusions presented in this paper. The single crystal approach appears to be the most conservative because it results in larger uncertainty for each age, while overlapping with the weighted mean ages.



**Fig. S5. Alternate Age Interpretations.** Our preferred interpretation of single crystals representing the eruptive age of each sample does not substantially offset our results from using weighted mean ages. For each sample, we compare the age of the youngest sample to the a weighted mean age calculated from the youngest few grains, and to a weighted mean age calculated using the maximum number of grains that yield an acceptable MSWD near 1. Even though ages from single crystals exhibit higher  $2\sigma$  uncertainty, we prefer the youngest zircon interpretation to avoid the effects of pre-eruptive zircon crystallization, as the weighted mean ages all appear biased slightly older. Calculated dates using the different interpretations are given in Table S2.

### Comparing with $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology

When compared to the most recent  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology results (20) for the Steens Basalt, we find a similar duration (150 ka compared with 210 ka) but timing 100 ka earlier. However, when the  $^{40}\text{Ar}/^{39}\text{Ar}$  ages are recalculated through the method of Renne

*et al.* (63) using the more recent Fish Canyon sanidine age of 28.201 Ma (21) instead of 28.02 Ma (63), the recalculated range of 16.75-16.54 Ma matches favorably with our results.

**Table S1. U-Pb Isotopic Data.** Data acquired by CA-ID-TIMS is presented following the references, with various corrections as specified in the notes beneath the table.

sample	Youngest Zircon										Weighted Means												
	zircon	age	const. partition coefficient			constant Th/U <sub>magma</sub>			Youngest Few Zircons				Maximum n allowed for MSWD = 1										
			uncertainty			uncertainty			addtnl zircons	n	uncertainty			MS WD	addtnl zircons	n	age	uncertainty			MS WD		
			X	Y	Z	age	X	Y			Z	X	Y					Z	X	Y		Z	
CRB1625	z15	16.653	0.063	0.071	0.073	16.655	0.062	0.070	0.072	7,27,36	4	16.654	0.050	0.057	0.059	0.018	al	6	16.680	0.042	0.052	0.055	0.82
CRB1624	z5	16.589	0.031	0.032	0.037	16.589	0.029	0.031	0.035	18,23	3	16.597	0.021	0.023	0.029	0.26	all	11	16.616	0.011	0.014	0.023	0.92
CRB1586	z4	16.572	0.018	0.018	0.026	16.582	0.013	0.014	0.023	3,15	3	16.571	0.016	0.017	0.024	0.086	2,9,23	6	16.579	0.014	0.015	0.023	0.94
CRB1634	z8	16.288	0.039	0.043	0.046	16.294	0.038	0.041	0.045	22	2	16.295	0.026	0.030	0.035	0.25	all -15	10	16.308	0.022	0.029	0.034	1.1
CRB1556	z12	16.254	0.034	0.037	0.041	16.264	0.032	0.035	0.039	13	2	16.256	0.025	0.029	0.033	0.014	all	7	16.268	0.022	0.027	0.032	0.88
CRB1519	z1_BS	16.210	0.043	0.044	0.047	16.208	0.043	0.043	0.046	1,16	3	16.236	0.032	0.032	0.037	1.6	13	4	16.237	0.031	0.032	0.036	1.1
CRB1533	z4_BS	16.066	0.040	0.040	0.043	16.065	0.038	0.039	0.042	3,25,34	4	16.059	0.029	0.030	0.035	0.19	28	5	16.068	0.028	0.030	0.034	1.3
CRB1506	z34	15.895	0.019	0.020	0.026	15.904	0.015	0.017	0.024	3,21	3	15.898	0.013	0.014	0.022	0.26	1,35	5	15.905	0.010	0.012	0.021	1.1

\*\*preferred interpretation\*\*

**Table S2. Alternate Age Interpretations.** We compare our preferred data interpretation of using the youngest, most precise zircon date for the age of the sample, with a constant Th/U partition coefficient to alternative interpretations. The youngest zircon age with a constant partition coefficient shows no more than 10 ka offset from the youngest zircon age obtained using a constant (Th/U)<sub>magma</sub>. The youngest zircon age can also be compared to weighted mean ages calculated from the youngest few zircons or a weighted mean taken from the maximum number of grains allowing an acceptable MSWD of 1. The effects of these interpretations are described in the text and illustrated in Fig. S5.

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Sample	Dates (Ma)							Composition					Isotopic Ratios							Corrections																			
	206Pb/ 238U		±2σ		207Pb/ 235U		±2σ		207Pb/ 206Pb		±2σ		% disc		Pb*		Pbc		Th/		206Pb/		208Pb/		207Pb/		207Pb/		Corr.		Blank								
	absolute	absolute	absolute	absolute	absolute	absolute	% disc	(pg)	(pg)	Pbc	U	U(magma)	204Pb	206Pb	238U	±2σ %	235U	±2σ %	206Pb	±2σ %	206Pb	±2σ %	207Pb	±2σ %	207Pb	±2σ %	coef.	model	Tracer										
a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p	q	r	s	t	u	v	w	x	y	z	aa	ab	ac	ad										
<b>CRB1506</b>																																							
z34	15.895	0.019	15.979	0.059	28.6	8.5	63.0	43.15	0.83	51.96	0.39	2.05	3315	0.13	0.0024551	0.095	0.0158661	0.369	0.0468923	0.341	0.399			SF	ET535														
z21	15.887	0.043	15.918	0.091	21	12	54.5	18.98	0.48	39.76	0.38	2.00	2545	0.12	0.0024538	0.260	0.0158055	0.574	0.0467363	0.491	0.519			SF	ET535														
z3	15.902	0.018	16.16	0.19	55	29	77.1	11.58	0.77	15.06	0.27	1.42	976	0.09	0.0024561	0.088	0.0160505	1.213	0.0474162	1.192	0.273			OC	ET2535														
z1	15.914	0.025	16.08	0.32	41	47	71.0	20.48	2.18	9.40	0.31	1.63	610	0.10	0.0024580	0.144	0.0159643	2.001	0.0471266	1.963	0.297			OC	ET2535														
z35	15.921	0.023	15.94	0.17	19	26	52.5	33.03	2.20	15.03	0.41	2.11	968	0.13	0.0024591	0.123	0.0158301	1.097	0.0467091	1.065	0.311			SF	ET535														
z31	15.938	0.071	16.1	1.0	35	149	67.6	9.43	3.06	3.09	0.43	2.16	206	0.14	0.0024618	0.447	0.0159518	6.345	0.0470161	6.219	0.313			OC	ET535														
z12	20.85	0.12	22.1	1.8	159	193	87.7	1.51	0.74	2.04	0.71	3.74	137	0.23	0.0032252	0.588	0.0219882	8.439	0.0494682	8.261	0.335			SF	ET535														
z16	39.16	0.14	38.5	1.9	-1	117	-667.9	1.71	0.46	3.75	0.53	2.79	248	0.17	0.0060791	0.346	0.0386766	4.934	0.0461636	4.845	0.287			SF	ET535														
z11	99.57	0.16	98.9	2.0	83	48	-17.2	10.21	1.37	7.44	0.34	1.79	497	0.11	0.0155515	0.164	0.1022996	2.074	0.0477304	2.033	0.289			SF	ET535														
z33	166.56	0.16	166.44	0.72	165	11	-0.2	20.84	0.61	34.15	0.38	2.00	2188	0.12	0.0261600	0.096	0.1781232	0.470	0.0494056	0.450	0.300			SF	ET535														
<b>CRB1533</b>																																							
z4_BS	16.066	0.040	16.08	0.52	18	76	50.0	5.16	0.78	6.62	0.71	3.74	393	0.23	0.0024817	0.238	0.0159665	3.243	0.0466827	3.169	0.347			OC	ET2535														
z25	16.044	0.089	15.7	1.4	-38	213	166.8	1.08	0.55	1.95	0.59	3.26	136	0.19	0.0024780	0.558	0.0155775	8.878	0.0456128	8.748	0.263			SF	ET535														
z34	16.045	0.059	16.05	0.86	17	128	47.7	1.28	0.39	3.25	0.72	3.79	208	0.23	0.0024783	0.363	0.0159351	5.417	0.0465648	5.327	0.278			SF	ET535														
z3	16.070	0.093	16.2	1.5	41	214	70.7	2.64	1.16	2.27	0.54	2.84	153	0.17	0.0024823	0.579	0.0161224	9.091	0.0471274	8.919	0.327			OC	ET2535														
z28	16.163	0.094	16.4	1.4	46	206	73.2	0.55	0.27	2.00	0.76	4.16	134	0.24	0.0024966	0.579	0.0162529	8.773	0.0472357	8.629	0.279			SF	ET535														
z14	16.171	0.057	15.96	0.75	-15	112	1221.3	1.62	0.41	3.94	0.64	3.47	252	0.21	0.0024979	0.346	0.0158488	4.759	0.0460388	4.643	0.366			SF	ET535														
z1_BS	16.234	0.018	16.22	0.13	14	19	41.6	10.59	0.41	25.62	0.44	2.32	1575	0.14	0.0025078	0.082	0.0161052	0.792	0.0465987	0.776	0.240			OC	ET2535														
z2_BS	16.568	0.015	16.63	0.11	25	15	57.3	14.29	0.47	30.27	0.46	2.42	1844	0.15	0.0025597	0.057	0.0165141	0.648	0.0468125	0.634	0.259			OC	ET2535														
z1	16.587	0.030	16.49	0.36	2	52	-8.2	15.30	1.70	8.98	0.40	2.11	569	0.13	0.0025626	0.169	0.0163729	2.221	0.0463590	2.174	0.314			OC	ET2535														
z31	17.37	0.13	17.3	2.0	3	279	-5.9	0.40	0.27	1.47	0.66	3.47	105	0.21	0.0026852	0.749	0.0171637	11.727	0.0463798	11.556	0.259			SF	ET535														
z3_BS	31.086	0.043	30.90	0.49	16	37	-31.9	4.75	0.38	12.47	0.44	2.32	775	0.14	0.0048202	0.135	0.0309028	1.604	0.0465184	1.544	0.475			OC	ET2535														
<b>CRB1519</b>																																							
z1_BS	16.210	0.043	16.12	0.62	2	92	6.3	2.35	0.45	5.19	0.48	4.00	331	0.15	0.0025028	0.266	0.0160033	3.882	0.0463965	3.815	0.281			OC	ET2535														
z13	16.26	0.19	16.1	2.9	-5	434	-65.8	1.25	1.42	0.88	0.37	3.08	75	0.12	0.0025110	1.209	0.0160067	18.282	0.0462531	17.980	0.281			SF	ET535														
z16	16.265	0.081	15.9	1.3	-40	191	165.0	2.28	1.01	2.26	0.49	4.08	159	0.16	0.0025114	0.503	0.0157810	7.978	0.0455941	7.852	0.280			SF	ET535														
z1	16.268	0.058	16.58	0.86	62	123	79.0	4.94	1.38	3.58	0.40	3.33	238	0.13	0.0025118	0.357	0.0164678	5.251	0.0475705	5.161	0.283			OC	ET2535														
z2_BS	16.298	0.043	16.69	0.63	74	88	81.8	4.29	0.86	4.99	0.40	3.33	325	0.13	0.0025165	0.261	0.0165823	3.775	0.0478131	3.710	0.279			OC	ET2535														
z4	16.34	0.10	16.3	1.6	7	231	24.7	1.99	1.00	1.98	0.39	3.25	140	0.13	0.0025227	0.640	0.0161605	9.745	0.0464810	9.578	0.292			OC	ET2535														
z2	16.414	0.081	16.8	1.2	67	168	80.1	2.00	0.75	2.67	0.47	3.92	179	0.15	0.0025346	0.496	0.0166531	7.175	0.0476742	7.040	0.303			OC	ET2535														
z4_BS	16.60	0.13	17.18	0.73	99	98	85.4	1.51	0.34	4.43	0.31	2.58	296	0.10	0.0025633	0.806	0.0170651	4.289	0.0483067	4.131	0.286			OC	ET2535														
z6	17.81	0.13	18.2	2.0	73	259	79.5	1.57	0.91	1.72	0.43	3.58	123	0.14	0.0027518	0.759	0.0181122	11.079	0.0477590	10.876	0.299			OC	ET2535														
z3_BS	78.734	0.035	78.86	0.27	83	8	8.4	53.71	1.09	49.21	0.09	0.75	3326	0.03	0.0122734	0.044	0.0807707	0.352	0.0477510	0.342	0.241			OC	ET2535														
<b>CRB1556</b>																																							
z12	16.254	0.034	16.32	0.44	26	64	59.3	1.54	0.26	5.91	0.35	1.89	397	0.11	0.0025109	0.200	0.0162068	2.733	0.0468346	2.678	0.308			SF	ET535														
z13	16.257	0.036	16.60	0.46	66	66	79.7	1.52	0.27	5.68	0.44	2.37	373	0.14	0.0025114	0.212	0.0164844	2.809	0.0476273	2.764	0.244			SF	ET535														
z18	16.295	0.063	16.32	0.95	21	139	54.3	1.03	0.37	2.77	0.31	2.75	198	0.10	0.0025159	0.387	0.0162103	5.867	0.0467507	5.765	0.295			SF	ET535														
z5	16.30	0.18	17.4	2.8	169	371	91.1	0.87	0.78	1.12	0.37	1.95	87	0.12	0.00																								

**Table 1: U-Pb Isotopic Data**

z18	16.606	0.051	16.633	0.730	21	105	51.5	1.74	0.48	3.65	0.43	2.32	248	0.14	0.0025655	0.301	0.0165205	4.424	0.0467243	4.349	0.280	SF	ET535
z2	16.606	0.039	16.672	0.519	26	74	58.3	2.89	0.53	5.47	0.62	3.32	345	0.20	0.0025656	0.225	0.0165595	3.136	0.0468326	3.075	0.300	SF	ET535
z21	16.610	0.043	16.967	0.596	68	83	79.6	26.93	4.92	5.47	0.51	2.63	344	0.16	0.0025663	0.255	0.0168545	3.539	0.0476536	3.471	0.300	OC	ET535
z3	16.616	0.046	16.287	0.789	-32	119	189.9	2.90	0.61	4.74	0.83	4.42	287	0.27	0.0025671	0.268	0.0161742	4.881	0.0457167	4.886	0.006	SF	ET535
z19	16.618	0.020	16.709	0.140	30	20	61.7	5.72	0.27	21.12	0.53	2.79	1309	0.17	0.0025675	0.098	0.0165964	0.843	0.0469021	0.833	0.155	SF	ET535
z15	16.627	0.027	16.681	0.253	24	36	56.3	2.91	0.24	12.16	0.61	3.26	745	0.20	0.0025689	0.149	0.0165685	1.529	0.0467982	1.482	0.355	SF	ET535
z7	16.635	0.067	16.951	0.993	62	138	78.1	2.07	0.71	2.91	0.64	3.47	191	0.21	0.0025700	0.402	0.0168385	5.905	0.0475405	5.800	0.293	SF	ET535
z16	16.643	0.044	16.946	0.597	60	83	77.5	1.24	0.25	4.98	0.81	4.37	301	0.26	0.0025713	0.256	0.0168336	3.553	0.0475026	3.483	0.307	SF	ET535
z17	16.654	0.047	17.008	0.671	67	93	79.5	1.05	0.23	4.47	0.85	4.58	270	0.27	0.0025730	0.278	0.0168964	3.977	0.0476482	3.907	0.284	SF	ET535
<b>CRB1625</b>																							
z15	16.653	0.063	17.17	0.94	90	128	84.0	0.71	0.24	2.97	0.55	3.00	199	0.18	0.0025728	0.374	0.0170557	5.499	0.0481022	5.407	0.278	SF	ET535
z36	16.64	0.039	18.0	2.6	202	337	92.3	1.91	1.54	1.24	0.49	2.32	92	0.16	0.0025719	1.073	0.0178838	14.806	0.0504555	14.506	0.313	OC	ET535
z7	16.66	0.13	17.8	2.0	170	258	90.9	3.48	2.07	1.69	0.58	3.05	116	0.19	0.0025733	0.792	0.0176465	11.262	0.0497570	11.057	0.292	OC	ET535
z27	16.67	0.14	16.9	2.2	52	307	74.5	1.09	0.85	1.29	0.56	2.95	97	0.18	0.0025752	0.846	0.0167991	13.068	0.0473335	12.859	0.278	SF	ET535
z38	16.68	0.17	16.6	2.5	4	358	2.7	0.30	0.25	1.22	0.53	2.79	93	0.17	0.0025774	1.021	0.0164797	15.253	0.0463940	14.864	0.410	SF	ET535
z12	16.754	0.085	17.1	1.3	66	177	78.9	0.58	0.26	2.19	0.59	3.21	151	0.19	0.0025885	0.510	0.0169849	7.580	0.0476109	7.449	0.289	SF	ET535
z1	17.297	0.026	17.25	0.26	11	36	27.1	8.01	0.71	11.32	0.64	3.37	690	0.21	0.0026731	0.136	0.0171381	1.541	0.0465208	1.502	0.325	SF	ET535
z11	17.84	0.11	19.5	1.8	231	208	92.7	0.54	0.32	1.68	0.52	2.74	121	0.17	0.0027580	0.647	0.0194136	9.158	0.0510748	9.000	0.277	SF	ET535
z17	18.578	0.040	18.92	0.51	62	63	75.1	1.49	0.24	6.16	0.63	3.32	385	0.20	0.0028724	0.210	0.0188112	2.701	0.0475195	2.642	0.318	SF	ET535
z2	18.643	0.055	18.50	0.76	0	97	-59.8	5.02	1.06	4.76	1.08	5.68	272	0.35	0.0028824	0.292	0.0183883	4.124	0.0462889	4.041	0.317	SF	ET535
z40	19.818	0.093	19.8	1.4	16	171	26.4	1.98	0.84	2.34	0.60	3.16	159	0.19	0.0030652	0.471	0.0196786	7.206	0.0465827	7.097	0.261	SF	ET535
z16	19.895	0.054	20.24	0.76	61	89	72.7	2.10	0.45	4.65	0.67	3.53	292	0.21	0.0030772	0.265	0.0201384	3.783	0.0474849	3.712	0.297	SF	ET535
z19	20.095	0.041	20.14	0.50	26	59	46.0	2.76	0.32	8.53	1.63	8.58	422	0.52	0.0031084	0.194	0.0200414	2.491	0.0467822	2.441	0.292	SF	ET535
z35	21.026	0.057	20.70	0.75	-17	87	417.2	3.88	0.59	6.52	1.35	7.11	346	0.43	0.0032533	0.268	0.0205982	3.645	0.0459403	3.592	0.231	SF	ET535
z20	23.393	0.047	23.75	0.61	61	61	66.7	1.60	0.25	6.34	0.57	3.00	402	0.18	0.0036217	0.195	0.0236754	2.611	0.0474321	2.564	0.274	SF	ET535
z13	23.482	0.080	23.7	1.2	42	117	54.9	1.26	0.37	3.38	0.57	3.00	223	0.18	0.0036356	0.338	0.0235863	4.977	0.0470738	4.892	0.283	SF	ET535
z21	23.923	0.039	23.96	0.45	27	45	34.8	6.55	0.67	9.75	0.90	4.74	561	0.29	0.0037042	0.156	0.0238775	1.901	0.0467726	1.857	0.319	SF	ET535
z23	47.954	0.074	47.59	0.82	29	41	-41.4	5.84	0.55	10.57	0.60	3.16	653	0.19	0.0074529	0.153	0.0479881	1.755	0.0467198	1.714	0.311	SF	ET535
z14	49.511	0.049	49.54	0.32	51	15	10.4	6.10	0.24	25.09	0.37	1.95	1618	0.12	0.0076963	0.098	0.0499996	0.664	0.0471386	0.631	0.393	SF	ET535

a Corrected for initial Th/U disequilibrium using radiogenic 208Pb and Th/U[magma] specified.

b Corrected for initial Pa/U disequilibrium using initial fraction activity ratio [231Pa]/[235U] = 1.10000.

c % discordance = 100 - (100 \* (206Pb/238U date) / (207Pb/206Pb date))

d Total mass of radiogenic Pb.

e Total mass of common Pb.

f Ratio of radiogenic Pb (including 208Pb) to common Pb.

g Th contents calculated from radiogenic 208Pb and 230Th-corrected 206Pb/238U date of the sample, assuming concordance between U-Pb Th-Pb systems.

h Th/U ratio of magma from which mineral crystallized.

i Measured ratio corrected for fractionation and spike contribution only.

j Measured ratios corrected for fractionation, tracer and blank.

k Two different blank models were used to reduce data - Outliers Culled model (OC), and Side Filaments (SF). Values are:

OC	206Pb/204Pb	18.168317±0.384235	SF	206Pb/204Pb	18.628271±0.317714
	207Pb/204Pb	15.348332±0.273090		207Pb/204Pb	15.796256±0.232017
	208Pb/204Pb	37.350513±0.773909		208Pb/204Pb	38.535874±0.375848

l Values for ET535 and ET2535 are found in ref. 31 and ref. 32.

## Chapter 4

### **Eruption history of the Columbia River Basalt Group constrained by U-Pb geochronology**

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*This chapter is in review at Geology, with authors J. Kasbohm, B. Schoene, and J. Murray*

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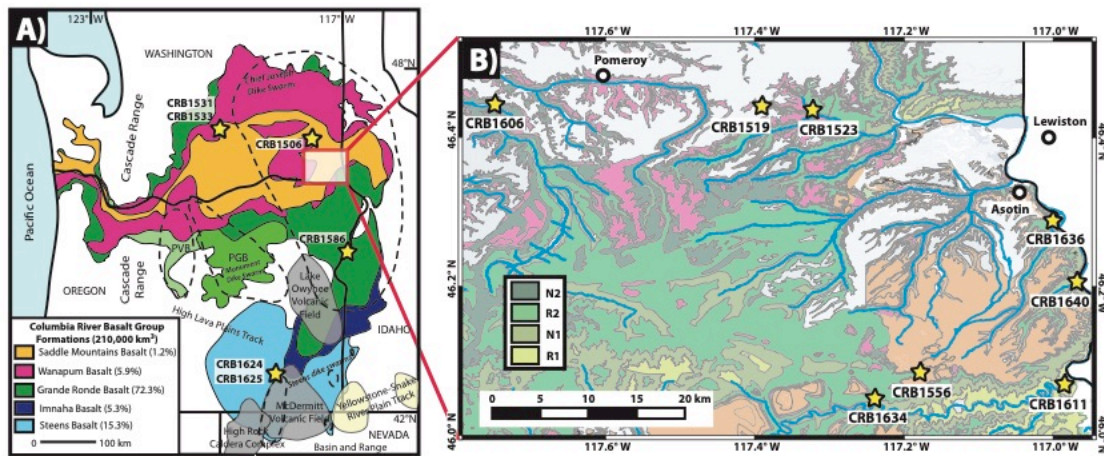
#### **ABSTRACT**

Large igneous provinces have been connected to a number of Earth's most severe environmental crises. A surge in detailed high-precision geochronological studies has revised estimates of the timing and tempo of their emplacement, which are necessary to assess causality in global perturbations. We present new U-Pb geochronology from zircon-bearing volcanic ashes in the Columbia River Basalt Group (CRBG), the youngest and best-studied continental flood basalt, which is temporally connected to the global warming and elevated CO<sub>2</sub> of the Miocene Climate Optimum. By combining new ages with our recently published dataset, we find that main phase CRBG volcanism occurred at a relatively constant rate of 0.3-0.5 km<sup>3</sup>/a, with a small likelihood of hiatuses beyond ~80 ka, and that the Grande Ronde Basalt (GRB), the largest CRB formation encompassing 72% of its total volume, was emplaced in 505±51/-61 ka beginning at

~16.57 Ma. Our model also yields ages for magnetic field reversals ongoing during CRBG emplacement, which can be used to improve calibration of Miocene paleoclimate records. While proxies suggesting elevated CO<sub>2</sub> levels from 16.5-15.8 Ma may be connected to GRB emplacement, any model invoking the CRBG as a continued source of CO<sub>2</sub> throughout the MCO (until ~14 Ma) requires cryptic outgassing long after eruptions ceased.

## **INTRODUCTION**

Large igneous provinces (LIPs), Earth's most voluminous volcanic events, have punctuated Earth history, leaving evidence for mass extinctions and climatic perturbations in their wake (Ernst & Youbi, 2017). Whether LIPs are associated with mantle plumes (e.g., Deccan Traps, Ontong Java Plateau), continental breakup (Central Atlantic Magmatic Province, Karoo-Ferrar), or combinations of the two (North Atlantic Igneous Province), their surface expression represents an end-member of intrusive and extrusive magmatism. In the past decade, new geochronology has yielded crucial constraints on the timing, duration, and volumetric rates of eruption for a number of LIPs (Blackburn et al., 2013; Burgess et al., 2017; Schoene et al., 2019). However, only a minority of LIPs possess the wide geographic exposure, well-defined stratigraphy, and datable material amenable to detailed geochronological studies (Kasbohm et al., in press). Here we report new temporal constraints on the Columbia River Basalt Group (CRBG), the youngest, best-preserved, and best-studied LIP, which is a well-suited testbed to quantify the tempo of LIP emplacement.



**Figure 1. A)** Overview map of the CRBG, with areal extents and volume estimates for each formation, and localities of other regional volcanic activity labeled. Dashed lines bracket source dike swarms, and the locations of geochronology samples are starred. In total, the Saddle Mountains Basalt, Picture Gorge Basalt (PGB) and Prineville Basalt (PVB) together comprise 2.6% of the total CRBG volume, and are not discussed further here, or included in any cumulative volume estimates. **B)** Geologic map of CRBG exposure in southeastern Washington.

The CRBG has been the subject of decades of effort to document its geochemistry, paleomagnetism, and mineralogy, leading to a well-defined volcanostratigraphy comprising five main formations and dozens of individual stratigraphic members, each with area and volume estimates obtained through mapping and coring campaigns (Reidel, 2015). The 210,000 km<sup>3</sup> of the CRBG were emplaced in the northwestern USA during the Miocene during active regional volcanism east of the Cascades subduction zone and High Lava Plains track, north of the Basin & Range and silicic caldera complexes, and west of the Yellowstone-Snake River Plain hotspot track (Fig. 1A).

The origin of the CRBG is debated. While some workers hypothesize a mantle plume source, suggesting that the CRBG represents initial impingement of the Yellowstone

plume head on the crust (Camp, 2013), others favor subduction-related mechanisms, such as a slab tear (Liu & Stegman, 2012) or slab rollback (Long et al., 2012), and still others favor an interaction of plume and slab (Coble & Mahood, 2012). The CRBG is also noteworthy for its temporal correlation with the Miocene Climate Optimum (MCO), an episode of global warming 17-15 Ma evidenced by paleoclimate proxies indicating a 4-6°C high-latitude sea surface temperature rise (Shevenell et al., 2004) and elevated atmospheric CO<sub>2</sub> levels at or above 400 ppm (Armstrong McKay et al., 2014).

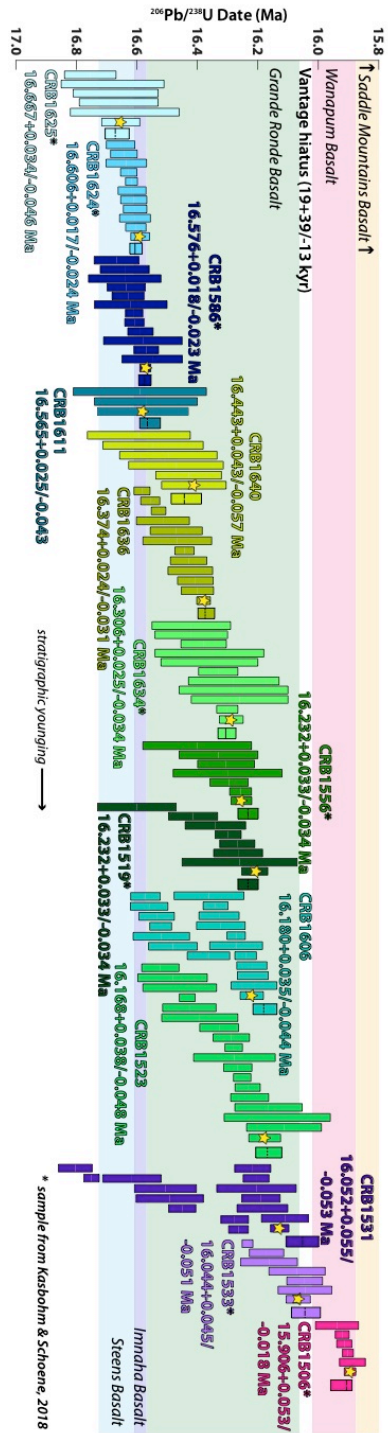
Prior geochronology for the CRBG lacked the accuracy and precision required to fully integrate eruptions into geodynamic models, or assess in detail its connection to the MCO. Barry et al. (2013) reviewed K-Ar and <sup>40</sup>Ar/<sup>39</sup>Ar geochronology obtained from CRBG basalts, and suggested that emplacement of the Steens, Innaha, Grande Ronde, and Wanapum Basalts occurred from 16.9-15.0 Ma. This age model, constructed from individual ages with low (~1 Ma) precision and in some cases poor accuracy, yielded numerous inconsistencies between the magnetic polarity of the basalts and the Geomagnetic Polarity Timescale (GPTS; Hilgen et al., 2012). More recent high-precision <sup>40</sup>Ar/<sup>39</sup>Ar and U-Pb zircon geochronology have provided a clearer timeline for CRBG eruptions by dating sanidine or zircon extracted from volcanic ashes or weathering horizons between lava flows (Kasbohm & Schoene, 2018; Mahood & Benson, 2017). A new U-Pb age model for the CRBG suggests that emplacement of 95% of the CRBG volume occurred in ~750 ka beginning at 16.65 Ma, with possible brief intervals of more rapid emplacement (Kasbohm & Schoene, 2018). However, our previous contribution constrained the timing of only one member of the Grande Ronde Basalt (GRB), the

largest CRBG formation comprising 72% of its total volume (Reidel, 2015). Here we provide new age constraints on six geochronology samples from the beginning, middle, and end of the GRB. These new data constrain the eruptive tempo of the CRBG and also place tighter age estimates on magnetic reversals observed in the basalt pile, which are critical for building a robust GPTS and therefore age models for climate proxy records.

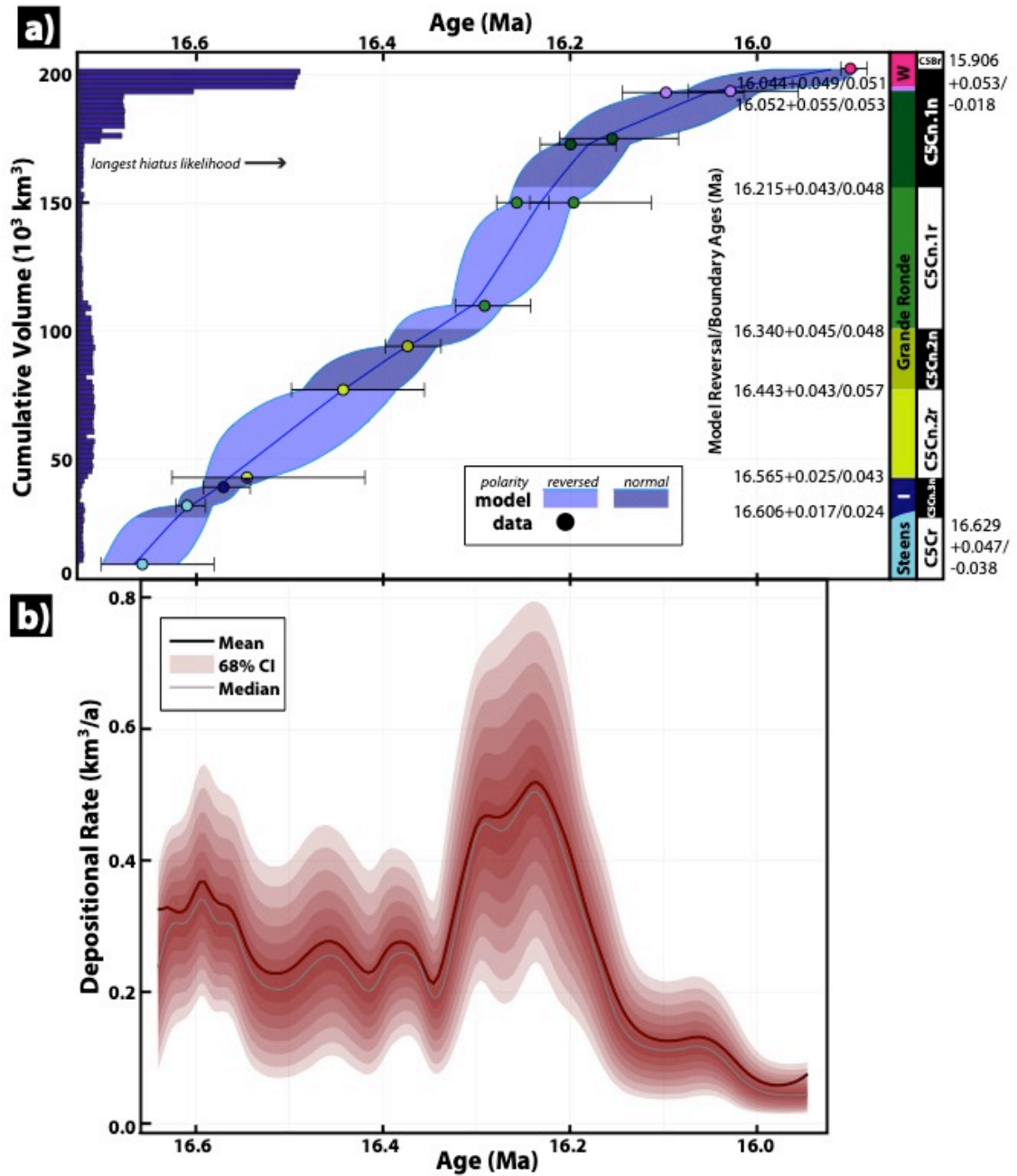
## **RESULTS**

We use U-Pb zircon geochronology by chemical abrasion – isotope dilution – thermal ionization mass spectrometry (CA-ID-TIMS) to provide accurate and precise age constraints on CRBG interbeds. These interbeds, manifest as ash layers, weathered flow top horizons containing ash material, or the volcanoclastic infill of brecciated basalt flow tops were sampled in central and southeast Washington (Fig. 1B). Individual zircons were separated from each sample and dated through CA-ID-TIMS at Princeton University (see Data Repository for materials and methods).

Individual zircon  $^{206}\text{Pb}/^{238}\text{U}$  dates from six GRB horizons are presented in Figure 2 with 95% confidence intervals, alongside our prior dataset (Kasbohm & Schoene, 2018). Dates within each sample spread beyond analytical uncertainty as a result of pre-eruptive crystallization derived from prolonged crystallization in the magma, or inheritance of older grains from the host rock or volcanic edifice (Cooper, 2015; Stelten et al., 2015). In Figure 2, we star the youngest and most precise zircon age as one estimate for the age of the interbed. As an additional approach to calculating an eruption age from disperse



**Figure 2.** Rank order plot of geochronological data presented in this study, with samples arranged in stratigraphic order (younging left to right), and height of error bars showing  $2\sigma$  uncertainty. The youngest, most precise single zircon age is starred, and the result of the MCMC age model is highlighted (the rightmost bar for each sample) and labeled as our preferred interpretation. Background shading indicates the timing of eruption for each CRBG formation. Samples with an asterisk are from Kasbohm & Schoene (2018).



**Figure 3.** **a)** Age model for cumulative volume erupted through the CRBG, based on eruptive ages (black lines) from known stratigraphic positions. Blue shading indicates 95% credible interval of the model, and is dark for intervals of normal polarity and light for reversed polarity. Indigo bars on the right indicate the likelihood of the longest CRBG hiatus (most likely 50-80 ka) occurring at each stratigraphic position. The age model also yields magnetic field reversal and formation boundary ages (labeled). **b)** Results from **(a)** for emplacement rates of the CRBG, averaged over 50 ka windows, shown with contours up to 68% credible intervals.

datasets, each sample was subjected to a Bayesian Monte Carlo Markov Chain (MCMC) model, which makes a probabilistic estimate of eruption age based on all of the dates and uncertainties of individual zircons from a sample (Keller et al., 2018); in all cases, the derived eruption ages overlap with the youngest zircon ages (Table DR2). Finally, eruption ages were input into an additional MCMC simulation (Schoene et al., 2019), which imposes stratigraphic order as a constraint to further refine eruption ages, and calculate volumetric eruption rates (Fig. 3), yielding our preferred model age for each CRBG sample (Fig. 2).

Our data yield a high-resolution age model for the vast majority of the CRBG that agrees well with our previous age estimates. The new data provide a more thorough interrogation of the GRB specifically. Interbeds immediately below the first and above the last GRB members constrain the duration of the GRB to  $505^{+51}/-61$  ka. The age model yields estimates for the timing of the magnetic field reversals bracketing the four magnetostratigraphic units of the GRB, corresponding to chrons C5Cn.2r-C5Cn.1n, as well as the preceding chron C5Cn.3n (Fig. 3). The ages for the bottom and near the top of the Vantage sedimentary interbed, the most prominent though not necessarily the longest-lived interbed in the CRBG (Barry et al., 2010), yield a duration of  $19^{+39}/-13$  ka. At its sampled type locality, the Vantage interbed exhibits a thin layer of white mud (CRB1531), interpreted as ancestral Columbia River deposits, overlain by 4 m of an ash-rich volcanoclastic lahar sourced from the Cascades (CRB1533) (Tolan et al., 2009). In the field, we observed that the overlying Basalt of Ginkgo (Wanapum Basalt) exhibits

load structures, indicating that the volcanoclastic unit was not yet lithified at the time of the Ginkgo eruption.

The modeled eruption rates calculated through the main phase of the CRBG (Steens, Innaha, and GRB) suggest an average emplacement rate of  $\sim 0.3 \text{ km}^3/\text{a}$  (Fig. 3). An exception to this average rate is evident during the emplacement of the Wapshilla Ridge Member, which appears to have been emplaced at  $\sim 0.5 \text{ km}^3/\text{a}$  during chron C5Cn.1r (R2). As we have previously reported, fluxes slow by an order of magnitude during the emplacement of the Wanapum Basalt, with an average rate of  $0.05 \text{ km}^3/\text{a}$  (Kasbohm & Schoene, 2018). Monte Carlo simulations suggest that the longest possible hiatus of CRBG volcanism was most likely 50-80 ka (Fig. DR4), which would have been most likely to occur in the uppermost portion of the GRB (Fig. 3).

## **DISCUSSION**

Our model for emplacement rates throughout the duration of the CRBG may be compared to other well-dated LIPs. U-Pb ID-TIMS geochronology shows that the CAMP, Deccan Traps, and Siberian Traps were also all emplaced in less than a million years, and the data are pointing towards models demarcated by periods of high eruptive flux  $10^4$ - $10^5$  years long interspersed with intervals of reduced effusion (see summary in Kasbohm et al., in press). For example, the Deccan Traps emplacement is shown to occur in four pulses of  $\leq 20 \text{ km}^3/\text{a}$  (Schoene et al., 2019); the Siberian Traps have been modeled to be emplaced as a few pulses lasting 10-100 ka (Pavlov et al., 2019). In the CAMP, some U-Pb dates from dikes and sills fall during apparent eruption hiatuses (Blackburn et

al., 2013; Davies et al., 2017), perhaps indicating that in all LIPS, lulls in eruptions need not be lulls in magmatism. In the case of the CRBG, where the stratigraphy is arguably better known than any other LIP, our data show that the longest eruption hiatus during CRBG emplacement was unlikely to be longer than 80 ka. The gradual rather than pulsed emplacement of the CRBG, as well as its smaller total volume, may partly explain why the CRBG is not associated with the more catastrophic environmental and ecological effects of other LIPs. More detailed geochronology is needed to assess whether apparent eruption hiatuses in some LIPs are simply a transition to intrusion-dominated magmatism or regional phenomena and an artifact of incomplete sampling.

Our age model can be used to calculate the frequency and rate of individual eruptions through the GRB. Field observations have provided the number of lava flows in each stratigraphic member (Reidel & Tolan, 2013), and thermal models (Petcovic & Dufek, 2005) combined with thermochronologic data (Karlstrom et al., 2019) have been used to show that feeder dike segments were active for at most 1-10 years with fluxes of 1-3 km<sup>3</sup>/a. With the simplistic assumption that each of the 112 GRB lava flows was sourced from 1 dike erupting over 10 years, we find a flow frequency of 1 flow per 2-6 ka for most of the GRB, apart from the interval between samples CRB1635 and CRB1634 (late N1-early R2), when it slows by an order of magnitude to 1 flow per ~11 ka. An interval of 1-10 ka between lava flows is consistent with the timescale on which sedimentary interbeds in the CRBG have been estimated to develop, based on the study of nutrient fluxes and palynoflora captured in these units, which are proxies for duration of exposure calibrated by modern interbeds in Hawaii (Jolley et al., 2008).

Our highly-resolved CRBG age model can yield further insight into the connection of the CRBG with the MCO. As we have previously discussed, one obstacle to comparing the timing of these events has been the disputed calibration of the Miocene Geomagnetic Polarity Timescale (GPTS), for which there are several proposals. Our new GRB ages show greater concordance with the astronomically tuned age model for IODP sites U1335 and U1336 (Kochhann et al., 2016) than with the Neogene GPTS in the Geologic Timescale 2012 (Hilgen et al., 2012), which is based on the spline fit of seafloor geomagnetic anomalies from 17-14 Ma, rather than astronomical tuning (Table DR3). Because some astronomically tuned Miocene climate records do not exhibit the same concordance with our age model (Billups et al., 2004; Pälike et al., 2006), it is important to utilize both tuning and geochronology to assess the timing of magnetic field reversals and gain a full understanding of sedimentation in tuned sections (Machlus et al., 2015; Sahy et al., 2017). Given good agreement between our radiometric ages and the age model of Kochhann et al. (2016), it could be used to recalibrate the Mid-Miocene GPTS, thereby anchoring other paleoclimate proxy records.

