# Solubility of Apatite, Monazite, Zircon, and Rutile in Supercritical Aqueous Fluids with Implications for Subduction Zone Geochemistry

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# Solubility of apatite, monazite, zircon, and rutile in supercritical aqueous fluids with implications for subduction zone geochemistry

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Solubilities of accessory minerals (apatite, monazite, zircon and rutile) in supercritical aqueous fluids have been measured to evaluate the role of these fluids in the mobilization of accessory mineral-hosted trace elements. We have characterized the effects on solubility of pH, $X_{H_2O}$ (addition of $CO_2$), pressure ($P = 1.0$–$3.0$ GPa), temperature ($T = 800$–$1200$ °C), and dissolved silicate and NaCl concentration.

Fluorapatite solubility in pure $H_2O$ is low, not more than 0.4 wt % at all conditions studied, but increases strongly with decreasing pH. Changes in $P$, $T$, $X_{H_2O}$, $M_{NaCl}$ (the molality of NaCl), and dissolved silicate concentration have comparatively little effect on apatite solubility. Monazite is even less soluble in $H_2O$ (not more than 0.2 wt %). Limited data suggests that monazite solubility increases with increasing $P$ and $T$ and with decreasing pH, but is insensitive to $M_{NaCl}$.

Zircon reacts with $H_2O$ to form baddeleyite ($ZrO_2$) + silica-rich fluid. $ZrO_2$ solubility in $H_2O$ and 1 M HCl is less than 0.2 wt %. Zircon, and therefore $ZrO_2$, solubility in *quartz-saturated* fluids ± HCl ± NaCl and in $H_2O$–$CO_2$ fluids is also very low. Rutile is more soluble than the other minerals examined, in the wt % range, and its solubility increases with increasing $P$ and $T$.

Results indicate that high $P$–$T$ aqueous fluids can dissolve significant amounts of Ti but very little Zr, and little phosphate unless the fluids are acidic. In most cases, apatite, monazite and zircon will remain present during episodes of aqueous fluid metasomatism and therefore will exert control, as 'residual phases', over element distribution. The higher solubility of rutile relative to other accessory minerals at high pressure may result in the depletion of high field strength elements relative to large ion lithophile elements observed in subduction zone volcanics.

## 1. Introduction and previous work

The association of volatile fluid metasomatism and loss or gain of accessory minerals suggests that volatile fluids dissolve, transport, and precipitate these minerals (Gieré 1990; Rubin *et al.* 1989; Sorenson & Grossman 1989). At issue here is whether supercritical aqueous fluids are capable of dissolving accessory minerals in sufficient quantity to be effective transport agents of the elements these minerals host. To test this we have measured the solubilities of the accessory minerals apatite, monazite, zircon, and rutile in various fluids. Before discussing the results we review the properties of each phase.

### (a) Aqueous fluids

We know little about the chemical properties of aqueous fluids above 0.5 GPa. Metamorphic fluids often contain large amounts of dissolved salts, including NaCl,

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KCl, $FeCl_2$ and $CaCl_2$ (Selverstone *et al.* 1990). Dissolved salts may be significantly dissociated at the high pressures of this study, and this serves to increase the ionic strength of the solution, which in turn may increase the solubility of ionic solids. Solubilities of silicate minerals in supercritical fluids are rarely more than several wt % at crustal conditions, but show a wide variation depending on fluid composition, ionic strength, mineral composition, and $P$ and $T$ (Holland & Malinin 1979). Aqueous fluids in equilibrium with most silicate rocks are rich in $SiO_2$, $Al_2O_3$, $Na_2O$ and $K_2O$, while CaO, MgO, and FeO are not as soluble. Addition of $CO_2$ to the fluid greatly reduces the solubilities of silicate components (Eggler 1987).

### (*b*) *Apatite*

Fluorapatite (FAp) is the most common end-member of the isomorphous series $Ca_5(PO_4)_3(OH,F,Cl)$. We therefore chose the nearly pure Durango FAp for study. The solubility reaction for FAp may be written:

$$Ca_5(PO_4)_3F_{(xt)} \rightleftharpoons 5\,Ca^{2+} + 3\,PO_4^{3-} + F^-. \qquad (1.1)$$

Even in the simplest four-component system (Ca, P, O and F), each of the aqueous species produced can form many different complexes. The phosphate ion may undergo stepwise association with $H^+$ to form the species $HPO_4^{2-}$, $H_2PO_4^-$ and $H_3PO_4$. As a result, high activity of $H^+$ (low pH) should increase the solubility of apatite. Calcium may form the complexes $CaOH^+$, $CaPO_4^-$, $CaHPO_4$ and $CaH_2PO_4^+$, while $F^-$ may associate to form HF. The value of $K_{eq}$ for (1.1) at 25 °C as determined experimentally by McCann (1968) is $8.6\,(\pm 1.3) \times 10^{-61}$. Measured solubilities in p.p.m. FAp increase strongly with decreasing pH, from 3.0 at pH 7.0 to 253 at pH 4.0, but appear insensitive to changes in ionic strength (McCann 1968).

