Decoupling of Zr-Hf during contact metamorphic anatexis of metabasalts and timing of zircon growth, Sudbury, Canada

Taus R.C. Jørgensen¹, Douglas K. Tinkham¹, C. Michael Lesher¹, and Joseph A. Petrus¹,²
¹Mineral Exploration Research Centre, Harquail School of Earth Sciences and Goodman School of Mines, Laurentian University, 935 Ramsey Lake Road, Sudbury, Ontario P3E 2C6, Canada
²School of Earth Sciences, University of Melbourne, Corner Swanston & Elgin streets, Parkville, VIC 3010, Australia

ABSTRACT

Whole-rock Zr-Hf systematics combined with zircon petrography, geochronology, and geochemistry in partially melted mafic rocks offer new insights into Zr-Hf decoupling processes during metamorphism. Zirconium and Hf are frequently used to interpret the petrogenesis of mafic igneous rocks, but their behavior during dehydration and partial melting is still controversial. The contact aureole of the 1850 Ma Sudbury Igneous Complex (SIC, Canada) includes pyroxene hornfels facies metabasalts with systematically strong negative whole-rock Zr/Zr* (down to 0.25) and Zr/Hf (down to 29.7) anomalies. This signature only occurs in the highest grade portions of the aureole where partial melting occurred proximal to the SIC, and indicates that Zr-Hf decoupling is linked to partial melting and melt segregation. In this zone, the metabasalts contain intergranular melt with rare interstitial and poikilitic zircon grains yielding an 1850 ± 24 Ma U-Pb age, connecting zircon growth to partial melting processes. In addition, zircon texturally overgrows the peak contact metamorphic mineral assemblage and locally shows straight crystal faces in microleucosomes. This is consistent with zircon crystallizing from trapped melt and in agreement with models suggesting that metamorphic zircon does not necessarily grow during peak pressure-temperature conditions. The apparent requirement for melt to facilitate zircon growth and Zr-Hf mobility illustrates the importance of melting for understanding zircon and Zr-Hf behavior in mafic rocks. An increased understanding of whole-rock Zr-Hf decoupling combined with zircon analysis provides the opportunity of better constraining high-temperature crustal processes involving silicate melts.

INTRODUCTION

Zr-Hf systematics are often essential to interpreting the petrogenesis of igneous and metamorphic mafic rocks, and thus important for understanding the evolution of the Earth’s crust and mantle. Although there are many studies exploring the behavior of Zr-Hf during the formation and metamorphism of mafic rocks (e.g., to understand element transfer in subduction zones), the Sudbury Igneous Complex (SIC, Canada) contact aureole provides a unique setting to evaluate the processes of partial melting and zircon growth in mafic rocks and relate it to the Zr-Hf behavior resulting in Zr/Hf fractionation and Zr/Zr* anomalies. Zirconium and Hf are thought to be largely immobile during metamorphism if partial melting occurs or until depths exceeding ~160 km are reached, where the properties of fluids and silicate melts converge to form a supercritical liquid capable of mobilizing Zr and Hf (Watson and Harrison, 1983; Rubatto and Hermann, 2003; Kessel et al., 2005). Decoupling of Zr-Hf is often negligible during igneous processes involving silicate melt, as is demonstrated by chondritic ratios in global geochemical reservoirs such as mid-oceanic ridge basalt (MORB; David et al., 2000). However, experimental data suggest that Zr is more compatible than Hf (i.e., $D^{\text{hydrous melt}}_{\text{Zr}} < D^{\text{hydrous melt}}_{\text{Hf}}$; where D is the partition coefficient) during subduction-related partial melting (1000 °C and 40 kbar) of average MORB (Kessel et al., 2005), resulting in higher Zr/Hf values in the restite. As such, the wide range of Zr/Hf observed in some blueschist and eclogite facies metabasalts (e.g., Sorensen et al., 1997; Zr/Hf from ~26–290 and an average of ~45 ± 6.3, 1 standard error), the remnants of subducted ocean crust, does not offer a clear picture on the processes controlling the decoupling of Zr-Hf.