Recent work modeling atmospheric CO<sub>2</sub> concentrations during the MCO based on the  $\delta^{11}\text{B}$  isotopic proxy show a brief increase at ~16.7 Ma, followed by sustained elevated levels from ~16.5-15.8 Ma (Sosdian et al., 2018). If the age models for these records are accurate, this pattern permits a connection between an increase in pCO<sub>2</sub> and the onset of CRBG magmatism. Elevated seawater temperatures, as recorded by  $\delta^{18}\text{O}$  in foraminifera, continued for another ~1.5 million years after the cessation of main phase volcanism,

(until ~14.5 Ma; Zachos et al., 2008). Our geochronology conclusively shows that all but ~1% of CRBG eruptions had ceased by ~15.9 Ma, and therefore, the CRBG cannot be invoked as a source of CO<sub>2</sub> through the entire duration of the MCO. In recent work using carbon cycle modeling to discern the connection between the MCO, CRBG, and the concurrent Monterey Carbon Isotope Excursion, Sosdian et al. (2020) suggest that elevated surface ocean dissolved inorganic carbon (DIC) throughout the MCO was caused by continuous eruption of the CRBG over millions of years, citing an outdated age model of CRBG emplacement rates, from Hooper et al., (2002). Since our new CRBG age model constrains the timing of volcanism to ~16.7-15.9 Ma, with eruptive fluxes double that of Hooper et al. (2002), we suggest that another mechanism of sustaining elevated DIC and seawater temperatures through this interval must be invoked after 15.9 Ma. One, perhaps unlikely, scenario is that elevated crustal geotherms sustained decarbonation reactions of carbon-rich sediments long after CRBG magmatism ceased. Another possible mechanism is a potentially slower silicate weathering feedback allowing for sustained warm conditions following the cessation of main phase CRBG volcanism. Both explanations require better data on the magnitude of each effect, especially since they play a role in explaining carbon cycle observations during other examples of LIP emplacement and environmental change, such as mass extinction events.

## **CONCLUSION**

Our new ages for the GRB and revised age model for the CRBG offer a uniquely detailed view of the dynamics of LIP emplacement. The GRB, representing 72% of total CRBG volume, was emplaced over  $505^{+51}_{-61}$  ka, with the longest hiatus unlikely to be longer

than 80 ka. The mostly constant and lower volumetric emplacement rates of 0.3-0.5 km<sup>3</sup>/a calculated through the main phase of CRBG volcanism likely contributed to its differing environmental effects from other LIPs; rather than association with a cataclysmic mass extinction, the CRBG instead was likely partly responsible for establishing the conditions of the MCO. Further studies that temporally constrain climatic fluctuations through the duration of the MCO and that input our new temporal constraints on CRBG volcanism into carbon cycle models for the MCO will allow for enhanced testing of this connection.

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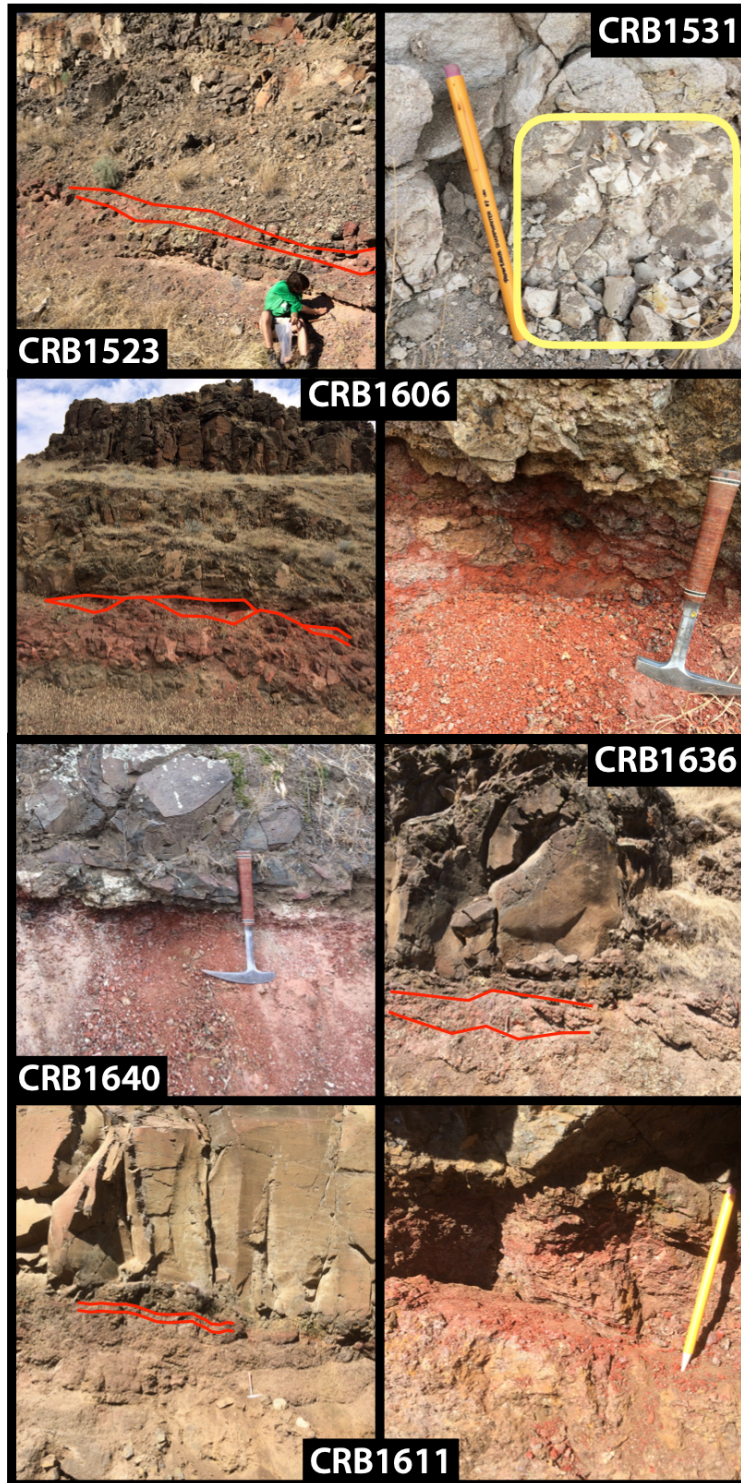
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## **SUPPLEMENTAL INFORMATION**

### **SAMPLE DESCRIPTIONS**

Samples dated in this study were collected from roadcuts or natural exposures in Washington, Oregon, and Idaho in summers 2015 and 2016. Detailed sample descriptions are provided here, in stratigraphic order from oldest to youngest; starred sample descriptions are reproduced from Kasbohm & Schoene (2018). Outcrop photographs are provided in Fig. DR1, and zircon photographs are provided in Fig. DR2.



**Fig. DR1. Geochronology Sample Photos.** Outcrop-scale and/or hand-sample scale photos of each geochronology sample are provided here, with stratigraphic younging from bottom to top (Photo credit: Jennifer Kasbohm, Princeton University).



**Fig. DR2. Zircon Photos.** Optical images of zircons under transmitted light are presented here, with stratigraphic younging from bottom to top. Zircons present a range of morphologies, but the majority are euhedral with sharp crystal terminations, indicating an igneous rather than detrital origin. The zircon yielding the youngest, most precise analysis for each sample is starred.

**CRB1625\* (42.67542°N, 118.68724°W, elevation 2255 m)**

This sample was collected from a ~0.5 m thick redbole between two Lower Steens Basalt flows, (based on the stratigraphy of (Johnson et al., 1998)) on the western side of Steens Mountain. The fine red sediment overlay a brecciated flow top and contained abundant vitreous microphenocrysts, black round lithic fragments, and subangular fragments of basaltic pumice up to 1 mm in size.

Fewer than 100 zircons were separated from this sample, and many of these grains are rounded and appear detrital. Some grains are euhedral, and ranged from equant to a high aspect ratio. Many grains are tinted orange, while some are clear. Forty grains were selected for analysis, and 19 were successfully dated. For this sample and the other samples described below, grains that were not successfully dated were lost at some stage of zircon chemistry prior to dating, or were dated and either did not fall on the Concordia line or exhibited a ratio of radiogenic Pb to common Pb that was  $\leq 1$ . Six of these grains were ca. 16.7 Ma, with a dispersion of 120 ka, while the other 13 are inherited. Both the Mid-Miocene and inherited grains exhibited a range of morphologies. The youngest grains were often euhedral, and ranged from equant to an aspect ratio of at least 4:1. While some of the young grains were glassy and transparent, others were opaque. While a few of the analyses exhibited elevated common Pb content ( $>1$  pg), others had low common Pb ( $<0.3$  pg) but also low radiogenic Pb content ( $<1$  pg), yielding generally less precise zircon ages for this sample than for the others in this study.

**CRB1624\* (42.66626°N, 118.56479°W, elevation 2966 m)**

This sample was collected from a ~0.5 m thick redbole interbedded between Upper Steens Basalt flows (60) at the East Rim Lookout on Steens Mountain. The sampled horizon was a fine pink sediment infilling a brecciated flow top, and contained abundant vitreous microphenocrysts with few dark round lithic fragments.

Hundreds of zircons were obtained from this sample, with a range of morphologies.

Generally, grains were angular to subangular, with fewer round detrital grains. The grains ranged from equant to higher aspect ratios, though few were acicular. Most of the grains are orange, while a few are clear and glassy. Twenty-three grains were selected for analysis, and 11 were successfully dated. The youngest grains appear to be the most euhedral, and range in size from <100 to over 300  $\mu\text{m}$ . All of the grains were found to be ca. 16.6 Ma, with a dispersion of <70 ka. The precision of these analyses is attributed to high radiogenic Pb content (up to 34 pg) of the grains and low common Pb content (often <0.3 pg) in the analyses.

**CRB1586\* (44.83067°N, 116.90138°W, elevation 641 m)**

This sample was collected from a ~0.5 m thick bed of lapilli tuff interbedded between columnar Innaha Basalt flows on route 71 south of Brownlee Dam in Idaho.

Accretionary lapilli are mm-cm scale and exhibit concentric banding around lithic nuclei.

Fewer than 50 zircons were separated from this sample, and are found to be glassy, somewhat blocky, and ranging in morphology from equant to tabular. Most of the grains

are around 100  $\mu\text{m}$  in length. Twenty-three grains were selected for analysis, and of these, 14 were successfully dated. One grain was found to be inherited, while the other 13 are dated to  $\sim 16.6$  Ma, with a dispersion of 120 ka. The youngest and most precise grains are among the largest analyzed, and have a high radiogenic Pb content (1-6 pg).

**CRB1611 (46.06924°N, 116.98544°W, elevation 266 m)**

This sample was collected from a  $\sim 0.2$  m layer of brecciated basalt flow top with red sedimentary infill overlying the Rock Creek Member of the Imnaha Basalt and underlying the Buckhorn Springs Member of the Grande Ronde Basalt (R1) along the Grande Ronde River near Rogersburg, WA (Stop 13 in (Reidel et al., 2016)). The sample consists of the fine-grained waxy red sediment, which was found outcropping in thin coherent layers as well as around some basalt clasts.

Fourteen grains were separated from this sample, and most of them appeared equant, glassy, and a mix of euhedral to somewhat rounded. All zircons were picked for analysis, and 6 were successfully dated. For this sample and the other samples described below, grains that were not successfully dated were lost at some stage of zircon chemistry prior to dating, or were dated and either did not fall on the Concordia line or exhibited a ratio of radiogenic Pb to common Pb that was  $\leq 1$ . Three of these grains were ca. 16.58 Ma, with a dispersion of 20 ka, while the other 3 were inherited. The successful analyses suffered from low radiogenic Pb content ( $< 1$  pg), potentially due to the small ( $\leq 100$   $\mu\text{m}$ ) size of the zircons, yielding generally less precise zircon ages for this sample than for the others in this study.

**CRB1640 (46.21153°N, 116.96839°W, elevation 271 m)**

This sample was collected from a ~0.5 m thick redbole overlying a Member of Center Creek lava flow and underlying an undifferentiated R1 Grande Ronde Basalt lava flow in the Schoolhouse Draw section of (Camp, 1976) near Asotin, WA. The sampled horizon was a fine red sediment with a few dark lithic fragments.

A few hundred zircons were obtained from this sample, with a range of morphologies, from small and equant to acicular grains a few hundred microns in length. Many grains were somewhat rounded, and some exhibited inherited cores. Most of the grains are orange, while a few were clear and glassy. Twenty-seven grains were selected for analysis, and 14 were successfully dated. Eight of the grains were inherited, while the other six grains were found to be ca. 16.5 Ma, with a dispersion of 180 ka. The youngest grains are prismatic, euhedral, and exhibit higher aspect ratios. Like CRB1611, the successful analyses suffered from low radiogenic Pb content (<1 pg), yielding generally less precise zircon ages for this sample than for the others in this study.

**CRB1636 (46.28875°N, 116.98751°W, elevation 218 m)**

This sample was collected from a ~1 m layer of brecciated basalt flow top with red sedimentary infill between lava flows of the Hoskin Gulch Member of the Grande Ronde Basalt (N1) along the Snake River south of Asotin, WA. The sample consists of the fine-grained red, pink, and orange sediment, with mm- to cm-scale dark lithic fragments and few vitreous microphenocrysts.

Approximately 60 zircons were separated from this sample, most of which with somewhat rounded crystal terminations and orange in color. Most of the grains are around 100  $\mu\text{m}$  in length, with a range of aspect ratios. Thirty-eight grains were selected for analysis, and of these, 21 were successfully dated. Nine grains were inherited, while the other 12 are dated to  $\sim 16.4$  Ma, with a dispersion of 150 ka. The youngest and most precise grains are among the largest or most euhedral analyzed, and have a high radiogenic Pb content ( $\sim 2$  pg).

**CRB1634\* (46.05072°N, 117.23906°W, elevation 538 m)**

This sample was collected from a redbole in the lower flows of the Wapshilla Ridge Member of the Grande Ronde Basalt, on Rattlesnake Grade in southeastern Washington. The redbole infills topography on the underlying brecciated flow top, with a maximum thickness of 0.3 m, but pinches out over a few meters width. The redbole contains a few mm-scale light and dark lithic fragments, with some vitreous phenocrysts.

Hundreds of zircons were obtained from this sample, ranging in size from 50-250  $\mu\text{m}$ . Most are orange in color but a few are clear. Half of the zircons presented an acicular morphology, 20% appeared equant, and the rest have a medium aspect ratio. Twenty-four zircons were selected for analysis, and eleven were successfully dated. All zircons were found to be ca. 16.3 Ma, with a dispersion of 160 ka. The youngest grains appear somewhat wide, clear, and euhedral, and the most precise analyses came from zircons with the greatest amount of radiogenic Pb (1-2 pg).

**CRB1556\* (46.08543°N, 117.17870°W, elevation 1145 m)**

This sample was collected from the same stratigraphic section as CRB1634, from a 0.6 m thick redbole between lava flows of the Meyer Ridge Member, immediately overlying the Wapshilla Ridge Member. The horizon was most coherent in its upper half, and displayed few vitreous phenocrysts and rare lithics.

The sample yielded 19 zircons, and all were picked for analysis; 7 were successfully dated. The zircons were either <100 µm and equant or larger and more tabular. A few were euhedral with pointy edges, while others appeared fragmented at the edges. The youngest, most precise analyses came from the largest grains. Even though these grains were not euhedral, they possessed the greatest amount of radiogenic Pb (1-2 pg). The grains exhibit a dispersion of 150 ka around ca. 16.3 Ma.

**CRB1519\* (46.44171°N, 117.39066°W, elevation 701 m)**

This sample was collected from a redbole found under a lava flow of the Meyer Ridge Member and overlying a lava flow Wapshilla Ridge Member, representing the same stratigraphic interval as CRB1556 but found 44 km away on US-12 east of Pomeroy, WA. The sample is fine-grained, with abundant vitreous microphenocrysts and few angular lithic fragments.

Hundreds of zircons were separated from this sample, and they appear mostly clear and glassy, with a few orange grains. Most present typical aspect ratio, while 10% are acicular and a few grains are equant. Many grains are subangular, with pointy tips

slightly worn down. Twenty-one grains were selected for analysis, and 10 were successfully dated. Two of the zircons analyzed were inherited, and appear somewhat opaque; five zircons were ca. 16.2 Ma but an age dispersion of 400 ka, outside the range of analytical uncertainty. The youngest grains each have one euhedral tip, are longer than 100  $\mu\text{m}$ , and the most precise analyses were for zircons with a higher radiogenic Pb content (2-4 pg).

**CRB1606 (46.44399°N, 117.74769°W, elevation 496 m)**

This sample was collected from a discontinuous ~0.7 m layer of red sedimentary infill of brecciated basalt flow top above the Member of Ortley and below the Fields Spring Member the Grande Ronde Basalt (N2), on Marengo Grade (Majorie Road) near Pomeroy, Washington. The sample is very-fine grained red to pink sediment with a few very fine light grains (possible phenocrysts) and very small, round, dark lithic fragments.

Approximately 1000 euhedral zircons were obtained from this sample, ranging in size from <100-250  $\mu\text{m}$ . Most grains were clear with a medium aspect ratio, while 10-20% of the grains were glassy, acicular, and prismatic. Forty-four zircons were selected for analysis, and eighteen were successfully dated. Zircons were found to be ca. 16.2-16.5 Ma, with a dispersion of 350 ka. The youngest grains appear especially elongate and acicular, and the most precise analyses came from zircons with 1-2 pg of radiogenic Pb.

**CRB1523 (46.43582°N, 117.32221°W, elevation 410 m)**

This sample was collected from a 10 cm, heterogeneous redbole found in the Fields Spring Member of the Grande Ronde Basalt (N2) on US-12 east of Pomeroy, WA, in the same stratigraphic transect as CRB1519.

Approximately 100 zircons were separated from this sample, and they are a mix of clear and glassy, and somewhat orange grains. Most are equant or present typical aspect ratio, while 10% are acicular. Many grains are slightly rounded. Fifty-three grains were selected for analysis, and 20 were successfully dated. Two of the zircons analyzed were inherited; the rest range in age from ~16.1-16.5 Ma. The youngest grains are mostly acicular and a few hundred microns long, and the most precise analyses were for zircons with a higher radiogenic Pb content (1-4 pg).

**CRB1531 (46.95243°N, 119.99783°W, elevation 227 m)**

This sample was collected from the lowermost unit of the Vantage Interbed type locality in Vantage, WA (Stop 7 in (Tolan et al., 2009)), which is 15 cm of a white mud, with possible spherules and tiny vitreous phenocrysts. The Vantage Interbed lies over the Basalt of Museum of the Sentinel Bluffs Member of N2 of the Grande Ronde Basalt, and under the Basalt of Ginkgo of the Frenchman Springs Member of the Wanapum Basalt.

Fewer than 100 zircons were obtained from this sample, and all are clear and prismatic, with a mix of rounded and euhedral grains. The zircons range in size from 100-200  $\mu\text{m}$ , and are a mix of equant and normal aspect ratio grains, while 10% of the grains are

acicular. Thirty-three zircons were selected for analysis, and 18 of these were successfully dated, with 15 grains found younger than 16.8 Ma. The age dispersion of these samples is greater than 700 ka, well beyond analytical uncertainty, suggesting pre-eruptive crystallization. The youngest grains are prismatic with a medium aspect ratio, and the most precise analyses are due to radiogenic Pb content >1 pg.

**CRB1533\* (46.95243°N, 119.99783°W, elevation 227 m)**

This sample was collected from 2 kg of 1-10 cm-scale pumice clasts embedded in the volcanoclastic sediments of the Vantage Interbed type locality in Vantage, WA (Stop 7 in Tolan *et al.* (61)). Phenocrysts in the pumice contained quartz and sanidine, and the sampled horizon consisted of 1.4 m of the total 5.6 m of the Vantage Interbed exposed at the outcrop. The Vantage Interbed lies over the Basalt of Museum of the Sentinel Bluffs Member of N2 of the Grande Ronde Basalt, and under the Basalt of Ginkgo of the Frenchman Springs Member of the Wanapum Basalt.

Several thousand zircons were obtained from this sample, and all are clear, prismatic, and euhedral. The zircons range in size from 50-300  $\mu\text{m}$ , and about 10% are equant grains, while 10% of the grains are acicular. Forty zircons were selected for analysis, and 11 of these were successfully dated, with 9 grains found younger than 17 Ma. The age dispersion of these samples is greater than 500 ka, well beyond analytical uncertainty, suggesting pre-eruptive crystallization. The youngest grains appear to be the most acicular in morphology, and the most precise analyses are due to high radiogenic Pb content of 5-15 pg.

**CRB1506\* (46.73914°N, 117.75500°W, elevation 470 m)**

This sample was collected from 0.3 m of a fine white crumbly ash, with few round lithic fragments and glassy phenocrysts, interbedded between the overlying Basalt of Lolo of the Priest Rapids Member of the Wanapum Basalt and the underlying Roza Member of the Wanapum Basalt, on WA-127 southeast of Endicott, WA.

Hundreds of zircons were obtained from this sample, most of which are clear and subangular to subrounded. While a few zircons were angular, none were acicular. Thirty-five grains were selected for analysis, and 10 were successfully dated. Four of these were inherited, and the remaining six grains have a uniform age distribution within  $2\sigma$  uncertainty, of ca. 15.9 Ma. The youngest and most precise dates were obtained from somewhat opaque, orange-tinted zircons that were euhedral, and had high radiogenic Pb content of 11-40 pg.

**METHODS**

Methods are as described in Kasbohm & Schoene (2018), Schoene *et al.* (2015) and Samperton *et al.* (2015).

**Zircon Separation and Preparation**

Zircons were separated from their host rock through standard methods of crushing, gravimetric-, and magnetic-separation techniques using a Bico Braun “Chipmunk” Jawcrusher, disc mill, hand pan, hand magnet, Frantz isodynamic separator, and methylene iodide. Zircons from the least magnetic and most dense mineral separate were

transferred in bulk to quartz crucibles and annealed in a muffle furnace at 900°C for 48 hours after Mattinson (Mattinson, 2005). After annealing, 20-40 zircon grains from each sample were photographed (Fig. DR2) and picked in reagent-grade ethanol for analysis. Given the low radiogenic Pb content of the samples, cathodoluminescence images were not obtained. Euhedral grains with a range of morphologies were selected, while those with visible cracks, inclusions, and cores were avoided. Individual grains were transferred using stainless steel picking tools to separate 3-mL Savillex Hex beakers containing distilled acetone and taken to the clean lab for analysis.

#### **U-Pb Zircon ID-TIMS Analysis**

Single zircon grains were loaded into 200  $\mu$ L Savillex “micro”-capsules with 100  $\mu$ L 29 M HF + 15  $\mu$ L 3N HNO<sub>3</sub> for a single leaching step in high-pressure Parr bombs at 185°C for 12 h to remove crystal domains affected by Pb loss (Mattinson, 2005). Grains were rinsed post-leaching in 6 N HCl, MQ H<sub>2</sub>O, 3N HNO<sub>3</sub>, and 29 M HF prior to spiking with EARTHTIME <sup>205</sup>Pb-<sup>233</sup>U-<sup>235</sup>U tracer and addition of 100 $\mu$ L 29 M HF + 15  $\mu$ L 3N HNO<sub>3</sub> (Condon et al., 2015; McLean et al., 2015). Zircons were then dissolved to completion in Parr bombs at 210°C for 48 h. Dissolved zircon solutions were subsequently dried down, dissolved in 100  $\mu$ L 6N HCl, and converted to chlorides in Parr bombs at 185°C for 12 h, after which solutions were dried again and brought up in 50  $\mu$ L 3N HCl. The U-Pb and trace element aliquots were then separated by anion exchange chromatography using 50  $\mu$ L columns and AG-1 X8 resin (200-400 mesh, chloride from Eichrom) (Krogh, 1973), and dried down with a microdrop of 0.015 M H<sub>3</sub>PO<sub>4</sub>. The dried U and Pb aliquot was

loaded in a silica gel emitter (Gerstenberger & Haase, 1997) to an outgassed zone-refined Re filament.

Isotopic determinations were performed using an IsotopX PhoeniX-62 thermal ionization mass spectrometer (TIMS) at Princeton University, with Pb analysis performed in peak-hopping mode on a Daly-photomultiplier ion-counting detector. A correction for mass-dependent Pb fractionation was applied using a Pb fractionation of  $0.182 \pm 0.041\%$ /amu, as determined by repeat measurements of NBS982 at Princeton. A Daly-photomultiplier deadtime of 28.8 ns was used, as determined by repeat measurements of NBS standards. Corrections for interfering isotopes under masses 202, 204, and 205 were made cycle-by-cycle by measuring masses 201 and 203 and assuming they represent  $^{201}\text{BaPO}_4$  and  $^{203}\text{Tl}$  and using natural isotopic abundances to correct for  $^{202}\text{BaPO}_4$ ,  $^{204}\text{BaPO}_4$ ,  $^{205}\text{BaPO}_4$ , and  $^{205}\text{Tl}$ .

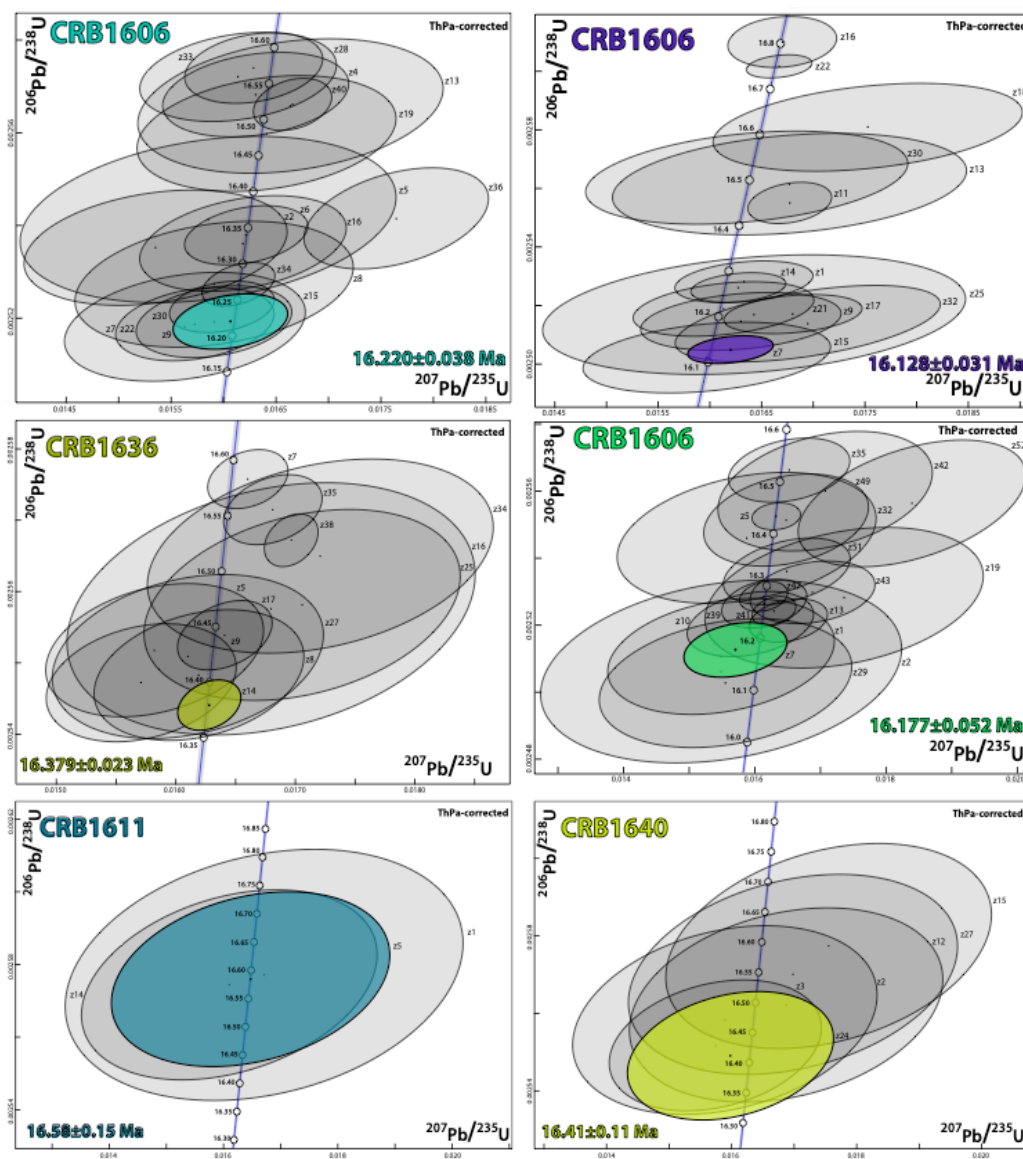
$\text{UO}_2$  measurements were performed in static mode on Faraday cups with a bulk U fractionation correction calculated from the deviation of measured  $^{233}\text{U}/^{235}\text{U}$  from the known tracer  $^{233}\text{U}/^{235}\text{U}$  ( $0.995062 \pm 0.000054$  ( $1\sigma$ )), and an oxide composition of  $^{18}\text{O}/^{16}\text{O}$  of 0.00205 was used (Nier, 1950). Data reduction was performed using the programs Tripoli and U-Pb Redux (Bowring et al., 2011; McLean et al., 2011) and the decay constants of Jaffey *et al.* (1971). All Pbc was attributed to laboratory blank with a mean isotopic composition determined by total procedural blank measurements (see Table DR1 for values). Uncertainties in reported U-Pb zircon dates are at the 95% confidence level and exclude tracer calibration and decay constant uncertainties. Correction for initial

$^{230}\text{Th}$  disequilibrium in the  $^{206}\text{Pb}/^{238}\text{U}$  system was made on a fraction-by-fraction basis by estimating  $(\text{Th}/\text{U})_{\text{magma}}$  using  $(\text{Th}/\text{U})_{\text{zircon}}$  determined by TIMS and a mean  $(\text{Th}/\text{U})_{\text{zircon-magma}}$  partition coefficient ratio of  $0.19 \pm 0.11$ , which encompasses the range of values for  $(\text{Th}/\text{U})_{\text{zircon-magma}}$  partition coefficients obtained from glasses from a variety of volcanic settings (Claiborne et al., 2018). Uncertainties for the resulting  $(\text{Th}/\text{U})_{\text{magma}}$  were also calculated on a fraction-by-fraction basis, propagating the uncertainty in the  $(\text{Th}/\text{U})_{\text{zircon-magma}}$  partition coefficient. We found in our prior work (Kasbohm & Schoene, 2018) that these corrections for  $^{230}\text{Th}$  disequilibrium affect our results by no more than  $\pm 10$  ka, compared to an alternative approach using a constant  $(\text{Th}/\text{U})_{\text{magma}}$  of  $3.5 \pm 1.0$ . Given the likelihood that the zircons in this study were crystallized from a variety of different magmatic systems, we prefer the constant partition coefficient approach for correcting Th/U disequilibrium.

## **U-PB AGE INTERPRETATIONS**

Given the physical characteristics of both rock samples and zircons, the geochronology samples for this study are interpreted to be volcanic in origin, and deposited by unrelated regional silicic volcanism during cessations in CRBG volcanism. The presence of phenocrysts, lithic fragments, and fragments of basaltic pumice found at the hand sample scale are consistent with ash deposits, and the euhedral and prismatic appearance of the zircons are consistent with magmatic textures, with little evidence for rounding seen in alluvial or eolian grains.

Full U-Pb isotope results are given in Table DR1, and Concordia plots for each sample are given in Fig. DR3. All dates are presented with  $2\sigma$  uncertainty, which represents internal errors only. In Table DR2, alternative age interpretations are also given with  $2\sigma$  uncertainties of  $\pm X/Y/Z$ . X is used for most of the geochronological uncertainty



**Fig. DR3. Concordia Plots for U-Pb ID-TIMS Geochronological Data.** U-Pb isotopic data for each analysis is available in Table DR1. Each ellipse is labelled and represents a zircon analysis, with the width of the ellipse representing  $2\sigma$  uncertainty. The youngest, most precise zircon age obtained for each sample is highlighted. The shading around the Concordia line represents uncertainties in the U decay constants. Almost all ellipses overlap with Concordia, indicating closed-system behavior.

described in this paper, and indicates internal uncertainties only for comparison with U-Pb dates from labs using ET-(2)535 tracer solution. Y also incorporates tracer calibration uncertainties for comparison with other U-Pb dates determined with different tracer solution. Z includes full systematic uncertainties, including decay constants, to allow for comparison with other radioisotopic dates or astrochronologically-determined timescales that may be tied to other radioisotopic dates that are not derived from the U-Pb system (Renne et al., 1998; Schoene et al., 2006).

### **Interpretation of Zircon Crystallization Age Spectra**

The zircons dated from each geochronology sample displayed a dispersion in ages ranging from 40-700 ka (apart from inherited grains). We interpret this as geological scatter caused by pre-eruptive zircon crystallization or incorporation of zircons from older material in the same volcanic system (Cooper, 2015; Stelten et al., 2015), because the dispersion in most cases goes beyond analytical uncertainty. In Table DR2, we present a variety of different age interpretations to address these complex age spectra. While we suggest that our simulated stratigraphic model ages, based on Bayesian eruption ages with a triangular prior, best address the geologic uncertainty inherent in these interpretations, Table DR2 shows that alternative interpretations yield overlapping results. Therefore, our main conclusions about the dynamics of CRBG emplacement do not depend on the mode of zircon age interpretation.

In Kasbohm & Schoene (2018), we presented the youngest, most precise zircon dates as best representing the ages of the horizons in the study, since that zircon likely crystallized closest in time to the eruption of the volcanic ash. However, even following chemical abrasion, subtle Pb-loss may be difficult to detect. Meanwhile, other geochronological studies use weighted means of several zircon dates to constraint the age of the sample. Although a weighted mean date has lower uncertainty than a single crystal age, it should only be used for homogeneous age populations where all scatter is caused by analytical uncertainty, which is not the best interpretation for our samples, given the complexity of pre-eruptive crystallization. As a mean route between these approaches, in some cases geochronologists calculate the weighted mean age of the youngest few grains. However, as described in Keller et al. (2018), a statistical model for Bayesian eruption ages incorporating timescales of zircon saturation provides a more objective approach for interpreting zircon age spectra, yielding more accurate if somewhat less-precise results. The only subjective element of these model ages is whether a uniform, bootstrapped, or triangular prior of zircon crystallization is chosen (Keller et al., 2018). We prefer the Bayesian eruptive ages, and suggest that a triangular prior, with linear increase of zircon mass as time passes, provides the most geologically relevant interpretation. To further refine our ages, we use a second Markov Chain Monte Carlo simulation taking into account the stratigraphic position and cumulative volume erupted by each sample in succession, and we use the outputs of this model in all figures and discussion in the paper.



Using these six different interpretations, we calculate ages for all of our samples and present them in Figure DR2. Ultimately, all of the interpretations produce overlapping ages, showing that our preferred interpretation does not bias the conclusions of our work.

## GEOMAGNETIC POLARITY TIMESCALE CALIBRATION

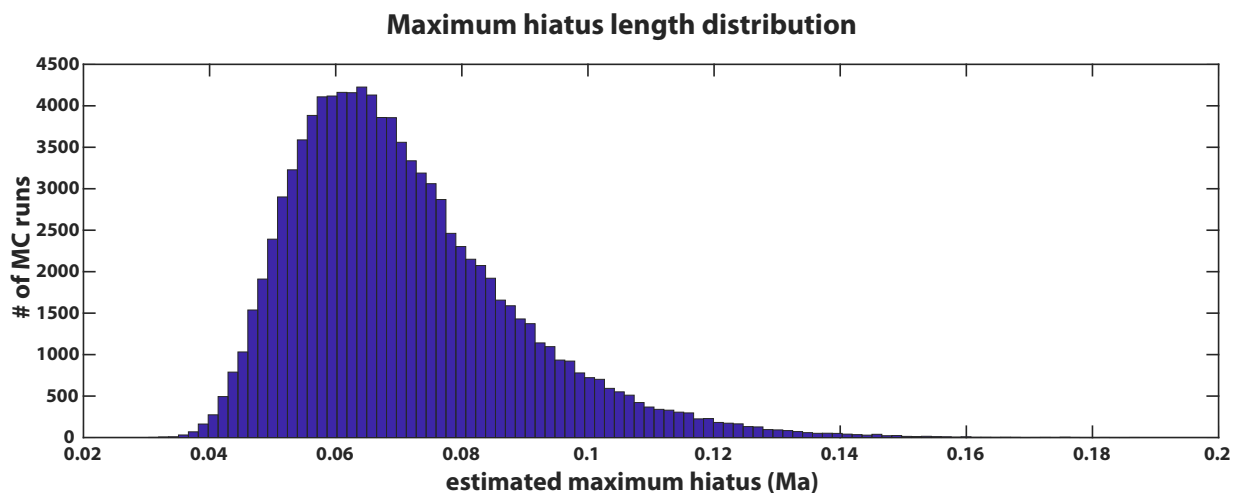
Our CRBG age model yields ages for magnetic field reversals that occurred during the emplacement of the basalts, as well as chron durations during this period, reported with 95% credible intervals. In Table DR3, we compare our reversal ages to astronomically tuned age models from Sites U1335 and U1336 (Kochhann et al., 2016), Site 1090 (Billups et al., 2004), Site 154 (Pälike et al., 2006), and spline fits from the Astronomically Tuned Neogene Timescale (ATNTS) from the Geologic Time Scale 2012 (Hilgen et al., 2012). We find the greatest agreement between our model and the tuning results of Kochhann et al. (2016).

Polarity Chron Onset	CRBG Reversal Age Model					Other GPTS Calibrations					Reversal Age Differences				
	Cumulative Volume (km <sup>3</sup> )	Reversal Age (Ma)	Maximum Reversal Age (Ma)	Minimum Reversal Age (Ma)	Chron Duration (ka)	U1335 Tuned Age (Ma)	U1336 Tuned Age (Ma)	1090 Tuned Age (Ma)	154 Tuned Age (Ma)	ATNTS 2012 Spline Age (Ma)	Δ CRBG Age - U1335 Age (Ma)	Δ CRBG Age - U1336 Age (Ma)	Δ CRBG Age - 1090 Age (Ma)	Δ CRBG Age - 154 Age (Ma)	Δ CRBG Age - ATNTS 2012 Age (Ma)
C5Br	202942	15.906	15.959	15.888	-	15.896	15.994	15.898	15.899	15.974	agrees	-0.035	agrees	agrees	-0.015
C5Cn.1n	157600	16.215	16.259	16.168	296+45/-63	16.242	16.261	16.161	16.162	16.268	agrees	-0.002	0.007	0.006	-0.009
C5Cn.1r	101600	16.340	16.385	16.292	126+55/-54	16.34	16.351	16.255	16.256	16.303	agrees	agrees	0.037	0.036	agrees
C5Cn.2n	77000	16.443	16.486	16.386	100+56/-58	16.415	16.434	16.318	16.319	16.472	agrees	agrees	0.068	0.067	agrees
C5Cn.2r	42800	16.565	16.590	16.522	122+51/-45	16.514	16.532	16.405	16.406	16.543	0.008	agrees	0.117	0.116	agrees
C5Cn.3n	23850	16.629	16.677	16.592	65+52/-38	16.582	16.637	16.498	16.499	16.721	0.01	agrees	0.094	0.093	-0.044

**Table DR3. Geomagnetic Polarity Timescale Calibration.** Using our stratigraphic CRBG age model, we provide here ages for polarity chron onsets and chron durations during CRBG emplacement, reported with 95% credible intervals. We compare our reversal ages to astronomically tuned age models from Sites U1335 and U1336 (Channell et al., 2013; Kochhann et al., 2016; Ohneiser et al., 2013), Site 1090 (Billups et al., 2004), Site 154 (Pälike et al., 2006), and the spline fit based on magnetic seafloor anomalies from the Astronomically Tuned Neogene Timescale (ATNTS) in Geologic Time Scale 2012 (Hilgen et al., 2012). We find the greatest agreement between our model and the tuning results of Kochhann et al. (2016).

## HIATUS DURATION CALCULATION

We query our Monte Carlo age model to find the length of the longest hiatus in each model run, and plot the results in the histogram in Figure DR4. This plot shows that the longest hiatus during CRBG emplacement was most likely 50-80 ka, and we show the likelihood of that longest hiatus occurring at each stratigraphic position in Figure 3.



**Figure DR4. Maximum hiatus length.** This histogram plots the frequency of durations for the longest hiatus calculated for each Monte Carlo simulation. The longest CRBG hiatus was most likely 50-80 ka.

**Table DR1. U-Pb Isotopic Data.** Data acquired by CA-ID-TIMS is presented following the references, with various corrections as specified in the notes beneath the table.

