THE POSSIBLE ROLE OF HYDROGEN IN THE SUBSTITUTION OF RARE EARTH ELEMENTS INTO ZIRCON

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Ion microprobe measurements have been made of trace element concentrations in zircon and surrounding fresh glass of 5 recently erupted rhyolites. In particular analyses have included not only rare earth elements (REE), but many of the elements that have been suggested to be incorporated into zircon. Y and the REE elements were found to be the dominant trace elements in the zircon and these elements varied by over an order of magnitude between grains despite a relatively constant REE content in the surrounding glasses. Strong correlations were observed between Y and all other REE except Ce and Eu. As has been previously observed, the REE partitioning coefficients (zircon/glass) increased strongly from La to Lu. The Ce partitioning was significantly higher than the neighbouring REE (as this element dominantly substitutes as the 4+ ion). Whereas it has been previously demonstrated that xenotime substitution occurs in zircon it is clear that in some strongly zoned crystals the P content is insufficient to permit complete charge balance. In the zircons analysed here there also appears to be insufficient P to permit charge balance. The P$_2$O$_5$ did not exceed 0.15 wt.% yet the total Y and REE oxide concentrations ranged up to about 2 wt.%. Concentrations of other trace elements were invariably very low (Li, Na, K, Be, Mg, Ca, Sr and Ba) less than 7 ppm and Al less than 5 ppm wt. Sc, Ti and Fe were less than 40 ppm wt. and V, Cr and Mn less than 1 ppm wt. F concentrations (7 to 200 ppm wt.) correlated poorly with Y and the REE but were about an order of magnitude too low to permit any major charge coupling with the REE. Although no zircon water standard was available, initial estimates of the water content suggest that the zircons contained between 0.01
to 0.09 wt.% H₂O (background approximately 0.008 wt.% H₂O). Somewhat surprisingly the H contents displayed a very good correlation with the Y (and REE) content. Further, although low, these water concentrations appear to be within (at least) 50% of that needed for the coupled substitution: \( \text{M}^{3+} + \text{H}^{+} \) replacing \( \text{Zr}^{4+} \). Subsequent H measurements of a strongly zoned pre-Cambrian zircon and two zircon standards also displayed correlations between Y and H that overlapped the trends observed for the recently formed crystals. It is possible that H, rather than P, is a common charge balancing element within the zircon structure and that its presence may not be related to metamictisation alone.