Rubatto and Hermann (2003) showed that zircon, when present in subducted oceanic crust, is the dominant host for Zr (>95%) and Hf (~90%), and thus segregated fluids and melts capable of dissolving zircon should be essential to the transfer of Zr and Hf in subduction zones. However, recent Zr mass balance models suggest that melting may not be crucial for understanding zircon behavior in mafic rocks (Kohn et al., 2015).

GEOLOGICAL SETTING

The two-pyroxene hornfels metabasalts reported in this study are part of the Elsie Mountain Formation (EMF), which has a minimum age of 2452.5 ± 6.2 Ma (Ketchum et al., 2013) and occurs in the lowermost Paleopetrozoic Huronian Supergroup in the Sudbury area, Canada (Fig. 1; Fig. DR1 in the GSA Data Repository¹). The EMF is the easternmost part of an ~200-km-long volcanic belt interpreted to represent flood basalts associated with continental rifting (Jolly et al., 1992). The EMF in the Sudbury area is composed of pillowed and massive basalts flows that form part of the footwall rock along the southern margin of the SIC (e.g., Innes, 1977; Jolly et al., 1992). The SIC is the remnant of an impact melt sheet that was initially superheated to ~1800 °C and had the geometry of a ~5-km-thick magma pond with a diameter exceeding 100 km (Lightfoot, 1993).
The dimensions and high temperature of the melt sheet resulted in extensive contact metamorphism of the underlying footwall rocks. The peak contact metamorphic assemblage and generally share contacts with more than one of these minerals. The nature of the contacts between zircon and associated phases varies, but zircon is typically subrounded against pyroxene and straight to subrounded against oxides and plagioclase. Rounded to subrounded inclusions of relatively Ca-rich plagioclase and lesser clinopyroxene in zircon are common. Locally, zircon is in contact with mainly plagioclase, and is locally interstitial between relatively Na-rich plagioclase (An<sub>90</sub> in sample FSTJ301; An—anorthite component of plagioclase) and polygonal granoblastic Ca-rich plagioclase (An<sub>60</sub> in sample FSTJ301; Fig. 2B).

Cathodoluminescence (CL) and backscattered electron (BSE) imaging of zircon reveals the local presence of sector zoning and otherwise verify fairly simple internal morphologies with little to no textual indication of metamictization (Fig. DR2). Shock metamorphic features reported in other Sudbury zircon (e.g., Thomson et al., 2014) are not present. Thorite, coffinite, xenotime, thortveitite, and other phases that are commonly described in hydrothermally reequilibrated zircon are not observed as inclusions in BSE, CL, or qualitative element map images (e.g., Th, Hf, Pb, and HREEs; Figs. DR2 and DR3). The qualitative element maps also show no signs of major nonstoichiometric elements (e.g., Ca and Al; Geisler et al., 2007).

**U-Pb and Trace Element Geochemistry**

Three zircon grains from two different thin sections of sample FSTJ301 were selected for U-Pb dating and trace element analyses by laser ablation–inductively coupled plasma–mass spectrometry (LA-ICP-MS; n = 13), and 56 samples were selected for whole-rock trace element analyses by solution ICP-MS. The
Whole-rock Zr/Zr* versus Zr/Hf plot showing the variations within EMF metabasalts: distal BHVO-2 (Hawaiian Volcanic Observatory standard BHVO-2 (Hawaiian Volcanic Observatory island basalts (OIB Zr/Hf = 41 ± 4; 2σ; David et al., 2000), whereas the Zr/Hf ratios of proximal metabasalts extend across and well past the range for MORB and C1 chondrite (MORB Zr/Hf = 37 ± 2; σ; C1 chondrite Zr/Hf = 36.52 ± 0.04; 2σ; David et al., 2000). The higher OIB-like Zr/Hf of distal metabasalts compared to MORB can be explained by differences in mantle source composition and/or degree of mantle partial melting (David et al., 2000), but the range of Zr/Hf in proximal metabasalts exceeds the variability that can be expected to be generated within the same basaltic unit by primary magmatic processes and must therefore have been produced during post-emplacement processes. The interpretation that the whole-rock Zr-Hf systematics documented in the proximal metabasalts are related to partial melting during contact metamorphism is strongly supported by the combination of zircon petrography, chemistry, and ages (Figs. 2 and 3); the presence of mesoscopic patchy, coalescing, dike-like leucosomes within the proximal metabasalts (Fig. DR5); a concordant U-Pb LA-ICP-MS age of 1839 ± 10 Ma for zircon in the patchy leucosomes, consistent with the timing of SIC contact metamorphism (Jorgensen, 2017); and corresponding whole-rock depletion in Th-LREEs relative to MREEs and HREEs with proximity to the SIC (Jorgensen, 2017). Furthermore, these data indicate that melting reached a critical threshold (>7%; Rosenberg and Handy, 2005) in the SIC contact aureole and that melt segregation mobilized Zr and to a lesser degree Hf, producing negative Zr-Hf anomalies and fractionation of Zr/Hf during the partial melting process. The Zr/Hf ratio within the proximal zone does not vary systematically with proximity to the SIC contact, so the systematically lower Zr/Zr* but variable Zr/Hf ratios suggest both elements were mobile during high-temperature contact metamorphism, but that local variations in melt compositions (e.g., Linnen and Keppler, 2002) may have influenced the relative mobilities of Zr-Hf.

