Solubility of hydrogen and ferric iron in rutile and TiO\(_2\) (II): Implications for phase assemblages during ultrahigh-pressure metamorphism and for the stability of silica polymorphs in the lower mantle

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Received 7 January 2004; accepted 14 January 2004; published 24 February 2004.

[1] The solubility of hydrogen in Fe\(_2\)O\(_3\)-doped rutile and TiO\(_2\) (II) at 1100°C has been experimentally determined. H incorporation in rutile is coupled to substitution of Fe\(^{3+}\) onto the octahedral Ti\(^{4+}\) site. In contrast, TiO\(_2\) (II) contains no structurally-incorporated hydrogen. The dominant Fe\(^{3+}\) incorporation mechanism in both phases is unrelated to H content, and involves substitution of Fe\(^{3+}\) onto octahedral Ti\(^{4+}\) sites, charge-balanced by oxygen vacancies. Substitution of Fe\(_2\)O\(_3\) into TiO\(_2\) (II) stabilizes the structure to much lower pressures than in the pure TiO\(_2\) system. Results indicate that Al-bearing stishovite could act as an important carrier of water in subducting oceanic crust, but that formation of the post-stishovite phase with the \(\alpha\)-PbO\(_2\) structure would represent a significant dehydration event at the base of the lower mantle.


1. Introduction

[2] Subduction of oceanic lithosphere provides a mechanism for transporting water into the deep Earth’s interior. Beyond the stability of hydrous phases, trace amounts of water can be stored in a large number of nominally anhydrous minerals (NAMs) [Bell and Rossman, 1992]. In subducting oceanic crust, NAMs could provide an effective mechanism for transporting water beyond the depths of sub-arc magmatism and even into the lower mantle.

2. Experimental Details

[7] Samples were synthesized using a starting mix of 95 wt% TiO\(_2\) (99.998%) and 5 wt% Fe\(_2\)O\(_3\) (99.95%) (unenriched in \(^{57}\)Fe) using piston-cylinder (0.5 to 3 GPa) and multi-anvil apparatus (5 to 7 GPa). Samples were loaded into welded Pt capsules lined with Re foil to prevent Fe-loss, along with 5 wt% distilled water. All experiments were run at 1100°C for more than 30 hours to ensure chemical homogenization and attainment of equilibrium defect structures [Mackwell and Kohlstedt, 1990]. Recovered samples were prepared as doubly polished thin sections of 150 to 200 μm thickness, or as doubly polished plates prepared from optically-aligned single crystals. Phases were identified by micro-Raman spectroscopy using published spectra for rutile and TiO\(_2\) (II) [Goresy et al., 2001] and...
powder X-ray diffraction, and hydrogen incorporation was studied using Fourier transform infrared spectroscopy [see Bolfan-Casanova et al., 2000]. Samples were further analyzed by electron microprobe (EMPA) and Mössbauer spectroscopy [see McCammon et al., 2004]. Water contents were calculated using the three published extinction coefficients for rutile: $15100 \pm 500 \text{ lmol cm}^{-1} \text{ nmol}^{-1}$ [Johnson et al., 1973], $3270 \text{ lmol cm}^{-1} \text{ nmol}^{-1}$ [Hammer and Beran, 1991] and $38000 \text{ lmol cm}^{-1} \text{ nmol}^{-1}$ [Maldener et al., 2001].

