



Cubic zirconia in $>2370^{\circ}\text{C}$ impact melt records Earth's hottest crust



Nicholas E. Timms^{a,*}, Timmons M. Erickson^a, Michael R. Zanetti^b, Mark A. Pearce^c, Cyril Cayron^d, Aaron J. Cavosie^{a,e}, Steven M. Reddy^a, Axel Wittmann^f, Paul K. Carpenter^g

^a Department of Applied Geology, Curtin University, Perth, GPO Box U1987, Western Australia 6845, Australia

^b University of Western Ontario, 1151 Richmond St, London, Ontario, N6A 3K7 Canada

^c CSIRO Mineral Resources, Australian Resources Research Centre, 26 Dick Perry Avenue, Kensington, WA 6151, Australia

^d Laboratory of ThermoMechanical Metallurgy (LMTM), PX Group Chair, École Polytechnique Fédérale de Lausanne (EPFL), Rue de la Maladière 71b, 2000 Neuchâtel, Switzerland

^e NASA Astrobiology Institute, Department of Geoscience, University of Wisconsin–Madison, Madison WI, USA

^f LeRoy Eyring Center for Solid State Science, Arizona State University, 901 S Palm Walk, Tempe, AZ, 85287, USA

^g Washington University in St Louis, Earth and Planetary Science Department and the McDonnell Center for Space Sciences; 1 Brookings Drive, St Louis MO, 63112, USA

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ABSTRACT

Bolide impacts influence primordial evolution of planetary bodies because they can cause instantaneous melting and vaporization of both crust and impactors. Temperatures reached by impact-generated silicate melts are unknown because meteorite impacts are ephemeral, and established mineral and rock thermometers have limited temperature ranges. Consequently, impact melt temperatures in global bombardment models of the early Earth and Moon are poorly constrained, and may not accurately predict the survival, stabilization, geochemical evolution and cooling of early crustal materials. Here we show geological evidence for the transformation of zircon to cubic zirconia plus silica in impact melt from the 28 km diameter Mistastin Lake crater, Canada, which requires super-heating in excess of 2370°C . This new temperature determination is the highest recorded from any crustal rock. Our phase heritage approach extends the thermometry range for impact melts by several hundred degrees, more closely bridging the gap between nature and theory. Profusion of $>2370^{\circ}\text{C}$ superheated impact melt during high intensity bombardment of Hadean Earth likely facilitated consumption of early-formed crustal rocks and minerals, widespread volatilization of various species, including hydrates, and formation of dry, rigid, refractory crust.

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1. Introduction

Shock wave propagation during hypervelocity impact can melt and vaporize both the impactor and target rocks (Melosh, 1989). The immediate, post-impact, thermal pulse far exceeds both ultra-high-temperature metamorphism in tectonic settings (Heisinger and Head, 2006; Korhonen et al., 2014) and the liquidus temperatures of target rocks, and is therefore important for the evolution of planet and asteroid surfaces. The heat associated with impacts had a profound significance on the early Earth, and has been shown to have affected processes in Earth's core (Arkani-Hamed and Ghods, 2011; Monteux et al., 2015; Sleep, 2016), mantle (Watters et al., 2009), crust and atmosphere (Marchi et al., 2016, 2014, 2013; Melosh, 2008).

Volatile depletion and isotope fractionation of Earth, Moon and other planetary bodies are attributed to giant basin-forming impacts (Albarede et al., 2013; Day and Moynier, 2014; Moynier et al., 2010; Pringle et al., 2014). Vaporization of target and impactor material during impacts is temperature dependant. Preferential mass-dependant volatile loss and isotope fractionation from impact melts can therefore locally influence subsequent remelting and rheological behavior, and so giant impacts and/or the cumulative effects of intense periods of impact bombardment have important geodynamic consequences (Albarede, 2009). These effects, in turn, have implications for the evolution and habitability of Earth's surface environment (Abramov and Mojzsis, 2009; Ryder, 2002), and, by extension, the habitability of extraterrestrial planetary bodies and exoplanets.