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Table DR1: U-Pb Isotopic Data

Sample	Dates (Ma)							Composition					Isotopic Ratios								Corr. coef.
	206Pb/238U		207Pb/235U		207Pb/206Pb		% disc	Pb* (pg)	Pbc (pg)	Pb*/Pbc	Th/U	Th/U(magma)	206Pb/204Pb	208Pb/206Pb	238U ±2σ %	207Pb/235U ±2σ %	207Pb/206Pb ±2σ %	208Pb/206Pb ±2σ %			
	absolute	±2σ	absolute	±2σ	absolute	±2σ													d	e	
<b>CRB1531</b>																					
z7	16.128	0.031	16.32	0.41	44	60	72.4	1.70	0.28	6.05	0.24	1.26	418	0.08	0.0024912	0.190	0.0162039	2.553	0.0471954	2.499	0.317
z15	16.110	0.078	16.1	1.2	13	177	39.6	0.887	0.40	2.23	0.42	2.21	159	0.14	0.0024885	0.487	0.0159743	7.493	0.0465771	7.357	0.309
z32	16.185	0.084	17.1	1.3	143	172	89.7	1.07	0.25	4.24	0.44	2.32	283	0.14	0.0025001	0.523	0.0169512	7.565	0.0491961	7.310	0.514
z9	16.190	0.064	16.4	1.0	50	140	74.6	1.45	0.53	2.75	0.50	2.63	188	0.16	0.0025009	0.396	0.0163039	5.948	0.0473036	5.850	0.277
z25	16.20	0.13	16.5	2.0	66	292	79.5	1.74	1.37	1.28	0.43	1.58	99	0.14	0.0025046	0.819	0.0164320	12.450	0.0476042	12.255	0.269
z17	16.206	0.043	16.92	0.67	120	92	87.9	0.922	0.22	4.25	0.45	2.37	283	0.14	0.0025033	0.267	0.0168077	3.976	0.0487173	3.906	0.294
z21	16.217	0.060	16.25	0.87	21	128	53.7	0.967	0.31	3.09	0.43	2.26	212	0.14	0.0025051	0.373	0.0161364	5.420	0.0467383	5.307	0.334
z14	16.264	0.033	16.39	0.46	35	67	67.0	2.18	0.35	6.29	0.80	4.21	377	0.26	0.0025124	0.202	0.0162799	2.825	0.0470170	2.775	0.278
z1	16.277	0.046	16.45	0.67	41	96	70.6	1.76	0.44	4.02	0.48	2.53	267	0.15	0.0025144	0.284	0.0163342	4.087	0.0471370	4.012	0.295
z11	16.450	0.045	16.89	0.40	80	56	82.5	2.93	0.40	7.33	0.49	2.58	470	0.16	0.0025414	0.277	0.0167771	2.416	0.0479012	2.354	0.278
z13	16.49	0.11	16.9	1.7	74	239	81.2	1.89	1.22	1.55	0.46	2.42	115	0.15	0.0025478	0.683	0.0167747	10.210	0.0477739	10.048	0.267
z30	16.51	0.10	16.5	1.6	12	225	35.5	0.723	0.41	1.78	0.44	2.32	130	0.14	0.0025499	0.626	0.0163611	9.524	0.0465561	9.349	0.311
z18	16.62	0.10	17.6	1.5	160	196	90.4	0.379	0.20	1.92	0.47	2.47	137	0.15	0.0025672	0.587	0.0175315	8.534	0.0495511	8.352	0.341
z22	16.750	0.025	16.79	0.32	22	45	53.1	4.09	0.46	8.86	0.55	2.89	556	0.18	0.0025880	0.152	0.0166753	1.904	0.0467524	1.866	0.287
z16	16.803	0.056	16.82	0.53	19	75	47.9	1.86	0.23	8.08	0.44	2.32	525	0.14	0.0025963	0.335	0.0167046	3.151	0.0466849	3.117	0.152
<b>CRB1523</b>																					
z7	16.177	0.052	15.82	0.79	-38	120	167.2	1.78	0.53	3.38	0.50	2.63	227	0.16	0.0024989	0.327	0.0157086	5.000	0.0456118	4.920	0.275
z29	16.11	0.12	15.7	1.9	-52	297	142.6	1.08	0.84	1.29	0.31	1.68	103	0.10	0.0024890	0.776	0.0155578	12.371	0.0453550	12.188	0.265
z2	16.14	0.18	15.6	2.8	-66	428	131.1	0.848	0.91	0.93	0.42	2.21	77	0.14	0.0024925	1.099	0.0154905	17.758	0.0450945	17.515	0.250
z1	16.16	0.11	15.6	1.7	-70	269	128.7	1.21	0.82	1.46	0.36	1.89	112	0.11	0.0024969	0.696	0.0154899	11.150	0.0450126	10.988	0.263
z10	16.227	0.063	16.0	1.0	-11	143	-385.2	1.52	0.58	2.64	0.32	1.68	189	0.10	0.0025067	0.390	0.0159363	6.043	0.0461298	5.937	0.302
z13	16.234	0.042	16.63	0.60	74	85	81.6	1.69	0.39	4.37	0.40	2.11	295	0.13	0.0025077	0.258	0.0165143	3.623	0.0477838	3.559	0.281
z41	16.252	0.028	16.41	0.33	40	48	69.6	2.89	0.37	7.89	0.36	1.89	523	0.12	0.0025105	0.175	0.0162960	2.050	0.0470994	2.005	0.299
z39	16.266	0.047	16.26	0.65	16	95	44.8	1.01	0.25	4.00	0.32	1.68	278	0.10	0.0025128	0.291	0.0161487	4.023	0.0466317	3.941	0.312
z19	16.28	0.13	17.5	2.1	186	279	91.9	0.497	0.40	1.25	0.36	1.89	98	0.12	0.0025145	0.839	0.0173651	12.213	0.0501095	11.978	0.311
z47	16.280	0.029	16.25	0.37	12	54	37.2	1.76	0.22	7.82	0.41	2.16	512	0.13	0.0025149	0.178	0.0161386	2.267	0.0465629	2.228	0.254
z43	16.288	0.060	17.0	1.0	118	131	87.7	0.931	0.33	2.83	0.31	1.63	202	0.10	0.0025162	0.372	0.0168834	5.638	0.0468873	5.556	0.252
z51	16.328	0.064	16.60	0.97	57	136	76.9	0.887	0.31	2.88	0.31	1.63	205	0.10	0.0025224	0.396	0.0164914	5.858	0.0474401	5.718	0.384
z32	16.39	0.13	16.0	2.0	-44	297	154.5	0.663	0.51	1.31	0.27	1.42	105	0.09	0.0025324	0.777	0.0158795	12.424	0.0454992	12.212	0.302
z49	16.426	0.088	16.6	1.3	41	179	70.0	3.18	1.53	2.08	0.32	1.68	153	0.10	0.0025376	0.545	0.0164811	7.617	0.0471247	7.480	0.285
z5	16.433	0.026	16.44	0.37	18	54	48.3	4.01	0.49	8.17	0.37	1.95	539	0.12	0.0025388	0.158	0.0163315	2.263	0.0466759	2.244	0.155
z52	16.46	0.12	18.5	1.7	294	208	94.7	0.462	0.26	1.80	0.35	1.84	134	0.11	0.0025427	0.749	0.0183993	9.431	0.0525054	9.117	0.452
z42	16.48	0.11	17.2	1.6	117	221	87.4	0.802	0.49	1.64	0.27	1.42	126	0.09	0.0025463	0.706	0.0170762	9.568	0.0468599	9.370	0.315
z35	16.522	0.062	16.64	0.92	34	132	65.2	1.39	0.47	2.94	0.42	2.21	204	0.13	0.0025526	0.376	0.0165273	5.596	0.0469805	5.499	0.290
<b>CRB1606</b>																					
z9	16.220	0.038	16.18	0.55	11	80	34.1	2.18	0.46	4.72	0.40	2.16	317	0.13	0.0025055	0.238	0.0160697	3.398	0.0465377	3.338	0.284
z15	16.213	0.076	15.7	1.1	-54	176	139.8	1.06	0.47	2.26	0.41	2.16	161	0.13	0.0025045	0.471	0.0156361	7.340	0.0453011	7.226	0.272
z7	16.216	0.051	15.84	0.76	-40	115	161.1	2.18	0.62	3.54	0.49	2.58	237	0.16	0.0025050	0.317	0.0157311	4.803	0.0455661	4.724	0.281
z22	16.220	0.050	16.03	0.74	-13	111	-1707.4	1.98	0.57	3.49	0.40	2.11	239	0.13	0.0025056	0.310	0.0159131	4.662	0.0460833	4.587	0.274
z30	16.240	0.036	16.10	0.50	-5	74	-75.0	6.33	1.19	5.31	0.50	2.63	345	0.16	0.0025087	0.221	0.0159885	3.127	0.0462431	3.074	0.274
z8	16.272	0.087	16.0	1.3	-20	199	346.3	1.46	0.71	2.05	0.61	3.21	141	0.19	0.0025136	0.541	0.0159148	8.334	0.0459409	8.204	0.271
z34	16.272	0.030	16.26	0.35	14	50	42.9	1.61	0.18	8.70	0.46	2.52	559	0.15	0.0025135	0.187	0.0161469	2.155	0.0466124	2.088	0.394
z2	16.322	0.080	15.5	1.3	-115	198	116.1	2.14	1.01	2.12	0.41	2.16	153	0.13	0.0025215	0.495	0.0153568	8.164	0.0441915	8.039	0.281
z16	16.328	0.066	16.30	0.98	13	143	38.1	2.31	0.73	3.16	0.95	5.00	192	0.31	0.0025224	0.409	0.0161900	6.082	0.0465719	5.962	0.323
z6	16.340	0.041	16.33	0.59	15	85	44.1	1.56	0.34	4.63	0.37	1.95	314	0.12	0.0025242	0.253	0.0162203	3.625	0.0466264	3.551	0.325
z5	16.36	0.12	16.0	1.8	-43	271	156.4	0.987	0.67	1.47	0.43	2.26	111	0.14	0.0025276	0.712	0.0158569	11.301	0.0455200	11.130	0.270
z36	16.363	0.070	17.76	0.88	211	112	92.7	1.23	0.30	4.15	0.53	2.79	271	0.17	0.0025278	0.434	0.0176500	4.983	0.0506627	4.829	0.394
z19	16.481	0.080	16.5	1.2	23	178	55.4	1.67	0.80	2.08	0.33	1.79	153	0.11	0.0025461	0.492	0.0164139	7.520	0.0467768	7.408	0.259
z13	16.519	0.093	16.8	1.5	51	206	74.4	1.15	0.65	1.78	0.34	1.79	133	0.11	0.0025521	0.571	0.0166423	8.745	0.0473162	8.613	0.263
z40	16.521	0.036	16.77	0.37	53	52	75.3	2.29	0.32	7.23	0.36	1.89	480	0.12	0.0025525	0.220	0.0166622	2.242	0.0473660	2.189	0.285
z4	16.535	0.059	16.42																		

z38	16.528	0.024	17.08	0.22	96	31	84.9	2.59	0.22	11.97	0.26	1.37	805	0.08	0.0025535	0.143	0.0169700	1.326	0.0482220	1.287	0.320
z35	16.556	0.032	16.93	0.41	70	57	80.3	1.33	0.20	6.63	0.40	2.11	438	0.13	0.0025577	0.191	0.0168160	2.455	0.0477047	2.398	0.333
z7	16.583	0.027	16.72	0.34	36	48	66.9	2.20	0.28	8.00	0.40	2.11	524	0.13	0.0025621	0.160	0.0166071	2.025	0.0470322	1.984	0.285
<b>CRB1640</b>																					
z24	16.41	0.11	16.1	1.6	-30	246	199.0	0.714	0.43	1.65	0.55	2.89	119	0.18	0.0025353	0.655	0.0159867	10.310	0.0457526	10.152	0.271
z3	16.43	0.11	15.9	1.7	-70	259	129.1	0.549	0.33	1.64	0.59	3.11	117	0.19	0.0025381	0.667	0.0157440	10.775	0.0450099	10.613	0.272
z2	16.47	0.16	16.0	2.4	-53	368	142.0	0.851	0.76	1.11	0.53	2.79	87	0.17	0.0025446	0.959	0.0158967	15.318	0.0453296	15.089	0.268
z12	16.50	0.16	17.0	2.5	87	347	83.7	0.865	0.78	1.10	0.59	3.11	85	0.19	0.0025485	0.985	0.0168759	14.852	0.0480489	14.619	0.268
z27	16.55	0.17	17.1	2.6	95	361	84.9	0.291	0.27	1.07	0.52	2.74	84	0.17	0.0025563	1.013	0.0169859	15.498	0.0482130	15.241	0.285
z15	16.59	0.17	17.7	2.6	166	340	90.8	0.668	0.61	1.10	0.50	2.63	86	0.16	0.0025637	1.035	0.0175560	14.836	0.0496888	14.549	0.309
<b>CRB1611</b>																					
z5	16.58	0.15	16.6	2.4	17	350	46.68	0.771	0.69	1.12	0.48	2.47	88	0.153	0.002562	0.94	0.0165	15	0.0467	15	0.276
z14	16.57	0.17	16.2	2.6	-36	383	172.75	0.513	0.46	1.11	0.49	2.58	87	0.157	0.002561	1.0	0.0161	16	0.0456	16	0.322
z1	16.59	0.22	16.8	3.5	51	490	74.20	0.480	0.62	0.77	0.48	2.53	66	0.153	0.002563	1.4	0.0167	21	0.0473	21	0.255

a Corrected for initial Th/U disequilibrium using radiogenic 208Pb and Th/U[magma] specified.

b Corrected for initial Pa/U disequilibrium using initial fraction activity ratio  $[^{231}\text{Pa}]/[^{235}\text{U}] = 1.10000$ .

c % discordance =  $100 - (100 * (206\text{Pb}/238\text{U date}) / (207\text{Pb}/206\text{Pb date}))$

d Total mass of radiogenic Pb.

e Total mass of common Pb.

f Ratio of radiogenic Pb (including 208Pb) to common Pb.

g Th contents calculated from radiogenic 208Pb and 230Th-corrected 206Pb/238U date of the sample, assuming concordance between U-Pb Th-Pb systems.

h Th/U ratio of magma from which mineral crystallized.

i Measured ratio corrected for fractionation and spike contribution only.

j Measured ratios corrected for fractionation, tracer and blank. Values for ET535 are found in Condon et al. (2015) and McLean et al. (2015). Blank model values are as follows:

206Pb/204Pb	18.628271±0.317714
207Pb/204Pb	15.796256±0.232017
208Pb/204Pb	38.535874±0.375848

## Chapter 5

### **High-precision U-Pb zircon geochronology of the Miocene Bisciario Formation, Contessa Section, Italy: A case study for requisite radiometric calibration of bio- and magnetostratigraphy**

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*This will be submitted to a journal with authors J. Kasbohm, B. Schoene, and A.*

*Montanari*

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#### **ABSTRACT**

The Contessa section near Gubbio, Italy has yielded numerous insights into Cenozoic Earth history. The deposition of bentonite layers containing zircon in the uppermost, Miocene portion of the section allows for the acquisition of absolute, high-precision ages through U-Pb zircon geochronology. Here, we present four ages from the Contessa – Il Testimone section, which revise prior  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology and provide new age constraints on the Bisciario Formation. We find that the section was deposited between ~22.3 and 20.1 Ma, with a hiatus lasting ~1 Ma in the lower Bisciario. Our results suggest that biostratigraphic data may be skewed by absence of foraminifera following their

regional first occurrence and preceding their last occurrence, as a result of poor preservation. Additionally, prior magnetostratigraphy overestimated the number of magnetic field reversals due to unreliable data. Given these inconsistencies and the presence of hiatuses in the section, we reject the recent suggestion that the Contessa section could serve as the Burdigalian Global Stratigraphic Section and Point. We suggest that wherever possible, absolute geochronology should be used to calibrate sedimentary sections, as a way to verify the accuracy of age models based on biostratigraphy, magnetostratigraphy, and astronomical tuning.

## **INTRODUCTION**

The Contessa section (Gubbio, Italy), is noteworthy for its nearly continuous sedimentary record of Cenozoic Earth history. Spanning the Jurassic to the Miocene, this section contains the ‘Selli’ and ‘Bonarelli’ black shales from which the Cretaceous Oceanic Anoxic Events were inferred, hyperthermal events in the early Paleogene and middle Eocene, and sedimentary evidence for intervals of tectonic activity in the Mediterranean (Montanari et al., 1997). Numerous bio-, chemo-, and magnetostratigraphic studies have been performed on this section (Coccioni et al., 2010; Jovane et al., 2007), and many portions of the section have been calibrated in age by astronomical tuning (Galeotti et al., 2010; Jovane et al., 2010).

The Early Miocene Bisciario Formation, near the top of the Contessa section, is noteworthy for its quantity of volcanoclastic layers that are interbedded with marly and glauconitic limestone. This unit is interpreted as representing the transition from pelagic

carbonate deposition to siliciclastic turbidite deposition in the Apennine foredeep, concurrent with a pulse of calc-alkaline intermediate volcanism elsewhere in the Mediterranean (Guerrera et al., 2015; Montanari et al., 1997). Because the volcanoclastic layers contained biotite and plagioclase suitable for dating through  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology, the Bisciario was included in an integrated study of the Early Miocene Contessa-II Testimone (CT) portion of section that combined  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology, biostratigraphy, chemostratigraphy, and magnetostratigraphy (Montanari et al., 1997). While astronomical tuning has not yet been successfully performed in the CT section, due to at least three documented hiatuses, the presence of bentonitic layers and advances in radiometric dating encourage an absolute calibration of magnetostratigraphic and biostratigraphic data produced from the 21 m exposed of this section.

Prior  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology from the CT section yielded ages of  $21.88 \pm 0.32$  Ma and  $19.67 \pm 0.30$  Ma through incremental heating of plagioclase separates. Paleomagnetic and biostratigraphic study suggested that nearly 5 Ma was represented in the CT and overlying CV section, from 22-17 Ma (Montanari et al., 1997). Here, we use high-precision U-Pb CA-ID-TIMS geochronology to produce four new bentonite ages from the CT section. We show that this section represents only 2 Ma of deposition, including an  $\sim 1$  Ma hiatus. We suggest that the paleomagnetic and biostratigraphic data obtained for this carbonate section may be unreliable, as a result of magnetic mineralogy and poor foraminiferal preservation. Even with our new high-precision geochronology, we reject the recent suggestion of Fabbrini et al. (2019) that the Aquitanian-Burdigalian GSSP (Global Stratotype Section and Point) be placed in the Contessa section, because of these

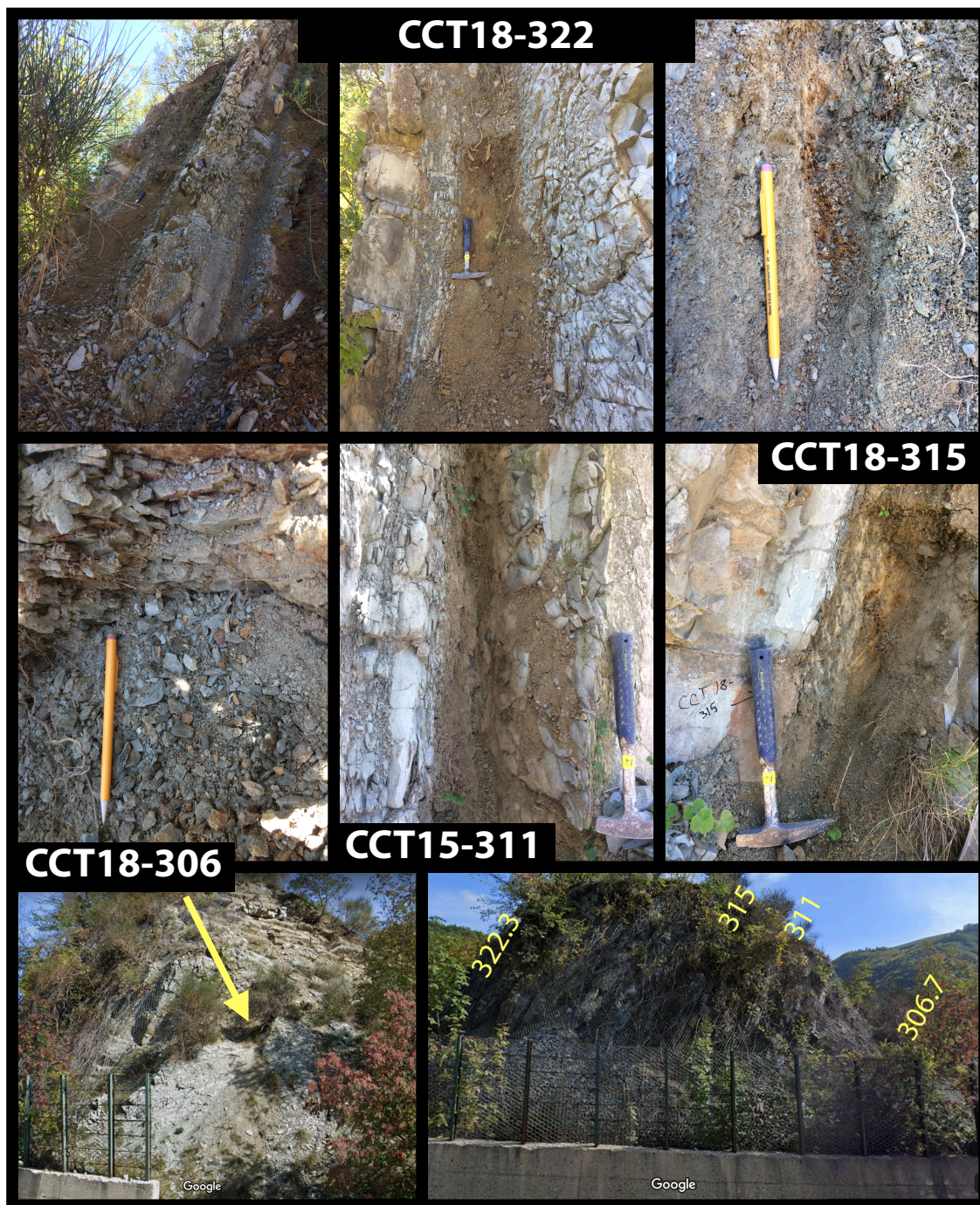
numerous inconsistencies when integrated stratigraphy is attempted. Our work shows the importance of absolute radiometric calibration of sedimentary records, to ground truth bio- and magnetostratigraphy and to more accurately determine the timing and tempo of changes in Earth's climatic and tectonic history.

## **METHODS**

Geochronology samples were collected from the CT section in September 2018 (Figure 1). The geochronology methods below are as described in Kasbohm & Schoene (2018), Schoene *et al.* (2015) and Samperton *et al.* (2015).

### *Zircon separation and preparation*

Zircons were separated from their host rock through standard methods of crushing, gravimetric-, and magnetic-separation techniques using a blender, shatterbox, hand pan, hand magnet, Frantz isodynamic separator, and methylene iodide. Zircons from the least magnetic and most dense mineral separate were transferred in bulk to quartz crucibles and annealed in a muffle furnace at 900°C for 48 hours after Mattinson (Mattinson, 2005). After annealing, 20-40 zircon grains from each sample were photographed (Figure 2) and picked in reagent-grade ethanol for analysis. Given the low radiogenic Pb content of the samples, cathodoluminescence images were not obtained. Euhedral grains with a range of morphologies were selected, while those with visible cracks, inclusions, and cores were avoided. Individual grains were transferred using stainless steel picking tools to separate 3-mL Savillex Hex beakers containing distilled acetone and taken to the clean lab for analysis.



**Figure 1: Contessa section outcrop photos.** Photos of geochronology samples are provided and labeled in the top two rows, with hammer or pencil for scale (Photo credit: Jennifer Kasbohm). The bottom row shows the position of each sample at outcrop scale (Photo credit: Google Street View).

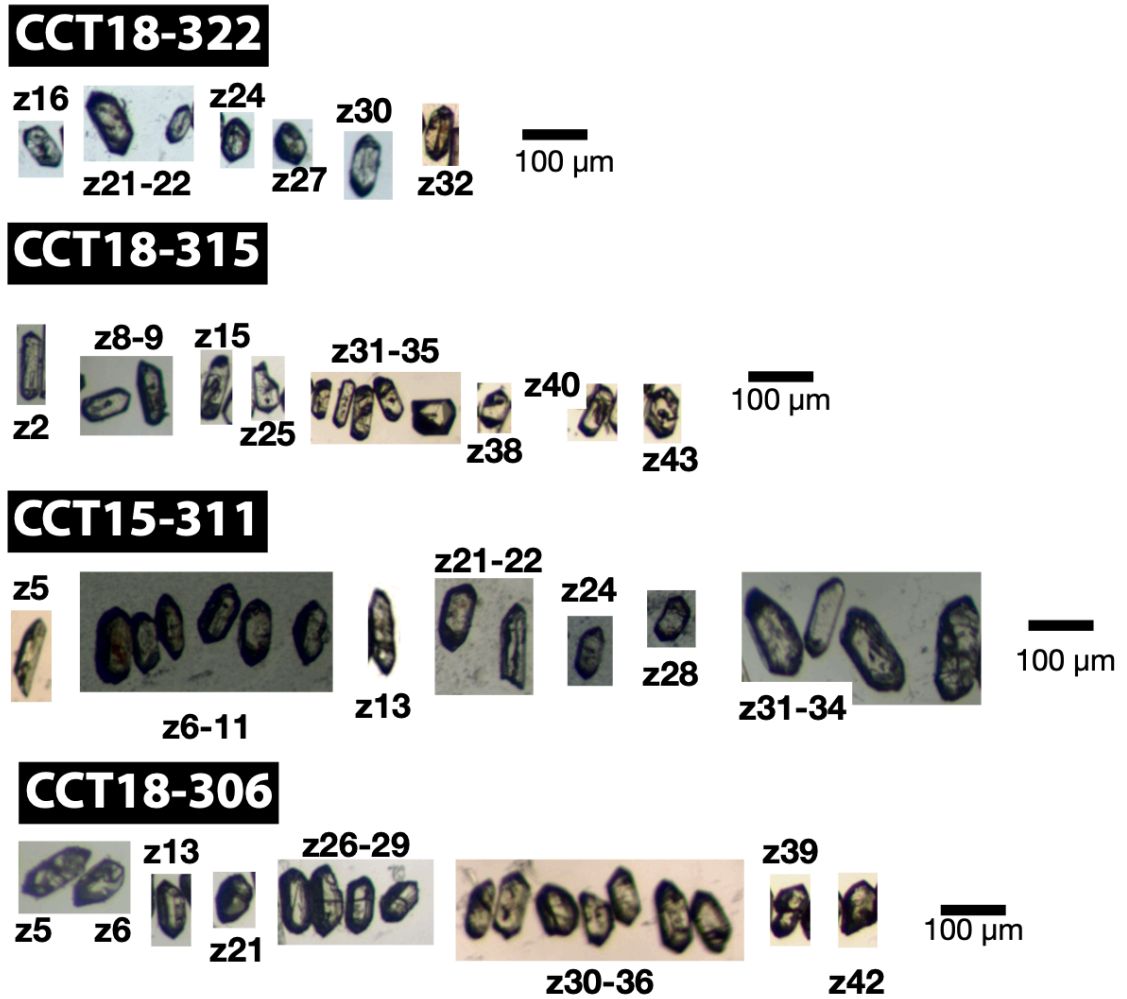
### *U-Pb zircon ID-TIMS analysis*

Single zircon grains were loaded into 200  $\mu\text{L}$  Savillex “micro”-capsules with 100  $\mu\text{L}$  29 M HF + 15  $\mu\text{L}$  3N  $\text{HNO}_3$  for a single leaching step in high-pressure Parr bombs at 185°C for 12 h to remove crystal domains affected by Pb loss (Mattinson, 2005). Grains were rinsed post-leaching in 6 N HCl, MQ  $\text{H}_2\text{O}$ , 3N  $\text{HNO}_3$ , and 29 M HF prior to spiking with EARTHTIME  $^{205}\text{Pb}$ - $^{233}\text{U}$ - $^{235}\text{U}$  tracer and addition of 100 $\mu\text{L}$  29 M HF + 15  $\mu\text{L}$  3N  $\text{HNO}_3$  (Condon et al., 2015; McLean et al., 2015). Zircons were then dissolved to completion in Parr bombs at 210°C for 48 h. Dissolved zircon solutions were subsequently dried down, dissolved in 100  $\mu\text{L}$  6N HCl, and converted to chlorides in Parr bombs at 185°C for 12 h, after which solutions were dried again and brought up in 50  $\mu\text{L}$  3N HCl. The U-Pb and trace element aliquots were then separated by anion exchange chromatography using 50  $\mu\text{L}$  columns and AG-1 X8 resin (200-400 mesh, chloride from Eichrom) (Krogh, 1973), and dried down with a microdrop of 0.015 M  $\text{H}_3\text{PO}_4$ . The dried U and Pb aliquot was loaded in a silica gel emitter (Gerstenberger & Haase, 1997) to an outgassed zone-refined Re filament.

Isotopic determinations were performed using an IsotopX PhoeniX-62 thermal ionization mass spectrometer (TIMS) at Princeton University, with Pb analysis performed in peak-hopping mode on a Daly-photomultiplier ion-counting detector. A correction for mass-dependent Pb fractionation was applied using a Pb fractionation of  $0.182 \pm 0.041\%$ /amu, as determined by repeat measurements of NBS982 at Princeton. A Daly-photomultiplier deadtime of 28.8 ns was used, as determined by repeat measurements of NBS standards. Corrections for interfering isotopes under masses 202, 204, and 205 were made cycle-by-

cycle by measuring masses 201 and 203 and assuming they represent  $^{201}\text{BaPO}_4$  and  $^{203}\text{Tl}$  and using natural isotopic abundances to correct for  $^{202}\text{BaPO}_4$ ,  $^{204}\text{BaPO}_4$ ,  $^{205}\text{BaPO}_4$ , and  $^{205}\text{Tl}$ .

$\text{UO}_2$  measurements were performed in static mode on Faraday cups with a bulk U fractionation correction calculated from the deviation of measured  $^{233}\text{U}/^{235}\text{U}$  from the known tracer  $^{233}\text{U}/^{235}\text{U}$  ( $0.995062 \pm 0.000054$  ( $1\sigma$ )), and an oxide composition of  $^{18}\text{O}/^{16}\text{O}$  of 0.00205 was used (Nier, 1950). Data reduction was performed using the programs Tripoli and U-Pb Redux (Bowring et al., 2011; McLean et al., 2011) and the decay constants of Jaffey *et al.* (1971). All Pbc was attributed to laboratory blank with a mean isotopic composition determined by total procedural blank measurements (see Table DR1 for values). Uncertainties in reported U-Pb zircon dates are at the 95% confidence level and exclude tracer calibration and decay constant uncertainties. Correction for initial  $^{230}\text{Th}$  disequilibrium in the  $^{206}\text{Pb}/^{238}\text{U}$  system was made on a fraction-by-fraction basis by estimating  $(\text{Th}/\text{U})_{\text{magma}}$  using  $(\text{Th}/\text{U})_{\text{zircon}}$  determined by TIMS and a mean  $(\text{Th}/\text{U})_{\text{zircon-magma}}$  partition coefficient ratio of  $0.19 \pm 0.11$ , which encompasses the range of values for  $(\text{Th}/\text{U})_{\text{zircon-magma}}$  partition coefficients obtained from glasses from a variety of volcanic settings (Claiborne et al., 2018). Uncertainties for the resulting  $(\text{Th}/\text{U})_{\text{magma}}$  were also calculated on a fraction-by-fraction basis, propagating the uncertainty in the  $(\text{Th}/\text{U})_{\text{zircon-magma}}$  partition coefficient. U-Pb data from each analysis is provided in Table 1.



**Figure 2: Zircon photos.** The zircons yielding dates from each geochronology sample are shown here, exhibiting magmatic morphologies (Photo credit: Jennifer Kasbohm).

## RESULTS

### *Sample descriptions*

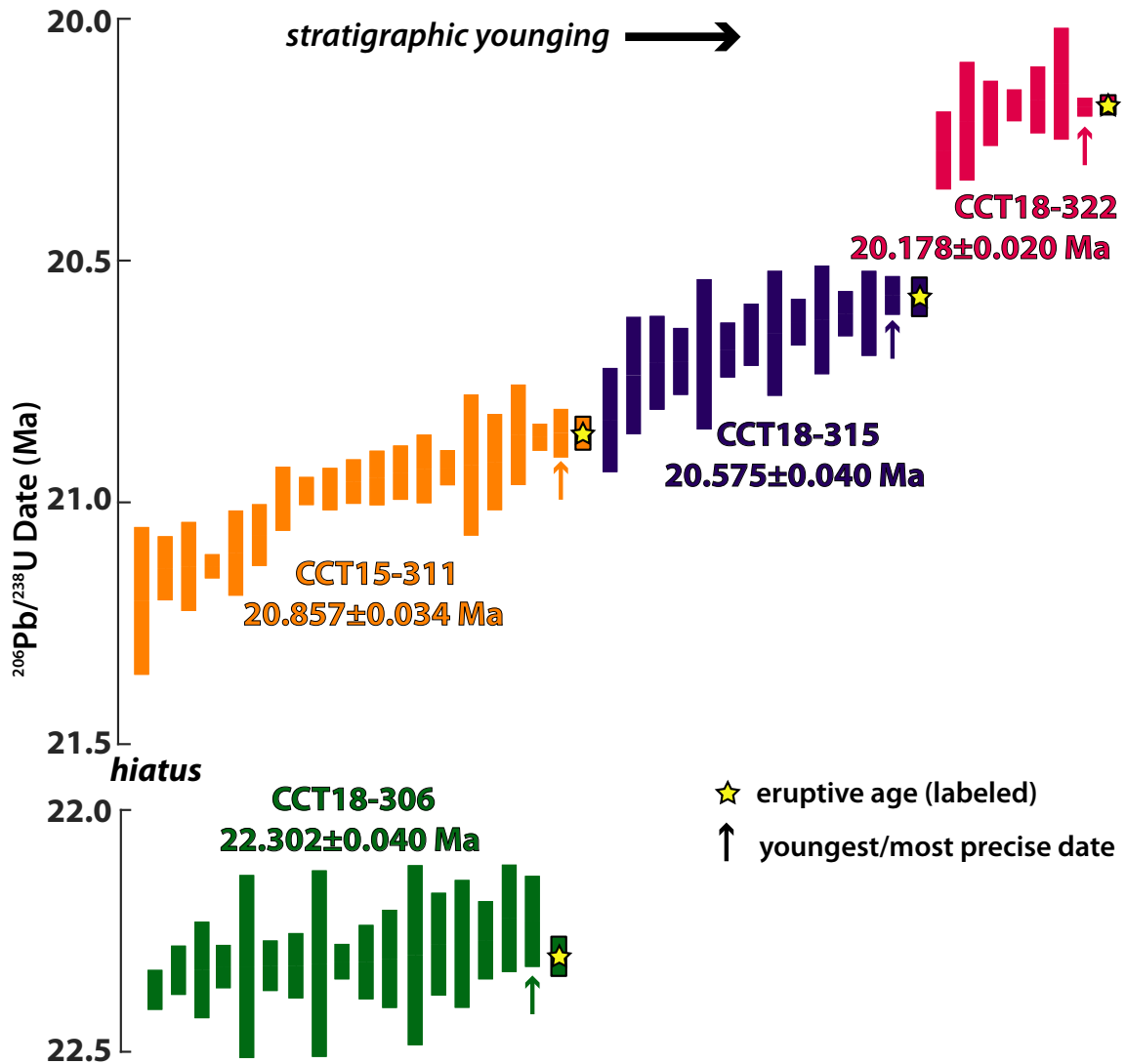
Outcrop photos of each sample are shown in Figure 1, and zircon images are displayed in Figure 2. Sample CCT18-306 was collected from section height 306.7 m, from the “Livello Raffaello.” With a thickness up to 40 cm, the Raffaello is a regional marker bed in the Umbria-Marche basin because it is the first volcanoclastic horizon in the Miocene, found just above the contact with the underlying Scaglia Cinerea (Guerrera et al., 2015).

At the CT section, the sample consists of 18 cm of bentonite, and it is thicker and more lithified than the other samples collected in this study; some excavation of a thin layer of recent cover was required to collect the sample. Zircons separated were ~100  $\mu\text{m}$  in length, euhedral, blocky, and prismatic, with pronounced terminations.

Sample CCT15-311 was collected from a stratigraphic height of 311.3 m, from a horizon also referred to as “CT-WAL” (Montanari et al., 1997). This bentonitic horizon is 15 cm thick, and is noted for the presence of biotite. This sample, as well as the following two bentonites, is recessed from the outcrop relative to the more resistant limestones on other side. Zircons extracted from this sample were euhedral and prismatic, and ranged in morphology from small (~100  $\mu\text{m}$ ) and equant to nearly 200  $\mu\text{m}$  and blocky, with a few thin grains.

Sample CCT18-315 was collected at height 315 m, and is ~10 cm thick. The bentonite was somewhat orange in color. Zircons dated from this sample were euhedral and prismatic, with pronounced terminations.

Sample CCT18-322 was collected at height 322.2 m, and is 40 cm thick. The bentonite was not well lithified, and exhibited discontinuous streaks of orange. It is the last volcanoclastic horizon in the CT section, just 50 cm below the end of the outcrop. Zircons separated from this sample were euhedral, blocky, and 50-100  $\mu\text{m}$  in length.

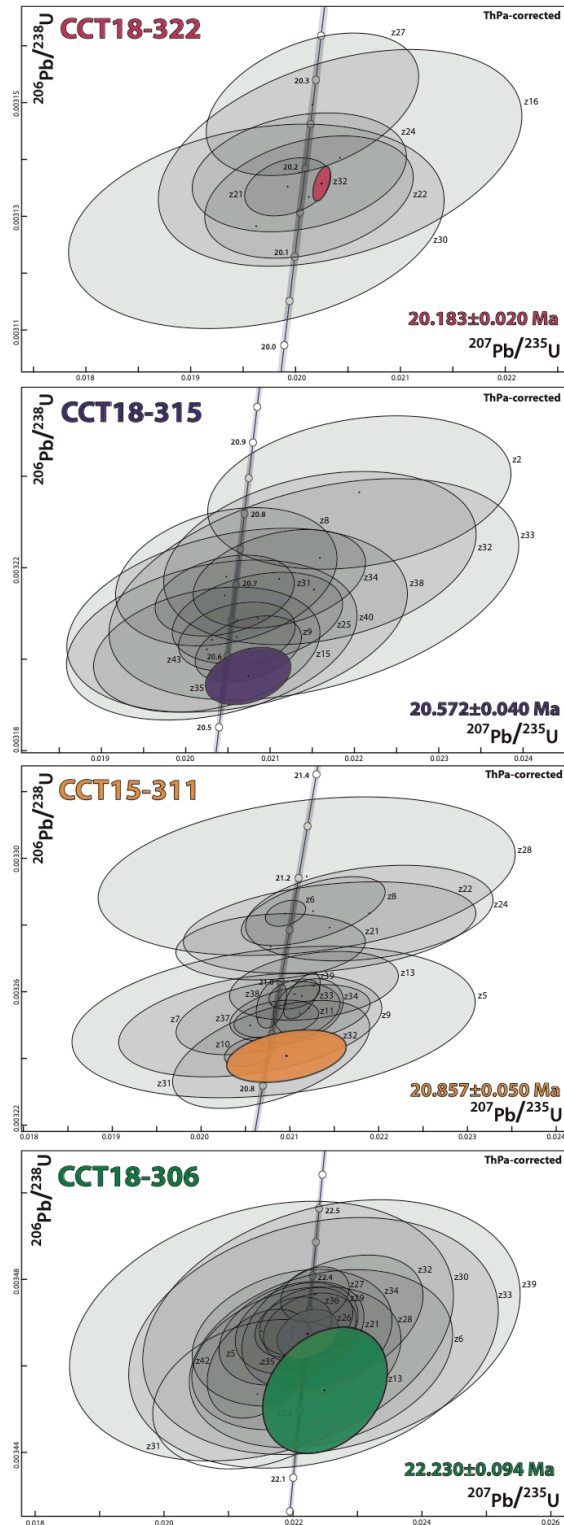


**Figure 3: Weighted mean plots.**  $^{206}\text{Pb}/^{238}\text{U}$  dates from each geochronology sample are plotted here, with stratigraphic younging of the younger three samples from left to right. Arrows indicate the youngest and most precise single analysis, and stars and labels show eruptive ages calculated from each sample, which we highlight as our preferred interpretation.

#### Sample ages

Individual zircon  $^{206}\text{Pb}/^{238}\text{U}$  dates from these four samples are shown in Figure 3, with 95% confidence intervals, and Concordia plots for each sample are found in Figure 4; each analysis overlaps with the Concordia line, indicating closed-system behavior.