The aqueous solution chemistry of apatite is further complicated by the following exchange reactions:

$$Ca_5(PO_4)_3F_{(xt)} + H_2O \rightleftharpoons Ca_5(PO_4)_3OH_{(xt)} + HF, \qquad (1.2)$$

$$Ca_5(PO_4)_3F_{(xt)} + HCl \rightleftharpoons Ca_5(PO_4)_3Cl_{(xt)} + HF. \qquad (1.3)$$

### (*c*) *Monazite*

Monazite is a rare-earth phosphate $\text{REE}(PO_4)$, with Ce and other light REE generally being the most abundant REE. A likely solubility reaction involving neutral species is:

$$\text{REE}(PO_4)_{(xt)} + 3H_2O \rightleftharpoons \text{REE}(OH)_3 + H_3PO_4. \qquad (1.4)$$

The effect pH will have depends on the relative values of the dissociation constants of $\text{REE}(OH)_3$ and $H_3PO_4$.

Limited data on solubility constants coupled with low concentrations of REE and P in seawater suggest that monazite is probably insoluble in aqueous fluids near ambient conditions. However, monazite in the epizone is considered to be of hydrothermal origin, suggesting it may be soluble under certain conditions (Overstreet 1967).

### (*d*) *Zircon*

Zircon ($ZrSiO_4$) is resistant to weathering and is concentrated in heavy mineral deposits. This behaviour, combined with the immobility of Zr during diagenesis and low-grade metamorphism, suggests a low solubility of zirconium compounds.

At ambient conditions the neutral tetrahydroxide species predominates for dissolved $ZrO_2$ over a wide range of pH, resulting in simple dissolution reactions and solubilities that are independent of pH. The dissolution of zircon involves the congruent solution of zircon followed by the precipitation of baddeleyite $ZrO_2$ (Tole 1985):

$$ZrSiO_{4(xt)} + 4H_2O \rightleftharpoons Zr(OH)_4 + H_4SiO_4, \tag{1.5}$$

$$Zr(OH)_4 \rightleftharpoons ZrO_{2(xt)} + 2H_2O. \tag{1.6}$$

Charged Zr species (e.g. $Zr(OH)_3^+$, $Zr(OH)_2^{2+}$, $Zr(OH)^{3+}$ or $Zr^{4+}$) will become increasingly important at high pressure. It seems likely that the neutral or possibly the +1 charged species will predominate at the conditions of our experiments.

At ambient conditions zircon is very insoluble, $K_{eq}$ for (1.5) being $2.48 \times 10^{-17}$, which for congruent solution and $\gamma_i = 1$ corresponds to $4.8 \times 10^{-9}$ mole $l^{-1}$ or 0.1 p.p.b. Si (Tole 1985). Maurice (1949) found that at 400 °C and 0.09 GPa for $ZrO_2:SiO_2 = 1$ the stable assemblage in acidic solutions is zircon; in near-neutral solutions it is zircon+baddeleyite; and in alkaline solutions it is baddeleyite+various zirconosilicates. Maurice (1949) states that zircon is very soluble in acidic solutions but presents little data to support this.

### (*e*) *Rutile*

The insolubility of rutile ($TiO_2$) makes titanium very immobile during weathering and low-grade metamorphism. In water below 400 °C and at low pressures, $Ti(OH)_4$ is the dominant species in solution (Barsukova *et al*. 1979). The solubility reaction is:

$$TiO_{2(xt)} + 2H_2O \rightleftharpoons Ti(OH)_4. \tag{1.7}$$

In 1 M NaCl the concentration of $Ti(OH)_4$ is $3.3 \times 10^{-8}$ mole $kg^{-1}$ at 300 °C (Barsukova *et al*. 1979). In solutions containing $F^-$, the solubility of rutile is higher and becomes pH dependent due to formation of complexes such as $Ti(OH)_4F_2^{2-}$ and $Ti(OH)_2F_4^{2-}$. Rutile is therefore most soluble in aqueous solutions with high fluoride content and low pH (Barsukova *et al*. 1979).