Initial thermal properties of impact melt also control their ability to digest pre-existing solid material and entrained debris (Onorato et al., 1978), including metals and sulphides essential

* Corresponding author.

E-mail address: n.timms@curtin.edu.au (N.E. Timms).

for forming impact-generated economic ore deposits (Keays and Lightfoot, 2004), their cooling rate (Onorato et al., 1978), and consequently the preservation of all pre-existing material and high-P phases formed during the passage of the shock wave (Tschauner et al., 2014). The highest temperature superheated melts (i.e., above the liquidus—the equilibrium temperature for complete melting) and vapor are produced during shock-release melting and frictional melting, whereas exhumation-related decompression melting is limited to sub-liquidus temperatures (Ahrens and O’Keefe, 1971; French and Koeberl, 2010; Melosh, 1989, 2005; Riller et al., 2010; Spray, 1998).

The critical melting temperature of target rocks depends on their composition, proximity to the impact site, initial conditions (Gibbons et al., 1975; Hörz et al., 2005; Stöffler, 1971) and porosity (Kieffer et al., 1976; Wünnemann et al., 2008). Vaporization temperature is taken as the highest vaporization temperature of oxides present in the system; in real systems, incongruent vaporization may occur over a range of temperatures (Ahrens and O’Keefe, 1971; Grieve et al., 1977; Lamoreaux et al., 1987; Lou et al., 1985). However, the complex behavior of silicates has made shock-related heating and, thus, the magnitudes of impact melt superheating and vaporization difficult to predict with any degree of certainty (Ahrens and O’Keefe, 1971). Accordingly, our understanding of temperatures achieved by impact melts necessarily relies on empirical constraints from the rock record via established geothermometers, which have inherently limited temperature ranges (Asimow and Giorso, 1998; Cherniak et al., 2007; Hart and Davis, 1978; Kubaschewski, 1982; Lindsley and Andersen, 1983; Sack and Giorso, 1991; Taylor et al., 2015). As there are large ranges between liquidus and vaporization temperatures for most rock types, maximum impact melt temperatures are largely unaccounted for, thus the effects of superheated melt may be underappreciated in planetary surface studies.

In the rock record, glass spherules and some types of microtektites contained within impact ejecta horizons provide *a priori* evidence for atmospheric condensation of silicate vapor (Glass and Simonson, 2012). In rare cases, nickel-rich magnesiowüstite inclusions in spherules indicate condensation temperatures >2300 °C (Kyte and Bohor, 1995). However, no direct geological evidence has been reported for high temperatures in contiguous impact melt rock, quenched ejected melt droplets (tektites), or impact melt-bearing breccia (suevite) because no geothermometers applicable to impact melt are calibrated beyond ~2000 °C (Asimow and Giorso, 1998; Cherniak et al., 2007; Hart and Davis, 1978; Kubaschewski, 1982; Lindsley and Andersen, 1983; Sack and Giorso, 1991; Taylor et al., 2015). Furthermore, models of impact melt formation often assume initial melt temperatures of ~1700 °C (Abramov et al., 2013; Onorato et al., 1978; Simonds, 1975), and in some cases allude to temperatures >2000 °C (Wünnemann et al., 2008).

In this study, we investigate the microstructure of zirconia (ZrO₂) produced during the dissociation of zircon (ZrSiO₄) in impact glass (quenched impact melt) sampled from the 28-km-diameter, 37.83 ± 0.05 Ma Mistastin Lake impact structure in northern Labrador, Canada (55°53’N; 63°18’W) (Marion and Sylvester, 2010; Sylvester et al., 2013). We present new thermometry based on reconstruction of the polymorphic transformation history of zirconia in a reaction rim around a zircon grain, an approach we refer to as phase heritage. Crystallographic relationships reveal the former presence of cubic zirconia, which definitively quantifies the minimum impact melt temperature to >2370 °C, far exceeding commonly assumed impact melt temperatures. These results thus present fundamental new constraints on the evolution of impact melts, and influence our understanding of the evolution of early planetary crust, when impact rates were orders of magnitude higher than now, substantial resurfacing by impact struc-

tures comparable to or larger in size than Mistastin Lake occurred (Marchi et al., 2014; Morbidelli et al., 2012), and all physical evidence of cratering was subsequently destroyed.