Within each sample, dates spread beyond analytical uncertainty, most likely as a result of



**Figure 4: Concordia plots.** Concordia plots from each sample are shown here, with the youngest and most precise analysis highlighted and labeled. Intersection with the Concordia line shows that the zircons crystallized in a closed system.

prolonged crystallization in the source magma, or inheritance of older grains from the volcanic edifice or host rock (Cooper, 2015; Stelten et al., 2015). For this reason, in Figure 3 we use arrows to point out the youngest and most precise age as one estimate for the age of each bentonite, and highlight these analyses in Figure 4. As an alternative approach to calculate eruptive ages from disperse datasets, zircon dates and uncertainties from each sample were incorporated into a Bayesian Monte Carlo Markov Chain (MCMC) model, which makes a probabilistic estimate of eruption age based on the dated population of grains from each sample (Keller et al., 2018). Since this approach eliminates all subjectivity and takes into account each zircon dated, we star and label these eruptive ages in Figure 3, and use these ages as our preferred interpretation for the age of each bentonite. However, we compare this interpretation to alternative approaches in Table 1, using youngest zircon or weighted mean ages, and we find that each interpretation produces overlapping ages. Thus, our chosen eruptive age interpretation does not affect the conclusions of this paper. Full U-Pb data is found in Table S1.

sample	Youngest Zircon					Weighted Means													Bayesian Eruptive Age with Bootstrapped Prior		
	zircon	age	uncertainty			Youngest Few Zircons					Maximum n allowed for MSWD = 1										
			X	Y	Z	addtnl	n	age	X	Y	Z	WD	addtnl	n	age	X	Y	Z			WD
CCT18-306	z13	22.230	0.094	0.095	0.098	31.42	3	22.246	0.054	0.055	0.060	0.73	all	17	22.320	0.016	0.021	0.032	1.0	22.302	0.040
CCT15-311	z32	20.857	0.050	0.052	0.057	31.10	3	20.863	0.024	0.027	0.035	0.043	5,9	5	20.868	0.023	0.027	0.035	0.44	20.857	0.034
CCT18-315	z35	20.572	0.040	0.043	0.048	9.15	3	20.590	0.029	0.035	0.041	0.86	25,38,40,43	7	20.609	0.022	0.028	0.036	1.1	20.575	0.040
CCT18-322	z32	20.183	0.020	0.022	0.030	21,22,30	4	20.180	0.016	0.019	0.029	0.28	all	7	20.185	0.015	0.019	0.028	1.0	20.178	0.020
																					**preferred interpretation**

**Table 1: Alternate Age Interpretations.** We compare our preferred eruptive age interpretation with other common ways to address complex zircon populations. All interpretations are internally consistent with little difference in age, showing that our selected interpretation will not affect the conclusions in this paper

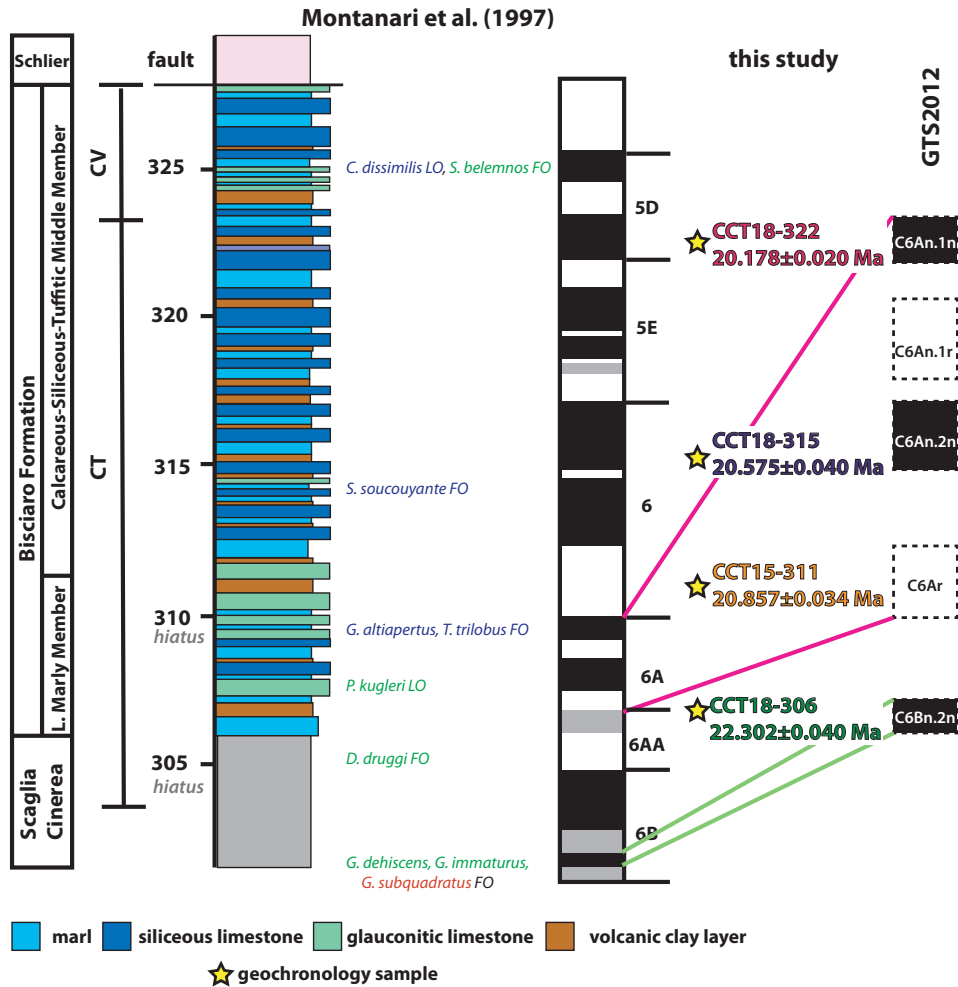
We find that the Raffaello bed, sampled in CCT18-306, is aged  $22.302 \pm 0.040$  Ma, compared to  $21.88 \pm 0.32$  Ma obtained through the  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology by Montanari

et al. (1997) using a Fish Canyon sanidine standard age of 27.84 Ma (Cebula et al., 1986). This age can be recalculated to  $22.16 \pm 0.3$  Ma with an updated Fish Canyon sanidine age of 28.201 Ma (Kuiper et al., 2008). Next, CCT15-311 is found to be  $20.857 \pm 0.34$  Ma, compared to the age of  $19.67 \pm 0.30$  Ma formerly obtained for this horizon (Montanari et al., 1997), recalculated to  $19.93 \pm 0.3$  Ma (Kuiper et al., 2008). Our age for CCT15-315 is  $20.575 \pm 0.040$  Ma, and our age for CCT15-322, at the top of the CT section, is  $20.178 \pm 0.20$  Ma.

## **DISCUSSION**

### *1. Zircon geochronology provides a new age model for the Miocene Contessa section*

Based on the appearance of both rock samples and zircons, we agree with the interpretation of Guerrera et al. (2015) that deposition of Bisciara Formation volcanics in the CT section represents primary ash fall. To complement their analysis of the mineralogy of the bentonites, which showed 50-75% volcanoclastic supply with a low ratio of reworked to primary grains, we present evidence based on zircon geochronology. The zircons obtained from all four dated bentonite horizons are euhedral and prismatic, consistent with magmatic textures, with little evidence for rounding seen in alluvial or eolian grains (Figure 2). Additionally, the grains dated from each sample comprise fairly uniform age populations, with numerous individual analyses overlapping with our estimated eruptive ages. Our ages reflect stratigraphic order, younging in a clearly resolvable manner from bottom to the top of the section (Figure 3).



**Figure 5: Summary of Contessa section stratigraphic data.** The stratigraphic section, paleomagnetic, and biostratigraphic data of Montanari et al. (1997) is reproduced here, alongside our geochronology results. Our ages may be correlated to the Geomagnetic Polarity Timescale presented in Hilgen et al. (2012). We show that polarity chrons inferred match the polarity of samples obtained at each height, though this may be accidental. Biostratigraphic data are color coded in the following manner: green when consistent with our geochronology, blue when consistent with foraminiferal absence, and red when inconsistent with geochronology and absence.

Given the internal consistency of our U-Pb ages, we suggest that they be used to construct a new age model for the CT section. Our ages suggest that biostratigraphy and magnetostratigraphy previously obtained in the CT section (Montanari et al., 1997) overestimate the amount of time represented in the section. Rather than being deposited

between 22 and 17 Ma, deposition occurred between ~22.3 and 20.2 Ma. With ~1.4 Ma elapsed between CCT18-306 and CCT15-315, our geochronology supports the biostratigraphic evidence for a substantial hiatus of ~1 Ma between these samples (Montanari et al., 1997).

We find that nearly all of the inconsistencies between our zircon ages and the prior bio-magnetostratigraphic calibration of the section can be resolved by foraminiferal absences and unreliable paleomagnetic data (Figure 5). While foraminiferal abundance and preservation in the Bisciaro Formation ranges from moderately good to very poor, at the CT section, foraminiferal preservation was poor due to recrystallization and deformation (Montanari et al., 1997). This may have led to the absence of foraminifera in the section subsequent to their regional first occurrence, or predating their expected last occurrence. For the most part, each biostratigraphic datum between our first and last geochronology samples either fits this pattern of absence, or falls where expected. We focus here primarily on the biostratigraphic data that falls between our geochronology samples, since we can provide older and younger bounding ages. We do note one exception to our absence hypothesis, in which the first occurrence of *G. subquadratus* occurs at 301.5 m, prior to our sample CCT18-306, dated to 22.3 Ma. However, this first occurrence is expected to be 21.09 Ma in the Mediterranean (Lirer et al., 2019). It is likely that sedimentary reworking may have allowed this species to be found before its anticipated first occurrence.

A number of foraminiferal boundaries are reported between CCT18-306 and CCT15-315, between 22.3 and 20.8 Ma. At 307.4 m, the last occurrence of *P. kugleri* is documented, which is expected to occur at 21.09 Ma in the Mediterranean, at the top of chron C6AA, based on sedimentation rate estimates from the Aquitanian GSSP section at Carrosio-Lemme, Italy (Lirer et al., 2019). This datum is consistent with our eruptive ages. Next, at 309.6 m, the first occurrences of *T. trilobus* and *G. altiapertura* are documented. Both of these data postdate their expected onset in the Mediterranean; *T. trilobus* is expected to first occur at 22.7 Ma, and *G. altiapertura* at 21.4 Ma (Lirer et al., 2019). While a hiatus was inferred based on the juxtaposition of these first occurrences (Montanari et al., 1997), the delayed onset of these first occurrences indicates that these foraminifera may be absent due to poor preservation at lower heights in the section, or due to sedimentary reworking. Additionally, the dinoflagellate cyst *S. soucouyantae* first occurrence occurs at 314 m, likely around 20.6 Ma. In GTS 2012, the same first occurrence is estimated to occur at 22 Ma, which fits the same pattern of absence.

The paleomagnetic data obtained from the CT section documented numerous magnetic field reversals, leading to the suggestion that magnetic polarity chrons C6B through C5D were present in the section (Montanari et al., 1997). By contrast, our U-Pb ages fall during chrons C6Bn.2n through C6An.1n, when compared to Geologic Timescale (GTS) 2012 (Hilgen et al., 2012). For the most part, the magnetic polarity obtained at the stratigraphic position of each geochronology sample matches the polarity inferred from GTS 2012 (Figure 5). However, this may be the result of chance, as the paleomagnetic data overestimates the number of magnetic field reversals present in the section. This

inaccuracy may be the result of numerous factors. The magnetic mineralogy of the sample was found to be multi-domain magnetite, which is recognized as an unreliable paleomagnetic recorder (Butler, 1992). Thermal demagnetization above 350°C led to erratic behavior, which is far lower than the 550-580°C unblocking temperatures that lead to reliable data. Rather than vector fitting of demagnetization directions through principle component analysis (Kirschvink, 1980), orthogonal projection diagrams were only visually inspected. Beyond these weaknesses with the data obtained, Montanari et al. (1997) also suggest that anomalous directions may arise through delayed remanence acquisition during lithification, bioturbation, and slow sedimentation rates of 2 m/Ma, based on  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology.

The large number of magnetic field reversals obtained from the prior paleomagnetic data,  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology, and the last occurrence of *C. dissimilis* at 325 m (in the CV portion of the section, which is across the highway but inferred as conformable with the top of CT), led to the inference that the top of the CT-CV section extended to ~17 Ma. However, our age for the top of the CT section, within 30 cm of the end of the outcrop, is  $20.178 \pm 0.020$  Ma. While we were unable to obtain geochronology samples from the CV section due to inaccessibility, we suggest that it may face the same obstacles of calibration as were present in the CT section. It is possible that the *C. dissimilis* last occurrence may occur prematurely relative to the Mediterranean record of this event at 17.03 Ma, based on astronomical tuning (Lirer et al., 2019), especially since it occurs concurrently with the first occurrence of calcareous nannofossil *S. belemnoides*, which is suggested to have been extant from 19-18 Ma (Raffi et al., 2006). The number of

magnetic field reversals observed in the uppermost portion of the section may also be either overestimated or miscorrelated. Alternatively, sedimentation rates slow significantly, or there is a depositional hiatus between the CT and CV sections.

Our work shows the importance of obtaining reliable age constraints on sedimentary records, from which major events in Earth's climate history are inferred. Unfortunately, carbonate rocks frequently lack the single-domain magnetite that produces reliable paleomagnetic records, and may be easily altered through diagenesis, tectonics, dissolution, or other processes that lead to poor foraminiferal preservation. The presence of hiatuses in the CT section complicates both assessments of biostratigraphic first and last occurrences as well as the assignment of reversal signatures to polarity chrons, and makes the section a poor target for astronomical tuning. High-precision geochronology not only reveals these stratigraphic issues, but also provides a new age model for the section, which can be used to re-calibrate the results of prior and future studies of the Bisciaro Formation at the Contessa section.

## *2. The Contessa section is not a suitable candidate for the Burdigalian GSSP*

A recent integrated stratigraphic study of another nearby outcrop of the Miocene Contessa section, which we will refer to as the Cementerie Barbetti Quarry (CBQ) section, was put forward as a candidate for the Aquitanian-Burdigalian GSSP (Global Stratotype Section and Point) (Fabbrini et al., 2019). This study reported the first occurrence of calcareous nannofossil *Helicosphaera ampliaperta*, which is one datum suggested for the Aquitanian-Burdigalian boundary, is accessible along the road to the

quarry, and in the opinion of the authors, produced concordant planktonic foraminifera, calcareous nannofossil, and paleomagnetic data from a well-preserved outcrop.

However, given its 1 km distance from the CT section, we suggest that the new CBQ section may be subject to some of the same concerns regarding imperfect paleomagnetic data and foraminiferal absence, leading to delayed first occurrences and premature last occurrences. Although principle component analysis was performed on the paleomagnetic data, and samples taken from the same horizon gave similar directions whether subject to thermal or alternating field demagnetization, the data is still not the best quality. Directional data with maximum angular deviation (MAD)  $>11^\circ$  was presented as “Group B” quality data, even though samples that show this level of uncertainty are typically excluded from paleomagnetic studies; they are included here because they are bracketed by directions with lower MADs. Additionally the k values of the mean directions are less than 10, indicating that the data included do not cluster well. The mean directions for each polarity group fail a reversal test, and one sampling horizon yielded both normal and reversed directions (Fabbrini et al., 2019). Despite these uncertainties, the polarity timescale suggested for the section also argues for a hiatus between chrons C6Br and C6AAn, which agrees with our radiometric constraints on the hiatus between CCT18-306 and CCT15-311.

While the foraminiferal preservation in the section is described as generally moderate, there are also intervals of poor preservation, particularly near the volcanoclastic horizons (Fabbrini et al., 2019). We can assess some of the foraminiferal boundaries that are

proximal to the volcanoclastic layer identified as the Raffaello level in the CBQ section, which we correlate to CCT-306; above, it is too challenging to correlate the five volcanoclastic horizons in the CBQ section with the other 3 horizons dated at CT. While *G. subquadratus* was found out of stratigraphic order at CT at 301.5 m, below the Raffaello level and prior to its expected first occurrence at 21.4 Ma (Lirer et al., 2019), it falls just above the Raffaello level at CBQ, which would work with our age for Raffaello of  $22.302 \pm 0.040$  Ma (Fabbrini et al., 2019). At CBQ, the first occurrence of *G. altiapertura*, also expected at 21.4 Ma, is found 6 m below Raffaello, which makes this datum out of order. The first occurrence of *T. trilobus* at CBQ falls 9 m below Raffaello, which is more concurrent with its expected onset of 22.8 Ma (Lirer et al., 2019).

However, the last occurrence of *P. kugleri* is marked at 65 cm below the Raffaello level (Fabbrini et al., 2019), which is in disagreement with the CT section, where it is found 70 cm above Raffaello (Montanari et al., 1997). This inconsistency could be explained by two options. First, the last occurrence at CBQ may precede the Mediterranean last occurrence at 21.09 Ma (Lirer et al., 2019), fitting the pattern of absence observed at CT. At CBQ, *P. kugleri* is described as rare, especially near the base and top of its occurrence, smaller in size, and hardly detectable, which lends support for this option. Alternatively, the Raffaello layer may represent a diachronous horizon, despite its designation as a regional marker bed.

Without a detailed interrogation of its accuracy, however, the biostratigraphic data from CBQ is used to infer that the hiatus described above occurs prior to Raffaello deposition,

whereas our data suggests it occurs afterwards. The last occurrence of *P. kugleri* is also used to suggest that the Raffaello layer is 21.09-21.08 Ma (Fabbrini et al., 2019), which is inconsistent with our eruptive age for this horizon. If the layers are the same age (which could be tested with zircon geochronology at CBQ), we suggest that the biostratigraphic age calibration of CBQ is incorrect, at least in this lower interval of the section. Above the Raffaello, there is better agreement between biostratigraphic and paleomagnetic data (Fabbrini et al., 2019).

The comparison of CBQ and CT shows the importance of obtaining high-precision geochronology as a check on biostratigraphic and magnetostratigraphic age calibration, especially for sections treated as possible GSSPs. Due to the biostratigraphic inconsistencies with our radiometric age model, paleomagnetic data that is not of the highest statistical quality, the presence of three major hiatuses in the section, and the difficulty of correlation with sections in its immediate vicinity, we suggest that the CBQ section not be adopted as a GSSP. Furthermore, selecting this section on the basis of its first occurrence of *Helicosphaera ampliapertura* should also be questioned, considering that this nannofossil is not common in marine records from ocean basins (Fabbrini et al., 2019), and thus cannot be broadly applied to find the Aquitanian-Burdigalian boundary in the ocean drill core record.

One recent study, from the very stratigraphic section we studied, proves this point. In a study of the Miocene Mediterranean Sr and Nd isotopic record, Cornacchia et al. (2018) collected samples from the CT section that were calibrated in age based on  $^{40}\text{Ar}/^{39}\text{Ar}$

geochronology from Montanari et al. (1997). One sample, two meters above the Raffaello layer, with an estimated age of 21.1 Ma and elevated  $^{87}\text{Sr}/^{86}\text{Sr}$  levels is suggested to be coeval with the Mi-1a event, reflecting increased continental runoff as a result of greater weathering during a transient glaciation (Cornacchia et al., 2018). The age model from CBQ based on bio- and magnetostratigraphy suggests that this event would postdate their estimated age of 21.09 Ma for the Raffaello, leading Fabbrini et al. (2019) to reject the correlation with the Mi-1a event. By contrast, an age of 21.1 Ma is concurrent with our radiometric age model, bounded by two high-precision eruptive ages, and furthermore, our age model could be used to refine the age estimates of the other CT samples presented in Cornacchia et al. (2018).

### *3. Geochronology may help constrain the provenance of the Bisciario volcanoclastics*

Petrography of the volcanoclastic layers of the Bisciario Formation have led to a debate on the source of these layers. Western Sardinia has been the leading candidate as the source of explosive volcanism that produced the Bisciario ashfall. Montanari et al. (1994) performed a grain size analysis of the felsic fraction of the Raffaello layer, and found that grain size decreased from southwest to northeast through the Umbria-Marche basin, consistent with ash carried by eolian transport from Sardinia. Assorgia et al. (1995) analyzed biotites present in the volcanoclastic units of the Bisciario and Schlier Formations, and found that their geochemistry matched that of the calc-alkaline volcanic sequence at Bosa, on the west coast of Sardinia. While  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology has been used to estimate the main phase of early Miocene volcanism on Sardinia to occur between 20.5 and 18 Ma (Gattacceca et al., 2007), this hypothesis could be further tested

by performing zircon geochronology on volcanic units in Sardinia, to see if any particular eruptions match our eruptive ages from the CT section. If these argon data are correct and complete, an alternative source of felsic volcanism may be required to explain the presence of the Raffaello level, which we have dated to 22.3 Ma.

By contrast, Guerrera et al. (2015) argue that while Sardinian volcanism may be responsible for fine-grained volcanoclastic pelites in the Bisciaro, it would be too distant to produce the turbiditic volcanoclastic horizons. Instead, they infer a more proximal source of volcanism, from the subduction of the Mesomediterranean microplate under Adria. However, there are no volcanic edifices preserved from this event, potentially as a result of rapid erosion, subsidence, or burial by underthrusting (Guerrera et al., 2015). Future high-precision geochronological studies in the Mediterranean could assist with identifying the provenance of the Bisciaro volcanoclastics, and correlating them with other early Miocene volcanoclastic deposits around the Mediterranean (listed in Guerrera et al., 2015).

## **CONCLUSION**

Our new U-Pb zircon eruptive ages at the CT section show the importance of the absolute calibration of the sedimentary sections that document Earth's climate history, when biostratigraphic and paleomagnetic data may be unreliable, and the section is not amenable to astronomical tuning. In stratigraphic sections with zircon-bearing volcanic ashbeds, absolute ages can and should be used to calibrate the bio- and magnetostratigraphic data by which the Geologic Timescale is constructed.

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**Supplemental Table 1: U-Pb Data.** Following the references, data acquired by CA-ID-TIMS is presented with various corrections as specified in the notes beneath the table.

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# Supplemental Table 1: U-Pb Data

Sample	Dates (Ma)							Composition					Isotopic Ratios									
	206Pb/		207Pb/		207Pb/		Pb*	Pbc	Pb*/	Th/	Th/	206Pb/	208Pb/	206Pb/	207Pb/		207Pb/	Corr.				
	238U	±2σ	235U	±2σ	206Pb	±2σ						(pg)	(pg)	Pbc	U	U(magma)	204Pb		206Pb	238U	±2σ %	235U
zircon	a	absolute	b	absolute	a,b	absolute	% disc	d	e	f	g	h	i	j	k	l	m	n	o	p	q	r
<b>CCT18-306</b>																						
z13	22.230	0.094	22.6	1.0	61	100	63.9	5.58	1.22	4.57	1.03	1.02	265	0.33	0.0034545	0.319	0.0225032	4.301	0.0472662	4.193	0.372	
z31	22.22	0.11	21.5	1.6	-53	182	151.4	2.09	0.85	2.45	0.82	4.32	158	0.26	0.0034397	0.503	0.0214532	7.572	0.0452544	7.456	0.261	
z42	22.269	0.081	21.59	0.82	-53	91	151.9	3.25	0.47	6.98	0.95	5.05	402	0.31	0.0034468	0.365	0.0214999	3.844	0.0452601	3.736	0.337	
z6	22.28	0.13	22.5	2.0	49	214	62.5	1.05	0.57	1.86	0.62	3.26	129	0.20	0.0034480	0.597	0.0224381	9.100	0.0472190	8.959	0.268	
z28	22.28	0.11	22.1	1.6	8	174	-22.1	2.97	1.15	2.58	1.05	5.53	157	0.34	0.0034481	0.480	0.0220570	7.356	0.0464155	7.242	0.269	
z33	22.30	0.19	22.4	2.8	34	303	50.0	3.89	2.68	1.45	1.03	5.42	97	0.33	0.0034516	0.840	0.0223228	12.841	0.0469265	12.653	0.255	
z34	22.31	0.10	22.1	1.5	-2	168	-189.1	3.17	1.17	2.72	1.10	5.79	163	0.35	0.0034528	0.458	0.0219911	7.049	0.0462134	6.944	0.258	
z26	22.314	0.037	22.32	0.47	23	50	32.9	3.74	0.43	8.74	0.97	5.11	496	0.31	0.0034537	0.165	0.0222310	2.137	0.0467057	2.096	0.285	
z21	22.315	0.077	22.1	1.1	-4	121	-274.9	2.37	0.62	3.82	1.06	5.58	223	0.34	0.0034538	0.347	0.0219816	5.116	0.0461797	5.014	0.325	
z30	22.32	0.19	21.6	3.0	-56	332	148.2	1.70	1.25	1.36	0.91	4.79	94	0.29	0.0034543	0.870	0.0215165	13.838	0.0451961	13.628	0.271	
z5	22.322	0.068	22.15	0.95	4	102	-61.0	4.19	0.96	4.37	0.95	5.00	258	0.31	0.0034550	0.304	0.0220613	4.320	0.0463313	4.244	0.280	
z35	22.322	0.052	22.36	0.72	26	76	38.1	4.57	0.81	5.67	0.93	4.89	331	0.30	0.0034550	0.235	0.0222656	3.238	0.0467601	3.182	0.270	
z39	22.32	0.19	22.7	2.9	62	304	68.9	1.52	1.10	1.38	0.91	4.79	95	0.29	0.0034553	0.853	0.0226009	12.951	0.0474612	12.757	0.259	
z36	22.324	0.045	22.10	0.59	-2	64	-182.7	4.07	0.57	7.18	1.03	5.42	405	0.33	0.0034553	0.202	0.0220084	2.699	0.0462169	2.654	0.259	
z32	22.33	0.10	22.7	1.4	62	144	69.2	3.09	0.96	3.23	0.92	4.84	197	0.30	0.0034564	0.450	0.0226160	6.215	0.0474774	6.050	0.397	
z29	22.331	0.051	22.30	0.72	19	77	22.7	1.68	0.29	5.74	0.82	4.32	344	0.26	0.0034565	0.229	0.0222086	3.261	0.0466211	3.205	0.275	
z27	22.372	0.041	22.43	0.53	29	56	42.8	3.89	0.48	8.02	0.95	5.05	458	0.31	0.0034628	0.185	0.0223437	2.383	0.0468194	2.346	0.239	
<b>CCT15-311</b>																						
z32	20.857	0.050	21.06	0.67	45	75	62.5	2.39	0.42	5.74	0.64	3.37	358	0.21	0.0032270	0.244	0.0209656	3.212	0.0471413	3.135	0.351	
z31	20.86	0.10	20.9	1.1	25	122	41.1	5.93	1.40	4.22	0.53	2.79	276	0.17	0.0032275	0.503	0.0207934	5.335	0.0467471	5.098	0.509	
z10	20.865	0.028	20.66	0.29	-4	33	-192.7	2.82	0.21	13.53	0.60	3.16	830	0.19	0.0032283	0.136	0.0205560	1.402	0.0462022	1.358	0.262	
z9	20.92	0.10	20.7	1.5	-9	171	-1354.4	2.16	0.86	2.53	0.67	3.53	167	0.22	0.0032363	0.479	0.0205585	7.208	0.0460936	7.061	0.336	
z5	20.92	0.15	20.9	2.3	21	258	33.3	0.76	0.49	1.56	0.65	3.42	111	0.21	0.0032372	0.703	0.0208212	10.905	0.0466690	10.741	0.264	
z11	20.928	0.036	20.95	0.47	24	54	39.1	2.18	0.28	7.85	0.70	3.68	477	0.22	0.0032381	0.175	0.0208526	2.288	0.0467269	2.242	0.299	
z7	20.931	0.071	20.75	0.92	-1	105	-105.6	1.14	0.28	4.09	0.58	3.05	265	0.19	0.0032385	0.342	0.0206469	4.474	0.0462605	4.351	0.392	
z37	20.939	0.056	21.21	0.78	53	87	67.0	1.43	0.26	5.44	1.25	6.58	297	0.40	0.0032397	0.270	0.0211179	7.873	0.0472980	3.652	0.348	
z34	20.950	0.056	21.31	0.39	62	43	71.3	6.32	0.55	11.46	0.59	3.11	707	0.19	0.0032414	0.271	0.0212124	1.354	0.0474846	1.806	0.245	
z38	20.957	0.046	20.90	0.17	14	19	14.8	72.82	2.87	25.40	1.22	6.42	1328	0.39	0.0032426	0.221	0.0207969	0.823	0.0465378	0.774	0.345	
z39	20.973	0.044	21.24	0.20	51	21	66.2	29.06	0.73	40.04	0.86	4.53	2264	0.28	0.0032450	0.210	0.0211401	0.974	0.0472705	0.863	0.604	
z33	20.977	0.029	21.15	0.29	41	32	59.7	5.09	0.40	12.86	0.56	2.95	798	0.18	0.0032456	0.139	0.0210551	1.362	0.0470721	1.321	0.342	
z13	20.992	0.066	21.37	0.95	64	105	72.1	2.19	0.54	4.01	0.87	4.58	243	0.28	0.0032481	0.318	0.0212761	4.469	0.0475291	4.387	0.291	
z21	21.068	0.064	20.9	1.1	0	123	-96.1	1.87	0.57	3.30	0.56	2.95	219	0.18	0.0032597	0.305	0.0207874	5.133	0.0462713	5.092	0.164	
z22	21.105	0.088	21.5	1.6	71	180	74.3	0.95	0.34	2.80	0.62	3.26	186	0.20	0.0032656	0.421	0.0214527	7.679	0.0476668	7.556	0.318	
z6	21.132	0.025	21.05	0.23	12	25	7.3	6.22	0.35	17.73	0.82	4.32	1022	0.26	0.0032698	0.119	0.0209562	1.081	0.0465031	1.045	0.353	
z24	21.133	0.092	22.0	1.4	117	148	83.5	1.45	0.54	2.68	0.62	3.26	178	0.20	0.0032699	0.439	0.0218992	6.364	0.0485951	6.256	0.279	
z8	21.136	0.066	21.36	0.81	47	87	63.4	1.61	0.24	6.68	1.25	6.63	360	0.40	0.0032704	0.316	0.0212672	3.811	0.0471842	3.643	0.560	
z28	21.20	0.15	21.3	2.3	31	261	49.3	1.18	0.76	1.56	0.65	3.42	111	0.21	0.0032809	0.726	0.0211940	11.080	0.0468717	10.900	0.279	
<b>CCT18-315</b>																						
z35	20.572	0.040	20.84	0.50	52	57	67.5	2.29	0.28	8.21	0.91	4.79	474	0.29	0.0031826	0.195	0.0207443	2.429	0.0472941	2.374	0.321	
z15	20.609	0.088	20.4	1.3	-10	158	-1454.6	1.15	0.43	2.65	0.70	3.68	174	0.22	0.0031884	0.429	0.0202535	6.628	0.0460914	6.525	0.270	
z9	20.610	0.047	20.85	0.63	48	71	65.1	1.28	0.20	6.46	0.80	4.21	386	0.26	0.0031885	0.228	0.0207465	3.036	0.0472115	2.961	0.363	
z40	20.62	0.11	20.4	1.7	-4	201	-196.5	2.23	1.03	2.15	0.80	4.21	141	0.26	0.0031905	0.549	0.0203139	8.480	0.0461988	8.329	0.306	
z43	20.627	0.048	20.71	0.69	30	79	50.1	3.09	0.56	5.48	0.89	4.74	324	0.29	0.0031912	0.235	0.0206107	3.356	0.0468632	3.297	0.283	
z38	20.65	0.13	20.7	2.0	28	231	47.0	1.44	0.76	1.91	0.88	4.63	125	0.28	0.0031948	0.630	0.0206137	9.796	0.0468168	9.633	0.289	
z25	20.653	0.064	21.0	1.0	55	114	68.9	2.10	0.55	3.81	0.83	4.37	234	0.27	0.0031953	0.314	0.0208543	4.843	0.0473568	4.757	0.304	
z31	20.685	0.057	20.57	0.82	7	95	-17.0	1.74	0.37	4.74	1.00	5.26	276	0.32	0.0032002	0.276	0.0204666	4.030	0.0464045	3.954	0.306	
z33	20.69	0.16	21.6	2.4	126	259	84.9	0.48	0.30	1.61	0.55	2.89	116	0.18	0.0032016	0.758	0.0215243	11.286	0.0487819	11.005	0.400	
z34	20.709	0.069	21.2	1.0	79	113	76.9	1.03	0.26	3.92	0.86	4.58	238	0.28	0.0032039	0.337	0.0211146	4.843	0.0478195	4.744	0.324	
z8	20.71	0.10	20.6	1.3	6	152	-23.3	0.58	0.20	2.87	0.69	3.63	187	0.22	0.0032043	0.472	0.0204854	6.410	0.0463875	6.301	0.264	
z32	20.74	0.12	21.7	1.8	129	199	85.2	0.53	0.27	1.96	0.74	3.89	132	0.24	0.0032084	0.591	0.0215957	8.578				

- d Total mass of radiogenic Pb.
- e Total mass of common Pb.
- f Ratio of radiogenic Pb (including  $^{208}\text{Pb}$ ) to common Pb.
- g Th contents calculated from radiogenic  $^{208}\text{Pb}$  and  $^{230}\text{Th}$ -corrected  $^{206}\text{Pb}/^{238}\text{U}$  date of the sample, assuming concordance between U-Pb Th-Pb systems.
- h Th/U ratio of magma from which mineral crystallized.
- i Measured ratio corrected for fractionation and spike contribution only.
- j Measured ratios corrected for fractionation, tracer and blank. Values for ET535 are found in Condon et al. (2015) and McLean et al. (2015). Blank model values are as follows:

$^{206}\text{Pb}/^{204}\text{Pb}$	$18.628271 \pm 0.317714$
$^{207}\text{Pb}/^{204}\text{Pb}$	$15.796256 \pm 0.232017$
$^{208}\text{Pb}/^{204}\text{Pb}$	$38.535874 \pm 0.375848$

## Chapter 6

# Radiometric constraints on the timing, tempo, and effects of large igneous province emplacement

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*This chapter is taken from*

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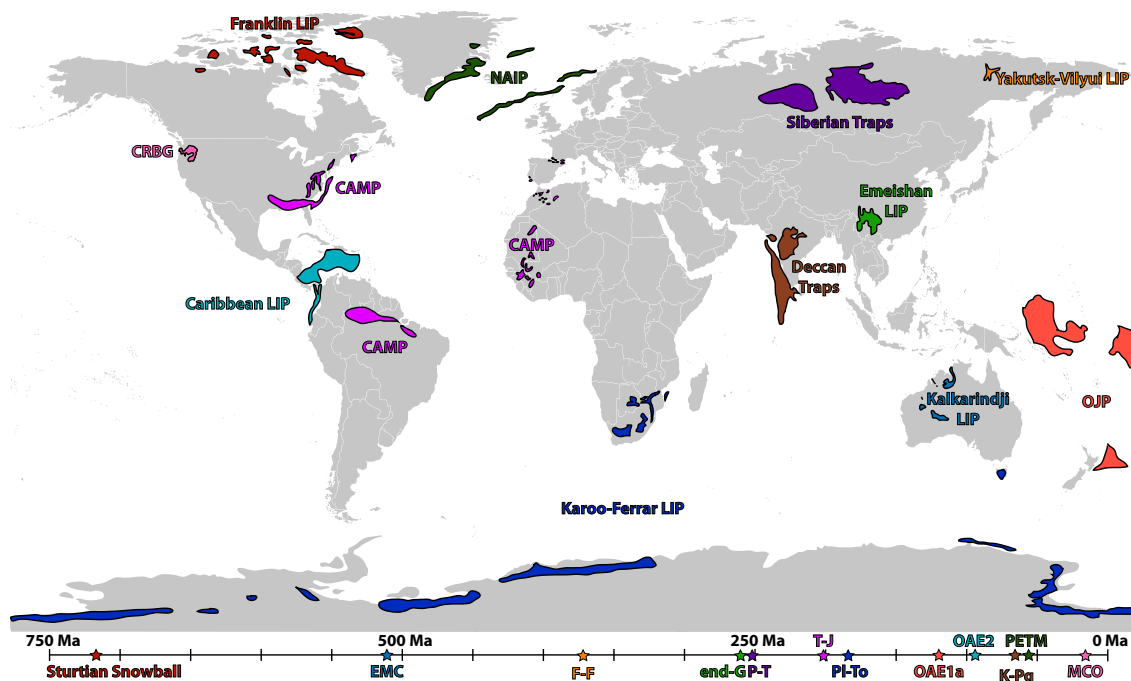
### ABSTRACT

There is an apparent temporal correlation between large igneous province (LIP) emplacement and global environmental crises, including mass extinctions. Advances in the precision and accuracy of geochronology in the past decade have significantly improved estimates of the timing and duration of LIP emplacement, mass extinction events, and global climate perturbations, and in general have supported a temporal link between them. In this chapter, we review available geochronology of LIPs and of global extinction or climate events. We begin with an overview of the methodological advances permitting improved precision and accuracy in LIP geochronology. We then review the

characteristics and geochronology of 12 LIP/event couplets from the past 700 Ma of Earth history, comparing the relative timing of magmatism and global change, and assessing the chronologic support for LIPs playing a causal role in Earth's climatic and biotic crises. We find that 1) improved geochronology in the last decade has shown that nearly all well-dated LIPs erupted in  $< 1$  Ma, irrespective of tectonic setting; 2) for well-dated LIPs with correspondingly well-dated mass extinctions, the LIPs began several hundred ka prior to a relatively short duration extinction event, and 3) for LIPs with a convincing temporal connection to mass extinctions, there seems to be no single characteristic that makes a LIP deadly. Despite much progress, higher precision geochronology of both eruptive and intrusive LIP events and better chronologies from extinction and climate proxy records will be required to further understand how these catastrophic volcanic events have changed the course of our planet's surface evolution.

## **INTRODUCTION (SEE ALSO CHAPTER 1)**

In this chapter, after describing the methodological advances that have led to improved accuracy and precision in geochronology, we will review the geochronology of 12 LIP – global environmental change couplets (Figure 1). We chose to focus on LIPs that coincided in time with a dramatic global environmental event, and further narrowed that focus to pairs wherein the LIP and/or the environmental event had been the subject of recent high-precision geochronological study. To complement our narrative review below, we also present a table detailing the samples included in our analysis (Tables 1 & 2). This new compilation is able to highlight some similarities and some differences



**Figure 1: Map of Large Igneous Provinces.** This map shows the current location of the large igneous provinces described in this chapter, after Bryan & Ferrari (2013). Below, a timeline shows the ages of the global events with which the LIPs are associated. LIP/event couplets are color-coded, and the ages of the LIPs overlap with the ages of the events shown on the timeline. Abbreviations (alphabetized): CAMP – Central Atlantic Magmatic Province; CRBG – Columbia River Basalt Group; EMC – Early-Middle Cambrian extinction; F-F – Frasnian-Famennian extinction; end-G – end-Guadalupian extinction; K-Pg – end-Cretaceous extinction; MCO – Miocene Climate Optimum; NAIP – North Atlantic Igneous Province; OAE – oceanic anoxic event; OJP – Ontong Java Plateau; PETM – Paleocene-Eocene Thermal Maximum; Pl-To – Pliensbachian-Toarcian boundary event; P-T – end-Permian extinction; T-J – end-Triassic extinction.

between LIPs that permit discussion of both the geodynamics of LIPs and their timing relative to environmental catastrophes.

### *Data reporting*

In the sections below and in Table 1, all U-Pb zircon dates reported are  $^{238}\text{U}/^{206}\text{Pb}$  dates, and all  $^{40}\text{Ar}/^{39}\text{Ar}$  are reported with the fluence monitor standard age used. All age uncertainties are reported in this paper at  $2\sigma$  or 95% confidence. When possible, the ages

in the text and table are reported at multiple levels of uncertainty, conventionally defined as: [X], the internal or random uncertainty, suitable for intra-lab comparison and inter-lab comparison when the same tracer is used; [Y], the uncertainty in tracer calibration or the age of the reference material used, for comparisons between labs using different ages or tracer solutions; and [Z], the uncertainty including decay constant uncertainty, permitting comparison between different geochronological methods (Schoene, 2014). High-precision U-Pb dates are calibrated with an EARTHTIME tracer, unless otherwise indicated in the text or in Table 1. To facilitate comparison of high-precision geochronology to that obtained for environmental crises, we have plotted the relative timing of both events with corresponding uncertainties in Figure 2.

Many of the datasets are plotted as probability density functions (Figures 3-7 & 9-10) to display the range of dates obtained from a LIP by various approaches; for plotting purposes, the maximum probability of each dataset included in these figures has been scaled to a probability of 1. It is important to note that none of these plots are meant to represent rates or pulses of magmatism – they simply are a way to display what dates have been produced from rocks sampled for comparison purposes. Determining eruptive or intrusive rates requires integration of geologic and stratigraphic data with geochronology (e.g. Siberian Traps, CAMP, Deccan, NAIP).

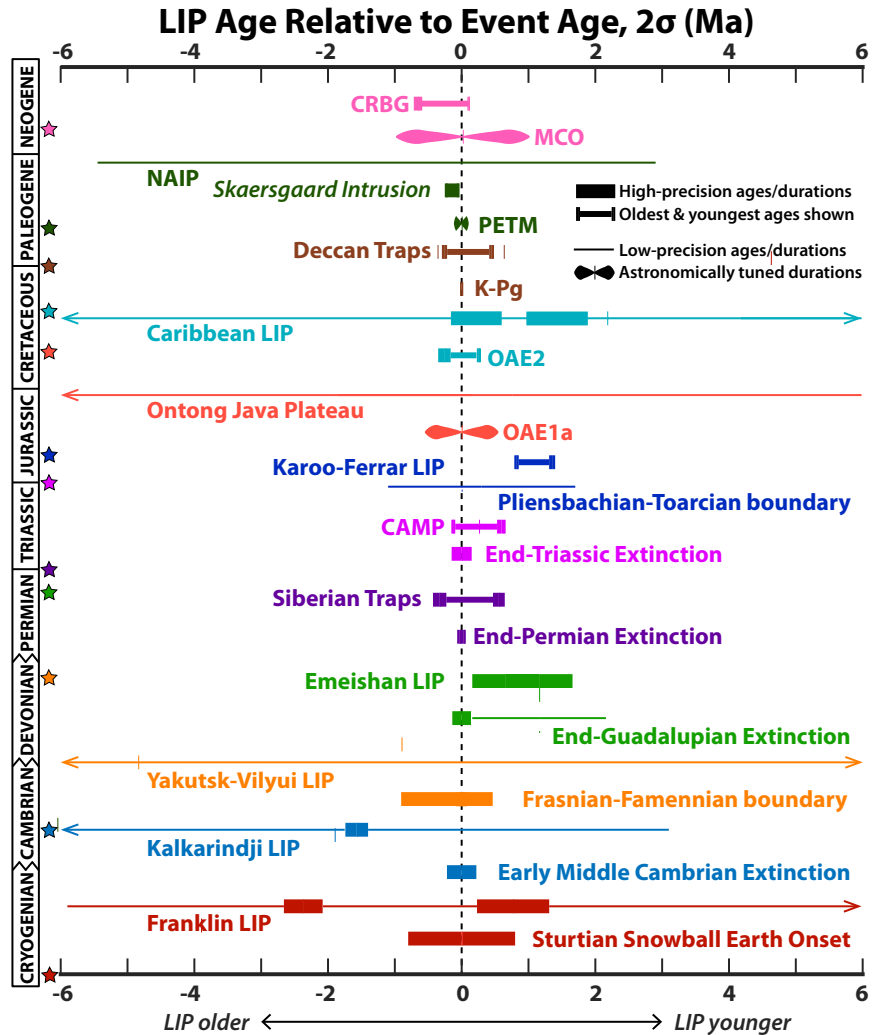


Figure 2: **Relative Timing of LIP Eruptions and Environmental Events.** This figure plots the timing and duration of each LIP, relative to that of the environmental event with which it is associated, plotted adjacently. For each couplet, 0 (black dashed line) is set at the most precise age constraint for the environmental change, or at the midpoint of the event's duration. Ages are plotted with  $2\sigma$  analytical uncertainties [X], except for the End-Guadalupian constraint, shown with [Y] to reflect comparison with different tracers, and Yakutsk-Vilyui LIP/Frasnian-Famennian, which are shown with [Z] to compare  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb results (arrows extending for the Yakutsk-Vilyui LIP indicate that the [Z] uncertainties extend beyond the bounds of the graph). The 0 line is removed for the Deccan Traps/K-Pg ages, since the high-precision extinction ages appear thinner than the line; U-Pb and  $^{40}\text{Ar}/^{39}\text{Ar}$  calibrations are plotted separately to avoid inclusion of systematic uncertainties. Wide lines represent high-precision ages or durations, and thin lines represent low-precision ages. For populations shaped like an "I", the oldest and youngest ages in a dataset are plotted with uncertainties, and there are a number of intervening high-precision ages between those bounds. The durations of OAE1a, the PETM, and the MCO have astronomical rather than radiometric age constraints, and so are demarcated with curved bars. Abbreviations are the same as those given for Figure 1.

