Title: The Effect of Element Substitution on Ti-in-Zircon Geothermometry in Volcanic Zircons from Mount Pinatubo, Philippines

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Publication: American Geophysical Union, Fall Meeting 2017, abstract #V43A-0511

Publication Date: 12/2017

Origin: AGU

Keywords: 3618 Magma chamber processes, MINERALOGY AND PETROLOGY, 3620 Mineral and crystal chemistry, MINERALOGY AND PETROLOGY, 3640 Igneous petrology, MINERALOGY AND PETROLOGY, 8499 General or miscellaneous, VOLCANOLOGY

Bibliographic Code: 2017AGUFM.V43A0511L

Abstract

Despite the extensive application of the Ti-in-zircon geothermometer, its accuracy in natural systems remains uncertain. In order to investigate the parameters contributing to Ti in zircon, we examined zircons from dacitic eruption products of Mount Pinatubo, Philippines, from the Pliocene (>2.5-2.7 Ma), 35000BP and 1991AD. All samples are unaltered and quenched from magmas at 790-825°C (Fe-Ti-oxide thermometry). Furthermore, the magma conditions of 1991 samples are well characterized: 780°C (cummingtonite rims on hornblende, Fe-Ti-oxide thermometry), 2 kbar pressure, 5.5-6.5 wt.% H2O and fO2 of NNO+1.6. Calculated zircon saturation temperatures are 760, 744 and 738°C (oldest to youngest). Zircon Ti concentrations are low (2.0-8.8 ppm), show positive covariation with U (35.6-639 ppm), Th (18.7-696 ppm), ∑REE (237-1310 ppm) and Y (247-1770 ppm), and negative covariation with Hf (7610-12000 ppm). The Ti-in-zircon geothermometer by Ferry and Watson (2007) yields mean temperatures of 690, 666 and 663°C (oldest to youngest), using TiO2 activity=0.6, SiO2 activity=1 and -40°C pressure correction. Therefore, temperatures calculated using this method are underestimated by >100°C. We suggest that elements in the Zr site impact the substitution of Ti in the Si site of zircon. Ti shows a positive covariation with Zr/Hf (37.0-57.3, r2=0.551). The ionic radius of Hf4+ is smaller than Zr4+, whereas cations like U4+, Th4+, REE3+ and Y3+ are larger. The departure from the ideal crystal configuration is evaluated using the parameter Zr/(Hf-x), whereby x=U4+, Th4+, ∑REE and Y3+. Ti contents are more strongly correlated with the parameter than Zr/Hf (r2=0.559, 0.565, 0.608, 0.616; respectively). This suggests that large cations replacing Zr strain the lattice, reducing the amount of Ti incorporated into zircon. This further suggests that ZrSiO4 activity is less than 1 in natural rocks, resulting in the systematic underestimation of Ti-in-zircon temperatures.