2. Methods and approach

We characterized the zircon grain and surrounding area *in situ* on a polished thin section with cathodoluminescence (CL), backscattered electron (BSE) imaging and wavelength dispersive spectroscopy (WDS). We used electron backscatter diffraction (EBSD) to verify the mineral assemblage and characterize and quantify the crystallographic orientation and microstructure of zirconia (ZrO₂) produced by the dissociation of zircon (ZrSiO₄). See Supplementary File for further information about data acquisition and processing. Crystallographic relationships among zirconia grains preserve the phase transformation history, or phase heritage, of zirconia polymorphs (Cayron et al., 2010; Kerschhofer et al., 2000). Transformations between mineral phases commonly occur with systematic crystallographic orientation relationships (e.g., Pearce et al., 2013). New phases tend to nucleate at multiple sites in one of several symmetrically equivalent orientations. The new grain orientations in the resulting polycrystalline microstructure are related by systematic misorientations, described by specific angular rotations around specific crystallographic axes that are strictly controlled by the symmetry relationships between the old and new phases. Therefore, the original (parent) crystal orientation can be inferred by combining the misorientations between the new (daughter) phase grains and the transformation relationships, even when the old crystal has been completely transformed. This concept of orientation-based phase heritage has been used to identify the former presence of high-temperature zirconia polymorphs in manufactured ceramics (Cayron et al., 2010; Chevalier et al., 2009) and kimberlites (Kerschhofer et al., 2000), and the high-pressure ZrSiO₄ polymorph reidite in impactites (Cavosie et al., 2016; Timms et al., 2017), and we use it here to investigate the thermal evolution of zircon entrained into impact melt.

The orientation relationships (OR) for the transformations from cubic–tetragonal–monoclinic zirconia due to cooling are well known from the literature on refractory ceramics, and measured orientations of low-temperature monoclinic zirconia (baddeleyite) can be used to reconstruct orientations of parent cubic grains, the highest temperature zirconia polymorph (Cayron, 2007; Cayron et al., 2010). This approach relies on $\langle a \rangle_{\text{cubic}} \rightarrow \langle a \rangle_{\text{tetragonal}}$ or $\langle c \rangle_{\text{tetragonal}}$, generating up to three possible unique tetragonal orientations from a single cubic grain. During subsequent tetragonal–monoclinic transformation upon further cooling, the following transformation rules apply:

$$\langle a \rangle_{\text{tetragonal}} \text{ OR } \langle c \rangle_{\text{tetragonal}} \rightarrow \langle b \rangle_{\text{monoclinic}}$$

plus either

$$\langle a \rangle_{\text{tetragonal}} \text{ OR } \langle c \rangle_{\text{tetragonal}} \rightarrow \langle a \rangle_{\text{monoclinic}}$$

(type 1 OR after Cayron et al., 2010)

or

$$\langle a \rangle_{\text{tetragonal}} \text{ OR } \langle c \rangle_{\text{tetragonal}} \rightarrow \langle c \rangle_{\text{monoclinic}}$$

(type 2 OR after Cayron et al., 2010)

allowing for up to four unique orientation variants from each tetragonal identity (Chevalier et al., 2009), totaling twelve possible monoclinic variants from a single cubic identity (Cayron et al., 2010).

The Python-based software combination of ARPGE and GenOVA were used to perform a crystallographic orientation analysis of baddeleyite (monoclinic zirconia) to reconstruct evidence for

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