<table>
<thead>
<tr>
<th>Pressure, GPa</th>
<th>Product</th>
<th>$\text{Fe}_2\text{O}_3$</th>
<th>TiO$_2$</th>
<th>Total</th>
<th>$\text{Fe}^{3+}$</th>
<th>Ti</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>Rutile</td>
<td>1.36(53)</td>
<td>98.21(67)</td>
<td>99.56(3)</td>
<td>0.01(1)</td>
<td>0.99(1)</td>
<td>1.01(1)</td>
</tr>
<tr>
<td>2.0</td>
<td>Rutile</td>
<td>2.76(8)</td>
<td>96.78(92)</td>
<td>99.55(95)</td>
<td>0.03(1)</td>
<td>0.98(1)</td>
<td>1.01(1)</td>
</tr>
<tr>
<td>3.0</td>
<td>Rutile</td>
<td>3.43(12)</td>
<td>95.90(39)</td>
<td>99.33(40)</td>
<td>0.03(1)</td>
<td>0.91(1)</td>
<td>1.00(1)</td>
</tr>
<tr>
<td>5.0</td>
<td>Rutile</td>
<td>3.22(32)</td>
<td>95.92(52)</td>
<td>99.14(30)</td>
<td>0.03(1)</td>
<td>0.98(1)</td>
<td>1.01(1)</td>
</tr>
<tr>
<td>6.0</td>
<td>TiO$_2$ (II)</td>
<td>4.80(21)</td>
<td>94.19(41)</td>
<td>98.99(37)</td>
<td>0.05(1)</td>
<td>0.96(1)</td>
<td>1.01(1)</td>
</tr>
<tr>
<td>7.0</td>
<td>TiO$_2$ (II)</td>
<td>4.81(22)</td>
<td>94.13(32)</td>
<td>98.94(28)</td>
<td>0.05(1)</td>
<td>0.96(1)</td>
<td>1.01(1)</td>
</tr>
</tbody>
</table>

3. Results

All recovered capsules contained a free fluid phase after the experiments. Results of phase identification and compositional analyses are listed in Table 1. Runs up to 5 GPa contained rutile and small amounts of ilmenite, while runs at 6 and 7 GPa contained only TiO$_2$ (II). No evidence for chemical zoning was noted in any samples. Fe$_2$O$_3$ contents increase in rutile from 0.5 to 3 GPa, but then remain constant at 5 GPa. Fe$_2$O$_3$ solubility in TiO$_2$ (II) is considerably higher than in rutile.

Infrared spectra for rutile are shown in Figure 1. All spectra consist of a single absorption band at 3295 cm$^{-1}$, which is strongly polarized, having a 95% component of vibration perpendicular to the crystallographic c axis. In contrast, IR spectra obtained from TiO$_2$ (II) contained no absorption bands over the region 4000–2500 cm$^{-1}$, implying an absence of structurally-incorporated hydrogen. In rutile, there is a variation in the intensity of the absorption band at 3295 cm$^{-1}$ with pressure, reflected in varying calculated water contents (Table 2). Quantitative determination of water contents in rutile is difficult because there are large disparities between published calibrations for rutile extinction coefficients. The calibration of [Johnson et al., 1968] is preferred because it was derived from a study of synthetic rutile, and gives calculated water contents more consistent with values determined for other high-pressure phases [Bell and Rossman, 1992; Ingrin and Skogby, 2000; Libowitzky and Rossman, 1997].