## 2. Experimental procedures

To make efficient and precise measurements of low mineral solubilities we developed a technique involving measurement of the weight loss of a single crystal (Ayers & Watson 1989). Briefly, the technique involves placing a weighed crystal in a capsule with a known amount of fluid, running at $P$ and $T$, then reweighing the fluid and crystal. To model natural solubility phenomena as closely as possible and facilitate interpretation, we used simple systems, with no more than three phases in a given experiment, and well-characterized natural crystals close to pure end-member compositions. Table 1 lists the experimental conditions and results.

All runs were done in a piston cylinder apparatus that maintains temperature at ±5 °C and pressure ±5%. Samples were run at nominal pressure. The ambient $fO_2$ of the assemblies is high, above Ni/NiO but in the fields of water stability and Fe-bearing olivine stability (Brenan & Watson 1991). This assures that $H_2O$ ($\pm CO_2$) will be the dominant species in the fluid (Eggler 1987). Several different capsules and pressure assemblies were used in these experiments, the details of which will be discussed in a future communication.

As a test of the single crystal technique we measured the solubility of rutile at 2.0 GPa and 1100 °C in 24 h runs using it and the double capsule method of Schneider & Eggler (1986). The two methods give the same results. Runs of greater duration

Table 1. *Experimental results*

(Tech., experimental technique, single crystal (Xt) or double capsule (DC); caps is the type of capsule used (ex: Ti+Pt signifies a Ti outer capsule with a Pt liner). Err. is the 1-sigma weighing error in wt%. Solubilities in wt% (= (wt loss crystal/wt fluid) 100). BD, below detection. Fo, forsterite; Ab, albite; 1 M = 1 molal of species indicated dissolved in $H_2O_5$ for $H_2O$-$CO_2$ fluids, $X_{H_2O} = 0.5$.)