## **Geochronology of 12 pairs of LIPs and environmental crises**

### ***Franklin LIP & Sturtian Snowball Earth***

The Neoproterozoic Franklin LIP consists of lava flows, dikes, and sills emplaced over 2.25 million km<sup>2</sup> stretching across northern Canada from Alaska to Greenland. As one of the largest dike swarms on Earth, it includes diabase dikes up to 20 m wide in mainland Canada, Baffin Island, and Greenland, with sills on Victoria Island, Northwest Territories, and Greenland (Denyszyn et al., 2009). The Natkusiak volcanics of Victoria Island represent the thickest extrusive member of the Franklin LIP, with a maximum thickness of ~1100 m (Cox et al., 2015).

Baddeleyite U-Pb ID-TIMS ages from Franklin dikes in Ellesmere Island, Devon Island, and Greenland indicate that the swarm was emplaced from 721±2 Ma to 712±2 Ma (Denyszyn et al., 2009). More recent work has yielded a baddeleyite date for a diabase sill from the Minto Inlier on Victoria Island of 716.33±0.54 Ma (Macdonald et al., 2010), and a U-Pb CA-ID-TIMS detrital zircon date of 719.47±0.29 Ma for a volcanoclastic unit in the Kikiktat volcanics in Arctic Alaska, which are interpreted to be connected to the Franklin LIP on the basis of this age overlap, proximity in paleogeography, and petrogenetic similarities (Cox et al., 2015). These dates from the Franklin LIP have been noted for their general synchronicity with the onset of the Sturtian Snowball Earth event, a period of global glaciation preceded by a large negative excursion in  $\delta^{13}\text{C}$  (Macdonald et al., 2010). The cooling that potentially caused the runaway ice albedo feedback, allowing for these conditions, is hypothesized to be connected to the emplacement of the

Franklin LIP (Macdonald et al., 2010). In this model, the equatorial paleolatitude for the Franklin LIP would have maximized CO<sub>2</sub> drawdown through the silicate weathering feedback (Goddéris et al., 2003; Macdonald et al., 2010). Further, the emplacement of the Natkusiak sills into sulfur-rich evaporites of the Shaler Supergroup could have allowed for cooling through injection of sulfate aerosols into the stratosphere (Macdonald & Wordsworth, 2017).

Maclennan et al. (2018) present CA-ID-TIMS zircon ages for the onset of Sturtian glaciation from tuffs underlying the Negash Diamictite of the Tambien Group in Ethiopia at  $719.68 \pm 0.46$  and  $719.68 \pm 0.56$ , as well as a tuff 2 m above the preceding nadir in  $\delta^{13}\text{C}$  at  $735.25 \pm 0.25$  Ma. Assuming a constant sediment accumulation rate in the basin, they suggest that the base of the diamictite was deposited at  $717.1 + 0.7 / - 0.9$  Ma. This estimate agrees well with findings from the Coal Creek Inlier in Yukon, Canada, where CA-ID-TIMS zircon dates bracket the onset of glaciation to between  $717.43 \pm 0.14$  Ma and  $716.9 \pm 0.4$  Ma (Macdonald et al., 2010, 2017). The previously mentioned sample from the Kikiktat Volcanics also underlies the Sturtian Hula Hula diamictite, providing another maximum age constraint for glaciation at  $719.47 \pm 0.29$  Ma (Cox et al., 2015), while a volcanoclastic interval within the Ghubrah diamictite in the Huqf Supergroup of Oman provides a minimum age constraint of  $711.5 \pm 0.3$  Ma. Collectively, these results indicate a globally synchronous onset for the Sturtian glaciation at the several million year level (Maclennan et al., 2018).

High-precision geochronology indicates concurrent onset of the Sturtian glaciation and Franklin sill emplacement on Victoria Island (Figure 2) (Macdonald et al., 2010), though baddeleyite dates suggest Franklin intrusions likely began a few million years earlier elsewhere in the province (Denyszyn et al., 2009). These age constraints leave open the possibility that weathering of the Franklin LIP could have contributed to the cooling climate prior to the Sturtian Snowball Earth, even if it may not have been the primary driver of the event.

Difficulties in sampling accessibility and preservation of the Franklin LIP result in a paucity of high-precision dates for the Franklin LIP relative to other, more accessible LIPs. While there is decent horizontal coverage across the regional breadth of the LIP, the lack of continuous preserved extrusive sections prohibit a comprehensive vertical sampling strategy, which would be the ideal way in which to assess eruption rates and durations in the province. To date, most ages have been generated from dikes and sills, which lack stratigraphic context and relative order, and it is thus unclear when the bulk of magmatism occurred (Macdonald et al., 2010). Additionally, the total volume emplaced by the Franklin LIP is unknown, which inhibits attempts to model climatic impact. While its equatorial paleolatitude provides a useful condition for maximizing CO<sub>2</sub> drawdown through silicate weathering, this effect may not have been as significant if the volume of the LIP was small.

### ***Kalkarindji LIP & Early-Middle Cambrian Extinction***

The Kalkarindji LIP was emplaced in Australia, and is the oldest known Phanerozoic LIP (Glass & Phillips, 2006). Encompassing the Antrim Plateau Volcanics and Table Hill Volcanics, among other units found to have similar geochemistry, the Kalkarindji is characterized by tholeiitic basalt to basaltic andesite dikes, sills, and lava flows emplaced over 2.1 million km<sup>2</sup> across northern and central Australia (Evins et al., 2009), with a minimum estimated volume of 500,000 km<sup>3</sup> (Glass & Phillips, 2006). Individual lava flows range from 20-200 m, and the thickest stratigraphic sections of the province expose a cumulative thickness of 1500 m (Jourdan et al., 2014). However, limited exposure prevents the development of robust stratigraphic division of the province.

U-Pb CA-ID-TIMS and <sup>40</sup>Ar/<sup>39</sup>Ar dates from distant regions of the Kalkarindji yield ages overlapping at 511 Ma (Jourdan et al., 2014). Zircons extracted from the Milliwindi dolerite dike in the northern portion of the province were dated through CA-ID-TIMS, and yielded a weighted mean age of 510.67±0.62 Ma ([Z]; MSWD = 2.0, n = 5).

Baddeleyites extracted from mafic enclaves, the product of Kalkarindji sills intruding basement rock in the Munro well, were dated with TIMS and yielded a concordant upper intercept crystallization age of 511±5 Ma (MSWD = 1.6). Plagioclase from dolerite sills in the Table Hill Volcanics, in the southern extent of the province, was dated via <sup>40</sup>Ar/<sup>39</sup>Ar to 510±4 Ma (MSWD = 0.74); pyroxene extracted from the same sills has been dated with <sup>40</sup>Ar/<sup>39</sup>Ar to 506.28±3.40 Ma ([X]; MSWD = 0.64) (Ware & Jourdan, 2018). Most of these ages agree within uncertainty, obscuring the relative order of emplacement

of these units and tentatively suggesting relatively brief emplacement of the province (Jourdan et al., 2014).

The Early-Middle Cambrian (EMC; Series 2-3, Stage 4-5) extinction is the first significant extinction following the Cambrian explosion, with more than 45% of genera going extinct (Jourdan et al., 2014). Reef-building archeocyaths and a variety of reef-dwelling organisms, including many trilobites suffered most prominently (Zhuravlev & Wood, 1996). The period is marked by oceanic anoxia, a positive excursion in  $\delta^{34}\text{S}$  (Hough et al., 2006), a negative excursion in  $\delta^{13}\text{C}$  (Gozalo et al., 2013), and sea-level fall recognized as the Hawke Bay regression, hypothesized to be caused by uplift resulting from a mantle plume (Williams & Gostin, 2000).

The age of the EMC extinction has been bracketed by ID-TIMS U-Pb zircon geochronology on air-abraded zircons from three different ash beds in the Somerset Street Member of the Hanford Brook Formation of New Brunswick, Canada, in the Cambrian Series 2, Stage 4, and dated with ID-TIMS following air abrasion (Landing et al., 1998). The youngest grains from each of these samples were all  $\sim 511$  Ma, thus the authors prefer a date of  $511 \pm 1$  Ma for the stratigraphic unit, which can be interpreted as a maximum age for the stratigraphic unit, though this date should be treated with caution as it was acquired before chemical abrasion was introduced to ID-TIMS (Mattinson, 2005), and without the use of the EARTHTIME spike (Condon et al., 2015). More recently, Harvey et al. (2011) performed CA-ID-TIMS zircon geochronology on an ashbed at the base of the Upper Comley Sandstone Formation in Shropshire, England, in the Cambrian

Series 3, Stage 5. The ash was dated to  $509.10 \pm 0.22/0.56/0.77$  Ma, yielding a minimum age for the EMC extinction.

The temporal connection between the eruption of the Kalkarindji LIP and the EMC extinction was noted by Glass & Phillips (2006), and strengthened by the most recent high-precision geochronology of both the LIP and extinction (Harvey et al., 2011; Jourdan et al., 2014). The precise minimum age of the EMC from Harvey et al. (2011) overlaps with the baddeleyite and  $^{40}\text{Ar}/^{39}\text{Ar}$  dates of Jourdan et al., (2014), though it postdates the zircon age obtained by Landing et al. (1998) by 1 Ma. This proximity in time, combined with analysis of volcanic breccias noting the explosive nature of some of the Kalkarindji volcanism, and sulfur concentration measurements from  $<50\text{-}1900$   $\mu\text{g/g}$ , leads to the suggestion that the Kalkarindji LIP played a causative role in the EMC extinction (Jourdan et al., 2014).

While there is strong evidence suggesting a temporal correlation between these two events, the resolution of the geochronology cannot discern the relative order of the extinction versus volcanism. There is a paucity of high-precision geochronology samples, which are from disparate regions (i.e., not from a single vertical section). Because all current dates overlap, the duration of Kalkarindji eruptions cannot yet be constrained other than by estimation of maximum and minimum durations based upon the uncertainty on these dates. The limited surface exposure of the LIP also inhibits calculation of volume estimates for the province.

### ***Yakutsk-Vilyui LIP & Frasnian-Famennian (Late Devonian) Mass Extinction***

The Yakutsk-Vilyui LIP was emplaced on the northeastern Siberian platform in a triple junction rift system associated with the Late Devonian breakup of the eastern margin of Siberia. Dikes, lava flows, sills, and layered basalt breccia, with some intercalated ashes and tuffs, are found in outcrops on the Lena, Markha, and Viluy rivers (Ricci et al., 2013). The Viluy rift, the NE/SW-striking branch of the triple junction, is 800 km long and 450 km wide, and is bounded by parallel dike swarms on either side that are 700 km in length (Ricci et al., 2013). There is a wide range in estimates for the volume of the Yakutsk-Vilyui LIP. Polyansky et al. (2017) tally the total length of middle Paleozoic mafic dikes in the region, multiplied by thicknesses of 50-250 m, in addition to the volume of basalts and sills calculated from borehole and surface exposure, to estimate a minimum volume for the province of 100,000-215,000 km<sup>3</sup>. Meanwhile, others estimate that over 300,000 km<sup>3</sup> erupted from the Viluy rift; if similar volumes were erupted from the other branches of the triple junction, the total volume emplaced by the Yakutsk-Vilyui LIP may have been up to 1 million km<sup>3</sup> (Ricci et al., 2013). The uncertainty in volume estimates may arise from the fact that exposure of the Yakutsk-Vilyui LIP is currently limited due to erosion, the overlying Siberian Traps LIP to the west, and thick Mesozoic sedimentary cover to the east (Ricci et al., 2013).

While there is a lack of high-precision geochronology for the Yakutsk-Vilyui LIP relative to other LIPs, <sup>40</sup>Ar/<sup>39</sup>Ar work by Courtillot et al. (2010) provide <sup>40</sup>Ar/<sup>39</sup>Ar plateau ages of 372.46±1.4 Ma and 362.36±1.8 Ma (2σ analytical uncertainties, recalculated with FCs = 28.201 Ma (Kuiper et al., 2008)). Incorporating these results with other new dates from

plagioclase phenocrysts separated from sills and lava flows, Ricci et al. (2013) also identify two separate  $^{40}\text{Ar}/^{39}\text{Ar}$  age groups, at  $366.6\pm 3.4$  and  $379.0\pm 3.4$  Ma ( $2\sigma$  total error, recalculated with FCs = 28.201 Ma (Kuiper et al., 2008)), although individual ages in each of these groups overlap with individual ages from the other group at the  $2\sigma$  level.

The Frasnian-Famennian mass extinction, as one of the “Big Five” mass extinctions of the Phanerozoic, resulted in the disappearance of >75% of marine species, particularly affecting reef systems, stromatoporoids, and benthic and planktonic marine invertebrates. The extinction took place in five pulses over a few Ma in the late Frasnian through early Famennian (McGhee, 2013). After the extinction began, there were two episodes of marine anoxia, known as the Kellwasser events, in the Upper Famennian, and a positive carbon isotope excursion (Joachimski et al., 2002; Joachimski & Buggisch, 1993). Hypotheses for the causal mechanism of the extinction include fluctuating sea level, bolide impact, the development of terrestrial plants (Algeo & Scheckler, 1998), and massive volcanism of the Yakutsk-Vilyui LIP (Racki, 1998; Ricci et al., 2013).

A bentonite horizon in uppermost Frasnian sediments in Steinbruch Schmidt, Germany, located 2.5 m below the Frasnian-Famennian boundary and between the Upper and Lower Kellwasser events, was dated with U-Pb ID-TIMS zircon geochronology to  $377.2\pm 1.7$  Ma; interpolating between this date and other ID-TIMS ages in the late Famennian led to an estimate of  $376.1\pm 1.7$  Ma for the Frasnian-Famennian boundary (Kaufmann et al., 2004). However, this date was found to be inconsistent with a Re-Os study that dated the Frasnian-Famennian boundary to  $372.4\pm 3.8$  Ma (Turgeon et al.,

2007) and with a Monte Carlo analysis used in the most recent Geologic Time Scale, which placed the boundary at  $372.2 \pm 1.6$  Ma (Becker et al., 2012). Following this disagreement, Percival et al. (2018) restudied the Steinbruch Schmidt bentonite with modern chemical abrasion U-Pb ID-TIMS zircon geochronology, and obtained a date of  $372.360 \pm 0.053/0.11/0.41$  Ma. This date overlaps with the Re-Os date and with statistically calibrated ages. The prior ID-TIMS date may be incorrect because it predates the introduction of the chemical abrasion technique (Mattinson, 2005), thereby leading to ambiguity in how to interpret a complicated age spectrum that may have resulted from unresolved Pb-loss. Several of the younger single crystal dates in that study, interpreted there as having been affected by Pb-loss, also overlap with the most recent CA-ID-TIMS date (Kaufmann et al., 2004).

Astronomical tuning of the Kellwasser horizons in a number of stratigraphic sections suggests a time interval of 400-450 ka between the Kellwasser horizons (De Vleeschouwer et al., 2017). With this estimate and assuming a constant sediment accumulation rate, Percival et al. (2018) place the Frasnian-Famennian boundary at  $371.86 \pm 0.08$  Ma, which postdates the  $^{40}\text{Ar}/^{39}\text{Ar}$  age for the Siljan impact crater in Sweden of  $377 \pm 2$  Ma (Reimold et al., 2005).

Given the sparse dates and low precision for Yakutsk-Vilyui LIP geochronology, it is possible that volcanic eruptions were concurrent with the Frasnian-Famennian boundary, and the pulses of extinction before and after the boundary. Alternatively, future high-precision dating of the LIP may find that these events are unrelated. An enrichment of

sedimentary Hg has been observed at or near the Frasnian-Famennian boundary in three different sedimentary records, indicating that, if Hg enrichment is a robust proxy-stratigraphic marker of active LIP volcanism, there may have been ongoing Yakutsk-Vilyui LIP activity during the Upper Kellwasser horizon (Racki et al., 2018).

### ***Emeishan LIP & End-Guadalupian (Late Permian) Mass Extinction***

The Emeishan LIP represents one of the primary eruptions of continental flood basalts on Pangea during the Late Permian. Approximately 300,000 km<sup>3</sup> erupted over 250,000 km<sup>2</sup> of the Yangtze craton (southwest China and northern Vietnam) in eastern Pangea, at roughly equatorial latitude (Shellnutt, 2014). However, the current exposure of the Emeishan LIP likely does not reflect its original extent, as the region has undergone extensive post-emplacement deformation due to the collision of the North China block and South China block during the Mesozoic, and the Indo-Eurasian collision during the Cenozoic (Shellnutt et al., 2012). The Emeishan LIP consists of flood basalts, layered mafic-ultramafic intrusions, and silicic plutonic rocks. Ultramafic (picritic) rocks are found in the lower half of the flood basalts, while silicic volcanic rocks (andesite, trachyte, rhyolite, ignimbrite) and basaltic andesites are found in the upper half. The thickness of the LIP ranges from 1-5 km in the west of the province to 0.2-2.6 km in the east, with an average thickness of 700 m (Shellnutt, 2014).

Geologic, paleontological, and paleomagnetic evidence suggest the Emeishan LIP erupted rapidly. In basalt sequences, few flows have weathered flow tops beneath overlying flows or sediments (Shellnutt, 2014). The majority of Emeishan units have

been identified as normal polarity thought to represent a single chron, with a few upper units indicating a reversed polarity, leading to the assessment that the LIP erupted in  $\leq 1$ -2 Ma (Ali et al., 2002; Zheng et al., 2010), corresponding to the Capit-N normal chron of the Geomagnetic Polarity Timescale (Henderson et al., 2012). The Emeishan LIP has also been the subject of numerous geochronological studies of volcanic and plutonic rocks, yielding more than 50 published  $^{40}\text{Ar}/^{39}\text{Ar}$ , U-Pb SHRIMP, U-Pb LA-ICP-MS, and U-Pb ID-TIMS ages, which range from the Capitanian ( $266 \pm 5$  Ma) through the early Triassic ( $246 \pm 4$  Ma) (Shellnutt et al., 2012) (Figure 3). This seemingly long duration, in conflict with the brief duration suggested by paleomagnetic studies, likely arises from inaccurate geochronologic studies, low precision of analyses, and uncertainty regarding the relationship between volcanic and plutonic rocks.  $^{40}\text{Ar}/^{39}\text{Ar}$  ages range from  $256.2 \pm 0.8$  to  $251.5 \pm 0.9$  Ma, suggesting that the Emeishan LIP emplacement extended past the Permian-Triassic boundary, concurrent with onset of Siberian Traps emplacement. Shellnutt (2014) interpret these younger ages as erroneous, compromised by open system behavior resulting from post-emplacement thermal resetting by regional tectonic events.

Recent high-precision U-Pb zircon CA-ID-TIMS dates have refined understanding of the timing and duration of Emeishan LIP emplacement. Shellnutt et al. (2012) reported three ages from diabase dikes, ranging between  $259.4 \pm 0.8$  Ma (MSWD = 0.2, n = 7) and  $257.6 \pm 0.5$  Ma (MSWD = 0.5, n = 6), and from four granites between  $259.6 \pm 0.5$  Ma (MSWD = 0.5, n = 5) and  $258.4 \pm 0.6$  Ma (MSWD = 1.8, n = 5), indicating emplacement over  $\sim 2$  Ma, consistent with age constraints from paleomagnetic data (Ali et al., 2002; Zheng et al., 2010). Shellnutt et al. (2012) also refuted the hypothesis that high-Ti rocks

represented the waning phase of volcanism, as the high-Ti diabase dikes seem to have erupted throughout the duration of the Emeishan LIP. Additionally, Zhong et al. (2014) dated a felsic ignimbrite in the uppermost portion of the Emeishan LIP lavas with U-Pb CA-ID-TIMS, reporting  $259.1 \pm 0.5$  Ma (MSWD = 0.7, n = 6) as the termination age for the Emeishan LIP. All of these dates were calibrated with a non-EARTHTIME tracer solution, but only reported analytical uncertainty [X]. Combined, these new data suggest that eruption of the Emeishan LIP may have lasted less than 1 Ma, and that volcanism ended more than 7 Ma before the Permian-Triassic boundary (Ramezani & Bowring, 2017).

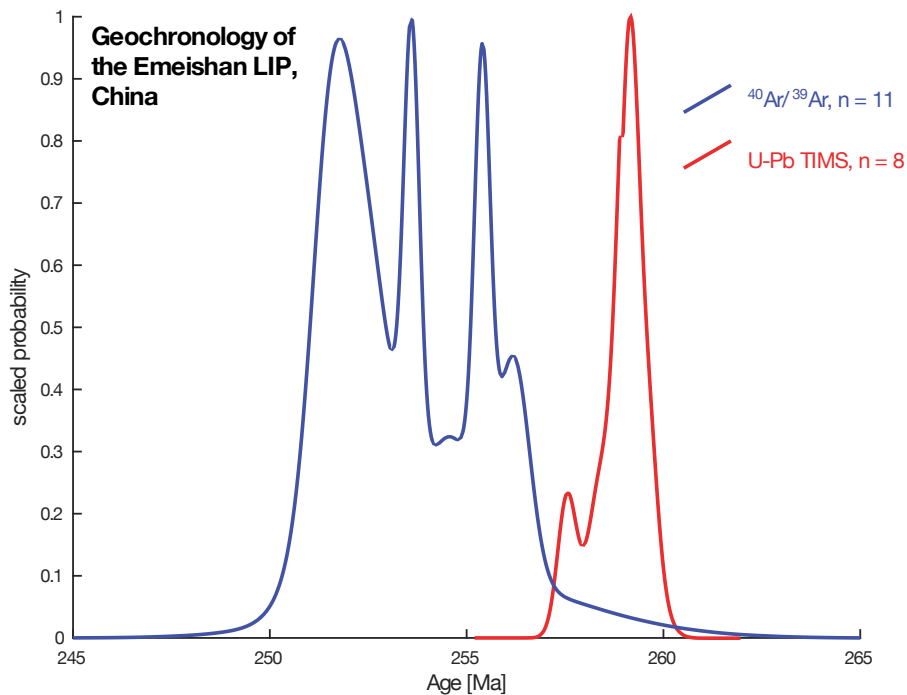


Figure 3: **Emeishan LIP geochronology.** Probability density function for  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-PbID-TIMS geochronology obtained for the Emeishan LIP, as compiled by Shellnutt, (2014).

The end-Guadalupian mass extinction affected both marine fauna and terrestrial flora and fauna, particularly affecting foraminifera, brachiopods, ammonoids, large bivalves, corals, and plants, though it was far less deadly than the Permian-Triassic mass extinction, which occurred only ~9 Ma later. It is also marked by fluctuations in seawater carbon isotopes and temperatures, and a major sea level regression (Chen et al., 2011; Ramezani & Bowring, 2017). The age of this event has been constrained through CA-ID-TIMS geochronology in both marine and terrestrial sections. Mundil et al. (2004) dated ash beds in the marine Shangsi section in central China above the Guadalupian-Lopingian boundary to  $259.1 \pm 1.0$  Ma (MSWD = 0.3, n=6) and  $260.8 \pm 0.8$  Ma (MSWD = 0.8, n = 5), providing a minimum age for the extinction, though obtained without the EARTHTIME tracer. On land, an ash bed in the lower Beaufort Group of the Karoo Basin in South Africa yielded a weighted mean age of  $260.259 \pm 0.081/0.14$  Ma ([X/Y]; MSWD = 1.5, n = 4, EARTHTIME spike) for the top of the *Tapinocephalus* assemblage zone (Day et al., 2015). Between the *Tapinocephalus* assemblage zone and the following *Pristerognathus* assemblage zone, there is a 74-80% loss of generic richness of all tetrapod fauna, particularly affecting the dinocephalian therapsids (Day et al., 2015).

Prior to publication of high-precision geochronology, the Emeishan LIP was implicated as a potential cause of, or contributor to, the end-Guadalupian mass extinction, as volcanic rocks were interbedded with Permian carbonates that exhibited the extinction (Wignall et al., 2009). The fact that the Emeishan LIP erupted through carbonate-rich sediments lends credence to this proposal, as the emplacement would have allowed for the degassing of thousands of gigatons of CH<sub>4</sub> and 40,000 Gt of CO<sub>2</sub> (Shellnutt et al.,

2012). Ganino & Arndt (2009) calculate that observed dolomite-to-marble host-rock thermal metamorphism would have produced 11-26 times more CO<sub>2</sub> than the degassing of magmatic CO<sub>2</sub> from the intrusion. δ<sup>18</sup>O evidence for warming immediately before the Guadalupian-Lopingian boundary may reflect such an influx of CO<sub>2</sub> (Chen et al., 2011). The shorter duration of Emeishan emplacement proposed by Shellnutt et al. (2012) and Zhong et al. (2014) suggest a more intense pulse of degassing of the carbonate-rich country rock that could have caused greater disruption to the biosphere.

The differing levels of precision on ages for Emeishan LIP emplacement and that for the ashes bracketing the end-Guadalupian extinction complicate interpretation of the temporal connection between these events (Figure 2). The most precise constraint on their coincidence is the maximum age of the end-Guadalupian extinction (Day et al., 2015), which suggests that extinction predates the Emeishan LIP (Shellnutt et al., 2012), though the LIP dates are an order of magnitude less precise. This allows for the both the absence or presence of a causal connection between Emeishan LIP magmatism and extinction. Uncertainties for Emeishan dates were not reported at the level to permit comparison of different tracers used [Y]; taking that systematic uncertainty into account would increase the uncertainty on each of the LIP dates, potentially allowing for greater overlap with the extinction constraint of Day et al. (2015). Some geochemical studies of end-Guadalupian sections from various sections globally indicate little climatic disturbance at the time (Sheldon et al., 2014) or a diagenetic, rather than environmentally-controlled carbon isotope excursion (Jost et al., 2014), which complicate the simple hypothesis of the Emeishan LIP causing the end-Guadalupian extinction.

Alternatively, if the extinction occurred closer in time to the minimum, less precise age constraint of Mundil et al. (2004), it may suggest coincidence with Emeishan LIP eruptions. Because the Emeishan dates and that of Mundil et al. (2004) were obtained in the same laboratory with the same tracer solution, these results can be compared considering analytical uncertainty [X] alone. While the Emeishan intrusions described above seem to have been emplaced in ~2 Ma duration around 259 Ma, the difficulty in directly correlating these intrusions with extrusive units does not preclude lavas having been erupted over a different duration. Obtaining ages from lava flows has not yet been possible due to the lack of zircons in basalt flows and thermal resetting affecting  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology (Shellnutt et al., 2012). Further, the uncertainty in eruptive duration, as well as having only a minimum estimate for the volume of the LIP, prohibits a robust calculation of effusion rate. Finally, obtaining high-precision dates from other sections capturing the end-Guadalupian extinction would aid in better assessing whether extinction was globally synchronous and contemporaneous with emplacement of the Emeishan LIP.

### ***Siberian Traps LIP & End-Permian Extinction***

The late Permian to early Triassic Siberian Traps LIP is the largest volume (~3 million  $\text{km}^3$ ) Phanerozoic continental magmatic province (Burgess & Bowring, 2015). Following implication of the Siberian Traps as a potential trigger of the end-Permian mass extinction, efforts to date the timing of LIP emplacement focused primarily on the mineralized intrusions of the Noril'sk region, using the  $^{40}\text{Ar}/^{39}\text{Ar}$  or U-Pb

geochronometers (Baksi & Farrar, 1991; Campbell et al., 1992; Dalrymple et al., 1995a; Kamo et al., 1996; Renne, 1995; Renne & Basu, 1991; Venkatesan et al., 1997). This work roughly constrained the timing of Siberian Traps emplacement from ~245 – 253 Ma (see review in Baksi, (2014)). Subsequent  $^{40}\text{Ar}/^{39}\text{Ar}$  on whole rock, plagioclase and biotite separates by Reichow et al. (2002, 2009) increased the overall footprint of Siberian Traps magmatism, and decreased the duration of magmatism to < 2 Ma, with the volumetric bulk of emplacement centered around ~250 Ma. Kamo et al. (2003) corroborated this approximate age via U-Pb geochronology on baddeleyite and zircon, suggesting magmatism occurred over an even shorter interval of ~ 1 Ma, and began immediately prior to  $251.7 \pm 0.4$  Ma (Figure 4). A relatively short duration of “main phase” LIP magmatism is consistent with observations from other LIPs (see other sections of this paper), however some  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb (SIMS and TIMS) geochronology suggests multiple pulses of Siberian Traps emplacement, and contemporaneous granitic magmatism potentially related to the LIP occurring until ~ 20 Ma after emplacement of the main volume (Ivanov et al., 2009, 2013 and references therein; Malitch et al., 2012; Paton et al., 2010; Reichow et al., 2016).

Advances in U-Pb ID-TIMS geochronology permitted reinvestigation of the timing and duration of Siberian Traps emplacement, with a focus on resolving the tempo of main-phase magmatism, the relative timing of pyroclastic, intrusive, and effusive extrusive components of LIP emplacement, and the relative timing of LIP emplacement and the end-Permian mass extinction. Application of the U-Pb CA-ID-TIMS protocol to sills, lavas, and pyroclastic rocks from throughout the LIP by Burgess & Bowring, (2015) and Burgess et al. (2017) suggests emplacement of the volumetric majority of the Siberian

Traps in three distinct stages, all of which occurred within  $\sim 1$  Ma. In this framework, the Siberian Traps magmatic activity began just prior to  $252.24 \pm 0.10$  Ma, and was characterized by initial pyroclastic eruptions followed by lava effusion. During this emplacement stage,  $\sim 2/3$  of the total volume of the LIP was emplaced ( $>1$  million  $\text{km}^3$ ). Stage 2 began at  $251.907 \pm 0.067$  Ma and was characterized by cessation of extrusion and the onset of widespread sill-complex formation. Intrusive magmatism continued throughout Stage 2 with no apparent hiatus (see also Svensen et al., 2009), with the close of Stage 2 at  $251.483 \pm 0.088$  Ma. Extrusion of lavas resumed after a  $\sim 420$  ka hiatus, marking the beginning of Stage 3, wherein both extrusive and intrusive magmatism continued until at least  $251.354 \pm 0.088$  Ma, an age defined by the youngest sill dated in the province (Burgess et al., 2017; Burgess & Bowring, 2015). Estimates of this relatively rapid eruption tempo are supported by magnetic secular variation data, which suggest the early large-volume Siberian Traps lavas were emplaced in a few pulses, each lasting between 10 kyr and 100 kyr (Pavlov et al., 2019).

Temporal coincidence and thus a causal relationship between Siberian Traps LIP emplacement and the end-Permian mass extinction has long been postulated (e.g., Rampino & Stothers, 1988), and efforts to understand the timing and duration of extinction and recovery, and to weigh probable trigger and kill mechanisms have progressed concomitantly with advances in radiometric dating. Early work established a broad timeline for extinction, with the Permian-Triassic boundary at  $\sim 251$  Ma (Bowring et al., 1998; Renne et al., 1995). Subsequent efforts utilizing both  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb datasets result in varied placement of the extinction timing, ranging from  $\sim 249 - 253$  Ma

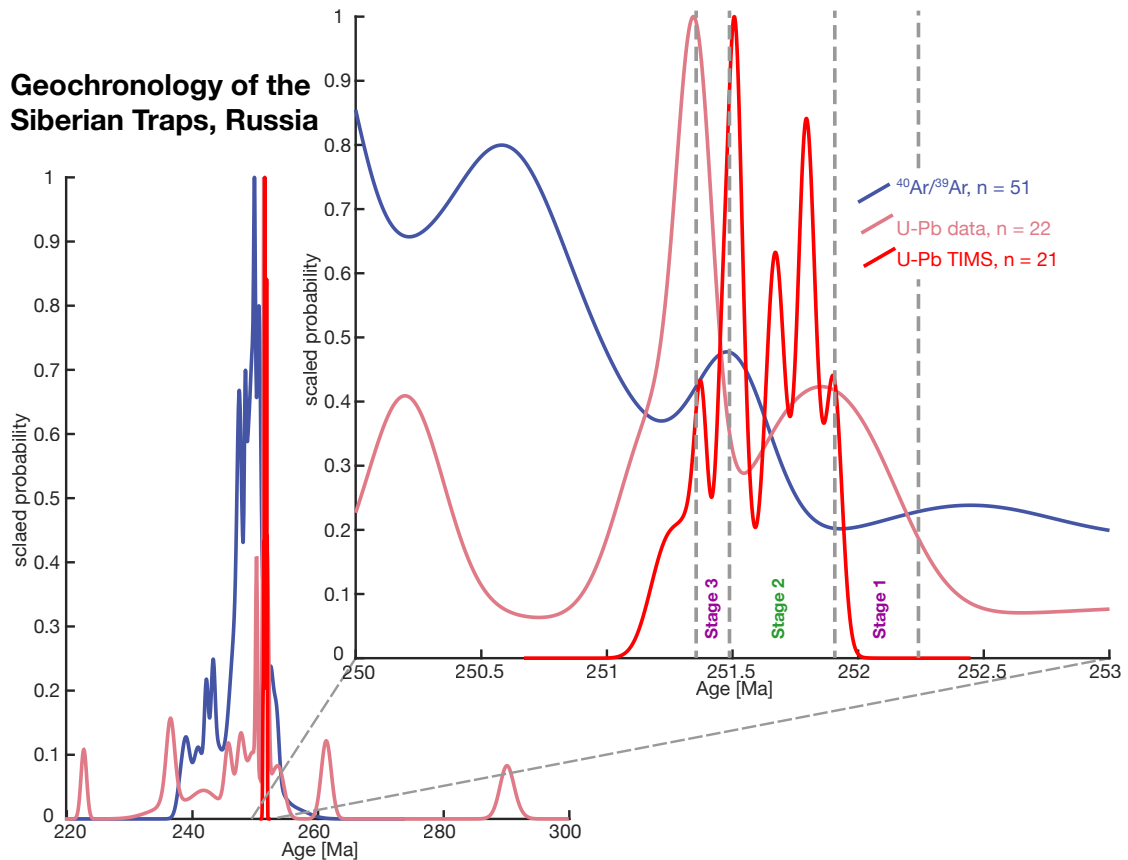


Figure 4: **Siberian Traps geochronology.** Probability density function for  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb ID-TIMS geochronology obtained for the Siberian Traps. U-Pb TIMS data from Burgess & Bowring (2015); references for other data as follows: Baksi & Farrar, 1991; Basu et al., 1995; Campbell et al., 1992; Dalrymple et al., 1995; Ivanov et al., 2005, 2009, 2013; Kamo et al., 1996, 2003; Malitch et al., 2012, 2010; Paton et al., 2010; Reichow et al., 2002, 2009; Renne, 1995; Renne & Basu, 1991; Svensen et al., 2009; Venkatesan et al., 1997; Vernikovsky et al., 2003; Walderhaug et al., 2005. The different stages of emplacement from Burgess & Bowring (2015) and Burgess et al. (2017) are labeled.

(Mundil et al., 2001, 2004; Reichow et al., 2009). Following the advent and broad adoption of the chemical abrasion protocol to single-grain zircon U-Pb TIMS geochronology, Shen et al., (2011) placed the P-T boundary at  $252.17 \pm 0.06$  Ma, with an extinction duration of less than 200 kyr based on bracketing zircon U-Pb TIMS dates. Subsequent to this work, further advances in zircon U-Pb TIMS analysis and data reduction protocol (see review in supplement to Burgess et al., (2014)) enabled an

increase in both accuracy and precision, leading Burgess et al., (2014) to place the Permian-Triassic boundary at  $251.902 \pm 0.024$  Ma, the onset of extinction just after  $251.941 \pm 0.037$  Ma, and cessation prior to  $251.880 \pm 0.031$  Ma, a maximum duration of  $\sim 60$  kyr. This punctuated extinction interval is corroborated by astrochronologic timescales developed for the interval, which suggest extinction over a maximum of  $\sim 80$  ka (Wu et al., 2013) or  $<40$  ka (Li et al., 2016). Employing similar methodology and protocol as Burgess et al., (2014), Baresel et al., (2017a) demonstrate synchrony of the Permian-Triassic boundary within the section dated by Burgess et al., (2014) and at two additional stratigraphic intervals in China, both characterized by much more rapid sediment accumulation rate prior to, and across the extinction interval. This synchrony permits Baresel et al., (2017b) to define a weighted mean Permian-Triassic boundary age of  $251.959 \pm 0.18$  Ma for China, and to suggest that at the resolution of their geochronology ( $\pm \sim 40$ ka), the extinction interval and timing of the Permian-Triassic boundary cannot be resolved from one-another. Shen et al., (2018) utilize an similar dating protocol to date zircon from one of the two expanded stratigraphic intervals studied by Baresel et al., (2017a). Shen et al., (2018) place the Permian-Triassic boundary at  $251.939 \pm 0.031$  Ma, and more tightly constrain the maximum duration of extinction to  $\sim 30$  kyr.

As the geochronologic, paleontologic, and paleostratigraphic datasets linking emplacement of the Siberian Traps and the end-Permian extinction have become more accurate, comprehensive, and precise, the plausibility of a causal connection has been affirmed (see review in Burgess et al., 2014; 2017), and has moved far beyond broad temporal coincidence and an assumption of causality. The paleophysiology selectivity of

the extinction (see review in Knoll et al., 2007), evidence for widespread ocean anoxia and geographic selectivity of extinction (e.g., Penn et al., 2018), and evidence for rapid global temperature increase (see Black et al., 2018; Kiehl & Shields, 2005; Sun et al., 2012), all point toward a massive influx of greenhouse gas into the atmosphere system immediately preceding the onset of mass extinction. Currently, general consensus suggests Siberian Traps magmatism likely drove this rapid input of extinction-triggering greenhouse gases via direct degassing from erupted lavas, and more importantly via metamorphism of sediments contacted by ascending and ponding magmas (e.g., Burgess et al., 2017; Ganino & Arndt, 2009; Svensen et al., 2009). Using this mechanism and the geochronology and emplacement age model of Burgess and Bowring, (2015), Burgess et al. (2017) propose that the initial pulse of Siberian Traps sill emplacement triggered the massive burst of greenhouse gases necessary to drive extinction. Because the ability of a LIP to drive massive environmental change is likely predicated on the tempo of magmatism, with faster emplacement rates more likely to overwhelm environmental buffering capacity, Burgess et al. (2017) suggest the initial pulse of sill emplacement led to sufficiently rapid gas generation. With conservative eruption rates of  $\sim 3\text{-}4 \text{ km}^3/\text{yr}$ , emplacement of Siberian Traps lavas may also have played a key role in rapid greenhouse gas generation (Burgess & Bowring, 2015).

### ***Central Atlantic Magmatic Province & End-Triassic Extinction***

The Central Atlantic Magmatic Province (CAMP) was erupted and emplaced in association with the initial breakup of Pangea ca. 200 Ma, and has been implicated in the end-Triassic mass extinction event. Due to its association with rifting, the CAMP was

highly fragmented and distributed on numerous continents such that its extent and volume have been difficult to estimate (Marzoli et al., 1999; McHone, 2003). The exposed volume of the CAMP is likely  $<1 \times 10^6 \text{ km}^3$ , whereas estimates of the total original volume are  $>2\text{-}3 \times 10^6 \text{ km}^3$  (Marzoli et al., 2018). Basaltic rocks of the CAMP have been identified in outcrop and drill core from North and South America, west Africa, and southern Europe. The chronology of the CAMP has been the subject of many studies over several decades, but here we focus on studies from the last  $\sim 20$  years, for which numerous compilations exist. Because of this fragmented record of CAMP emplacement and eruption, it is hard to know how representative the geochronologic record is of the actual eruption and intrusion history, which is important when comparing emplacement timing to the end-Triassic mass extinction. Nonetheless, a combination of geochronological, geochemical and geological work has assembled a framework of global correlations for the magmatic history of the CAMP that serve geologic and biologic events. For example, observations of eruptive stratigraphic sections, where well-exposed, record three main eruptive pulses of lavas separated by sedimentary horizons. These pulses are often unique geochemically, and can be correlated between isolated CAMP sections on different continents (Bertrand, 1991; Blackburn et al., 2013; Deenen et al., 2010; Marzoli et al., 2004, 2019; Olsen et al., 2003; Whiteside et al., 2007).

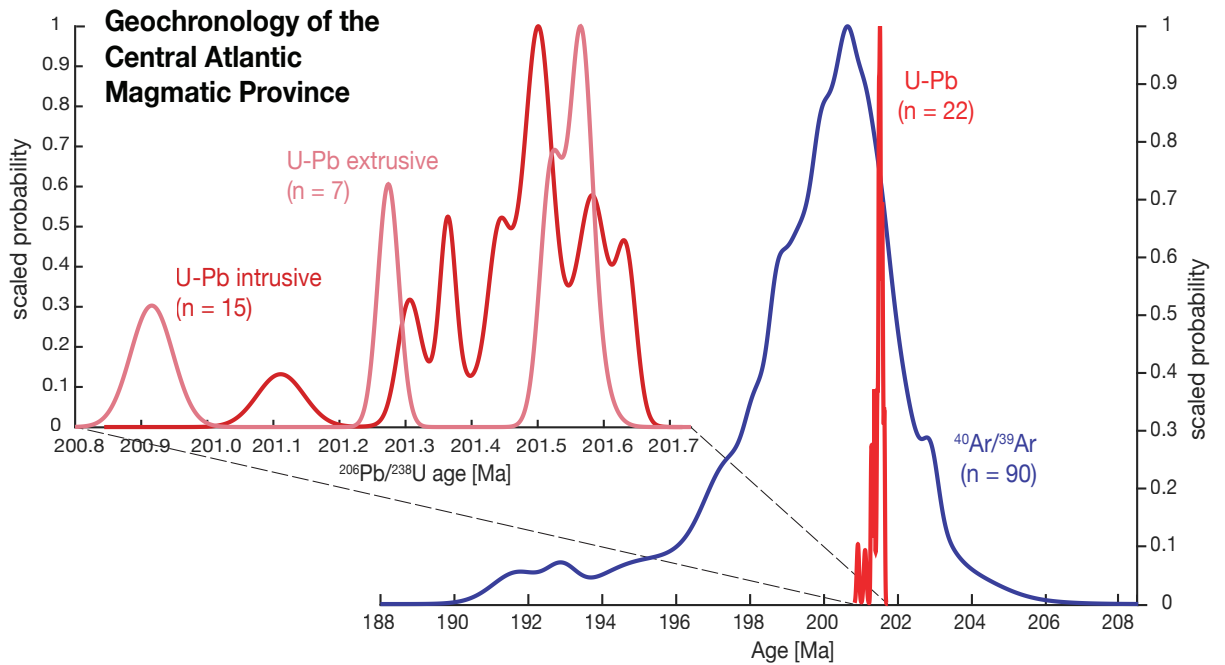


Figure 5: **CAMP geochronology.** Probability density function for  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb ID-TIMS geochronology obtained for the CAMP, as compiled by (Marzoli et al., 2018, 2019), with some additional data from Heimdal et al. (2018).