4. H And Fe$^{3+}$ Incorporation Mechanisms in Rutile and TiO$_2$ (II)

The single absorption band in IR spectra obtained from rutile is consistent with H incorporation coupled with Fe$^{3+}$ substitution onto the octahedral (Ti$^{4+}$) site. The anisotropic nature of this absorption band is consistent with an H position close to $\frac{1}{2} \frac{1}{2} \frac{1}{2}$, with vibration of the OH dipole just off of a shared octahedral edge, as proposed by Swope et al. [1995] on the basis of results from a neutron diffraction study of natural rutile. Variation in OH stretching frequencies in IR spectra obtained from natural rutiles with different minor element compositions [Vlassopoulos et al., 1993] supports the idea that H and trivalent cations form defect clusters in the rutile structure, where $M^{3+}$ substitution onto an octahedral Ti$^{4+}$ site is locally charge balanced by H association with an O atom surrounding the octahedral site. However, Fe contents in rutile synthesized in this study are several orders of magnitude higher than calculated water contents, implying that there must be an additional mechanism for Fe incorporation. The absence of a broad band in IR spectra centered around 5000–6000 cm$^{-1}$ precludes the presence of octahedral or interstitial Ti$^{3+}$ in the samples [Khomenko et al., 1998]. Fe incorporation could be charge-balanced by oxygen vacancies in the rutile structure, similar to the incorporation mechanism proposed for Al in Al-doped rutile grown at ambient pressure [Gesenhues and Rentschler, 1999]. A similar incorporation mechanism could operate in the TiO$_2$ (II) phase, which contains higher Fe contents than rutile, but contains no structurally-incorporated H. Operation of this mechanism in both phases is consistent with the results of Mössbauer spectroscopy. Spectra obtained from both phases (Figure 2) consist of a single quadrupole doublet, implying the presence of only Fe$^{3+}$. The center shifts in both samples are similar (0.376 (rutile) and 0.368 (TiO$_2$ II) mm/s relative to Fe), indicating similar octahedral Fe$^{3+}$ environments in both phases. The linewidth and quadrupole splitting in the rutile spectrum are significantly larger than in the TiO$_2$ (II) spectrum. The greater line width in the rutile spectrum could be due to greater

Figure 1. FTIR spectra obtained from water- and Fe$_2$O$_3$-saturated rutile synthesized at 2.0 GPa using radiation polarized perpendicular (solid line) and parallel (dotted line) to crystallographic c axis.
variation in the Fe$^{3+}$ environment compared to TiO$_2$ (II), which would be consistent with two mechanisms for Fe$^{3+}$ incorporation in rutile (i.e. charge-balanced by structurally-incorporated H, and by O vacancies), but only one mechanism of Fe$^{3+}$ incorporation in TiO$_2$ (II) (charge-balanced by oxygen vacancies). The larger quadrupole splitting in the rutile spectrum could imply greater site distortion, or be related to lattice strain or some other effect. Mössbauer spectra obtained from both phases indicate that Fe$^{3+}$ is in 6-fold coordination. Therefore, if Fe$^{3+}$ incorporation is charge-balanced by O vacancies, octahedral Fe$^{3+}$ and O vacancies must be decoupled and not form defect clusters.

Variation in Fe$_2$O$_3$ content with pressure appears to be unrelated to calculated water contents (Figure 3), which is consistent with the idea that the dominant mechanism for charge-balancing Fe$^{3+}$ incorporation involves O vacancies. However, water solubility in rutile does vary significantly as a function of pressure. The pressure dependence of water solubility in NAMs is governed by water fugacity and the volume change, $\Delta V_s$, of the host structure due to incorporation of OH groups. This relationship can be expressed in terms of the general solubility equation

$$c_{\text{OH}} = A f_{\text{H}_2\text{O}} \exp\left(-P\Delta V_s/RT\right)$$

(1)

where $c_{\text{OH}}$ is water solubility, $A$ is a temperature-dependent constant, $f_{\text{H}_2\text{O}}$ is water fugacity, $P$ and $T$ are run pressure and temperature, and $R$ is the gas constant). Data on water solubility in rutile were fitted to equation (1) for different values of $n$. The equation of state for H$_2$O of Pitzer and Sterner [1994] was used to calculate water fugacities (listed in Table 2). A meaningful fit of the data was only achieved for $n = 0.5$, with values of 12.485 cm$^3$/mol and 9.128 ppm/bar$^{0.5}$ refined for $A$ and $\Delta V_s$, respectively. Therefore, water solubility in the synthetic rutile is proportional to the square root of water fugacity, implying that water is incorporated in the structure as isolated hydroxyl groups. This is consistent with the proposed coupled Fe$^{3+}$, H$^+$ substitution mechanism.

