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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 ^{IV}Si, presumably in interstitial sites. Rutile recovered from 6 GPa, 1600 °C contains about 0.6 wt% SiO_2, incorporated both as ^{VI}Si (~90%) and ^{IV}Si (~10%). TiO_2-II, synthesized at 12 GPa, 1200 °C, contains only ^{VI}Si. The chemical shift for ^{VI}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