Modern geochronology for the CAMP includes both  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb data. While hundreds of K-Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  data exist, recent compilations have focused on the most reliable data, typically comprised of hand-picked plagioclase separates from both intrusive and extrusive units that cover the entirety of known CAMP stratigraphy (Marzoli et al., 2018, 2019). Recent compilations (Marzoli et al., 2018, 2019) contain ~90 step heating plateau dates, each typically with uncertainties of  $\pm 1\text{-}2$  Ma, that when plotted together range over ~10 Ma, from 204-192 Ma (Figure 5). However most analyses fall within a briefer window of about 1-2 Ma centered around 200 Ma, relative to an age for the Fish Canyon Sanidine neutron fluence monitor from Kuiper et al. (2008) of 28.201 Ma (Jourdan et al., 2009; Knight et al., 2004; Marzoli et al., 2011, 2018, 2019; Nomade et al., 2007). These data form an asymmetric distribution with younger tails that generally

correspond to lavas high in the stratigraphy in Morocco, but also include some intrusive rocks (Nomade et al., 2007).

U-Pb geochronology on the CAMP has been carried out primarily on sills and dikes that, because of slow cooling rate and internal differentiation, crystallized zircon (Blackburn et al., 2013; Davies et al., 2017; Dunning & Hodych, 1990; Heimdal et al., 2018; Krogh et al., 1987). However, several thick basaltic lava flows in North America that are also zircon-bearing and dated with high precision (Blackburn et al., 2013; Davies et al., 2017; Schoene et al., 2010). A high precision baddeleyite date from the mafic Freetown Layered Complex, Sierra Leone, has been published but these data show large dispersion and are ca. 2 Ma younger than other U-Pb dates, perhaps indicating Pb-loss (Callegaro et al., 2017). Other estimates for the timing of the main eruptions come from CAMP flows in Morocco and North America are derived from correlating dated sills with flows geochemically (Blackburn et al., 2013). The U-Pb data, similarly to the  $^{40}\text{Ar}/^{39}\text{Ar}$  data, show that the CAMP erupted in  $<1$  Ma. However, all the of the U-Pb dates produced so far fall from 201.6 to 200.9 Ma, with precision of  $\pm 20\text{-}50$  ka. In North American stratigraphic sections, younging upwards is maintained and durations of hiatuses between the three main basalt formations are consistent with predictions from cyclostratigraphic analysis of sedimentary interbeds (Blackburn et al., 2013).

The apparent discrepancy in timescales derived from  $^{40}\text{Ar}/^{39}\text{Ar}$  versus U-Pb geochronology likely derives from the relatively larger uncertainties associated with the reported  $^{40}\text{Ar}/^{39}\text{Ar}$  dates. However, excess dispersion in the  $^{40}\text{Ar}/^{39}\text{Ar}$  dates, demonstrated

by high MSWDs on weighted means of culled datasets (Jourdan et al., 2009; Marzoli et al., 2018, 2019; Nomade et al., 2007), suggests that either the  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology has dated rocks that have not been sampled by U-Pb geochronology, or that some  $^{40}\text{Ar}/^{39}\text{Ar}$  dates were affected by open-system behavior, excess Ar, or Ar recoil. Given the larger dataset obtained by  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology, it is possible that younger dates represent a more prolonged lifetime of the CAMP than sampled by U-Pb geochronology. Most of the anomalously young dates (i.e. <198 Ma) are from older studies (Baksi & Archibald, 1997; Deckart et al., 1997; Marzoli et al., 1999; Verati et al., 2005) and have not been re-dated by U-Pb or  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology for confirmation. Regardless, these younger dates, if accurate, likely represent a volumetrically small portion of the CAMP, so it seems likely that the majority of the magmatism fell within a period of <1 Ma between ca. 201.6-200.9 Ma (Davies et al., 2017; Marzoli et al., 2018).

The CAMP is implicated in the end-Triassic mass extinction event, and geochronology has both supported and refined that assertion (Marzoli et al., 1999; Pálffy et al., 2000b; Schoene et al., 2010). The extinction event is recognized in both the terrestrial and marine biospheres (Tanner et al., 2004), though the position of the extinction interval is defined based on ammonite biostratigraphy (Guex et al., 2004; Von Hillebrandt et al., 2007). The extinction event has been dated by U-Pb zircon ID-TIMS geochronology in three locations: the Queen Charlotte Islands, western Canada; the Pucara Basin, Peru; and New York Canyon, Nevada, USA. The zircon data from the Queen Charlotte Islands location was complicated, and potentially affected by Pb-loss, giving a weighted-mean date of  $199.6 \pm 0.3$  Ma ( $2\sigma$ , [X])(Pálffy et al., 2000b). Data from the Pucara Basin

represent the efforts of three studies, with more than a dozen zircon dates spanning the interval from the Norian-Rhaetian boundary to the Haetangian-Sinemurian boundary (Guex et al., 2012; Schoene et al., 2010; Wotzlaw et al., 2014). The resulting age for the Triassic-Jurassic boundary is  $201.36 \pm 0.17$  Ma, defined as the first occurrence of Jurassic ammonite *Psiloceras Spelae*. The onset of the end-Triassic extinction is represented by the last occurrence of Triassic ammonite *Choristoceras Crickmayi* and the onset of an initial carbon isotope excursion (Guex et al., 2004; Lindström et al., 2017), which is most closely stratigraphically associated with an ashbed dated at  $201.51 \pm 0.15$  Ma (Schoene et al., 2010; Wotzlaw et al., 2014). These dates are corroborated by a single ashbed date from Nevada that occurs near the Triassic-Jurassic boundary (Schoene et al., 2010). Another widely cited date for the Triassic-Jurassic extinction comes from the Newark basin, where a palynological turnover event occurs just below the lowermost CAMP basalt, the Orange Mountain Basalt (Whiteside et al., 2007). Using cyclostratigraphy to generate an age model below the basalt, Blackburn et al., (2013) calculate an age of  $201.564 \pm 0.015$  Ma for the extinction event. However, whether or not the palynological event is representative of the global extinction event remains disputed (Cirilli et al., 2009), so we consider the date from the ammonite extinction record in Peru at  $201.51 \pm 0.15$  Ma to be a more conservative and accurate date for the onset of the end-Triassic extinction.

The oldest high-precision U-Pb date of CAMP magmatism comes from an intrusion in west Africa, and is  $201.635 \pm 0.029$  Ma (Davies et al., 2017), likely older than the date of the extinction event from Peru, and ca. 100 ka older than the date from the Newark Basin.

In the Newark Basin, the oldest high-precision date from extrusive volcanism associated with the CAMP is that of the North Mountain Basalt and Orange Mountain Basalts (correlated geochemically with Palisades Sill), at  $201.566 \pm 0.031$  /  $201.481 \pm 0.021$  Ma (dates from Blackburn et al., 2013; Schoene et al., 2010) and  $201.520 \pm 0.034$  Ma (Blackburn et al., 2013), respectively. The North Mountain Basalt was recently redated in Davies et al. (2017), and they adopt an age that averages existing data to get  $201.498 \pm 0.028$  Ma. A date from the Amelal Sill in the Argana Basin in Morocco is  $201.564 \pm 0.054$  Ma (Blackburn et al., 2013), which was placed within the intermediate lavas stratigraphically. Marzoli et al. (2019) report an additional date from the Amelal Sill of  $201.569 \pm 0.042$  Ma, but correlate their sample with the stratigraphically lower lavas, implying rapid eruption for the lower and intermediate basalts in Morocco. Thus, it has become increasingly clear that the end-Triassic extinction coincides within tens of ka of the onset of extrusive CAMP volcanism in eastern North America and may postdate the beginning of sill emplacement by up to 100 ka. Underlining this observation is that the timescales of intrusive and extrusive magmas may not coincide (Figure 5), though it is difficult to say at this point because high-precision dates on lavas are not very abundant. Understanding this record, and continuing to search for older CAMP magmatic events will help tie down more precisely the timing of the onset of magmatism to the onset of extinction. Furthermore, higher-precision dates that can be tied closely to biostratigraphic and stable isotope data for the extinction interval itself will be key to understanding cause and effect in the end-Triassic biotic crisis.

### ***Karoo-Ferrar LIP & Pliensbachian-Toarcian Boundary Event***

The Karoo-Ferrar LIP is comprised primarily of basaltic lavas, sills, and dikes, and was emplaced in the early Jurassic during breakup of Gondwana (e.g., Elliot, 2013; Elliot & Fleming, 2008; Fleming et al., 1997; Pálffy & Smith, 2000; Svensen et al., 2012). At present, the LIP extends over multiple continents, with the two primary portions of the LIP being the Karoo, which is found in South Africa, and the Ferrar, which crops out predominantly in Antarctica, with volumetrically subordinate intrusive rocks found in Australia, Tasmania, and New Zealand (Elliot & Fleming, 2004, 2008). Volume estimates for the entire province are on the order of  $2.5 \times 10^6 \text{ km}^3$  (Cox, 1988; Encarnación et al., 1996). This LIP has received considerable attention due to emplacement of the province in broad temporal coincidence with global environmental perturbations in the early Jurassic, near the Pliensbachian-Toarcian boundary (Pl-To), and the possibility that LIP magmatism triggered these instabilities (e.g., Burgess et al., 2015; Huang & Hesselbo, 2014; Jourdan et al., 2008; Moulin et al., 2017; Sell et al., 2014; Suan et al., 2008; Svensen et al., 2012).

Early efforts to date Karoo-Ferrar magmatism suggested broad synchrony between emplacement of disparate portions of the LIP, and a total emplacement duration of  $>10$  Ma (see review in Burgess et al., 2015). For the Karoo, initial work was primarily done via the  $^{40}\text{Ar}/^{39}\text{Ar}$  chronometer, with a total duration of sill and lava emplacement eventually constrained to  $\sim 3$  Ma including uncertainty on dates (Duncan et al., 1997; Encarnación et al., 1996; Jourdan et al., 2005, 2007, 2008; Moulin et al., 2011). The idea of a protracted emplacement interval for the Karoo has subsequently been revised, with

zircon U-Pb TIMS dates suggesting a much narrower emplacement interval of  $< 0.5$  Ma starting at  $\sim 182.7$  Ma (Corfu et al., 2016; Svensen et al., 2012). Further U-Pb TIMS work on zircon and baddeleyite by Sell et al. (2014) indicate that Karoo intrusive magmatism progressed over 2 Ma, however there is some debate as to whether all of these rocks are associated with the main phase of Karoo LIP magmatism, and whether baddeleyite dates were affected by Pb-loss (Corfu et al., 2016; Sell et al., 2016). Similarly, a protracted emplacement interval characterized by multiple, shorter-lived episodes of voluminous eruption is supported by K-Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  work by Moulin et al. (2017). One U-Pb TIMS zircon date by Burgess et al. (2015) falls within the largest-volume pulse defined by Moulin et al. (2017), and is slightly older than, but within uncertainty of the older sample dated by Sell et al. (2014) and emplacement range defined by Svensen et al. (2014). At present, dates characterized by the highest analytical precision suggest emplacement of the Karoo over less than 1 Ma, while less precise but more stratigraphically inclusive K-Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  dates suggest Karoo emplacement over nearly 10 Ma (Figure 6).

For the Ferrar, initial dating efforts by U-Pb and  $^{40}\text{Ar}/^{39}\text{Ar}$  chronometers constrained emplacement duration to between  $\sim 1$ -2 Ma (e.g., Duncan et al., 1997; Encarnación et al., 1996; Fleming et al., 1997; Foland et al., 1993; Heimann et al., 1994; Minor & Mukasa, 1997). Subsequent CA-ID-TIMS U-Pb zircon dates by Burgess et al. (2015) significantly decreased this range, suggesting emplacement over  $349 \pm 49$  kyr, with magmatism starting by  $182.779 \pm 0.033$  Ma and persisting until at least  $182.430 \pm 0.036$  Ma. This duration is consistent with U-Pb ID-TIMS baddeleyite dating of Ferrar rocks from

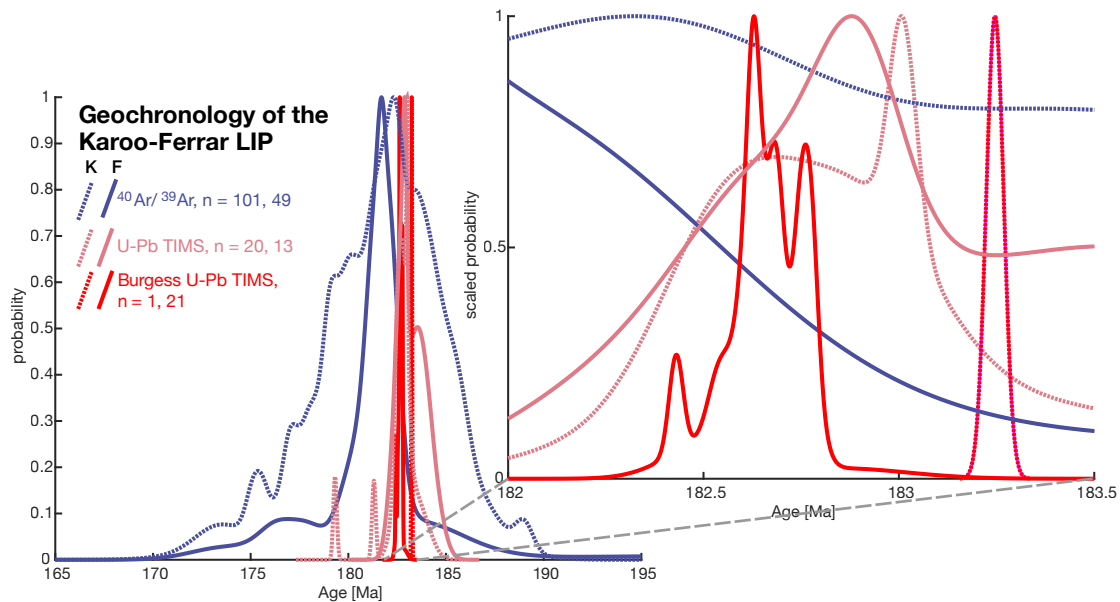


Figure 6: **Karoo-Ferrar LIP geochronology.** Probability density function for  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb ID-TIMS geochronology obtained for the Karoo-Ferrar LIP, highlighting high-precision U-Pb results of Burgess et al. (2017). References for other age data as follows: Antonini, 1998; Brewer et al., 1996; Duncan et al., 1997; Elliot et al., 1999; Encarnación et al., 1996; Fleming et al., 1997; Foland et al., 1993; Le Gall et al., 2002; Hargraves et al., 1997; Heimann et al., 1994; Ivanov et al., 2017; Jones et al., 2001; Jourdan et al., 2005, 2007, 2008; Minor & Mukasa, 1997; Moulin et al., 2017; Riley et al., 2005; Sell et al., 2014; Svensen et al., 2012; Ware & Jourdan, 2018.

Tasmania by Ivanov et al. (2017), within the bounds of  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  pyroxene and plagioclase geochronology on Tasmanian dolerites by Ware and Jourdan (2018), and falls within the bounds defined for the Karoo by Sell et al. (2014) and Svensen et al. (2012). Together, these datasets indicate broadly contemporaneous magmatism in what are now two geographically disparate Ferrar provinces. Extending this correlation with the Karoo requires temporal resolution beyond what currently exists for the Karoo. Estimates of average emplacement tempo for the Karoo-Ferrar are similarly precarious due to uncertainty on eruption duration and total province volume, as LIP erosion and concealment by Antarctic ice may bias volume estimates. Based on the range in eruption duration from the Karoo and Ferrar of between 10 Ma and 1 Ma, reasonable estimates for

average eruption tempo range from 0.25 – 2.5 km<sup>3</sup>/my, with the potential for short-lived (< 100 ka) higher flux pulses within the broader LIP emplacement interval.

Broad coincidence between Karoo-Ferrar LIP emplacement and the PI-To biotic crises and oceanic anoxic event (OAE) has been recognized for decades (e.g., Sepkoski, 1986). Recent work indicates multiple extinction events at this time, with the two most impactful events occurring coincident with the PI-To boundary and in the early Toarcian (see review in Moulin et al., 2017). This time period is also characterized by multiple large amplitude excursions in the carbon isotope record, evidence for widespread ocean anoxia, global warming and cooling events, and fluctuations in sea level (e.g., Al-Suwaidi et al., 2010; Boulila et al., 2014; Guex et al., 2012; Huang & Hesselbo, 2014; Pálffy et al., 2002; Suan et al., 2008, 2011, and many others). Determining coincidence between Karoo-Ferrar LIP emplacement and environmental perturbations in the early Jurassic requires not only a stratigraphically comprehensive, accurate, and precise age model for LIP emplacement, but also on the PI-To boundary date, and the timing and tempo of various environmental perturbations. The absolute temporal record of the LIP is in this instance more thoroughly characterized than geochronology of the environmental crises.

Accepting the PI-To boundary age from Palfy et al. (2000) of 183.6 +1.7/-1.1 Ma, which is consistent within uncertainty with constraints from Sell et al. (2014), Ferrar emplacement occurs within uncertainty of the boundary date and carbon cycle perturbation and is contemporaneous with the onset of the early Jurassic carbon isotope excursion, extinction, and ocean anoxia (Burgess et al., 2015). A more detailed temporal relationship between Ferrar emplacement and Toarcian perturbations is difficult to

ascertain due to large uncertainty in the timing and tempo of these events (e.g., Boulila et al., 2014; Hesselbo et al., 2007; Hesselbo & Pienkowski, 2011). Age uncertainty on the timing and, importantly, tempo of Karoo eruption/emplacement is high relative to that on the Ferrar, which further exacerbates efforts to conclusively link emplacement with environmental perturbation. Recent geochronology efforts do not preclude coincidence, but additional high-precision geochronology with age uncertainty smaller than the duration of events being compared is required to make robust comparison.

### ***Cretaceous Oceanic LIPs & Oceanic Anoxic Events***

The Cretaceous is marked by the prevalence of oceanic LIP eruptions and Oceanic Anoxic Events, which appear to be broadly correlative. OAEs were brief episodes of disturbance to the carbon cycle, with enhanced organic carbon burial, evidenced by the widespread deposition of black shales, and positive carbon isotope excursions of 1.5–2‰ (Jenkyns, 2010). They are associated with global warming, sea level rise, and the drowning of carbonate platforms (Jenkyns, 2010). OAEs appear to have been concurrent with the eruptions of the Cretaceous oceanic flood basalts, which may have provided excess carbon to the ocean that allowed for greater marine productivity, and pCO<sub>2</sub> to the atmosphere, allowing for global warming that accelerated the hydrological cycle, increasing continental weathering and nutrient discharge to the ocean (Ogg et al., 2012). Greater productivity allowed for an increase in organic matter, which placed a greater demand for oxygen in the water column as it was buried, leading to widespread anoxia (Jenkyns, 2010) as the warm global climate did not allow for cold oxygenated bottom water (Schlanger & Jenkyns, 1976). Here we will focus on two of the largest Cretaceous

oceanic LIPs, Ontong Java Plateau and the Caribbean LIP, because they are connected to the two most widespread OAEs, the Early Aptian OAE1a, and the Cenomanian-Turonian OAE2 (the Selli and Bonarelli events, named for their initial recognition in Italy).

#### *Ontong Java Plateau & OAE1a*

The Ontong Java Plateau (OJP) is the largest oceanic large igneous province and largest series of volcanic eruptions in the last 250 Ma, with an estimated volume of 60 million km<sup>3</sup> over an area of 2 million km<sup>2</sup> in the southwestern equatorial Pacific (Courtillot & Renne, 2003). The Greater OJP also includes the minor plateaus of Manahiki, Hikurangi, and South Kerguelen, and is exposed above sea level in the Solomon Islands Arc (Kerr, 2014), and the eastern portion of the plateau is thought to have been emplaced near or at sea level (Chambers et al., 2004).

Given its uniform normal polarity and biostratigraphy, the OJP is thought to have formed in the early Aptian, during the Cretaceous normal polarity superchron (Tarduno et al., 1991). All radioisotopic geochronology in the OJP has been performed using the <sup>40</sup>Ar/<sup>39</sup>Ar method, primarily on whole-rock samples. Mahoney et al. (1993) report that six whole-rock samples from ODP Site 807 yield eruption ages indistinguishable from one another, with a weighted mean value of 122.3±2.0 Ma (range from 124.7±4.4 Ma to 119.9±5.2 Ma). Ages results from Site 289, which was sampled 500 km away, and from the island of Malaita, over 1600 km away, overlap with this mean value. Further dating from exposed OJP basement on the Solomon Islands yielded ages overlapping with the 122 Ma age group (Tejada et al., 1996, 2002). These early studies also had suggested a second

pulse of volcanism at ~90 Ma, given ages obtained from ODP Site 803 (Mahoney et al., 1993) and the island of Sigana (Tejada et al., 1996). However, these younger ages are thought to be affected by argon recoil, given the low potassium content of the rocks and the few plateau heating steps used to obtain the ages, and thus should be interpreted as minimum ages (Chambers et al., 2002). Total fusion ages on plagioclase crystals extracted from OJP basalts sampled at ODP Site 1184, in the eastern salient of the plateau, yield a weighted mean age of  $123.5 \pm 3.6$  Ma, overlapping with the age population obtained elsewhere in the plateau (Chambers et al., 2004).

Though these ages lack the precision of more recent  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb studies on other LIPs, they do suggest that OJP volcanism was occurring simultaneously across a widespread area at ~122 Ma. It cannot yet be assessed whether volcanism occurred on the short timescale of other LIPs in <1 Ma, or if it occurred in the 9 Ma permitted by the range of dates, which would allow calculated emplacement rates to vary over an order of magnitude (Fitton & Godard, 2004). With the current data, there is no apparent geographic age progression, though this may be obscured by the precision of the ages and by the limitations of sampling over only 9 m – 2 km of stratigraphy at a given sampling site (Tejada et al., 1996, 2002).

OAE1a, also known as the Selli event, is recognized for its apparent concurrence with the emplacement of the OJP in the early Aptian. It is marked by the deposition of organic-rich black shales in all major ocean basins, and a complex geochemical signature in  $\delta^{13}\text{C}$ , with a negative excursion followed by a major positive excursion (Menegatti et al.,

1998). The influx of light carbon causing the negative excursion is thought to result from injection of CO<sub>2</sub> from submarine volcanic outgassing (Larson & Erba, 1999; Tejada et al., 2009), or by the dissociation of methane hydrates (Jahren, 2002). The biostratigraphic record of the event is manifested by first, an increased speciation of calcareous nannofossils, followed by a drastic decrease in the calcification of these fossils as well as of planktonic foraminifera, known as the “nannoconid crisis” (Erba, 1994).

While there are no radiometric ages available for OAE1a, two different astronomical tuning models have attempted to constrain the duration of the event, even though the astronomical solution of Laskar et al. (2004) does not apply in the Cretaceous. Li et al. (2008) correlate the carbon isotope records from Italy, Mexico, and the Iberian shelf to estimate a 1.27 Ma duration for OAE1a, with the initial negative  $\delta^{13}\text{C}$  excursion occurring over 27-41 ka. Meanwhile, Malinverno et al. (2010) suggest a duration of OAE1a of  $1.11 \pm 0.11$  Ma through astronomical tuning of the Cismon APTICORE borehole in Italy. They suggest that the record be tied to the base of polarity chron M0r, formerly estimated at 121 Ma (Channell et al., 1995), making the timing of OAE1a from 120.21 to 119.11 Ma. However, a review of advances in Early Cretaceous geochronology suggest that the base of chron M0r, which is also the Barremian-Aptian boundary, is conservatively between 123.8-121.8 Ma, following U-Pb CA-ID-TIMS and  $^{40}\text{Ar}/^{39}\text{Ar}$  studies (Corfu et al., 2013; He et al., 2008; Midtkandal et al., 2016; Olierook et al., 2019). Thus, the timing of OAE1a is likely to have occurred at least 1 Ma if not a few Ma earlier than previously suggested. This time period would be a fruitful interval to pursue more high-precision age constraints, to better ascertain the timing of this boundary and OAE1a.

The current state of geochronology for OJP and OAE1a allows for correlation of the events, since the ages for OJP overlap with the age assigned to OAE1a at ~120 Ma, though at an order of magnitude lower resolution. Higher-precision ages are required to improve this correlation, and to assess a causal relationship between oceanic LIP volcanism and this global climate event at the same resolution as other events in this chapter. Geochronology of the OJP is hindered by sample availability: there have been only a few ODP cores to drill into OJP basement, and it is exposed above sea level in only a few small islands, inhibiting wide sampling across both area and depth of the province. Furthermore, there is no description of felsic ashbeds or gabbroic intervals in the basalts that may potentially yield zircon. Additionally, the low K content of the basalts has limited the precision of  $^{40}\text{Ar}/^{39}\text{Ar}$  dating (Fitton & Godard, 2004).  $\text{pCO}_2$  proxy records suggest that the documented shift to lighter oceanic  $^{187}\text{Os}/^{186}\text{Os}$  isotopes (Bottini et al., 2012; Tejada et al., 2009), reflecting volcanogenic mantle values, was concurrent with the rise in oceanic  $\text{CO}_2$ , strengthening the connection between OJP emplacement and the carbon cycle perturbation of OAE1a (Naafs et al., 2016).

### *Caribbean LIP & OAE2*

The Caribbean LIP consists of 4.5 million  $\text{km}^3$  (Kuroda et al., 2007) of highly faulted basaltic or picritic lavas and sills, layered gabbros, and ultramafic rocks interpreted to be a remnant of an eastern Pacific oceanic plateau that was inserted between North and South America. These rocks were obducted and exposed around the Caribbean margin and the northwestern coast of South America, and exhibit a thickness of 8-20 km (Sinton

et al., 1998). With carbonized tree trunks and corals occasionally interbedded with the basalts, parts of the LIP appear to have been emplaced subaerially or in shallow water (Kerr, 2014). The limited presence of interbedded sediments and ash layers in the Caribbean LIP suggest rapid eruptions with few hiatuses (Kerr, 2014).

Like the OJP, most age constraints for the Caribbean LIP are based on whole rock  $^{40}\text{Ar}/^{39}\text{Ar}$  dates, constrained by biostratigraphic ages of surrounding sediments, which indicate that much of the LIP was emplaced before the Coniacian (89.8-86.3 Ma (Ogg et al., 2012)). These dates similarly suffer from low precision as most of the rocks sampled were tholeiitic, with low  $\text{K}_2\text{O}$  content (Sinton et al., 1998; Snow et al., 2005). The primary pulse of Caribbean LIP volcanism seems to have occurred between 92 and 88 Ma (ranging from  $92.0 \pm 9.6$  to  $87.9 \pm 4.2$  Ma), as evidenced by dates from outcrops on Haiti, Colombia, Costa Rica, Curacao, as well as from DSDP cores sampling the Venezuelan basin (Kerr et al., 2003; Sinton et al., 1998). More recent whole rock  $^{40}\text{Ar}/^{39}\text{Ar}$  dating has yielded a weighted mean of four dates of  $93.96 \pm 0.38$  Ma for the Dumisseau Formation in Haiti, and  $92.75 \pm 0.46$  Ma for a sample from Curacao (Snow et al., 2005). These dates suggest that volcanism was broadly synchronous across the region over a short period of time, potentially 1-2 Ma. A second set of ages from basalts in Columbia, a sill in Curacao, volcanics in Haiti, and from DSDP Site 152 reveal a younger phase of volcanism from 76-72 Ma, which is as extensive in area as the first phase, but is likely less voluminous, and may be related to extension as the plateau was emplaced in its current location (Sinton et al., 1998).

OAE2 was first recognized as a 1 m thick package of laminated black shale with total organic carbon content >30% in the Umbria-Marche region of Italy (Schlanger & Jenkyns, 1976). The black shale has been found across the globe, most prominently in pelagic Atlantic settings, Caribbean, and Alpine-Mediterranean areas, and to a lesser extent in north Africa and Asia (Jenkyns, 2010). This global distribution suggests a widespread reducing environment, occurring in the context of a major sea level transgression, higher global temperatures with elevated pCO<sub>2</sub>, and a positive carbon isotope excursion of 4-5‰, reflecting increased rates of productivity and organic carbon burial (Jenkyns, 2010). The timing of this event, overlapping the Cenomanian-Turonian boundary, is also coincident with an extinction event in which 26% of known genera were lost, particularly affecting more than half of ammonoid and brachiopod genera (Kerr, 2014). Oceanic LIP volcanism has been implicated as a potential cause of OAE2 because of this loss in deep marine biota, the geochemical signature of black shales resembling oceanic plateau, and the increase in productivity related to a greater flux of nutrients provided by volcanism (Kerr, 2014).

Sedimentary sections containing the records of OAE2 have been astronomically tuned to suggest a range of possible durations of the event: 1.8 Ma for the Bonarelli level in central Italy, with the event beginning at 94.21 or 93.72 Ma (Mitchell et al., 2008), 430-445 ka for the Wunstorf section in northern Germany (Voigt et al., 2008), 600 ka for the Greenhorn Formation in the western USA (Meyers et al., 2001; Sageman et al., 2006). A recent high-precision U-Pb zircon geochronology study of bentonites bracketing OAE2 in the Yezo Group of Japan has refined the timing and duration of the event, which begins

at  $94.436 \pm 0.093 / 0.14$  Ma ([X/Z], MSWD = 0.8, n = 5), and ends at  $93.920 \pm 0.031 / 0.11$  Ma ([X/Z], MSWD = 2, n = 3) (Du Vivier et al., 2015). This age model yields a duration of 392-640 ka, in broad agreement with prior astrochronological constraints. The age model's timing for OAE2 also overlaps with the Cenomanian-Turonian Boundary age of  $93.90 \pm 0.07 / -0.09$  Ma, ( $\pm 0.15$  Ma) [X/Z], which was derived from intercalibrated  $^{40}\text{Ar}/^{39}\text{Ar}$ , U-Pb, and astrochronology of the Western Interior Seaway (Meyers et al., 2012).

Given its observed temporal coincidence, the Caribbean LIP has frequently been implicated as one of the causes of OAE2, though other LIPs, such as the High Arctic LIP (Polteau et al., 2016) and the flood basalt volcanism from the rifting of Madagascar (Storey et al., 1995; Turgeon & Creaser, 2008) have also been implicated as possible causes. However, high-precision geochronology studies of these LIPs will be required to better understand this connection, now that the occurrence of OAE2 is well-constrained to  $\sim 94$  Ma (Figure 2). With uncertainty on the order of a few million years, many of the ages used to suggest a first main phase of Caribbean volcanism at 92-88 Ma overlap with the OAE2 zircon ages (Kerr et al., 2003; Sinton et al., 1998; Du Vivier et al., 2015), including the higher-precision  $^{40}\text{Ar}/^{39}\text{Ar}$  dates from the Dumisseau Formation (Snow et al., 2005). While it is also possible that the main phase of the Caribbean LIP eruption could have postdated OAE2 entirely, and may in fact align better with the Turonian-Coniacian boundary (Ogg et al., 2012), a variety of osmium isotope records suggest that a large magmatic pulse triggered the onset of OAE2 (Turgeon & Creaser, 2008; Du Vivier et al., 2014). While the Caribbean LIP suffers from its fragmentary, fault-bounded nature,

complicating sampling across its full vertical stratigraphy and horizontal extent, higher-precision ages would allow for a better understanding of its timing, duration, effusion rate, and connection to OAE2.

### ***Deccan Traps & End-Cretaceous Extinction***

In the late Cretaceous at *ca.* 90 Ma the Indian subcontinent rifted from Madagascar, marking the initial drift of India towards Eurasia, an event that culminated in the Himalayan Orogeny (Besse & Courtillot, 1988; Raval & Veeraswamy, 2003). The impingement of the Reunion plume under the western Indian margin occurred *ca.* 66 Ma, which resulted in the eruption of the Deccan Traps flood basalt province. As outlined below, the timing of the Deccan Traps corresponds well with the end-Cretaceous mass extinction event, though whether it played a role in that disaster remains heavily debated due to the simultaneous occurrence of the Chicxulub bolide impact and the evidence that the impact coincided with the potentially very rapid extinction of marine organisms (Keller et al., 2012; Schulte et al., 2010).

The Deccan Traps covers ~500,000 km<sup>2</sup> of western India, with estimated volumes ranging from 1-2 million km<sup>3</sup> (Jay & Widdowson, 2008; Richards et al., 2015; Self et al., 2008). Large uncertainties in the total volume derive from both the portion of the Deccan that is eroded and also from the amount of basaltic magma that is currently below sea level on the continental shelf off the west coast of India. However, by comparison to other flood basalts, the stratigraphy of the Deccan Traps is well exposed along the western margin of the 1000 m elevation Deccan plateau, called the Western Ghats, where

deep erosion down to the coastal plain has resulted in outstanding exposure of the volcanic stratigraphy. As a result, geological, paleomagnetic, and geochemical studies conducted over several decades have generated a very well-characterized stratigraphy of the Deccan Traps relative to many other flood basalt provinces (Beane et al., 1986; Chenet et al., 2007, 2008, 2009; Khadri et al., 1988; Subbarao et al., 2000).

The stratigraphy of the Deccan Traps has been divided into twelve formations within three subgroups that can be well correlated over ~80,000 km<sup>2</sup> surrounding the Western Ghats. The stratigraphy becomes less certain towards the east, south and north, though geochemical and paleomagnetic data have been used to correlate with the Western Ghats (Courtillot et al., 2000; Jay & Widdowson, 2008; Schöbel et al., 2014; Self et al., 2008; Shrivastava & Pattanayak, 2002). As one spectacular example, basalt flows exposed in quarries on the southeast coast of India are thought to have traveled 1000s of km within the Krishna-Godavari paleo river valley from the Western Ghats into the Indian Ocean. Paleomagnetic, geochemical and chronologic data support an affiliation with the Deccan Traps, though exact correlations have yet to be confirmed (Keller et al., 2008; Knight et al., 2003; Self et al., 2008). While these peripheral flows are important for understanding of the overall evolution of the Deccan Traps, they are volumetrically less significant and therefore perhaps less important for understanding the paleoclimatic implications of the Deccan eruptions.

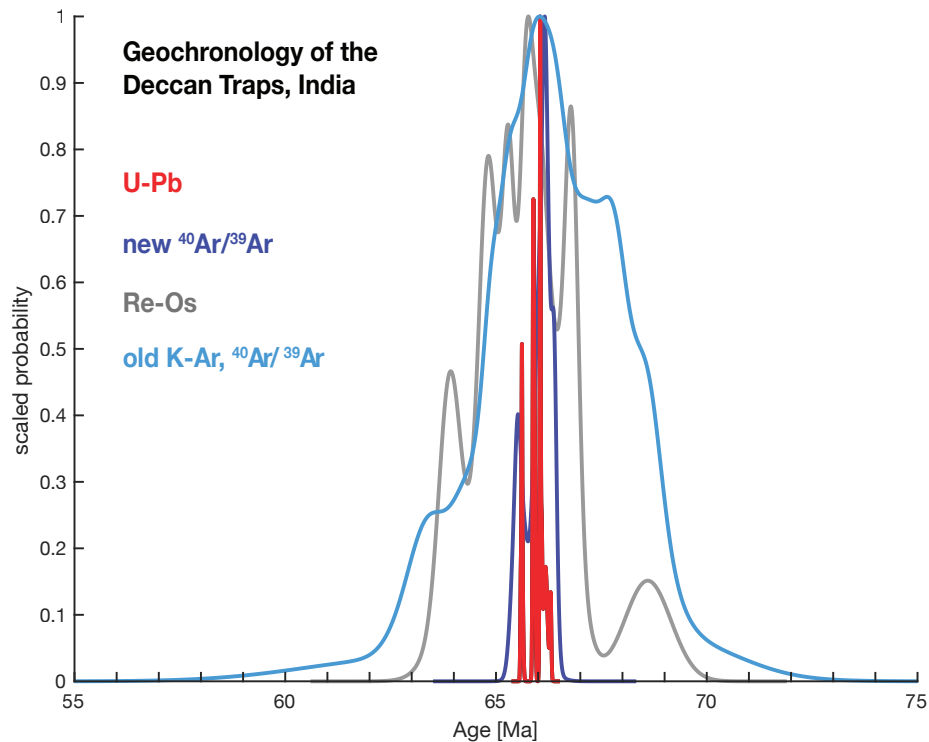


Figure 7: **Deccan Traps geochronology.** Probability density function for Re-Os,  $^{40}\text{Ar}/^{39}\text{Ar}$ , and U-Pb ID-TIMS geochronology obtained for the Deccan Traps. U-Pb data are from Schoene et al. (2019), new  $^{40}\text{Ar}/^{39}\text{Ar}$  data are from Sprain et al. (2019), Re-Os data is from Allègre et al., (1999) and old K-Ar and  $^{40}\text{Ar}/^{39}\text{Ar}$  are from Baksi (1994), Chenet et al. (2007), Courtillot et al. (1986, 1988, 2000), Duncan & Pyle (1988), Hofmann et al. (2000), Hooper et al. (2010), Knight et al. (2003), Pande (2002), Venkatesan et al. (1993).

Because portions of the Deccan Traps are interstratified with sediments containing late Cretaceous flora and fauna, they have been long known to potentially overlap with the end-Cretaceous mass extinction (McLean, 1985). K-Ar,  $^{40}\text{Ar}/^{39}\text{Ar}$ , Re-Os geochronology and paleomagnetic data were gathered over several decades (Allègre et al., 1999; Baksi, 1994; Chenet et al., 2007; Courtillot et al., 1986, 1988, 2000; Duncan & Pyle, 1988; Hofmann et al., 2000; Hooper et al., 2010; Knight et al., 2003; Pande, 2002; Venkatesan et al., 1993), which confirmed that the majority of the eruptions occurred during chron C29r (now known to be between ca. 66.3 and 65.6 Ma), but beginning and finishing

during normal polarity (Chenet et al., 2009; Courtillot et al., 2000) (Figure 7). Chron 29r contains the end-Cretaceous mass extinction and the Cretaceous-Paleogene boundary, which has been defined as the timing of the Chicxulub impact (see review in Smit, 1999). However, uncertainties of  $\pm 1-2$  Ma or more on the dates for the Deccan Traps prevented a high-resolution correlation of the Deccan Traps with the Chicxulub impact and the biotic crisis. Additionally, the age uncertainties, when combined with paleomagnetic data, led several authors to conclude that an early pulse of volcanism as old as 68 Ma predated the main phase in the western Ghats sections (Chenet et al., 2007), indicating a total duration of volcanism to be several millions of years.

Two recent ongoing efforts using  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb geochronology have established a much higher resolution timeline for the eruption of the Deccan Traps. The  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology has focused on multi-grain plagioclase separates from Deccan basalt flows (Renne et al., 2015; Sprain et al., 2019), whereas the U-Pb geochronology is based on dating single zircons from volcanic ash interstratified with the basalts (Schoene et al., 2015, 2019). Both datasets show that over 90% of the Deccan Traps erupted between  $\sim 66.3$  and 65.6 Ma, and therefore do not support a prolonged eruption over millions of years in the Western Ghats. Neither of the studies have dated the C30n portion of the Deccan Traps nor the topmost formations, so the total duration cannot yet be calculated.

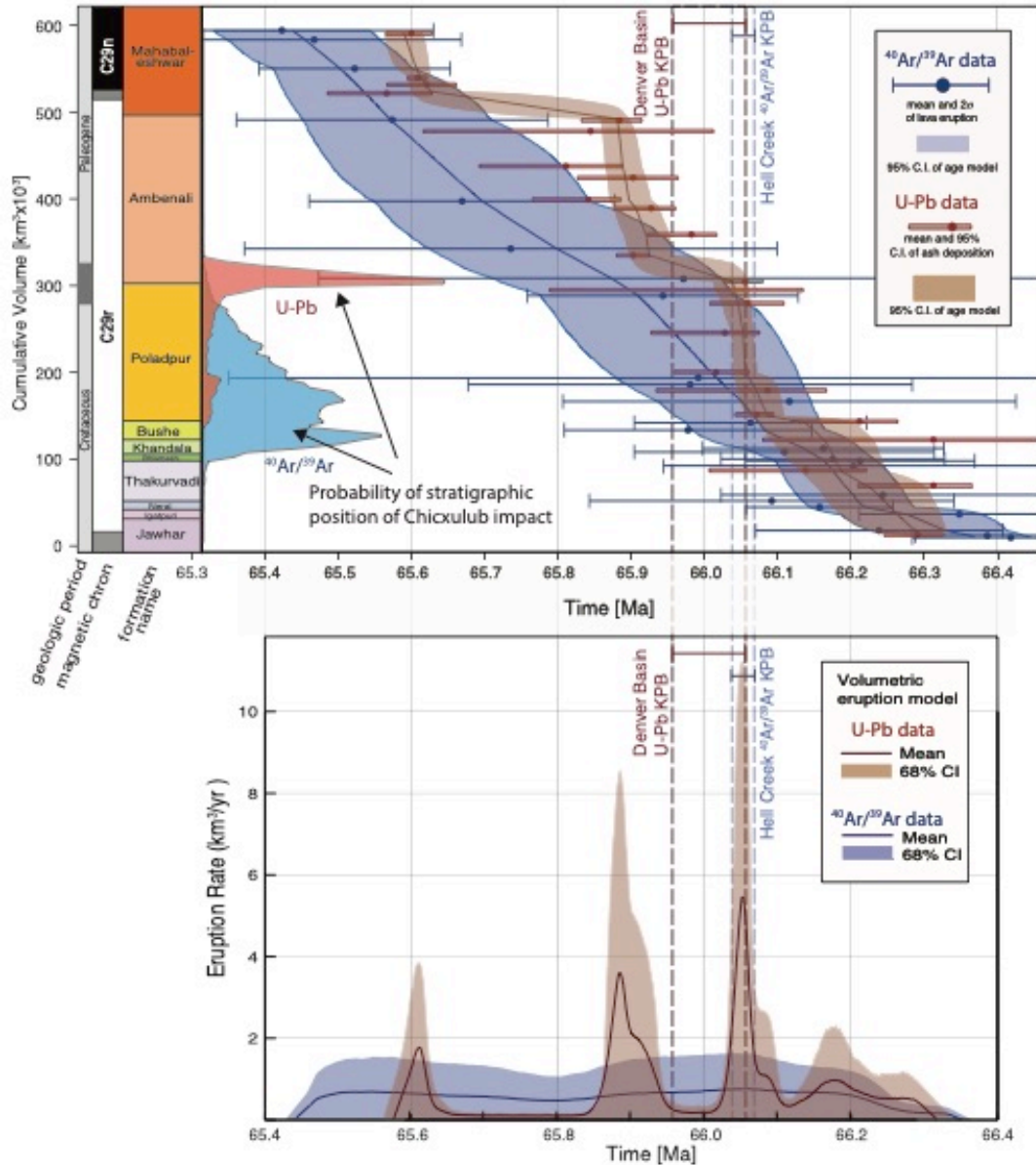


Figure 8: **High-precision geochronology from the Deccan Traps, India.** Compilation of recently published  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb datasets (Sprain et al., 2019; Schoene et al., 2019), compared using the same Bayesian techniques for generating an eruptive age model from each dataset. Upper plot shows the age of stratigraphic units versus the cumulative volume of basalt, using the volume model of Richards et al., (2015). Lower plot shows the corresponding volumetric eruptive rate. Methods are outlined in Schoene et al., (2019). As an output of the same model, the probabilistic position of the Chicxulub impact within the Deccan Traps for each dataset is shown, using the Chicxulub U-Pb date from Clyde et al. (2016) and the  $^{40}\text{Ar}/^{39}\text{Ar}$  date from Sprain et al. (2018), compared to the age model derived from each method.