| run | solid | fluid | $P$/GPa | $T/(10^3\ °C)$ | $t$/h | tech. | caps | pH | wt% | err. |
|---|---|---|---|---|---|---|---|---|---|---|
| R07 | rutile | $H_2O$ | 2.0 | 1.1 | 23 | Xt | Pt | — | 0.96 | 0.04 |
| R10 | rutile | $H_2O$ | 2.0 | 1.1 | 42 | Xt | Pt | — | 1 | 0.03 |
| R12 | rutile | $H_2O$ | 2.0 | 1.1 | 24 | DC | Pt | — | 1 | 0.08 |
| R13 | rutile | $H_2O$ | 2.8 | 1.1 | 24 | DC | Pt | — | 5.9 | 0.03 |
| R20[a] | rutile | $H_2O$ | 2.0 | 1.1 | 22.5 | Xt | Ti+Pt | — | 1.6 | 0.05 |
| Ap02 | FAp | $H_2O$ | 2.0 | 1.1 | 24 | Xt | Ni | — | 0.35 | 0.06 |
| Ap06 | FAp | $H_2O$ | 1.0 | 1.1 | 24 | Xt | Ni | 5 | 0.44 | 0.05 |
| Ap08 | FAp | $H_2O$ | 2.0 | 1.1 | 23 | Xt | Ni+Pt | — | 0.33 | 0.08 |
| Ap10 | FAp | $H_2O$ | 2.0 | 1.1 | 48 | Xt | Nb+Pt | 2.1 | 0.25 | 0.05 |
| Ap11 | FAp | $H_2O$ | 1.0 | 1.0 | 26 | Xt | Ni+Pt | 5 | 0.17 | 0.05 |
| Ap12 | FAp | 1 M NaCl | 1.0 | 1.0 | 24 | Xt | Ti+Pt | — | 0.14 | 0.05 |
| Ap13 | FAp+Fo | $H_2O$ | 1.0 | 1.0 | 24 | Xt | Ti+Pt | — | 0.17 | 0.05 |
| Ap15 | FAp | $H_2O$ | 1.0 | 1.2 | 24 | Xt | Ti+Pt | 1.8 | 0.13 | 0.05 |
| Ap17[a] | FAp+Ab | $H_2O$ | 1.0 | 1.0 | 45 | Xt | Ti+Pt | — | 3.0 | 0.05 |
| Ap18 | FAp | $H_2O$ | 1.0 | 1.0 | 25.5 | Xt | Ni | — | BD | 0.05 |
| Ap20 | FAp+Ab | $H_2O$ | 1.0 | 1.0 | 24 | Xt | Ti+Pt | 8 | 0.067 | 0.05 |
| Ap21 | FAp | 1 M HCl | 1.0 | 1.0 | 66 | Xt | Ti+Pt | 0.52 | 2.1 | 0.05 |
| Ap22 | FAp | $H_2O$ | 1.0 | 0.8 | 46.5 | Xt | Ti+Pt | 7 | 0.1 | 0.05 |
| Ap24 | FAp | $H_2O$ | 3.0 | 1.0 | 24 | Xt | Ti+AgPd | 7 | BD | 0.05 |
| Ap25 | FAp | $H_2O$–$CO_2$ | 1.0 | 1.0 | 24 | Xt | Ti+Pt | — | 0.06 | 0.04 |
| M01 | monazite | $H_2O$ | 2.0 | 1.1 | 24 | Xt | Ni | — | 0.09 | 0.04 |
| M02 | monazite | $H_2O$ | 2.8 | 1.1 | 24 | Xt | Ni | — | 0.2 | 0.05 |
| M03 | monazite | $H_2O$ | 1.0 | 1.0 | 24 | Xt | Ni+AgPd | — | 0.14 | 0.05 |
| M05 | monazite | $H_2O$ | 1.0 | 0.8 | 24 | Xt | Ti+AgPd | neut | BD | 0.05 |
| M07[b] | monazite | 1 M HCl | 1.0 | 1.0 | 24 | Xt | Ti+Pt | acidic | 0.36 | ? |
| M08 | monazite | 1 M NaCl | 1.0 | 1.0 | 24 | Xt | Ti+Pt | neut | 0.12 | 0.06 |
| Z02 | zircon | $H_2O$ | 2.0 | 1.1 | 24 | Xt | Ni | — | 3.4 | 0.05 |
| Z06 | zircon | $H_2O$ | 2.0 | 1.1 | 26 | Xt | Ni+AgPd | neut | 6.9 | 0.06 |
| Z08 | zir+qtz | $H_2O$ | 1.0 | 1.0 | 24 | Xt | Ni+AgPd | neut | 0.17 | 0.05 |
| Z09 | zir+qtz | 1 M HCl | 1.0 | 1.0 | 24 | Xt | Ni+AgPd | acidic | 0.12 | 0.05 |
| Z11 | zir+qtz | 1 M NaCl | 1.0 | 1.0 | 24 | Xt | Ni+AgPd | >= 10 | low | — |
| Z13 | zircon | $H_2O$ | 1.0 | 1.0 | 24 | Xt | Ni+AgPd | neut | 5.3 | 0.05 |
| Z14 | zircon | 1 M HCl | 1.0 | 1.0 | 24 | Xt | Ti+Pt | acidic | 5.0 | 0.05 |
| Z15 | zircon | $H_2O$–$CO_2$ | 1.0 | 1.0 | 24 | Xt | Ti+Pt | — | BD | 0.05 |

[a] Solubility high due to recrystallization in temperature gradient.

[b] Crystal broke during experiment; measured solubility may be artificially high.

listed in table 1 confirm that 24 h is sufficient to achieve equilibrium, as demonstrated in other studies of fluid/mineral systems (Brenan & Watson 1991; Schneider & Eggler 1986).

For some experiments the pH of quenched fluid was measured using litmus paper, and for three experiments (Ap 10, 15 and 21) using a pH microelectrode. Although quench pH is not equivalent to pH at run conditions, it is a measure of the relative activity of $H^+$ at $P$ and $T$.

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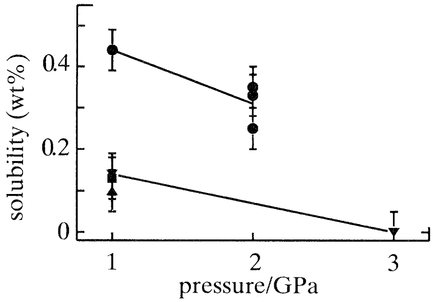

Figure 1. Apatite solubility in wt % as a function of pressure and temperature. Errors bars represent ±1$\sigma$ weighing errors. ▲, 800 °C; ▼, 1000 °C; ●, 1100 °C; ■, 1200 °C.

