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

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The Ti content of zircon (ZrSiO\textsubscript{4}) can be used as a geothermometer, which is widely used to interpret past tectono-thermal 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\textsubscript{2} (\textit{aSiO\textsubscript{2}} quartz/coesite) and TiO\textsubscript{2} (\textit{aTiO\textsubscript{2}} rutile) and (ii) pressure due to differences in the molar volumes of the ZrTiO\textsubscript{4} and TiSiO\textsubscript{4} components relative to ZrSiO\textsubscript{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 °C 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 1s to 3d 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 \textit{aSiO\textsubscript{2}}\textsubscript{quartz/coesite} and \textit{aTiO\textsubscript{2}}\textsubscript{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 °C and by 50 – 100 °C, respectively.