However, U-Pb geochronology of the same outcrop originally reported to be 67-68 Ma (Chenet et al., 2007) and of transitional polarity was shown to represent the C30n-C29r transition at ca. 66.3 Ma (Schoene et al., 2015), supporting a short duration.

Both the recent  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb datasets (Renne et al., 2015; Schoene et al., 2015, 2019; Sprain et al., 2019) have excellent coverage of the entire Deccan stratigraphy and reveal good agreement between the two methods, but a direct comparison of absolute ages remains difficult. This is because of systematic uncertainties between the  $^{40}\text{Ar}/^{39}\text{Ar}$  to U-Pb dating methods that arise from the decay constants and physical constants of both the  $^{238}\text{U}$  and  $^{40}\text{K}$  decay schemes (Min et al., 2000; Renne et al., 1998, 2010; Schoene et al., 2006), which are discussed in the Dating Methods section. Given these uncertainties, we refrain from comparing the  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb data at better than the 200 kyr level, but instead focus on the datasets and calculated eruption rates internally and compare to geochronology from the same system for assessing their temporal relation to the Chicxulub impact.

Because of the spectacular exposure and preservation of the Deccan Traps in the western Ghats, the  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb datasets can be combined with models for the relative volumes of each formation (Richards et al., 2015) and used to calculate volumetric eruption rates for the flood basalts. Doing so with the U-Pb dataset reveals that the Deccan Traps erupted in four major pulses, separated by relative lulls in volcanism of up to 100 ka (Figure 8). The  $^{40}\text{Ar}/^{39}\text{Ar}$  dataset, in contrast, shows roughly constant eruption rates over the entirety of the Deccan Traps.

However, the comparably large uncertainties associated with the  $^{40}\text{Ar}/^{39}\text{Ar}$  dataset make it impossible to test the presence of pulses identified by the U-Pb dataset. A challenge facing both dating methods in calculating eruption rates is the large uncertainties in the volume models for the flood basalt, in addition to the unknown volume or age of basalts located offshore to the west of the Indian margin. Furthermore, the intrusive component of the Deccan Traps is poorly exposed compared to other LIPs, and thus difficult to compare to the eruption record. As a result, estimating volatile release associated with the Deccan Traps remains a challenge.

The end-Cretaceous mass extinction has not been directly dated. Terrestrial records have low stratigraphic resolution, making it difficult to pinpoint an extinction horizon, and no geochronology has been published from marine records. However, ejecta material from the Chicxulub impact has been well dated by both U-Pb and  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology. Given the stratigraphic correspondence between the impact ejecta and the peak marine extinction, these dates may also calibrate the timing of the extinction. U-Pb dates on impact ejecta come from zircon geochronology of ashbeds bracketing Chicxulub ejecta in the Denver Basin, Colorado (Clyde et al., 2016); the  $^{40}\text{Ar}/^{39}\text{Ar}$  date comes from both sanidine extracted from ashbeds bracketing Chicxulub ejecta in Hells Creek, Montana, and on glassy tektites defining the Cretaceous-Paleogene boundary from both Haiti and Columbia (Renne et al., 2013, 2018; Sprain et al., 2018). Both U-Pb and  $^{40}\text{Ar}/^{39}\text{Ar}$  datasets show that the Deccan Traps began several hundred thousand years before the Chicxulub impact and continued for a similar duration afterwards. It has been

hypothesized that seismic energy from the impact itself may have influenced the eruption of the Deccan Traps, for example by leading to an increase in eruption rates (Renne et al., 2015; Richards et al., 2015). While the  $^{40}\text{Ar}/^{39}\text{Ar}$  dataset cannot rule this model out (Sprain et al., 2019), the U-Pb dataset shows a pulse of eruptions likely beginning before the impact and a decrease afterwards, suggesting the Chicxulub impact and Deccan Traps were completely independent of one another (Schoene et al., 2019).

There remains much to learn about what the effect of the Deccan Traps may have been on the end-Cretaceous mass extinction event. Several datasets have argued for a role for Deccan Traps in late Maastrichtian ecological changes, such as a warming and cooling event evidenced by oxygen isotopes records in foraminifera (Barnet et al., 2017; Li & Keller, 1998; Tobin et al., 2012) and fossil leaf evolution (Wilf et al., 2003), evidence for biologic disturbance in the lead-up to the Chicxulub impact (Henehan et al., 2016; Petersen et al., 2016; Punekar et al., 2014; Wilson, 2014; Wilson et al., 2014), and a significant change in silicate weathering documented by seawater Os isotopes (Ravizza & VonderHaar, 2012; Robinson et al., 2009). The pulse of Deccan volcanism identified in the U-Pb dataset that begins within tens of ka before the Chicxulub impact may hint at a closer temporal link between volcanism and the main extinction event. However, environmental, climate, and biologic records within this timeframe do not paint a clear picture as to what the effect of volcanism was. Some evidence of a hyperthermal event prior to the Chicxulub impact in Elles, Tunisia, has been suggested (Thibault et al., 2016), but corroborating records are scarce. A better understanding of the contribution of the Deccan Traps to the end-Cretaceous mass extinction and recovery period will require

continued stratigraphic work generating very high resolution biotic and proxy records, geochronology from marine sections, as well as continued geochronology on the Deccan Traps to test recently established eruptive histories, including the intrusive history.

### ***North Atlantic Igneous Province & Paleocene-Eocene Thermal Maximum***

The North Atlantic Igneous Province (NAIP) initiated when the proto-Icelandic plume impinged on the base of Greenland (Larsen et al., 1999; Richards et al., 1989).

Magmatism initiated as a result ca. 61-62 Ma in what is now West and East Greenland, Baffin Island, the Faeroe Islands, and throughout the British Isles (Saunders, 2016).

Magmatism continued during rifting of east Greenland and Europe, where inferred plume magmatism is superimposed on mid-ocean ridge magmatism of the mid-Atlantic ridge, forming thickened crust ridges leading towards Iceland (Saunders, 2016; Saunders et al., 1997). In addition to the exposed basalt stratigraphy associated with the NAIP, abundant submarine sills have been imaged seismically along the continental margins (so-called “seaward dipping reflectors (White et al., 1987)), some of which have been dated from drill core and shown to be synchronous with the NAIP (Svensen et al., 2010). Given the fragmentary nature of the NAIP and the abundance of submerged intrusive rocks, the volume of the NAIP has been difficult to determine. An estimate of pre-erosion volume for extrusive rocks of ~1.8 million km<sup>3</sup> is often cited (Eldholm & Grue, 1994), and estimates for the total magmatic volume including intrusive rocks range between 5-10 million km<sup>3</sup> (Eldholm & Grue, 1994; White et al., 1987). Despite potentially being one of the largest LIPs, there is no mass extinction associated with the NAIP. However, geochronology suggests that peak magma production rates may have coincided with the

Paleocene-Eocene boundary and the associated hyperthermal event (the PETM). Testing this correlation requires high-precision geochronology on both basalts, intrusive rocks, and sedimentary sections that contain the PETM.

Published geochronology for the NAIP includes data from the  $^{40}\text{Ar}/^{39}\text{Ar}$ , K-Ar, U-Pb, Re-Os, and Rb-Sr methods. In a recent comprehensive review of existing geochronology, (Wilkinson et al., 2017) rejected the vast majority of these dates based on criteria including poor data quality, incomplete data reporting, dubious interpretations, ambiguous data handling, and questionable sample quality. Their resulting database focuses on subaerial sampling localities and includes between ~80 and 120  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb dates; the number of acceptable dates depends predominantly on whether groundmass, glass, or whole-rock data were included for  $^{40}\text{Ar}/^{39}\text{Ar}$  data (Figure 9a). Our summary here focuses on their more restrictive database that contains only pure mineral separates, given that whole-rock, groundmass and glass  $^{40}\text{Ar}/^{40}\text{Ar}$  dates are too often inaccurate (see other sections of this paper).

The majority of dates within the subset are  $^{40}\text{Ar}/^{39}\text{Ar}$  dates from a handful of studies on basalts and gabbros from west Greenland, east Greenland, the Faeroe Islands and the British Isles (Figure 9b). Both intrusive and extrusive samples have been dated, and some studies (Larsen et al., 2014, 2016; Storey et al., 2007b) focus on sampling from known stratigraphic sections in order to make regional correlations and estimate volumetric eruption rates. Modern ID-TIMS U-Pb geochronology for the NAIP is sparse. Eight dates have been published, from the British Isles (Chambers et al., 2005; Hamilton et al., 1998)

and from submarine cores off the coast of Norway (Svensen et al., 2010). One study of the Skaergaard intrusion in East Greenland was not included on the compilation of (Wilkinson et al., 2017), in which construction of the mafic complex was estimated to be between  $56.02 \pm 0.02$  and  $55.84 \pm 0.02$  Ma (Wotzlaw et al., 2012).

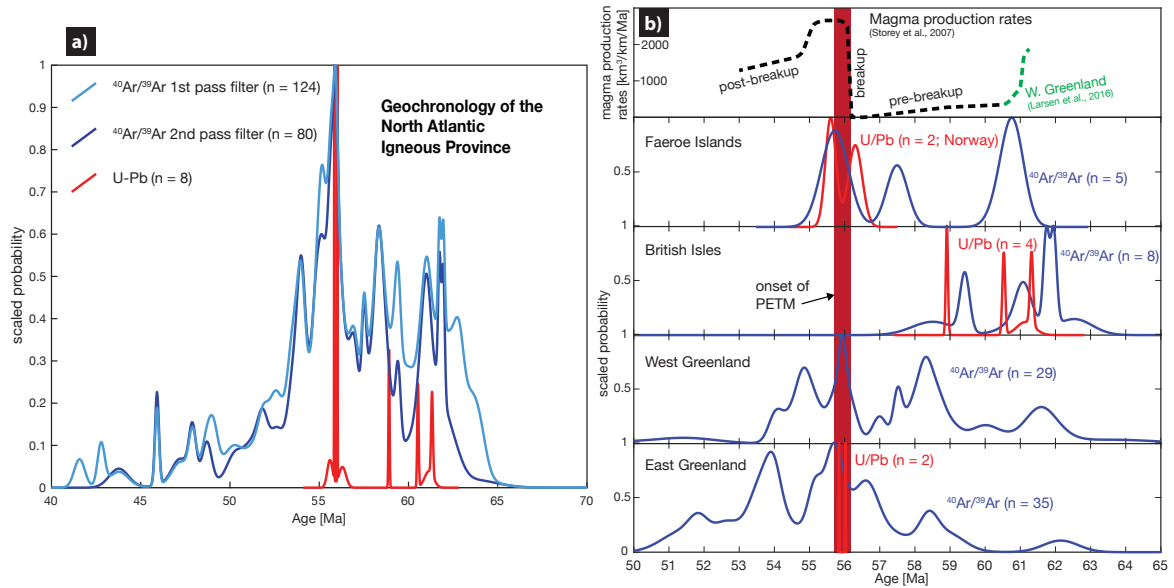


Figure 9: **NAIP geochronology.** Probability density function for  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb ID-TIMS geochronology obtained for the NAIP, as compiled by Wilkinson et al., (2017). The first pass filter of Wilkinson et al. (2017) eliminated dates in the NAG-TEC database adversely affected by poor data quality, incomplete data reporting, dubious interpretations, ambiguous data-handling, and questionable sample quality. The second pass filter removes whole-rock, groundmass, and glass  $^{40}\text{Ar}/^{39}\text{Ar}$  dates, leaving only dates from pure mineral separates.

The results show that magmatism began in the early Paleocene and continued well beyond the Paleocene-Eocene boundary. These geochronologic data have led to the hypothesis that the NAIP was erupted and intruded in two main phases, one that predates the initial breakup of Greenland, North America and Europe ca. 63-61 Ma, and a second beginning ca. 56 Ma (Larsen et al., 2014, 2016; Storey et al., 2007a, 2007b). Wilkinson et

al., (2017) argue that, given their full compilation of available geochronology, this gap in magmatism is less significant. However, assessing changes in the rates of magmatism that may define different phases requires robust volumetric estimates of eruption rates, which are difficult to calculate given the fragmentary preservation of the NAIP. In an attempt to reconcile this, Storey et al., (2007a, 2007b) combined stratigraphically resolved  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology from eastern Greenland with estimates of volumes of each formation to calculate an order of magnitude increase in eruption rates that defines the onset of the second phase of magmatism ca. 56 Ma. In a similar effort in western Greenland, (Larsen et al., 2016) also calculate higher eruption rates in the pre-breakup phase prior to ca. 61 Ma.

The most severe hyperthermal event in the Cenozoic, the Paleocene-Eocene Thermal Maximum (PETM), may overlap with the onset of the second phase of NAIP magmatism. The PETM is marked globally in marine and terrestrial stratigraphic records. It is recorded by both a negative  $\delta^{13}\text{C}$  anomaly of carbonate and organic carbon of several permil, and also a negative  $\delta^{18}\text{O}$  anomaly in foraminifera that indicates a warming of seawater of 3-4° (Cui et al., 2011; Zachos et al., 2001, 2005). The duration of the PETM has been estimated to be either 170 ka or 220 ka, by cyclostratigraphy on astronomically tuned sediments (Röhl et al., 2007) and extraterrestrial  $^3\text{He}$  accumulation (Murphy et al., 2010), respectively. The absolute timing of the onset of the PETM has been calibrated through a combination of U-Pb and  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology on volcanic ashbeds and cyclostratigraphic estimation of the time between the onset and stratigraphic position of the ashbed (Charles et al., 2011; Jaramillo et al., 2010; Storey et al., 2007a; Westerhold et

al., 2009). These result in a range of estimates spanning 500 ka between ca. 55.7 and 56.2 Ma, despite reported uncertainties on the geochronology of 100 ka or better. The uncertainties in these estimates derive from both the uncertainties in standard ages used for  $^{40}\text{Ar}/^{39}\text{Ar}$  dates, the interpretation of the U-Pb zircon data, and the assumptions inherent in cyclostratigraphy, for example that observed cyclicity is caused by Milankovitch cycles and that there are no hiatuses.

There is agreement that the PETM was likely driven by delivery of a large amount of isotopically light carbon to the ocean-atmosphere system, but the source and isotopic composition of that carbon remain debated. Possible sources include methane hydrate dissociation (Dickens et al., 1995), organic carbon volatilization through contact with NAIP sills (Svensen et al., 2004, 2010), weathering of exposed organic-rich epicontinental seaways (Higgins & Schrag, 2006), and mantle carbon derived directly from NAIP magmatism (Gutjahr et al., 2017). It is difficult to reconcile the negative carbon isotope shift of the PETM with mantle carbon extracted from the NAIP, thus explaining the attraction to methane hydrate or organic carbon volatilization. However, Gutjahr et al., (2017) argue based on the pH of seawater derived from boron isotope measurements combined with carbon isotope mass balance that volcanic/mantle carbon was an important source of  $\text{CO}_2$  for the driving the PETM. In order to resolve this issue, more stratigraphically linked, high-precision geochronology is necessary from the NAIP to calculate eruption rates during the break-up phase of the magmatism. Also, the differences in estimates for the onset of the PETM need to be resolved (Charles et al., 2011), likely through a combination of geochronology and potentially cyclostratigraphy

in sections that record the PETM. It is unlikely that cyclostratigraphic estimates for the timing of the PETM alone will have the accuracy to resolve this question (Westerhold et al., 2012).

### ***Columbia River Basalt Group & Miocene Climate Optimum***

The Columbia River Basalt Group (CRBG), the youngest, smallest, and best-preserved continental flood basalt, erupted 210,000 km<sup>3</sup> of lava over Washington, Oregon, and Idaho, USA from ~17-6 Ma. Due to its accessibility, it has been the subject of numerous stratigraphic, paleomagnetic, geochemical, mapping, and geochronological studies, providing an unparalleled level of detail for LIP researchers. The province has been divided into five formations (Steens Basalt, 15.3% of total volume; Innaha Basalt, 5.3%; Grande Ronde Basalt, 72.3%; Wanapum Basalt, 5.9%, and Saddle Mountains Basalt, 1.2%), and each of these has been subdivided into 2-24 stratigraphic members based on mineralogy, geochemistry, and paleomagnetic signature. Volume estimates exist for each member, consisting of 1-20 tholeiitic basalt to basaltic andesite lava flows (Reidel, 2015).

For decades, K-Ar and <sup>40</sup>Ar/<sup>39</sup>Ar geochronology techniques have been used in order to assess the timing and duration of CRBG volcanism. However, large uncertainties (>1 Ma) in these analyses, with ages overlapping despite known stratigraphic order, have precluded the development of an unambiguous chronology. The most recent review of <sup>40</sup>Ar/<sup>39</sup>Ar dates for the basalts (Figure 10) suggests an age model of Steens Basalt erupting from 16.9-16.7 Ma, the Innaha Basalt from 16.7-16.0 Ma, the Grande Ronde Basalt from 16.0-15.6 Ma, the Wanapum Basalt from 15.6-15.0 Ma, and the Saddle

Mountains Basalt in small events between 15 and 6 Ma (Barry et al., 2013). This age model yields several inconsistencies with the Geomagnetic Polarity Timescale (GPTS) (Hilgen et al., 2012) – for example, the universally normally magnetized Innaha Basalt would have erupted during an interval with two complete magnetic field reversals, while the Grande Ronde Basalt, which does exhibit two complete reversals, would have erupted during a reversed chron.

Recent high-precision geochronological studies using both  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb methods have provided a reassessment of the CRBG age model. Since plagioclase phenocrysts extracted from basalt contain low concentrations of  $\text{K}_2\text{O}$ , and basaltic groundmass can be easily altered, Mahood & Benson (2017) performed  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology on feldspar phenocrysts extracted from rhyolitic and trachytic tuffs intercalated with and below the Steens Basalt. Improving on the precision of prior studies by an order of magnitude, the oldest tuff in their study of the Main Scarp section of the southern Pueblo Mountains is dated at  $16.699\pm 0.028$  Ma, and the youngest tuff is  $16.601\pm 0.048$  Ma. Twenty-four lava flows comprising 230 m of section were emplaced between the tuffs, allowing for the calculation of an average eruption rate of 2.4 m/ka (1.3-11 ka at 95% confidence interval). With these constraints, they estimate that the Steens Basalt erupted from  $\sim 16.75$ - $16.54$  Ma, and that the Steens Mountain geomagnetic reversal occurred at  $16.602\pm 0.028$  Ma (all dates re-calculated with Fish Canyon Sanidine age of 28.201, (Kuiper et al., 2008), and expressed with  $2\sigma$  model error).

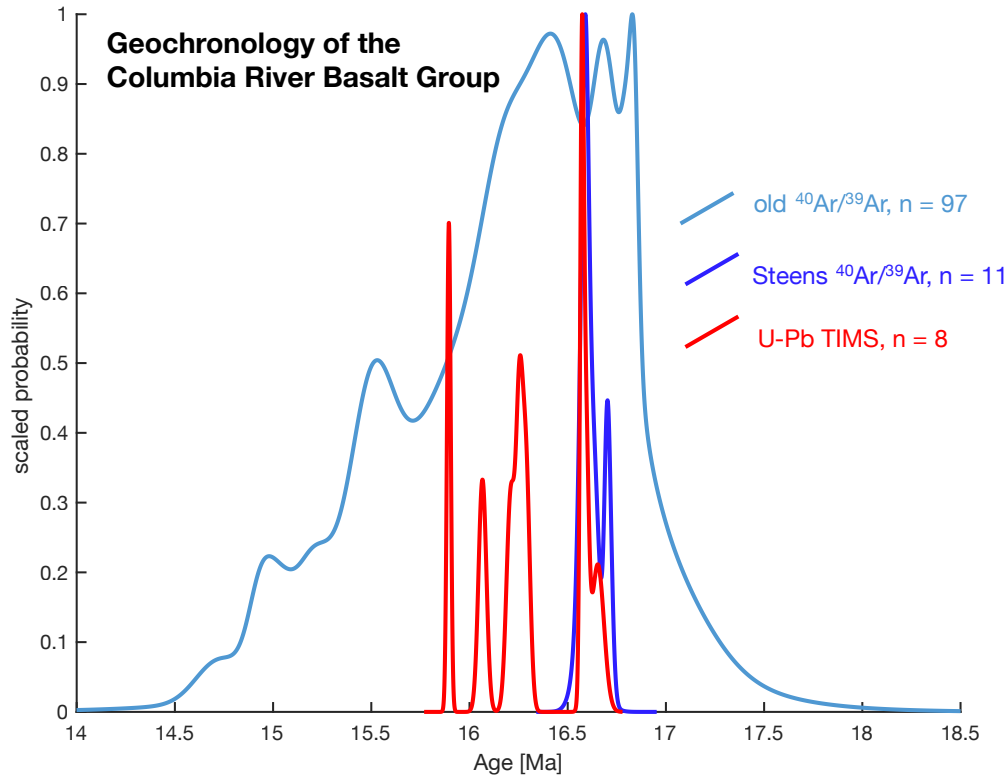


Figure 10: **CRBG geochronology**. Probability density function for  $^{40}\text{Ar}/^{39}\text{Ar}$  and U-Pb ID-TIMS geochronology obtained for the CRBG, comparing the compilation of  $^{40}\text{Ar}/^{39}\text{Ar}$  dates by Barry et al. (2013) to age constraints on the Steens Basalt (Mahood & Benson, 2017) and CRBG zircon geochronology (Kasbohm & Schoene, 2018). Dates for Saddle Mountains Basalt are omitted.

A similar approach was undertaken by Kasbohm & Schoene (2018), who extracted zircons from silicic ash beds interbedded throughout the CRBG stratigraphy, and dated them with U-Pb geochronology through CA-ID-TIMS. Zircon ages show that 95% of the eruptive volume was emplaced in  $758 \pm 66$  ka, 2.4 times faster than previous estimates (Camp, 2013), between  $16.653 \pm 0.063$  Ma in the Lower Steens Basalt, and  $15.895 \pm 0.019$  Ma in the upper Wanapum Basalt. Zircon dating in the Steens Basalt gives good agreement with the results of Mahood & Benson (2017). The volume estimates for CRBG stratigraphic members allow the calculation of an average effusion rate of  $0.334 \pm 0.042$  km<sup>3</sup>/year for the Steens, Imnaha, and Grande Ronde Basalts; volcanism

slows during the emplacement of the Wanapum Basalt, to a rate of  $0.055 \pm 0.014$   $\text{km}^3/\text{year}$ . The samples also indicate at least one effusive pulse of volcanism; the Wapshilla Ridge Member, which comprises 20% of the total CRBG volume, was emplaced at an average rate of  $1.18 \text{ km}^3/\text{year}$ , though the dates for the top and bottom of the member overlap with  $\sim 30$  ka precision, permitting extremely rapid eruption.

A connection between the emplacement of the CRBG and the  $\sim 17$ - $15$  Ma Miocene Climate Optimum (MCO) has long been suggested (Hodell & Woodruff, 1994). This interval was marked by elevated high-latitude sea surface temperatures  $4$ - $6^\circ\text{C}$  above background (Shevenell et al., 2004), with a benthic  $\delta^{18}\text{O}$  minimum, a benthic  $\delta^{13}\text{C}$  maximum, and an inferred reduction in high-latitude ice sheet extent (Armstrong McKay et al., 2014). Vertebrates migrated poleward as temperatures warmed, with increased species originations (Böhme, 2003). A variety of  $\text{pCO}_2$  proxy records, including stomata (Kürschner et al., 2008), alkenone (Zhang et al., 2013), and  $\delta^{11}\text{B}$  (Foster et al., 2012) proxies indicate a possible doubling of atmospheric  $\text{CO}_2$  levels to  $>400$  ppm concurrent with the warming. CRBG volcanism has been suggested as the source of the  $\text{CO}_2$  that led to this warming, and the prior age model for volcanism (Barry et al., 2013) offered a reasonable temporal overlap for these events.

However, there are no radiometric dates calibrating the timing and duration of the MCO, inhibiting an assessment of its connection to the CRBG, particularly in light of new high-precision age models for flood volcanism. The early- and middle-Miocene has proven to be the most difficult interval of the Neogene for establishing precise independent

chronologies in the marine sediments that exhibit the MCO, due to problems obtaining undisturbed stratigraphic sections that yield reliable magnetostratigraphy, biostratigraphy, astronomical tuning, and radiometric ages (Hilgen et al., 2012). All Miocene time scales depend in some way on correlation with the GPTS, for which there are currently several proposals. The most recent, Geologic Time Scale 2012 (Hilgen et al., 2012), notes that the interval from 17-14 Ma is the only portion of the Neogene GPTS that is not calibrated by astronomical tuning of a core with reliable magnetostratigraphy. Instead, this interval was calibrated by seafloor anomaly profiles of the Antarctic and Australian plates, and assuming a relatively constant spreading rate to give a 23.03 Ma age for the Oligocene-Miocene boundary. Proxy records of the MCO use a variety of age models that yield conflicting accounts of the timing of the event, inhibiting the ability to compare its timing to that of CRBG eruptions (Foster et al., 2012; Holbourn et al., 2007, 2015).

In the absence of radiometric ages for the MCO, one way forward, as suggested by Kasbohm & Schoene (2018), may be to focus on MCO records with reliable magnetostratigraphy. By integrating U-Pb zircon dates into the magnetostratigraphic framework of the CRBG, Kasbohm & Schoene (2018) suggest four absolute age constraints on the ages of magnetic field reversals concurrent with CRBG eruption. These absolute ages differ from all prior calibrations of the GPTS, indicating that prior GPTS age models may be in error. However, isotopic records of the MCO that also yielded magnetostratigraphy may be aligned with the proposed GPTS recalibration, and compared to the zircon-derived age model for CRBG eruptions. At Sites 1090 (Billups et al., 2004; Channell et al., 2003) and U1335 (Kochhann et al., 2016), the decline in

benthic  $\delta^{18}\text{O}$ , a proxy for deep-ocean temperature, occur in chron C5Cr, which is the same chron in which CRBG eruptions began with the Lower Steens Basalt, and reach a nadir during chrons C5Cn.3n-C5Cn.1r, during which time the Grande Ronde Basalt was erupting. The astronomically tuned record from U1335 suggests that the decline in  $\delta^{18}\text{O}$  may have begun 100-200 ka before the onset of Steens eruptions. This offset may be explained by the onset of cryptic degassing of  $\text{CO}_2$  as magma migrated through CRBG dike swarms (Armstrong McKay et al., 2014), or it may suggest that these events are unrelated. Further work improving age models for the MCO is required in order to determine its relationship to the CRBG.

Regardless of adjustments to individual proxy records that may occur through refining MCO age models, global proxy data (Zachos et al., 2008) indicate that the MCO continued for  $\sim 1$  Ma after the termination of all but the smallest CRBG eruptions by  $15.895 \pm 0.019$  Ma (Kasbohm & Schoene, 2018). A continuation of warm temperatures following the cessation of volcanism may be explained by the long response time of the silicate weathering feedback, which may occur on 200-500 ka time scales (Stolper et al., 2016), allowing for volcanogenic  $\text{CO}_2$  drawdown over 1 Ma. Alternatively, the CRBG may not be the primary driver for the MCO. Other explanations include changing dynamics of the East Antarctic Ice Sheet (Foster et al., 2012) and changes in global oceanic circulation (Holbourn et al., 2014).

## DISCUSSION

Our review of high-precision geochronology of LIPs and their corresponding environmental perturbations permits new insights to be gained toward understanding the temporal overlap of these events (Figure 2), and potential patterns across these LIP/event couplets in three different areas: (1) the duration and dynamics of LIP magmatism; (2) correlation of LIP magmatism with mass extinctions and environmental change; and (3) challenges and future opportunities in geochronology to better assess how LIPs disrupt the Earth system.

### *Duration and dynamics of LIP magmatism*

Continued improvement in the accuracy and precision of both U-Pb and  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronometers, and their widespread application to LIP rocks, have progressively narrowed estimates for the total duration of LIP emplacement in most cases (Figures 3-9). In particular,  $^{40}\text{Ar}/^{39}\text{Ar}$  and K-Ar datasets published before *ca.* 2010 seemed to indicate eruption durations of at least several Ma for most LIPs, whereas recent refinements, predominantly by U-Pb geochronology, have drastically shortened that duration to < 1 Ma. This pattern of decreasing emplacement duration as age accuracy and precision increase applies to the Emeishan LIP, Siberian Traps, CAMP, Karoo-Ferrar, Deccan Traps, and CRBG. Improved LIP age models also agree with magneto- and cyclostratigraphic timescales, as demonstrated by new age models for the CAMP, Deccan Traps, and CRBG (Blackburn et al., 2013; Kasbohm & Schoene, 2018; Schoene et al., 2015), which yield ages for magnetic field reversals in the basalt stratigraphy that are largely concordant with reversal ages suggested by astronomical tuning (Kochhann et al.,

2016; Westerhold et al., 2008), and, in the case of the CRBG, yield better agreement with reversal ages proposed by the Geologic Time Scale 2012 (Hilgen et al., 2012) than the most recent  $^{40}\text{Ar}/^{39}\text{Ar}$  age model (Barry et al., 2013). While these LIPs are sourced from a variety of geodynamic processes (related to mantle plumes, continental rifting, or upwelling related to subduction), they seem to have been emplaced in a characteristically brief timeframe, placing constraints on how long voluminous eruptions can be sustained.

One notable exception to the < 1 Ma emplacement duration is the NAIP (Figure 9), which shows magmatism extending over several million years. The changing geographic locus of emplacement may result from the movement of the North American and Eurasian plates over the hotspot thought to supply magma, and/or a varying contribution of mid-ocean ridge magmatism to erupted volume. Meanwhile, the other LIPs described in this chapter lack sufficient high-precision geochronology to sufficiently resolve emplacement duration at the ~ 1 Ma level

In addition to a better understanding of overall emplacement duration, better dates have led to a more complete knowledge of the relative timing of intrusive and extrusive magmatism. For those LIPs with sufficiently high precision geochronology and comprehensive sample coverage to resolve the timing of intrusion and extrusion (Siberian Traps, CAMP, Ferrar LIP, and NAIP), all permutations are seen, indicating that there is no characteristic pattern for the order of intrusive and extrusive emplacement of LIPs. For example, in the Siberian Traps, “Stage 1” extrusive magmatism is followed by “Stage 2” intrusion, which is followed by contemporaneous intrusion and extrusion in “Stage 3”

(Burgess et al., 2017). For the CAMP, while further sampling may reveal new insights, currently geochronology is consistent with intrusion slightly predating extrusive magmatism, although both are ongoing through most of the LIP's duration (Davies et al., 2017; Figure 5). In the Ferrar, weighted mean ages for sills are mostly older than the dates for lavas, though there is considerable overlap among individual zircon analyses from lavas and sills (Burgess et al., 2015). In the case of the NAIP, the highest-precision dates indicate contemporaneous extrusive and intrusive magmatism throughout the relatively long duration of emplacement. However, U-Pb dates, which have been instrumental in refining the timelines of other LIPs, are still scarce in the NAIP. For the Franklin and Kalkarindji LIPs, high-precision dates have been obtained only from intrusive units (Cox et al., 2015; Jourdan et al., 2014; Macdonald et al., 2010), while in the Deccan Traps and CRBG, high-precision age constraints have been provided only for lava flows (Kasbohm & Schoene, 2018; Mahood & Benson, 2017; Schoene et al., 2015, 2019; Sprain et al., 2019). For the remaining LIPs, both intrusive and extrusive rocks have been dated, but these dates lack the precision necessary to discern the relative order of emplacement style.

Continued improvement in radiometric dating accuracy and precision has also led to hypotheses regarding eruptive pulses within the overall LIP emplacement duration. These pulses are manifested as short periods of high-tempo volcanism punctuating periods of relative quiescence, and have been documented via U-Pb geochronology in the Siberian Traps, CAMP, Deccan Traps, and CRBG. The CAMP age model of Blackburn et al. (2013) suggests CAMP emplacement in three discrete pulses over an ~700 kyr

emplacement duration, with the astrochronologically determined timing and duration of hiatuses (totaling ~600 ka) supported by U-Pb zircon dates. Similarly, Schoene et al. (2019) propose Deccan Traps emplacement occurred in four high-output pulses, with durations ranging from 50-200 ka, while Kasbohm & Schoene (2018) suggest that the emplacement of the Wapshilla Ridge Member of the CRBG, which comprises 20% of the total LIP volume, likely occurred over tens of ka. In the Siberian Traps, a study of magnetic secular variation suggests that a large portion of magma was emplaced in as little as ~10 ka, though this estimate does not take into account the length of hiatuses (Pavlov et al., 2019). Models for pulsed eruptions of LIPs need to be tested with additional geochronology from a broader area to test whether the apparent hiatuses are simply changes in depositional locations or eruptive center migration. This is a challenge given the large geographic distribution of LIPs and also variable preservation.

#### *Correlation of LIP magmatism with environmental change and biotic extinctions*

While a broad temporal overlap of LIPs and environmental perturbations was once sufficient to hypothesize a causal relationship (e.g., Courtillot & Renne, 2003), progressively higher precision geochronology of LIPs and their corresponding crises has enabled a more detailed interrogation of this hypothesis. In Figure 2, we present the relative timing (zero is set as the age or midpoint timing of environmental event) and total duration of each event, incorporating the most recent geochronology (with  $2\sigma$  uncertainty). This visualization shows the progress made in assessing the relative timing of these events and the plausibility of a causal connection, as well as fruitful areas

to pursue future work. While all of the pairs of events show temporal overlap, for many, uncertain age constraints on at least one of the events hinders the assessment of the possible effects of LIP emplacement. A minority of pairs have high-precision age constraints for both events: Siberian Traps/End-Permian Extinction, CAMP/End-Triassic Extinction, Deccan Traps/End-Cretaceous Extinction, and the CRBG/MCO. The CRBG and MCO show the as-yet unique relationship of the climate event apparently beginning before LIP volcanism, though it is necessary to obtain absolute age constraints on the MCO in addition to its current astronomical calibration. If the MCO were shown to begin before CRBG emplacement, it would suggest that either other processes, such as changing ocean circulation patterns and fluctuations in the East Antarctic Ice Sheet, were more important in driving the MCO (Foster et al., 2012; Holbourn et al., 2014), or that cryptic degassing of the CRBG affected climate prior to the start of extrusive volcanism (Kasbohm & Schoene, 2018). Efforts to find evidence for cryptic degassing in other LIPs are described in the following section, and could be applied to the CRBG.

For the other three couplets (Siberian Traps, CAMP, and Deccan), geochronology suggests emplacement beginning ~100-300 ka prior to the onset of corresponding extinction. For the Siberian Traps, Svensen et al. (2009) propose that the most lethal aspect of the LIP was widespread sill emplacement into an organic-rich sedimentary basin, and Burgess et al. (2017) observe that the end-Permian extinction coincides with the beginning of emplacement Stage 2, dominated by sill emplacement. For the CAMP, the timing of the first intrusive emplacement in western Africa and sill emplacement into an organic-rich basin in Brazil also overlaps with the End-Triassic Extinction (Davies et

al., 2017; Heimdal et al., 2018). In the Deccan Traps, Schoene et al. (2019) resolve the largest pulse of Deccan volcanism immediately before the end-Cretaceous mass extinction, suggesting that the LIP may have played a role, along with the Chicxulub impact, in creating catastrophic conditions for the biosphere. The Deccan Traps emplacement and the K-Pg event do not adhere to the model of Burgess et al. (2017), which argues that the emplacement of sills into a volatile-rich sedimentary basin makes a LIP deadly, rather than voluminous extrusive volcanism or dyke emplacement. A significant volume of intrusive rocks have not been described, and the rocks through which the Deccan was emplaced are not obviously volatile-rich relative to those of the Siberian Traps, leading Burgess et al. (2017) to suggest that the Chicxulub impact would have played an equal if not greater role in causing the extinction as Deccan emplacement. Alternatively, the pronounced increase in Deccan effusion rate just prior to extinction (Schoene et al., 2019) would have been accompanied by more rapid loading of deadly gases into the atmosphere, potentially creating high-stress conditions immediately prior to the Chicxulub impact.

Broadly, Figure 2 and the information reviewed above allow LIP – environmental crisis couplets to be divided into three groups: (1) LIPs connected to mass extinctions (Kalkarindji, Yakutsk-Vilyui, Emeishan, Siberian, CAMP, Deccan), (2) LIPs associated with oceanic anoxic events (Karoo-Ferrar, OJP, Caribbean LIP), and (3) LIPs related to global climate perturbations without mass extinction or oceanic anoxic events (Franklin, NAIP, CRBG). With existing datasets, it is premature to develop a single general model describing why certain LIPs drive specific environmental feedbacks. For example, LIP

size doesn't seem a uniquely deadly trait, as the largest LIP, OJP, was not the most deadly to the biosphere, though its underwater emplacement seems to have disrupted ocean chemistry (Naafs et al., 2016). Nor is duration a unique indicator of deadliness, as the CRBG is of comparable lifespan to the Siberian Traps, CAMP, and Deccan Traps, but is not related to a mass extinction, though it is disputed whether the Deccan Traps played a role in the end-Cretaceous extinction. In every case, the duration of LIP volcanism continues beyond the age of the extinction, indicating that the simple presence of magmatic activity is insufficient to create lasting climatic distress; other aspects of LIP emplacement, such as effusion rate or emplacement style, are likely to drive the short-lived perturbations. While the Franklin LIP's original location in the tropics is hypothesized to be a necessary condition for the onset of the Sturtian Snowball Earth through CO<sub>2</sub> drawdown via silicate weathering (Goddéris et al., 2003; Macdonald et al., 2010), this mechanism does not explain why larger LIPs that were emplaced at the equator (Kalkarindji LIP, CAMP, Caribbean LIP, Deccan Traps) did not also cause similarly dramatic global cooling events. It is likely that the effect a LIP had on the climate and biosphere is at least partly a reflection of the weaknesses inherited in that particular climate or ecosystem state, which have yet to be fully characterized. Further high-precision geochronology in conjunction with development of paleoclimate and biostratigraphic records, and a better understanding of the causes, isotopic composition, and quantity of volatile release will be necessary to improve our understanding of the temporal connection between LIPs and their corresponding environmental catastrophes.

### *Challenges and Future Opportunities*

Geological limitations to improving LIP geochronology occur on macroscopic and microscopic scales. At the macroscopic scale, there is a limit to stratigraphically comprehensive sample collection due to access (particularly for oceanic LIPs), and in some cases, to erosive or depositional processes, which may eliminate much of the LIP stratigraphy from the rock record. At the microscopic scale, obtaining precise geochronology depends on finding the necessary minerals.  $^{40}\text{Ar}/^{39}\text{Ar}$  studies require unaltered minerals, and even when ideal minerals are isolated, can still be hindered by a lack of radiogenic parent isotope and therefore low precision. While U-Pb ID-TIMS zircon studies yield ages with greater precision, they can only be applied to LIPs from which zircons can be extracted from gabbroic segregations or interbedded ashes. A promising approach to improving the precision of  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology of LIPs may also lie in targeting interbedded ash deposits that contain K-feldspar, which can yield much higher precision than plagioclase (Mahood & Benson, 2017), though it may be prone to similar issues of pre-eruptive residence time as seen in zircon geochronology of ashes (Andersen et al., 2017).

For many LIPs, these geological limitations have impeded the calculation of magmatic volumes and the creation of a detailed timeline for eruptions across the original horizontal extent of the LIP and the vertical stratigraphy of eruptions. For example, the limited exposure and relatively low-precision ages of the Kalkarindji LIP make it difficult to ascertain the overall duration of volcanism and the total volume emplaced; current geochronology permits this LIP to have erupted rapidly or over  $\sim 10$  Ma (Figure 2). Well-

established volcanostratigraphies based on geochemistry and magnetic polarity of the basalts have been constructed for only a minority of LIPs (e.g., Siberian Traps, CAMP, Deccan Traps, CRBG), as both widespread exposure and somewhat complete vertical sections remain for these events. Without this detail, however, it is difficult to assess volumetric eruptive rates, which may be as important as overall emplacement volume to the environmental impact of LIPs.