The wide range in Zr/Hf ratios in some compilations of high-pressure metabasalt (e.g., Sorensen et al., 1997) are difficult to interpret. Nonetheless, Rubatto and Hermann (2003) demonstrated that significant Zr-Hf mobilization in this environment is likely to occur only if the liquid phase is silicate melt rather than a hydrous fluid. This is consistent with observations here, i.e., the distal metabasalts all underwent variable amounts of dehydration during SIC contact metamorphism, but dehydration by itself is incapable of significantly mobilizing Zr-Hf, which also seems true for incipient melting below the melt segregation threshold. This is also supported by experimental work on average MORB at pressures below 6 GPa, where
Zircon Behavior in Mafic Rocks

The whole-rock Zr-Hf systematics from EMF metabasalts described here required melting and melt segregation. As segregation ceased, minuscule amounts of zircon eventually formed from trapped melt films. This suggests that although the extent to which melting reactions have been observed to affect zircon consumption and growth in felsic rocks is not nearly as pronounced in mafic rocks (Kohn et al., 2015), melting is also critical for understanding zircon behavior in mafic rocks.

CONCLUSIONS

The combination of well-established methods, i.e., whole-rock Zr-Hf geochemistry, zircon petrography, geochemistry, and U-Pb geochronology, have provided the first outline of the partial melt and melt segregation zone in EMF metabasalts along the southern SIC contact aureole. The observations illustrate the importance of melting for mobilization and decoupling of Zr-Hf, and zircon behavior in mafic rocks. The results also highlight conclusions from mass-balance studies (Roberts and Finger, 1997; Kohn et al., 2015) that metamorphic zircon cannot automatically be assumed to have grown during peak-metamorphic conditions. Whole-rock Zr-Hf systematics have the potential to differentiate between dehydration and partial melting processes in metamorphosed mafic rocks. In combination with zircon analyses, such an approach might help constrain processes and conditions during subduction of oceanic crust as well as in low-pressure and high-temperature settings, e.g., basal sheeted dike-gabbro boundaries proximal to axial magma chambers (1–2 km beneath the seafloor), and in proximal metamorphic contact aureoles around igneous intrusions and impact melt sheets.

ACKNOWLEDGMENTS

Financial support was provided by grants from the Centre for Excellence in Mining Innovation, Vale Ltd., Glencore Ltd., and the Natural Sciences and Engineering Research Council of Canada (CRD 381555–09 to P. Jugo, Tinkham, and Lesher; Discovery Grant 327218–2009 to Tinkham; Discovery Grants 203171–2007 and 203171–2012 to Lesher; PDF-487902-2016 to Petrus). We are grateful to James Beard, Aaron Cavosie, and Fernando Corfu for very constructive and helpful reviews of the manuscript. Jorgensen thanks Richard Stern for discussions on how to successfully analyze the studied zircon. Field and logistical support was provided by Vale Ltd., and we thank Peter Lightfoot and Lisa Gibson of Vale for their assistance.

REFERENCES CITED


Manuscript received 7 August 2017

Revised manuscript received 20 November 2017

Manuscript accepted 21 November 2017

Printed in USA