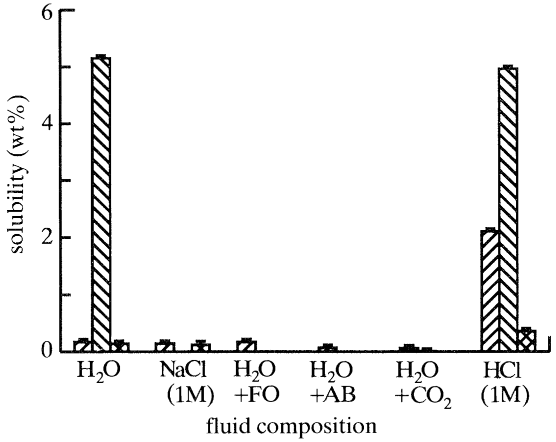

Figure 2. Solubilities of apatite, zircon, and monazite in wt % at 1.0 GPa and 1000 °C as a function of fluid composition. Error bars represent 1$\sigma$ weighing errors. ▨, Apatite; ▧, zircon; ▩, monazite. Fo, forsterite; Ab, albite; 1 M = 1 molal of the indicated species.

## 3. Experimental results

### (*a*) *Apatite*

To our surprise, apatite did not melt or recrystallize even at conditions as extreme as 1200 °C and 1.0 GPa. The solubility of apatite in $H_2O$ decreases with increasing pressure (figure 1). Temperature dependence is less systematic, with solubility increasing over the range 800–1100 °C and then dropping to a lower value at 1200 °C.

The most important result is the generally low solubility compared with silicates, which have solubilities of several wt % at similar conditions (Schneider & Eggler 1986). The total range of measured solubility is 0.10 wt % at 1.0 GPa and 800 °C to 0.44 wt % at 1.0 GPa and 1100 °C. This range is very small compared with the range at ambient conditions as a function of pH, suggesting that $P$ and $T$ have a much smaller affect on solubility than pH. In fact, experiments for which quench pH was measured show solubilities very close to values at ambient conditions at the same pH. Low quench pH values suggest that exchange reactions like (1.2) and (1.3) occur.

The effect on solubility of changing fluid composition is variable as shown in figure 2, which includes results for apatite, monazite, and zircon at 1.0 GPa and 1000 °C. No change in the solubility of FAp on addition of NaCl to $H_2O$ is evident. This

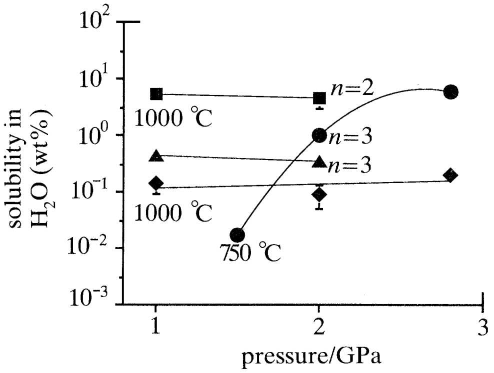

Figure 3. Solubilities in wt% of apatite, monazite, zircon and rutile in $H_2O$ as a function of pressure at 1100 °C (except where noted). Error bars represent $\pm 1\sigma$ weighing errors except where $n$, the number of determinations, is greater than one. In this case error bars represent $\pm 1\sigma$ on multiple determinations. ●, Rutile; ▲, apatite; ◆, monazite; ■, zircon.

suggests there is neither complexing of $Na^+$ or $Cl^-$ with dissolved apatite components nor a dependence of solubility on ionic strength, agreeing with the results of McCann (1968).

To test whether dissolved silicate material influences solubility, runs with added forsterite (Fo) and albite (Ab) were done. Results show no effect of dissolved silicate concentration on apatite solubility. The effect of $CO_2$ on apatite solubility was tested by loading oxalic acid to give a fluid composition $X_{H_2O} = 0.5$, $X_{CO_2} = 0.5$. Solubility dropped to about one third of the value for pure $H_2O$. Finally, the effect of pH was tested by adding 1 M HCl. As expected, solubility greatly increased to 2.1 wt%, showing that pH is the most important determinant of apatite solubility at high $P$ and $T$ just as it is at ambient conditions.

### (*b*) *Monazite*

Monazite is even less soluble than apatite at the conditions studied. Solubility appears to increase with increasing $P$ (figure 3), and at 1.0 GPa it increases with increasing $T$ (table 1). Solubilities range from detection (not more than 0.05 wt%) at 1.0 GPa and 800 °C to 0.2 wt% at 2.8 GPa and 1100 °C.

