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H and Fe³⁺ solubility in rutile and TiO₂ (II): Effects on phase stability, and the role of silica polymorphs in the lower mantle

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Previous studies have shown that at pressures of 6-8 GPa, rutile transforms to a phase with the α -PbO₂ structure, known as TiO₂ (II). Despite the possible importance of this phase transition for thermobarometry, it has only been bracketed in the pure TiO₂ system. In natural rutile, coupled substitution of pentavalent (e.g. Nb⁵⁺) and trivalent (e.g. Fe³⁺) cations maintains charge neutrality. Alternatively, substitution of lower valency cations may be charge-balanced by incorporation of H. Rutile is well-known for the great affinity which it shows towards H incorporation, and as such, provides a useful model for investigating the effects of H incorporation in other NAMs.

We have performed experiments to determine the solubility of H and Fe₂O₃ in rutile and TiO₂ (II) up to 10 GPa, and the effects of H and Fe³⁺ on phase stability. H incorporation in rutile is coupled to substitution of Fe³⁺ onto the octahedral Ti⁴⁺ site. In contrast, TiO₂ (II) contains no structurally-incorporated hydrogen. Results suggest that examination of water contents of rutile inclusions in UHP rocks could be used to confirm whether the inclusions were exsolved as rutile or as TiO₂ (II). The dominant Fe³⁺ incorporation mechanism in both phases is, however, unrelated to H content, and involves substitution of Fe³⁺ onto octahedral Ti⁴⁺ sites, charge-balanced by oxygen vacancies. Substitution of Fe₂O₃ into TiO₂ (II) stabilizes the structure to much lower pressures than in the pure TiO₂ system, and implies that application of data on rutile stability in the pure TiO₂ system may lead to significant overestimation of pressure.

The TiO₂ system provides a lower pressure analogue to the SiO₂ system, and results on Fe³⁺ and H solubility in rutile and TiO₂ can provide information on Al³⁺ and H incorporation in stishovite and post-stishovite phases, and to assess the role of silica polymorphs in subducting MORB under lower mantle conditions. Results indicate that, while Al-bearing stishovite could act as an important carrier of water, formation of the post-stishovite phase with the α -PbO₂ structure would represent a significant dehydration event at the base of the lower mantle. Furthermore, Al substitution in silica polymorphs could have an important influence on phase stability, and could increase the likelihood of α -PbO₂ structure silica being stable at the base of the lower mantle.

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Influence of transition metals on hydrogen incorporation in orthopyroxene

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Water plays a crucial role for many physical properties (e.g., rheology, electrical conductivity) of the Earth's mantle as well as for magma generation during partial melting. Orthopyroxene as an important constituent of the Earth's upper mantle is able to incorporate several hundred ppm (wt) H₂O and might therefore be regarded as a major host for water in the Earth's upper mantle. Hydrogen incorporation can be enhanced by simultaneous incorporation of trivalent cations by coupled substitutions.

In this study we investigate the influence of trivalent transition metal cations Fe³⁺ and Cr³⁺ on the water solubility and the incorporation mechanism in orthopyroxene. In a series of high pressure syntheses at 25 kbar enstatite single crystals containing various amounts of Fe and Cr were synthesized and analysed by electron microprobe, Mößbauer spectroscopy and polarised FTIR-spectroscopy on oriented crystal sections. Strongest infrared absorptions occurred in all cases when n_{γ} was parallel to the electric field vector E of the incident light, weakest absorptions occurred for n_{β} //E. With increasing concentrations of trivalent transition metal the OH-dipole is tilted towards n_{β} and away from n_{γ} , and additional OH-bands between 3250 and 3350 cm⁻¹ as well as above 3400 cm⁻¹ are observed, consistent with the generation of new hydrogen sites and a distortion of the polyhedral chains. Infrared spectra taken from samples synthesized with D₂O exhibit OD absorption bands in the range between 2200 and 2600 cm⁻¹. The OD bands are in terms of positions and intensities equivalent to all OH bands observed previously, but reveal due to a smaller band width (i.e., higher resolution) a weak peak splitting also for the OD band at 2300 cm⁻¹ (equivalent to the OH band at 3070 cm⁻¹), which has not been observed in the OH range.

As shown before for Al³⁺, the amount of the incorporated OH correlates well with the concentration of trivalent cations in the crystal, consistent to the exchange mechanisms Cr³⁺ + H⁺ \leftrightarrow 2 Mg²⁺, Fe³⁺ + H⁺ \leftrightarrow 2 Mg²⁺ and Fe³⁺-Tschermak substitution. Comparison of the infrared spectra of Fe- and Cr-bearing enstatites to Al-bearing synthetic orthopyroxenes and to natural orthopyroxenes from the Earth's upper mantle strongly suggests that coupled substitutions involving Al³⁺ dominate the H⁺ incorporation in orthopyroxenes from the upper mantle.