In situ U/Pb geochronology of baddeleyite by LA-ICPMS

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Baddeleyite (ZrO_2) is a useful U-Pb chronometer for determining magmatic crystallization ages of silica-poor rocks that failed to form zircon. In situ baddeleyite dating has been plagued by analytical problems, however, limiting its application. Crystal orientation effects produce unacceptably large variations in $^{206}Pb/^{238}U$ ratios measured by ion microprobe so that ages must be determined from $^{207}Pb/^{206}Pb$ ratios alone. Laser ablation-inductively coupled plasma mass spectrometry (LA-ICPMS) analyses have produced $^{206}Pb/^{238}U$ and $^{207}Pb/^{235}U$ ratios that plot in arrays extending far above concordia, suggesting severe laser-induced Pb/U fractionation. Correction procedures for instrumental mass bias, in particular the extent of matrix effects between baddeleyite and common zircon standard reference materials (SRMs) used for calibration of measured isotope ratios, are poorly defined. We have dated two baddeleyites of known (TIMS) age using a Finnigan ELEMENT-XR magnetic sector ICPMS coupled to a GeoLas 193 nm ArF excimer laser ablation system. The baddeleyites are from carbonatite in the Phalaborwa Complex in South Africa (PHB; 2059.8± 0.8 Ma) and gabbroic anorthosite of the Duluth gabbro complex at Forest Center, Minnesota (FC-1; 1099.0± 0.6 Ma). Two methods commonly used for LA-ICPMS U-Pb dating were tested. The first involved spot analysis (40 micron beam, 5 Hz, 3 J/cm^2) and calibration of isotopic ratios by standard-sample-standard bracketing with zircon 91500 as the calibrant. The second employed raster analysis (10 micron beam, 10 Hz, 5 J/cm^2, making a 40 by 40 micron box pattern) and Pb/U determinations by the "intercept" method. Mass bias corrections are made by reference to a tracer solution of Tl-Bi-^{233}U-^{237}Np (with a composition defined by reference to zircon SRMs) aspirated into the argon plasma at the same time as sample ablation. Both spot and raster analyses exhibited laser-induced U/Pb fractionation during analysis, but the degree of fractionation was much more severe for the spot analyses. PHB baddeleyite exhibited much more fractionation than FC-1 baddeleyite. The reason is unclear but may be related to polysynthetic twinning on {100} being less well-developed in FC-1. Pb and U are heterogeneously distributed in the PHB baddeleyite: there is much less scatter on Pb/U ratios when it is drilled perpendicular to the {100} planes than when drilled parallel to them, suggesting that Pb/U ratios are more homogeneous at the scale of laser sampling in this orientation. Both zircon SRM and tracer solution calibration methods produced inadequate mass bias corrections for measured Pb/U and $^{207}Pb/^{206}Pb$ ratios and erroneous ages for analysed baddeleyites. LA-ICPMS U-Pb ages with accuracies comparable to those determined for zircon can be attained using raster analyses, intercept corrections, and a tracer solution calibrated for baddeleyite.

Efficiency of Cl recycling during subduction of oceanic crust: Constraints from melt inclusions in HIMU lavas

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The amount of chlorine that is recycled into the deep mantle through subduction processes is poorly constrained. Estimates of the chlorine content in recycled, dehydrated oceanic crust range from <50 ppm [1] up to ~200 ppm [2,3].

In order to better constrain the Cl content in subducted crust, we have examined Cl concentrations as well as Cl/K_2O and Cl/Nb ratios in olivine-hosted melt inclusions in HIMU lavas from the island of Raivavae, Austral Islands. Raivavae lavas span a wide range of lead isotopic values, with $^{206}Pb/^{204}Pb$ ranging from ~19.3 to 21.3. Previous isotopic and trace element studies suggest that Raivavae lavas derive from a mantle source containing ancient dehydrated oceanic crust.

Chlorine and K_2O concentrations range from 40-1070 ppm and 0.22-3.5 wt.% respectively. The majority of Cl/K_2O ratios range from 0.01-0.12 and Cl/Nb ratios range from 5-25. Cl/K_2O and Cl/Nb ratios are positively correlated with $^{206}Pb/^{204}Pb$ and negatively correlated with $^{207}Pb/^{206}Pb$. In addition, a positive correlation exists between Cl/K_2O and Nb/Zr. No correlation exists between host olivine forsterite content and Cl concentration or Cl/K_2O ratios.

The lack of correlation between host forsterite content and inclusion Cl/K_2O and the correlation between Cl/K_2O and Pb-isotopes suggest that Cl contents and Cl/K_2O ratios in HIMU lavas are not controlled by shallow assimilation processes. This contradicts the previous suggestion of [1], who argued that elevated Cl/K_2O ratios in some Raivavae lavas resulted from assimilation of Cl-rich brine. Instead, the high Cl/Nb and Cl/K_2O ratios observed in the HIMU samples suggest that the HIMU source is preferentially enriched in Cl.

Because Nb should be largely retained in subducted oceanic crust during slab dehydration, we can use the average Cl/Nb ratio observed in inclusions from HIMU lavas (~18) to estimate a Cl concentration in recycled oceanic crust. For an average N-MORB Nb content of 5.6 ppm, we estimate ~100 ppm Cl in subducted oceanic crust after slab dehydration, intermediate between previous estimates of [1] and [3]. Given an estimated Cl content in altered oceanic crust of ~157-322 ppm [2], we estimate ~30-65% of the Cl in altered crust is retained in the slab after subduction-induced dehydration and eventually returned to the deep mantle.

References

[1] Lassiter *et al.*, Earth Planet. Sci. Lett. 202 (2002) 525-540.
[2] Philippot, *et al.*, Earth Planet. Sci. Lett. 161 (1998) 33-44.
[3] Stroncik and Haase, Geology 32 (2004) 945-948.