Considering fluid composition (figure 2), the solubility of monazite in 1 M NaCl is the same as in $H_2O$ at the same conditions. As with apatite, ionic strength does not affect the solubility. This may be a result of monazite dissolving as neutral species, or more unlikely, complete association of NaCl at these conditions. For 1 M HCl an increase in solubility is similar to the results obtained for apatite: decreasing the pH increases the solubility. Presumably low pH keeps phosphate in the protonated form, decreasing the activity of $PO_4^{3-}$ and thereby increasing solubility of these minerals.

### (*c*) *Zircon*

Zircon proved more difficult to study because of precipitation of baddeleyite (see (1.5) and (1.6)) on the surface of the crystal in runs containing pure $H_2O$. In some cases baddeleyite was removed by heating the crystal in concentrated HF, in which zircon is virtually insoluble. This allowed measurement of the weight loss of *zircon*, upon which the stated solubilities are based. Analysis of Zr in quench silicate suggests that the solubility of $ZrO_2$ in the fluid is low, between 700–1800 p.p.m. in equilibrium with zircon and quartz.

In pure $H_2O$ the solubility of zircon at 1.0 GPa and 1000 °C is 5.3 wt%, and at 2.0 GPa and 1100 °C the average of two runs is 5.2%, suggesting $P$ and $T$ have little effect (figure 3). In 1 M HCl baddeleyite still formed, and the measured solubility is again close to 5 wt% (figure 2). Addition of $CO_2$ to the fluid, however, decreased the solubility to below detection. Like that of other silicates (Eggler 1987), zircon solubility decreases with dilution of $H_2O$, in this case by $CO_2$.

Experiments on the assemblage zircon–baddeleyite–$H_2O$ did not give a clear idea of how much zircon could be dissolved by a silica-bearing fluid. We therefore tried experiments on the assemblage zircon–quartz–$H_2O$, but found retrieved crystals to have several micrometres thick layers of quench silicate mineral on their surfaces. To obtain a solubility we estimated the weight of the layer using two techniques: by calculation from its thickness and probable density, and by soaking the crystal in concentrated HF to remove the silica layer and reweighing. Averaging the results gave the weight loss of zircon and the calculated solubilities listed in table 1. Solubility of zircon in quartz-saturated fluids is very low, regardless of whether HCl or NaCl is present.

### (*d*) *Rutile*

Recrystallization of rutile in the temperature gradient of the piston cylinder assembly required us to use a different technique. Rutile was run in horizontally positioned noble metal capsules surrounded by graphite; these runs yielded results showing a high degree of precision (table 1).

In runs in which recrystallization occurred, observation of run products and of the position of the capsule with respect to the hotspot suggested that rutile solubility increases with increasing temperature. Solubility also increases with increasing pressure, from 1 wt% at 2.0 GPa, 1100 °C to 5.9 wt% at 2.8 GPa, 1100 °C (figure 3). The solubility of rutile at 1.5 GPa and 750 °C is 0.017 wt% (Schneider & Eggler 1986), in agreement with the $P$–$T$ trends observed in this study.

### (*e*) *Summary*

Our measurements suggest that most accessory minerals are not very soluble in supercritical aqueous fluids of near-neutral pH. A comparison of solubilities in $H_2O$ at 2.0 GPa and 1100 °C shows an increase in the order monazite < apatite < rutile < zircon (figure 3). The high apparent solubility of zircon results from its consumption by silica-undersaturated $H_2O$ to form baddeleyite + silica-rich fluid. The actual solubility of $ZrO_2$ is low. Rutile is significantly soluble in water at very high $P$ and $T$, and because its solubility strongly depends on $P$ and $T$, it may be more or less soluble than the other minerals depending on conditions. The phosphates apatite and monazite are less soluble, and their solubilities less dependent on $P$ and $T$. Their solubilities are, however, pH dependent, and in low-pH fluids apatite in particular can be very soluble. The fluid-compositional variables $M_{\mathrm{NaCl}}$, dissolved silicate concentration, and $X_{\mathrm{CO_2}}$ do not increase the solubilities of apatite, zircon, or monazite (figure 2).

One important variable that we have yet to investigate is $a_{\mathrm{F^-}}$. Studies at lower $P$–$T$ (Barsukova *et al.* 1979) show that the ionic character of $F^-$ makes it a good complexing anion for Ti, and maybe for Zr and REE (Gieré 1990). It is clear that not just any fluid can transport incompatible elements in significant quantities.

