Silicon coordination in rutile and TiO$_2$-II at ambient and high pressures: Si-29 NMR

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ABSTRACT

The structural environment of silicon dissolved in rutile and α-PbO$_2$-structured TiO$_2$ (TiO$_2$-II) was probed using $^{29}$Si MAS NMR on $^{29}$Si-enriched samples. At 1 atm, about 0.01 wt% SiO$_2$ is incorporated into TiO$_2$ as $^{29}$Si, presumably in interstitial sites. Rutile recovered from 6 GPa, 1600 °C contains about 0.6 wt% SiO$_2$, incorporated both as $^{29}$Si (~90%) and $^{30}$Si (~10%). TiO$_2$-II, synthesized at 12 GPa, 1200 °C, contains only $^{30}$Si. The chemical shift for $^{30}$Si in TiO$_2$-II is slightly less negative than that for rutile, and the peak is split, suggesting either a more complex mechanism of substitution or a different response to quenching or decompression in the lower-symmetry structure. Future thermodynamic studies of the TiO$_2$-SiO$_2$ solid solution will have to take into account the mixed coordination environment of the Si in TiO$_2$ at low pressures.

Keywords: Crystal structure, rutile, TiO$_2$-II, high-pressure studies, NMR spectroscopy

INTRODUCTION

The solubility of SiO$_2$ in the various polymorphs of TiO$_2$, and the mechanism of incorporation of the dissolved Si, are of interest both for high-pressure petrology and for technological materials. The fact that stishovite (stable above about 9 GPa at mantle temperatures) is isostructural with rutile suggests that there should be significant solid solution at high pressures, which could in principle be used as a geothermobarometer (Stebbins 1992; Vinograd et al. 2008; Ren et al. 2009). At least at lower pressures, where the stable silica polymorph is coesite or quartz, there could be a strong pressure effect on solubility, given the expected large negative molar volume change on transition from tetrahedral ($^{16}$Si) to octahedral ($^{18}$Si) silicon coordination. Such an effect can be seen in the study of Gaetani et al. (2008) on rutile solubility in silicate melts; their data on SiO$_2$ concentrations in the rutile coexisting with rhyodacitic or haplobasaltic melts (Fig. 1) reveal a systematic increase from about 0.06 to 0.3 wt% SiO$_2$ with pressure increasing from 1 atm to 3.5 GPa. This raises the possibility that Si in rutile could be used as a “probe” to estimate the amount of $^{18}$Si in high-pressure melts, if the thermodynamics and structure of the substitution were well constrained.

Reports of high concentrations of Si in natural rutiles are scant in the literature. A comprehensive survey of rutiles from high (>1 GPa) to ultra-high pressure (UHP) (up to 4.5 GPa) rocks by Zack et al. (2004) yielded typical concentrations of only ~100 wt ppm, with a maximum of 929 ppm, as measured by laser-ablation ICP-MS. On the other hand, Schulze (1990) reported SiO$_2$ contents of 0.25–0.29 wt% for massive rutile in nodules from the Kamfersdam and Kimberley kimberlite pipes in South Africa. Mposkos and Kostopoulos (2001) measured 0.43 wt% SiO$_2$ in a rutile inclusion in garnet from the Rhodope UHP province in Greece. Finally—and most spectacularly—Yang et al. (2003) measured concentrations of 11–15 wt% SiO$_2$ in rutile from a chromitite in the Luobusa ophiolite in Tibet, apparently metamorphosed under UHP conditions (Yang et al. 2007).

This last report motivated an experimental study of Si solubility in TiO$_2$ as a function of pressure and temperature (Ren et al. 2009). The experiments were conducted in the stability fields of rutile and its high-pressure polymorph, α-PbO$_2$-structured TiO$_2$ (or TiO$_2$-II), and possibly even into the stability field of the still higher-pressure baddeleyite-structured polymorph. These authors found SiO$_2$ contents in TiO$_2$—coexisting with coesite or stishovite—ranging from a few tenths of 1 wt% at 1500 °C to a maximum of about 5 wt% at 2000 °C and 23 GPa.

![Figure 1](image-url) SiO$_2$ content of rutile coexisting with rhyodacitic melt (closed circles) or haplobasaltic melt (open squares) at 1350 °C, from experiments of Gaetani et al. (2008), showing systematic increase with pressure.

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