Geological limitations may also affect the age calibration of environmental events, as radiometric dating of these events would require volcanic ash deposition in the middle of the sedimentary successions in which they are recorded, which is rarely the case. Future geochronological studies of environmental crises would also benefit from a horizontal approach, which would assess the synchronicity of an event across different geographic locations (e.g., Baresel et al., 2017a, 2017b; Schoene et al., 2010), as well as a vertical approach, which would provide a greater number of dates constraining not only an extinction horizon, but also any biogeochemical or paleoecological changes that occur before or after that horizon (e.g., MacLennan et al., 2018; Shen et al., 2018; Du Vivier et al., 2015). When radiometric dating cannot be used to constrain the timing of environmental events, astronomical tuning methods may be effectively used to obtain age models, specifically in the Cenozoic for events like the MCO (Kochhann et al., 2016). Improving assessments of the timing, duration, and synchrony of these events at a global scale will not only yield greater insights into their connection to LIP emplacement, but also will provide better temporal constraints to calibrate future versions of the Geologic Time Scale.

Overcoming analytical limitations will also be necessary to provide more detailed assessments of the timescales of LIP eruption and environmental change. Even with methodological advances yielding U-Pb zircon ages with precision to better than  $\pm 0.1\%$ , this resolution is inadequate to address the relative order of LIPs and climatic perturbations that are several hundred Ma old. For younger LIPs, such as the Deccan Traps and CRBG, with geochronological uncertainty on the order of 10-30 ka, a more nuanced account of LIP eruptions can be generated, which indicates rapid pulses of voluminous eruptions and periods of relatively slow, or quiescent eruptions (Kasbohm & Schoene, 2018; Schoene et al., 2019). If analytical limits to absolute precision for eruption and emplacement dates can be overcome, it might be possible to observe such pulsed volcanism in older LIPs.

With new high-precision geochronology improving age constraints on both LIP emplacement and environmental perturbations, demonstrating a simple age overlap for event couplets is insufficient to assess whether or not LIPs play a causative role in these events. Instead, it becomes essential to consider the timing and timescales of different climatic effects of LIPs that may not be recorded in the rock record, such as volatile, aerosol, and particulate release, acid rain, and ozone depletion, and how these are temporally related to intrusive and extrusive LIP emplacement. The effects of ozone depletion from  $\text{Cl}_2$ , acid rain, and cooling due to sulfate aerosols occur on the timescales of months to years (Wignall, 2001), far below both the analytical precision of today's most precise radiometric ages and the typical temporal resolution of the rock record. The

environmental effects of CO<sub>2</sub> release, evident on 10 ka–100 ka timescales (Wignall, 2001) may be more easily captured by pCO<sub>2</sub> proxy records, and compared to LIP emplacement age models with 10 ka–100 ka resolution. With this resolution already obtained, these age models provide crucial temporal constraints for researchers seeking to model the environmental effects of LIP volcanism.

To constrain the timing of CO<sub>2</sub> liberation from LIPs, it may be possible to date rocks that show geological evidence for degassing. For example, Svensen et al. (2010) performed U-Pb zircon geochronology on NAIP sills sampled in drill core offshore Norway, which contain contact aureoles indicative of violent gas release from organic-rich host sediments, as well as a connection to hydrothermal vent complexes; these ages thereby constrain the timing of degassing. Obtaining ages for other intrusive units in contact with metamorphosed organic-rich sediments, for which studies have modeled the amount of CO<sub>2</sub> and methane released (Aarnes et al., 2011; Ganino & Arndt, 2009), would be a fruitful target for future geochronology. Stratigraphic proxy records, such as Hg concentration in sediments and osmium isotope records (Bottini et al., 2012; Tejada et al., 2009; Turgeon & Creaser, 2008; Du Vivier et al., 2014), are proving to be promising for identifying volcanic episodes in sedimentary basins that are distant from LIPs .

The goal of this review was to show how high-precision geochronology has progressively reinforced and refined temporal correlations between LIP emplacement and global environmental perturbations, and to seek out patterns in LIP eruption that may suggest when and how LIPs directly trigger these perturbations. The relative efficacy of various

LIP characteristics (area, volume, effusion rate, host rock composition) in driving situational change is dependent on a number of factors, paramount of which is accurately knowing the timing and duration of both events to a level of precision on par or better than the durations of the events themselves. As discussed, this has been and continues to be a main goal of the broader geochronologic community. Without accurate and precise dates and rates, the detailed role of LIPs in driving environmental change, and why some LIPs are more deadly than others, will remain frustratingly opaque.

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## **SUPPLEMENTAL TABLES (following References)**

**Table 1: High-Precision Geochronology of LIPs.** This table compiles individual high-precision ages of LIPs, with stratigraphic and geographic context, the method by which an age was obtained, statistical information required to report the appropriate uncertainty, and references to the original studies in which these ages were presented. For comprehensive summaries of high-quality  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology from the CAMP and NAIP, readers are directed to Marzoli et al. (2018, 2019) and Wilkinson et al. (2017). All U-Pb studies included are U-Pb CA-ID-TIMS. Abbreviations for Mineral: a = anorthoclase, b = baddeleyite, pl = plagioclase, ps = perovskite, s = sanidine, z = zircon. Abbreviations for Age interpretation: WMA = weighted mean age; WMA-YF = weighted mean age of youngest few zircons; YZ = youngest zircon; TPB = triangular prior in Bayesian age model. Abbreviations for Tracer/Standard used: ET = EARTHTIME; FCs = Fish Canyon Sanidine; BGC = Berkeley Geochronology Center tracer.

**Table 2: High-Precision Geochronology of Environmental Events.** This table compiles individual high-precision ages of global change events, with stratigraphic and geographic context, the method by which an age was obtained, statistical information required to report the appropriate uncertainty, and references to the original studies in which these ages were presented. All U-Pb studies included are U-Pb CA-ID-TIMS. Abbreviations for Mineral: a = anorthoclase, af = alkali feldspar, z = zircon. Abbreviations for Age interpretation: MCMC = Markov Chain Monte Carlo; WMA = weighted mean age; WMA-YF = weighted mean age of youngest few zircons; YZ = youngest zircon. Abbreviations for Tracer/Standard used: ET = EARTHTIME; FCs = Fish Canyon Sanidine.

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Table 1: High-Precision Geochronology of Large Igneous Provinces

LIP	Formation(: Member) and/or Location	Lithology	Method	Mineral	Sample	Age	[X]	[Y]	[Z]	MSWD	n	Age interp.	Tracer/ Standard	Reference
Franklin LIP	intruding Wynniatt Formation	diabase sill	U-Pb	b	S8	716.33	0.54			0.6	5	WMA		Macdonald et al., 2010
Franklin LIP	Kikiktat Volcanics, Alaska	volcaniclastic	U-Pb	z	F624B	719.47	0.29			0.57		WMA	ET535	Cox et al., 2015
Kalkarindji LIP	Milliwindi	dolerite dike	U-Pb	z	Z01	510.67	0.17	0.30	0.62	2.0	5	WMA	ET2535	Jourdan et al., 2014
Emeishan LIP	Daheishan syenite	syenitic pluton	U-Pb	z	DHS-1	259.1	0.5			0.5	5	WMA	BGC	Shellnutt et al., 2012
Emeishan LIP	Woshui syenite	metaluminous syenite	U-Pb	z	GS05-067	259.6	0.5			1.5	6	WMA	BGC	Shellnutt et al., 2012
Emeishan LIP	Huangcao syenite	fayalite+quartz bearing syenite	U-Pb	z	GS05-059	258.9	0.7			0.7	5	WMA	BGC	Shellnutt et al., 2012
Emeishan LIP	Cida granite	granite	U-Pb	z	GS04-143	258.4	0.6			1.8	5	WMA	BGC	Shellnutt et al., 2012
Emeishan LIP	Dyke intruding Baima peralkaline syenite	mafic dyke	U-Pb	z	GS05-005	259.2	0.4			1.9	8	WMA	BGC	Shellnutt et al., 2012
Emeishan LIP	Dyke intruding Baima peralkaline syenite	mafic dyke	U-Pb	z	GS03-105	259.4	0.8			0.2	7	WMA	BGC	Shellnutt et al., 2012
Emeishan LIP	Dyke intruding Woshui syenite	mafic dyke	U-Pb	z	GS03-111	257.6	0.5			0.5	6	WMA	BGC	Shellnutt et al., 2012
Emeishan LIP	Binchuan section, subunit P2-5	felsic ignimbrite	U-Pb	z	JW-1	259.1	0.5			0.7	6	WMA	BGC	Zhong et al., 2014
Siberian Traps	Bratsk/Padunskii	sill	U-Pb	z	A10-23-1	251.681	0.063	0.091	0.28	1.2	8	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Bratsk/Padunskii	sill	U-Pb	z	A10-23-2	251.539	0.056	0.086	0.28	1.2	11	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Bratsk/Padunskii	sill	U-Pb	z	A10-23-3	251.460	0.051	0.083	0.28	1	12	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Nepa/lower sill/Scholokhovskoie pipe	sill	U-Pb	z	194/35/860	251.354	0.088	0.110	0.29	0.4	4	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Nepa/Scholokhovskoie pipe	sill	U-Pb	z	SHI-3085	251.501	0.071	0.097	0.29	0.34	10	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Lower Tungussskaya	sill	U-Pb	z	LT10-1-1	251.786	0.054	0.085	0.28	0.69	8	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Lower Tunguska	sill	U-Pb	z	LT10-2-2	251.795	0.070	0.096	0.29	1.3	14	WMA	ET2535	Burgess & Bowring, 2015

**Table 1: High-Precision Geochronology of LIPs**

Siberian Traps	Lower Tunguska	sill	U-Pb	z	NT12-5-4	251.74	0.18	0.19	0.33	0.65	2	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Bratsk/Oktybroskoe deposit	sill	U-Pb	z	S68-700	251.509	0.044	0.079	0.28	1.4	13	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Bratsk/Oktybroskoe deposit	sill	U-Pb	z	O-6832	251.504	0.059	0.088	0.28	0.36	8	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Noril'sk/Kharaelakh	sill	U-Pb	z	KZ1818-1691	251.71	0.14	0.16	0.31	0.13	3	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Noril'sk/Talnakh	sill	U-Pb	z	KZ1799-1195	251.801	0.088	0.110	0.29	0.45	10	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Noril'sk/Chemogorsky	sill	U-Pb	z	R06-05	251.660	0.064	0.092	0.28	0.7	9	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Noril'sk/Noril'sk 1	sill	U-Pb	z	G22-105-2	251.64	0.10	0.12	0.30	0.48	11	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Noril'sk/Noril'sk 1	sill	U-Pb	z	G22-63-5	251.907	0.067	0.094	0.29	0.7	2	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Noril'sk/Noril'sk 1	sill	U-Pb	z	G22-65-0	251.813	0.065	0.092	0.28	1	5	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Daldykansky	sill	U-Pb	z	N12-3-2	251.376	0.050	0.082	0.28	1.1	7	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Maymecha-Kotuy	lava	U-Pb	ps	K08-14-3	252.20	0.12	0.16	0.31	1.1	15	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Maymecha-Kotuy	lava	U-Pb	ps	K09-6-1	252.27	0.11	0.15	0.31	1.1	12	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Maymecha-Kotuy	welded tuff	U-Pb	z	M09-11-1	251.901	0.061	0.089	0.28	1.6	21	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Maymecha-Kotuy	welded tuff	U-Pb	z	M09-12-1	251.483	0.088	0.110	0.29	1.1	7	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Angara river	pyroclastic breccia	U-Pb	z	A10-13-3	256.56	0.46	0.51	0.58		1	WMA	ET2535	Burgess & Bowring, 2015
Siberian Traps	Noril'sk	pyroclastic breccia	U-Pb	z	SG2610.4	255.58	0.38	0.43	0.51		1	YZ	ET2535	Burgess & Bowring, 2015
CAMP	North Mountain Basalt	Lava	U-Pb	z	NMB-03-1	201.38	0.02	0.22	0.31	1.2	20	WMA	ET535 or ET2535	Schoene et al., 2010
CAMP	North Mountain Basalt, Canada	Lava	U-Pb	z	AVC-1-2	201.522	0.064	1.4	1.4	0.71	8	WMA	ET2535	Blackburn et al., 2013
CAMP	North Mountain Basalt, Canada	pegmatite lens in lava	U-Pb	z	NMB_03	201.523	0.028	0.059	0.22	1.5	10	WMA	ET2535	Davies et al., 2017
CAMP	North Mountain Basalt, Canada	Lava (base of flow)	U-Pb	z	SU1201	201.440	0.047	0.71	0.23	3.5	13	WMA	ET2535	Davies et al., 2017

**Table 1: High-Precision Geochronology of LIPs**

CAMP	Amelal Sill (Argana Basalt correlate), Morocco	Sill correlated as lava	U-Pb	z	MOR	201.564	0.054	0.075	0.23	0.93	10	WMA	ET2535	Blackburn et al., 2013
CAMP	Palisades Sill, New Jersey, USA	Sill correlated as lava	U-Pb	z	NB08-13	201.515	0.033	0.02	0.22	1.7	10	WMA	ET2535	Blackburn et al., 2013
CAMP	Butner Diabase, North Carolina, USA	Sill correlated as lava	U-Pb	z	Butner Diabase	200.916	0.064	0.075	0.23	1.5	14	WMA	ET2535	Blackburn et al., 2013
CAMP	Preakness Basalt, New Jersey, USA	Lava	U-Pb	z	NB08-12	201.274	0.032	0.062	0.22	0.71	15	WMA	ET2535	Blackburn et al., 2013
CAMP	York Haven Diabase, Pennsylvania, USA	Sill	U-Pb	z	YORK	201.509	0.035	0.063	0.22	0.77	6	WMA	ET2535	Blackburn et al., 2013
CAMP	Rapidan Sheet, Virginia, USA	Sill	U-Pb	z	030507-2	201.498	0.033	0.062	0.22	0.44	5	WMA	ET2535	Blackburn et al., 2013
CAMP	Rossville Diabase, Pennsylvania, USA	Sill	U-Pb	z	ROSSGPH	201.305	0.034	0.063	0.22	1.4	6	WMA	ET2535	Blackburn et al., 2013
CAMP	Messejana dyke, Spain	dyke	U-Pb	z	MD48	201.585	0.034	0.063	0.22	2	8	WMA	ET2535	Davies et al., 2017
CAMP	Shelborne dyke, Canada	dyke	U-Pb	z	SD1_2	201.364	0.084	0.099	0.24	0.01	2	WMA	ET2535	Davies et al., 2017
CAMP	Foum Zguid dyke, Morocco	dyke	U-Pb	z	AN731	201.111	0.071	0.089	0.23	1.7	3	WMA	ET2535	Davies et al., 2017
CAMP	Hodh Sill, Mauritania	gabbro sill	U-Pb	z	HD38	201.440	0.031	0.061	0.22	4	7	WMA	ET2535	Davies et al., 2017
CAMP	Foura Djalón sill, Guinea	Sill	U-Pb	z	GUI22-26	201.493	0.051	0.073	0.23	1.5	8	WMA	ET2535	Davies et al., 2017
CAMP	Kakoulima intrusion, Guinea	Sill (layered ultramafic intrusion)	U-Pb	z	GUI126	201.635	0.029	0.06	0.22	1.8	16	WMA	ET2535	Davies et al., 2017
CAMP	Amazonia sill high Ti, Brazil	gabbro sill	U-Pb	z	RP113	201.364	0.023	0.057	0.22	1.88	9	WMA	ET2535	Davies et al., 2017
CAMP	Amazonia sill low Ti, Brazil	gabbro sill	U-Pb	z	RP126	201.525	0.065	0.076	0.23	1.2	9	WMA	ET2535	Davies et al., 2017
CAMP	Tarabuco sill, Bolivia	Sill	U-Pb	z	Bol	201.612	0.046	0.07	0.23	1.2	5	WMA	ET2535	Davies et al., 2017
CAMP	Amelal sill, Morocco	Sill	U-Pb	z	LV34	201.569	0.042			1.1	4	WMA	ET2535	Marzoli et al., 2019
CAMP	Solimões Basin, Brazil	Sill	U-Pb	z	Amostra 8	201.470	0.089	0.13	0.25	0.16	3	WMA-	ET535	Heimdal et al., 2018
CAMP	Amazonas Basin, Brazil	Sill	U-Pb	z	1-MA-1-PA-2883.18	201.477	0.062	0.11	0.24	1.7	5	WMA	ET535	Heimdal et al., 2018

**Table 1: High-Precision Geochronology of LIPs**

Ferrar LIP	Storm Peak, Central Transantarctic Mountains (CTM)	uppermost lava	U-Pb	z	85-76-63	182.43	0.04	0.06	0.20	1.6	7	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Mt. Bumstead, CTM	lowermost lava	U-Pb	z	96-55-2	182.48	0.20	0.21	0.28	0.81	3	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Mt. Bumstead, CTM	uppermost lava	U-Pb	z	96-52-1	182.54	0.20	0.21	0.28	1	4	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Nilsen Plateau, CTM	sill	U-Pb	z	96-65-11	182.59	0.08	0.093	0.22	0.94	6	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Mt. Picciotto, CTM	sill A	U-Pb	z	85-4-18	182.633	0.049	0.069	0.21	1.3	9	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Mt. Picciotto, CTM	sill B	U-Pb	z	85-4-4	182.616	0.049	0.068	0.21	0.47	4	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Dawson Peak, CTM	sill	U-Pb	z	85-5-6	182.635	0.068	0.100	0.22	1.4	6	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Wahl Glacier, CTM	sill	U-Pb	z	85-6-16	182.643	0.055	0.073	0.21	0.2	6	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Roberts Massif, CTM	sill	U-Pb	z	96-74-6	182.746	0.054	0.072	0.21	0.7	7	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Rougier Hill, CTM	sill	U-Pb	z	96-51-67	182.753	0.037	0.060	0.20	0.9	10	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Mt. Falla, CTM	sill	U-Pb	z	90-63-6	182.779	0.033	0.061	0.20	0.98	14	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Dawson Peak, CTM	sill	U-Pb	z	90-3-12	182.85	0.34	0.35	0.40	0.23	2	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Brimstone Pea, South Victoria Land (SVL)	uppermost lava	U-Pb	z	97-55-1	182.635	0.077	0.090		0.9	4	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Bull Pass, SVL	basement sill	U-Pb	z	05-06-01	182.680	0.038	0.061	0.20	0.84	8	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Pandora Spire, SVL	Penepplain sill	U-Pb	z	A-236-A	182.689	0.038	0.061	0.20	0.87	6	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Labyrinth Intrusion, SVL	intrusion	U-Pb	z	04-03-04	182.750	0.048	0.067	0.21	0.74	7	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Pearse Valley, SVL	basement sill	U-Pb	z	90-76-13	182.776	0.059	0.098	0.22	0.78	6	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Red Hill, Tasmania	sill	U-Pb	z	97-17	182.540	0.059	0.075	0.21	1.1	6	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Forrestal granophyre, Dufek intrusion	Granophyre	U-Pb	z	PRR-8633	182.700	0.050	0.066	0.21	0.85	7	WMA	ET535 or ET2535	Burgess et al., 2015
Ferrar LIP	Lexington granophyre, Dufek intrusion	Granophyre	U-Pb	z	PRR-09305	182.629	0.029	0.056	0.20	1.3	11	WMA	ET535 or ET2535	Burgess et al., 2015

**Table 1: High-Precision Geochronology of LIPs**

Karoo LIP	New Amalfi Sheet, South Africa	intrusion	U-Pb	z	I-247	182.246	0.045	0.066	0.21	0.74	5	WMA	ET535 or ET2535	Burgess et al., 2015	
Deccan Traps	Jawhar Fm (lower)	coarse grained gabbro veinlets	U-Pb	z	DEC13-30	66.296	+0.037 /-0.030	+0.042 /-0.038	+0.081 /-0.080				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Thakurvadi Fm (lower-middle)	redbole	U-Pb	z	RBAB	66.225	+0.077 /-0.071	+0.078 /-0.075	+0.104 /-0.104				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Thakurvadi Fm (middle)	redbole	U-Pb	z	RBAG	66.185	+0.061 /-0.056	+0.068 /-0.060	+0.094 /-0.093				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Khandala Fm (uppermost)	redbole	U-Pb	z	RBBQ	66.161	+0.066 /-0.069	+0.070 /-0.073	+0.099 /-0.101				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Bushe Fm (2m below Poladpur Fm)	redbole	U-Pb	z	RBBL	66.132	+0.069 /-0.058	+0.071 /-0.064	+0.100 /-0.096				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Poladpur Fm (10 m above Bushe contact)	breccia fill redbole	U-Pb	z	RBBI	66.088	+0.032 /-0.026	+0.043 /-0.034	+0.081 /-0.077				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Poladpur Fm (middle)	breccia fill redbole	U-Pb	z	RBBM	66.07	+0.031 /-0.028	+0.036 /-0.032	+0.077 /-0.078				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Poladpur Fm (middle)	breccia fill redbole	U-Pb	z	RBBR	66.055	+0.017 /-0.018	+0.026 /-0.024	+0.074 /-0.073				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Poladpur Fm (middle)	redbole	U-Pb	z	RBBJ	66.052	+0.015 /-0.018	+0.023 /-0.023	+0.073 /-0.072				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Poladpur Fm (upper)	redbole	U-Pb	z	RBBS	66.047	+0.017 /-0.020	+0.025 /-0.027	+0.073 /-0.073				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Poladpur Fm (uppermost)	redbole	U-Pb	z	RBAW	66.044	+0.019 /-0.022	+0.026 /-0.028	+0.073 /-0.073				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Poladpur Fm (uppermost)	redbole	U-Pb	z	RBX	66.039	+0.022 /-0.030	+0.027 /-0.029	+0.074 /-0.075				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Ambenali Fm (lower)	breccia fill redbole	U-Pb	z	RBBH	65.926	+0.035 /-0.028	+0.045 /-0.036	+0.081 /-0.079				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Ambenali Fm	breccia fill redbole	U-Pb	z	RBBF	65.92	+0.032 /-0.031	+0.039 /-0.040	+0.080 /-0.079				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Ambenali Fm (middle)	redbole	U-Pb	z	RBB2	65.905	+0.033 /-0.033	+0.042 /-0.045	+0.082 /-0.082				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Ambenali Fm (middle)	breccia fill redbole	U-Pb	z	RBAY	65.895	+0.032 /-0.030	+0.042 /-0.041	+0.082 /-0.081				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Ambenali Fm (middle)	redbole	U-Pb	z	RBAO	65.889	+0.029 /-0.028	+0.041 /-0.043	+0.081 /-0.080				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Ambenali Fm (middle)	redbole	U-Pb	z	RBAN	65.885	+0.027 /-0.029	+0.042 /-0.044	+0.081 /-0.082				TPB	ET2535	Schoene et al., 2019
Deccan Traps	Ambenali Fm (middle-upper)	redbole	U-Pb	z	RBP	65.879	+0.024 /-0.029	+0.045 /-0.053	+0.084 /-0.086				TPB	ET2535	Schoene et al., 2019

**Table 1: High-Precision Geochronology of LIPs**

Deccan Traps	Ambenali Fm (upper)	redbole	U-Pb z	RBO	65.875	+0.022	+0.047	+0.085	TPB	ET2535	Schoene et al., 2019
						-0.042	-0.057	-0.088			
Deccan Traps	Mahableshwar Fm	redbole	U-Pb z	RBE	65.631	+0.053	+0.059	+0.088	TPB	ET2535	Schoene et al., 2019
						-0.030	-0.037	-0.080			
Deccan Traps	Mahableshwar Fm	redbole	U-Pb z	RBF	65.62	+0.028	+0.033	+0.075	TPB	ET2535	Schoene et al., 2019
						-0.021	-0.029	-0.075			
Deccan Traps	Mahableshwar Fm	greenbole	U-Pb z	DEC13-09	65.614	+0.015	+0.024	+0.073	TPB	ET2535	Schoene et al., 2019
						-0.017	-0.025	-0.073			
Deccan Traps	Mahableshwar Fm (middle-upper)	redbole	U-Pb z	RBG	65.59	+0.026	+0.032	+0.077	TPB	ET2535	Schoene et al., 2019
						-0.027	-0.033	-0.075			
Deccan Traps	Jawhar Fm	lava	<sup>40</sup> Ar/ <sup>39</sup> Ar	pl	KAS15-2	66.234	0.168	0.186	38	WMA	FCs = 28.294; Sprain et al., 2019
											Renne et al.,
Deccan Traps	Jawhar Fm	lava	<sup>40</sup> Ar/ <sup>39</sup> Ar	pl	KAS15-3	66.413	0.134	0.158	45	WMA	FCs = 28.294; Sprain et al., 2019
											Renne et al.,
Deccan Traps	Neral Fm	lava	<sup>40</sup> Ar/ <sup>39</sup> Ar	pl	MG7	66.153	0.100	0.132	36	WMA	FCs = 28.294; Sprain et al., 2019
											Renne et al.,
Deccan Traps	Thakurvadi Fm	lava	<sup>40</sup> Ar/ <sup>39</sup> Ar	pl	BOR14-1	65.912	0.136	0.158	38	WMA	FCs = 28.294; Sprain et al., 2019
											Renne et al.,
Deccan Traps	Bhimashankar Fm	lava	<sup>40</sup> Ar/ <sup>39</sup> Ar	pl	KHK15-1	66.171	0.152	0.176	36	WMA	FCs = 28.294; Sprain et al., 2019
											Renne et al.,
Deccan Traps	Khandala Fm	lava	<sup>40</sup> Ar/ <sup>39</sup> Ar	pl	MAT14-6	66.105	0.204	0.224	53	WMA	FCs = 28.294; Sprain et al., 2019
											Renne et al.,
Deccan Traps	Khandala Fm	lava	<sup>40</sup> Ar/ <sup>39</sup> Ar	pl	MAT14-7	66.158	0.164	0.186	57	WMA	FCs = 28.294; Sprain et al., 2019
											Renne et al.,
Deccan Traps	Bushe Fm	lava	<sup>40</sup> Ar/ <sup>39</sup> Ar	pl	VER14-3 (pooled)	65.974	0.168	0.186	86	WMA	FCs = 28.294; Sprain et al., 2019
											Renne et al.,
Deccan Traps	Bushe Fm	lava	<sup>40</sup> Ar/ <sup>39</sup> Ar	pl	POL15-2	66.059	0.158	0.180	43	WMA	FCs = 28.294; Sprain et al., 2019
											Renne et al.,
Deccan Traps	Poladpur Fm	lava	<sup>40</sup> Ar/ <sup>39</sup> Ar	pl	KJA14-1	65.977	0.302	0.316	##	WMA	FCs = 28.294; Sprain et al., 2019
											Renne et al.,
Deccan Traps	Poladpur Fm	lava	<sup>40</sup> Ar/ <sup>39</sup> Ar	pl	KJA15-1 (pooled)	65.988	0.638	0.658	44	WMA	FCs = 28.294; Sprain et al., 2019
											Renne et al.,
Deccan Traps	Poladpur Fm	lava	<sup>40</sup> Ar/ <sup>39</sup> Ar	pl	KJA14-2 (pooled)	65.94	0.184	0.202	91	WMA	FCs = 28.294; Sprain et al., 2019
											Renne et al.,
Deccan Traps	Poladpur Fm	lava	<sup>40</sup> Ar/ <sup>39</sup> Ar	pl	POL15-1 (pooled)	66.112	0.308	0.324	72	WMA	FCs = 28.294; Sprain et al., 2019
											Renne et al.,
Deccan Traps	Ambenali Fm	lava	<sup>40</sup> Ar/ <sup>39</sup> Ar	pl	AMB14-4	65.968	0.496	0.508	28	WMA	FCs = 28.294; Sprain et al., 2019
											Renne et al.,

**Table 1: High-Precision Geochronology of LIPs**

Deccan Traps	Ambenali Fm	lava	$^{40}\text{Ar}/^{39}\text{Ar}$	pl	AMB14-5	65.733	0.362	0.376	50	WMA	FCs = 28.294; Renne et al.,	Sprain et al., 2019		
Deccan Traps	Ambenali Fm	lava	$^{40}\text{Ar}/^{39}\text{Ar}$	pl	AMB15-1 (pooled)	65.667	0.208	0.228	50	WMA	FCs = 28.294; Renne et al.,	Sprain et al., 2019		
Deccan Traps	Mahableshwar Fm	lava	$^{40}\text{Ar}/^{39}\text{Ar}$	pl	AMB14-13	65.521	0.130	0.156	65	WMA	FCs = 28.294; Renne et al.,	Sprain et al., 2019		
Deccan Traps	Mahableshwar Fm	lava	$^{40}\text{Ar}/^{39}\text{Ar}$	pl	AMB14-14	65.466	0.200	0.220	40	WMA	FCs = 28.294; Renne et al.,	Sprain et al., 2019		
Deccan Traps	Mahableshwar Fm	lava	$^{40}\text{Ar}/^{39}\text{Ar}$	pl	PAN15-3	65.422	0.206	0.224	51	WMA	FCs = 28.294; Renne et al.,	Sprain et al., 2019		
NAIP	Tardree Rhyolite (between Antrim Plateau Volcanics), UK	Rhyolite	U-Pb	z	Tardree forest	61.32	0.09		1.1	6	WMA	Oslo 205Pb-235U tracer	Ganerød et al., 2011	
NAIP	Vøring margin sill, offshore Norway	Sill	U-Pb	z	Utgard Upper Sill	55.6	0.3	0.4		4	WMA	Oslo 235U-205Pb-202Pb tracer	Svensen et al., 2010	
NAIP	Vøring margin sill, offshore Norway	Sill	U-Pb	z	Utgard Lower Sill	56.3	0.4	0.5		1	YZ	Oslo 235U-205Pb-202Pb tracer	Svensen et al., 2010	
NAIP	Skaergaard Intrusion, lower zone b, East Greenland	gabbroic pegmatite sill	U-Pb	z	SK-218	55.960	0.018	0.031	0.064	1.4	7	WMA	ET535 or ET2535	Wotzlaw et al., 2012
NAIP	Skaergaard Intrusion, Basistoppen Sill, East Greenland	tholeiitic sill	U-Pb	z	BZN	55.895	0.018	0.031	0.064	0.51	8	WMA	ET535 or ET2535	Wotzlaw et al., 2012
NAIP	Skaergaard Intrusion, Sandwich Horizon, East Greenland	ferrodiorite sill	U-Pb	z	SH-428	55.838	0.019	0.032	0.064	0.1	5	WMA	ET535 or ET2535	Wotzlaw et al., 2012
CRBG	Steens Basalt	Tuff 1 in Main Scarp	$^{40}\text{Ar}/^{39}\text{Ar}$	a	TB-124	16.592		0.028				WMA	FCs = 28.02; Renne et al.,	Mahood & Benson, 2017
CRBG	Steens Basalt	Tuff 2 in Main Scarp	$^{40}\text{Ar}/^{39}\text{Ar}$	a	TB-125	16.606		0.034				WMA	FCs = 28.02; Renne et al.,	Mahood & Benson, 2017
CRBG	Steens Basalt	Tuff 3 in Main Scarp	$^{40}\text{Ar}/^{39}\text{Ar}$	pl	TB-128A	16.499		0.104				WMA	FCs = 28.02; Renne et al.,	Mahood & Benson, 2017
CRBG	Steens Basalt	Tuff 4 in Main Scarp	$^{40}\text{Ar}/^{39}\text{Ar}$	pl	TB-128B	16.490		0.090				WMA	FCs = 28.02; Renne et al.,	Mahood & Benson, 2017
CRBG	Steens Basalt	Ignimbrite in East Creek	$^{40}\text{Ar}/^{39}\text{Ar}$	pl	ML-316	16.513		0.120				WMA	FCs = 28.02; Renne et al.,	Mahood & Benson, 2017
CRBG	Steens Basalt	Tuff 5 in Main Scarp	$^{40}\text{Ar}/^{39}\text{Ar}$	pl	TB-129	16.495		0.048				WMA	FCs = 28.02; Renne et al.,	Mahood & Benson, 2017

**Table 1: High-Precision Geochronology of LIPs**

CRBG	Steens Basalt	Tuff in Rosebriar Creek	$^{40}\text{Ar}/^{39}\text{Ar}$	pl	TB-382	16.532	0.046			1	WMA	FCs = 28.02; Renne et al., 1998	Mahood & Benson, 2017
CRBG	above Steens Basalt	Alkali rhyolite lava capping Main Scarp	$^{40}\text{Ar}/^{39}\text{Ar}$	s	TB-130	16.485	0.028			1	WMA	FCs = 28.02; Renne et al., 1998	Mahood & Benson, 2017
CRBG	above Steens Basalt	Tuff capping Steens Basalt in East Creek	$^{40}\text{Ar}/^{39}\text{Ar}$	pl	TB-397	16.474	0.042			1	WMA	FCs = 28.02; Renne et al., 1998	Mahood & Benson, 2017
CRBG	above Steens Basalt	Tuff in Cottonwood Creek	$^{40}\text{Ar}/^{39}\text{Ar}$	s	TB-103A	16.475	0.054			1	WMA	FCs = 28.02; Renne et al., 1998	Mahood & Benson, 2017
CRBG	above Steens Basalt	Tuff of Monument Basin	$^{40}\text{Ar}/^{39}\text{Ar}$	s	TB-101	16.479	0.042			1	WMA	FCs = 28.02; Renne et al., 1998	Mahood & Benson, 2017
CRBG	Steens Basalt: Lower Steens	Redbole	U-Pb	z	CRB1625	16.653	0.063	0.071	0.073	1	YZ	ET535	Kasbohm & Schoene, 2018
CRBG	Steens Basalt: Upper Steens	Redbole	U-Pb	z	CRB1624	16.589	0.031	0.032	0.037	1	YZ	ET535	Kasbohm & Schoene, 2018
CRBG	Imnaha Basalt	Lapilli tuff	U-Pb	z	CRB1586	16.572	0.018	0.018	0.026	1	YZ	ET2535	Kasbohm & Schoene, 2018
CRBG	Grande Ronde Basalt: Wapshilla Ridge (lower)	Redbole	U-Pb	z	CRB1634	16.288	0.039	0.043	0.046	1	YZ	ET535	Kasbohm & Schoene, 2018
CRBG	Grande Ronde Basalt: Meyer Ridge / Wapshilla Ridge (upper)	Redbole	U-Pb	z	CRB1556	16.254	0.034	0.037	0.041	1	YZ	ET535	Kasbohm & Schoene, 2018
CRBG	Grande Ronde Basalt: Meyer Ridge / Wapshilla Ridge (upper)	Redbole	U-Pb	z	CRB1519	16.210	0.043	0.044	0.047	1	YZ	ET2535	Kasbohm & Schoene, 2018
CRBG	Wanapum Basalt: Frenchman Springs / Grande Ronde Basalt: Sentinel Bluffs (Vantage Interbed)	Pumice clasts	U-Pb	z	CRB1533	16.066	0.040	0.040	0.043	1	YZ	ET2535	Kasbohm & Schoene, 2018
CRBG	Wanapum Basalt: Priest Rapids (Basalt of Rosalia) / Roza	Ash	U-Pb	z	CRB1506	15.895	0.019	0.020	0.026	1	YZ	ET535	Kasbohm & Schoene, 2018

**Table 2: High-Precision Geochronology of Environmental Events**

Event	Location	Formation	Lithology	Method	Mineral	Sample	Age	[X]	[Y]	[Z]	MSWD	n	Age interp.	Tracer/ Standard	Reference
Sturtian Glaciation	Tambien Group, Ethiopia	Upper Mariam Bohkahko Formation	tuffaceous siltstone	U-Pb	z	SAM-ET-03	719.68	0.56	0.64	1.0	0.54	3	WMA	ET535 or ET2535	MacLennan et al., 2018
Sturtian Glaciation	Tambien Group, Ethiopia	Upper Mariam Bohkahko Formation	tuffaceous siltstone	U-Pb	z	SAM-ET-04	719.68	0.46	0.54	0.94	1.3	8	WMA	ET535 or ET2535	MacLennan et al., 2018
Sturtian Glaciation	Tambien Group, Ethiopia	over contact betw Didikama & Matheos	crystal-rich tuff	U-Pb	z	T46-102_2Z	735.25	0.25	0.39	0.88	0.36	5	WMA	ET535 or ET2535	MacLennan et al., 2018
Sturtian Glaciation	Bald Hill, Coal Creek Inlier, Canada	Mount Harper Volcanic Complex	quartz-phyric rhyolite	U-Pb	z	F837B	717.43	0.14			0.8	7	WMA	ET535	Macdonald et al., 2010
Sturtian Glaciation	Tango Tarn, Coal Creek Inlier, Canada	Eagle Creek Fm	green/pink brecciated tuff	U-Pb	z	F840A	716.47	0.24			1.1	6	WMA	ET535	Macdonald et al., 2010
Sturtian Glaciation	SW inlier, Coal Creek Inlier, Canada	Mount Harper Volcanic Complex	welded rhyolitic tuff	U-Pb	z	15PM06	718.1	0.3	0.5	0.9	0.42	4	WMA	ET535	Macdonald et al., 2017
Sturtian Glaciation	SW inlier, Coal Creek Inlier, Canada	Mount Harper Volcanic Complex	welded rhyolitic tuff	U-Pb	z	15PM08	718.1	0.2	0.4	0.8	0.98	6	WMA	ET535	Macdonald et al., 2017
Sturtian Glaciation	Bald Hill, Coal Creek Inlier, Canada	Mount Harper Volcanic Complex	rhyolite flow	U-Pb	z	F837A	717.8	0.2	0.4	0.8	0.64	4	WMA	ET535	Macdonald et al., 2017
Sturtian Glaciation	Bald Hill, Coal Creek Inlier, Canada	Mount Harper Volcanic Complex	rhyolite flow	U-Pb	z	F837C	717.7	0.3	0.5	0.9	0.29	3	WMA	ET535	Macdonald et al., 2017
Sturtian Glaciation	Tango Tarn, Coal Creek Inlier, Canada	Eagle Creek Fm	green tuff in diamictite	U-Pb	z	F917-1	716.9	0.4	0.5	0.9	1.5	5	WMA	ET535	Macdonald et al., 2017
Sturtian Glaciation	Jabal Akhdar region, Oman Mtns	Ghubrah Formation	tuffaceous sandstone	U-Pb	z	WM 54	711.52	0.20	0.31	1.09	0.18	5	WMA	ET535?	Bowring et al., 2007
Early-Middle Cambrian Extinction	Shropshire, England	Upper Comley Sandstone Formation	bentonite	U-Pb	z	Comley ub	509.1	0.22	0.56	0.77	0.51	7	WMA	ET535	Harvey et al., 2011

**Table 2: High-Precision Geochronology of Environmental Events**

Frasnian-Famennian boundary end-	Steinbruch Schmidt Quarry, Germany	Bed 36	bentonite	U-Pb z	Bed 36 bentonite	372.36	0.053	0.11	0.41	1.47	8	WMA	ET2535	Percival et al., 2018
Guadalupian Extinction	Sutherland, Northern Cape Province, South Africa	Poortjie Member, Tekloof Formation, Beaufort Group	white tuff 3.5 m above basal sstn	U-Pb z	K1202-B1	260.259	0.081	0.14	0.31	1.5	4	WMA-YF	ET535	Day et al., 2015
End-Permian Extinction	Meishan, China	Changhsing Formation, Bed 25; extinction onset	ash	U-Pb z	Bed 25-MBE0203	251.941	0.037		0.28	1.3	16	WMA	ET2535	Burgess et al., 2014
End-Permian Extinction	Meishan, China	Yinkeng Formation, Bed 28; extinction onset	ash	U-Pb z	Bed 28-MBE0205	251.880	0.031		0.28	0.76	13	WMA	ET2535	Burgess et al., 2014
End-Triassic Extinction	Pucara Basin, North Peru	onset of $\delta^{13}C$ excursion	ash	U-Pb z	LM4-86	201.510	0.15				1	YZ; MCMC	ET2535	Schoene et al., 2010; Wotzlaw et al., 2014
OAE2 (beginning)	Yezo Group, Hokkaido, Japan	Saku Formation, Hakkin Member	bentonite (felsic tuff)	U-Pb z	HK017	94.436	0.093		0.14	0.8	5	WMA-YF	ET2535	Du Vivier et al., 2015
OAE2 (next; beginning)	Yezo Group, Hokkaido, Japan	Saku Formation, Hakkin Member	bentonite (felsic tuff)	U-Pb z	CT103	94.536	0.170		0.21	0.4	6	WMA-YF	ET2535	Du Vivier et al., 2015
OAE2 (end)	Yezo Group, Hokkaido, Japan	Saku Formation, Hakkin Member	bentonite (felsic tuff)	U-Pb z	HK018	93.92	0.031		0.11	2	3	WMA-YF	ET2535	Du Vivier et al., 2015
K-Pg boundary	Kiowa Core, Denver Basin, USA	D1 sequence; 1 ft above boundary	ash	U-Pb z	KJ10-04	66.019	0.024	0.038	0.08	0.94	5	WMA	ET535	Clyde et al., 2016
K-Pg boundary	Bowring Pit, Denver Basin, USA	D1 sequence; 1.5 ft below boundary	ash	U-Pb z	KJ08-157	66.082	0.022	0.037	0.08	0.78	12	WMA	ET535	Clyde et al., 2016
K-Pg boundary	Bowring Pit, Denver Basin, USA	D1 sequence; 3.2 ft above boundary	ash	U-Pb z	KJ04-70	65.889	0.027	0.044	0.083	1.1	11	WMA	ET535	Clyde et al., 2016
K-Pg boundary	Denver Basin, USA	D1 sequence	K-Pg boundary	U-Pb z		66.021	0.024	0.039	0.081				interpolated age	Clyde et al., 2016
K-Pg boundary	Hell Creek, Montana, USA	Hell Creek Fm / Fort Union Formation	Iridium Coal layer	$^{40}Ar/^{39}Ar$ af	IrZ	66.052	0.016		0.086		730	pooled WMA	FCs = 28.294; Renne et al., 2011	Sprain et al., 2018
PETM	Longyearben, Spitsbergen, Norway	Frysjaodden Fm, mid-excursion	bentonite	U-Pb z	SB01-1	55.785	0.034	0.066	0.086	0.88	5	WMA-YF	ET535	Charles et al., 2011