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The effect of pressure on the Ti site in zircon: Implications for the Ti-in-zircon thermometer

LAURA CRISP[1,2], ANDREW BERRY[2], ANTONY BURNHAM[2], LAURA MILLER[3] AND MATTHEW NEWVILLE[4]

[1]University of Wisconsin-Madison
[2]Australian National University
[3]Monash University
[4]University of Chicago

Presenting Author: lcrisp@wisc.edu

The Ti content of zircon ($ZrSiO_4$) can be used as a geothermometer, which is widely used to interpret past tectonothermal conditions. Ti could substitute for Si or Zr in zircon, which would result in opposing responses of Ti solubility to (i) the activities of SiO_2 ($aSiO_2^{quartz/coesite}$) and TiO_2 ($aTiO_2^{rutile}$) and (ii) pressure due to differences in the molar volumes of the $ZrTiO_4$ and $TiSiO_4$ components relative to $ZrSiO_4$. Previous calibrations of the Ti-in-zircon thermometer assume that Ti occupies the Si-site, and X-ray absorption near edge structure (XANES) spectroscopy has confirmed that Ti is tetrahedrally coordinated on the Si-site at atmospheric pressure.

Ti-bearing zircons were prepared at 1400 ^oC and nominal pressures from 0.0001 to 6.5 GPa using a flux-method that produced crystals up to 50 microns in size. Ti *K*-edge XANES spectra for zircons prepared at < 4.0 GPa are characterised by an intense pre-edge peak (attributed to the 1*s* to 3*d* transition) that is consistent with Ti in tetrahedral coordination on the Si-site. The intensity of this peak is proportional to the amount of Ti on the Si-site, and decreases abruptly > 4.0 GPa, indicating a change in the coordination of Ti. This change is also supported by Ti-O bond lengths determined from extended X-ray absorption fine structure (EXAFS) spectra. The proportion of Ti on each site varies systematically with pressure, with equal proportions of Ti on both sites at ~ 4.4 GPa. This change in site is consistent with a systematic decrease in the Ti content of these zircons with increasing pressure when $aSiO_2^{quartz/coesite}$ and $aTiO_2^{rutile} = 1$. As a result, an updated model for estimating zircon crystallisation temperatures from the Ti content has been derived.

Application of this new model to zircons from the mantle and ultra-high pressure (UHP; > 3.0 GPa) terranes, where the proportion of Ti on the Zr-site in zircon should be significant, gives crystallisation temperatures that are in good agreement with independent estimates, compared to those predicted using the previous Ti-in-zircon model, which are underestimated by ~ 300 ^oC and by 50 – 100 ^oC, respectively.