## 4. Petrological implications

### (a) *Comparison of accessory mineral solubilities in aqueous fluids and silicate melts*

Accessory minerals are generally less soluble in aqueous fluids than in silicate melts at the same conditions (table 2). Silicate melts therefore have a greater potential for transport of accessory mineral components than aqueous fluids. However, the differences in the abilities of silicate melts and aqueous fluids to dissolve accessory minerals shown in table 2 probably represent maxima. Accessory minerals are less soluble in more silica-rich or differentiated silicate melt compositions. Also, lowering of pH and possibly the presence of complexing anions such as $F^-$ will increase accessory mineral solubilities in aqueous fluids. Thus some aqueous fluids may be more effective solvents than some silicate melts.

### (b) *Estimation of fluid/rock ratios from solubility measurements*

It is instructive to calculate the minimum fluid/rock ratio required to add a given amount of each phase to a rock. The mass balance equation is:

$$M^{\mathrm{rock}} C^{\mathrm{rock}}_{\mathrm{AM}} = M^{\mathrm{fl}} C^{\mathrm{fl}}_{\mathrm{AM}} + M^{\mathrm{rock}}_{\mathrm{i}} (C^{\mathrm{rock}}_{\mathrm{AM}})_{\mathrm{i}}, \tag{4.1}$$

where $M^{\mathrm{rock}}_{\mathrm{i}}$ is the initial mass of rock, and the concentration of accessory mineral ($C_{\mathrm{AM}}$) in a phase is in wt%. In the simplest model a fluid saturated in the accessory mineral AM enters the rock, deposits its entire load of the mineral and exits the rock. In this case, the initial and final masses of rock are roughly equal (i.e. $M^{\mathrm{rock}} \approx M^{\mathrm{rock}}_{\mathrm{i}}$). Assuming, then, that there is no pre-existing AM in the rock, we can calculate the fl/rock ratio *per wt%* AM *introduced* (i.e. $C^{\mathrm{rock}}_{\mathrm{AM}} = 1$) from:

$$M^{\mathrm{fl}}/M^{\mathrm{rock}} = 1/C^{\mathrm{fl}}_{\mathrm{AM}}. \tag{4.2}$$

Using measured solubilities in $H_2O$ at 2.0 GPa and 1100 °C (table 2) gives fl/rock values necessary to introduce 1 wt% of each accessory mineral as *ca.* 3 for Ap, *ca.* 1 rutile, *ca.* 11 for monazite, and *ca.* 6 for zircon (for quartz-saturated $H_2O$).

This simple model almost certainly greatly underestimates the required fluid/rock ratio, because a fluid will precipitate only a small part of its dissolved accessory mineral content unless its is completely consumed in hydration reactions (which is not possible for the fluid/rock ratios we are discussing). In addition, for processes occurring specifically in subduction zones, temperatures corresponding to 1.0–2.0 GPa are considerably lower than 1100 °C, so accessory mineral solubilities will be lower than the values used above. Fluid/rock ratios required to add a given amount of accessory mineral will be correspondingly higher.

One way a fluid can transport large quantities of components of insoluble accessory minerals is to carry only some of those components. For example, a fluid carrying $PO_4^{3-}$ and $F^-$ may move through a depleted harzburgite that contains negligible Ca. Upon entering an eclogite $a_{\mathrm{Ca}^{2+}}$ will increase and apatite will precipitate. In this way a smaller volume of fluid is required to add a given amount of accessory mineral to a rock.

### (c) *Implications of rutile solubility for HFSE depletion in island-arc basalts*

In the past, the depletion of high field strength elements (HFSE) relative to REE in island arc basalts (IAB) was often attributed to residual rutile in the source region of IAB. However, Ryerson & Watson (1987) showed that rutile is too soluble in basaltic

Table 2. *Mineral solubilities in* $H_2O$ *and basalts in wt%*

| mineral | $H_2O$ | basalt | reference for basalt |
|---|---|---|---|
| apatite | 0.4 | 6.0 | Watson (1980) |
| monazite | 0.1 | 1.8 | Rapp *et al.* (1987) |
| rutile | 1.0 | 5.0 | Ryerson & Watson (1987) |
| zircon | 0.2 | 0.6 | Watson & Harrison (1983) |

melt to be residual during partial melting. Fractionation of HFSE from REE by some process is required by the chemistry of IAB, and that fractionation may be caused by aqueous fluids. The source of fluid is the subducted slab.