5. Implications for the Storage of Water in the Mantle

5.1. TiO$_2$ Polymorphs

Rutile is only an accessory mineral in UHP eclogite, and so its role in terms of water incorporation in subducting
crust is probably limited. Transformation of rutile to TiO₂ (II) during subduction probably represents a minor dehydration event. Any water released could be incorporated in omphacite, which can contain increasing amounts of water at higher pressures due to an increase in the number of vacancies on the M2 site [Smyth et al., 1991]. However, incorporation of minor elements into the rutile structure could have an important impact on phase stability. In the present study, the transition from rutile to TiO₂ (II) was noted at 5–6 GPa, which is considerably lower than in the pure TiO₂ system [Withers et al., 2003]. This effect is probably due to the high solubility of Fe in the high-pressure phase. In fact, with bulk compositions richer than 5 wt % Fe₂O₃, the transformation pressure could be even lower, because in the present study the high-pressure TiO₂ (II) phase is not Fe-saturated. The pressure at which rutile breaks down to TiO₂ (II) could, therefore, be strongly dependent upon the Fe³⁺ and other minor element content. It has been suggested that the presence of TiO₂ (II), or evidence of its former existence, in UHP rocks could be used to determine peak metamorphic conditions. Use of data on the stability of TiO₂ (II) in the pure TiO₂ system could lead to a significant overestimation of pressure.

[13] Examination of water contents of rutile in UHP eclogites could provide a useful means for determining whether rutile inclusions in other phases were originally TiO₂ (II). TEM investigations of rutile inclusions in minerals such as garnet in UHP rocks have revealed the presence of TiO₂ (II) lamellae [Hwang et al., 2000]. It has been proposed that these structures indicate that the inclusion was originally TiO₂ (II) that has reverted back to rutile during exhumation. If this is correct, then the water content of the whole inclusion should be minimal (due to the zero solubility of water in the TiO₂ (II) structure). In contrast, if the inclusion was exsolved as rutile, which has a high water solubility, then the water content should be quite high. If conditions were right for the chemical isolation of such inclusions, determination of present water contents could, in theory, be used to support arguments for the former existence of the TiO₂ (II) phase.

5.2. SiO₂ Polymorphs

[14] Stishovite, a high-pressure silica polymorph, is isostructural with rutile. Stishovite can also contain structurally-incorporated H via a similar mechanism as noted in rutile [Pawley et al., 1993], where H incorporation is related to Al³⁺ substitution onto the octahedral Si³⁺ site. Stishovite could act as an important repository for water in subducting oceanic crust in the lower mantle, and may provide a mechanism for water transport deep into the lower mantle [Chung and Kagi, 2002; Panero et al., 2003]. At approximately 50 GPa, stishovite undergoes a phase transition to a CaCl₂-type structure, and then at higher pressures, to a phase with the α-PbO₂ structure (i.e. isostructural with the TiO₂ (II) phase) [Hemley et al., 2000]. This high-pressure phase of silica may be stable at the core-mantle boundary [Murakami et al., 2003]. Data on water solubility in rutile and TiO₂ (II) can therefore be used to place constraints on the possible role of silica in subducting oceanic crust under lower mantle conditions. Substitution of Fe³⁺ onto octahedral Ti⁴⁺ sites in rutile and TiO₂ (II), probably charge balanced by O vacancies, has a strong effect on the stability of the two phases. By analogy, Al substitution in silica polymorphs may influence phase stability, and may make the appearance of α-PbO₂ silica at the base of the lower mantle more likely. This effect may be heightened in silica, because the difference in ionic radii between octahedrally-coordinated Si⁴⁺ and Al³⁺ (13.5 pm) is larger than that between octahedrally coordinated Ti⁴⁺ and Fe³⁺ (9.0 pm). The phase transition from rutile to TiO₂ (II) has a marked effect on water solubility in the system. A similar effect in silica could result in a significant dehydration event in subducted oceanic crust at the base of the lower mantle, and throughout geological history, would provide an effective mechanism for hydration of the lower mantle.

[15] Acknowledgments. We wish to thank Hupert Schultz, Detlef Krauss and Dan Frost for technical assistance. This manuscript benefited from reviews by Hans Keppler and Kei Hirose.

References


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