Dehydration of amphibole in the slab occurs at roughly 35 kbar (3.5 GPa) and 800 °C (Peacock 1990). At these conditions rutile is much more soluble in $H_2O$ than phases such as monazite and apatite that concentrate REE. As fluid ascends into the overlying mantle wedge it heats up to about 1100 °C (Peacock 1990), allowing it to dissolve even more rutile. Therefore fluid derived from dehydration of the subducted slab could flux the overlying mantle wedge, preferentially dissolving rutile and depleting the wedge in HFSE relative to REE and at the same time hydrating it to lower the solidus temperature. Subsequent partial melting of the source region would result in characteristically HFSE-depleted IAB. This scenario of fluid production in the slab by amphibole dehydration, fluxing of the overlying mantle wedge, and subsequent melting of peridotite in the wedge to form IAB is supported by thermal models and phase equilibria (Davies & Stevenson 1991; Peacock 1990). However, depending on the thermal model used it is possible that rutile may be less soluble than the REE-concentrating phases when fluid is released from the slab and metasomatizes the source region of IAB.

In closing, we note that there exist several problems with invoking rutile aqueous solubility to explain the HFSE anomaly. Most significant among these may be that IAB shows negative anomalies for all HFSE including Zr and Hf, and yet the latter two are controlled not by rutile but zircon, which we have shown to be relatively insoluble in aqueous fluids. Also, it is difficult to devise a model in which aqueous fluids can exist in a subduction zone and cause large-scale chemical transport over long periods of time. Partial melting will consume any fluids, so any modification of the source region must occur before basalt generation. If there is induced convection in the mantle wedge, fluids must continuously chemically modify fresh peridotite introduced to the source region (Davies & Stevenson 1991). In addition, aqueous fluids in equilibrium with silicate minerals show a marked preference for alkali metals and alkaline earths relative to REE (Brenan & Watson 1991), yet there is no fractionation of these elements in IAB.

Regardless of the role of rutile and aqueous fluids in subduction zones, our data show that Ti is significantly soluble in aqueous fluids at high $P$ and $T$. The scale and significance of aqueous fluid transport of Ti is controlled by the thermal structure of the region, phase stabilities, and the fluid transport mechanism.

### (*d*) *Geologic evidence of aqueous fluid transport of accessory mineral components*

Examples in the literature of accessory mineral mobility linked to volatile fluids are abundant. Based on their study of garnet amphibolites from a palaeosubduction zone, Sorenson & Grossman (1989) concluded that accessory mineral components were introduced by fluids. More direct evidence of fluid transport is given by

Selverstone *et al.* (1990) in their study of eclogites from a palaeosubduction zone in the Tauern Window of Austria. Fluid inclusions in these rocks contain $H_2O$, $CO_2$, and various salts, along with daughter minerals that include rutile, apatite, NaCl, and carbonate. The presence of the daughter minerals suggests that phosphorus and titanium (among other elements) are highly soluble in saline fluids at high pressure (2.0 GPa).

Addition of a whole suite of accessory minerals including zirconolite, rutile and apatite to a contact metamorphic marble has been documented by Gieré (1990). This study concludes that fluids derived from adjacent calcalkaline plutons metasomatized the country rock, and that fluorine and phosphorus in the fluid complexed with REE, HFSE, and actinides (Gieré 1990). In another setting, hydrothermal zircons in an intrusive igneous complex have been described by Rubin *et al.* (1989). Fluids derived from late-stage melts enriched in $F^-$ are believed to transport zircon (Rubin *et al.* 1989).

In many cases of accessory mineral enrichment reported in the literature the enrichment is attributed to hydrothermal fluids, but the enriched rocks are in close proximity to a zone of partial melting (Gieré 1990; Rubin *et al.* 1989; Sorenson & Grossman 1989). The connection may result from exsolution of an aqueous fluid from a late-stage crystallizing magma high in $F^-$ (Gieré 1990; Rubin *et al.* 1989). Fluorine is known to complex with Ti (Barsukova *et al.* 1979) and may complex with the other highly ionic ions such as Zr and REE. Such fluids also have low pH (Ayers & Eggler 1991), which should increase the solubility of many accessory minerals. Accessory minerals would precipitate as pH increases due to fluid-country rock interaction. One potential problem with this scenario is that $F^-$ partitions preferentially into the melt relative to the fluid (see references in Ayers & Eggler 1991). Further study on the effect of $F^-$ on the aqueous solubility of accessory minerals in required.

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