

# CONTROLS ON THE SATURATION OF SN-NB-TA-ZR-HF MINERALS IN GRANITIC MELTS

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## Summary

In order to evaluate whether it is reasonable that a mineral has crystallized from a silicate melt, the solubility of that mineral in the melt must be known. If at saturation the concentrations of the mineral-forming elements in the melt in question are at reasonable levels, then the ensuing question is what process(es) is/are controlling mineral crystallization. Experiments have been conducted with these thoughts in mind to place constraints on the origins of magmatic cassiterite, columbite, tantalite, zircon and hafnon mineralization. Magmatic cassiterite crystallization from peraluminous melts is most likely caused by late-stage oxidation of granitic melt. By contrast cassiterite is very soluble in peralkaline melts at all redox conditions and is unlikely to occur as a magmatic mineral. The crystallization of columbite and tantalite from peraluminous melts can be explained by cooling, however if the melt contains high concentrations of Li and F, tantalite saturation and to a lesser extent columbite saturation is less likely. Very high concentrations of Nb or Ta are required for columbite-tantalite saturation in peralkaline melts, similar to cassiterite. Tantalite was more soluble than columbite in all the subaluminous and peraluminous melts investigated, indicating that the activity coefficient of  $\text{Ta}_2\text{O}_5$  is lower than that of  $\text{Nb}_2\text{O}_5$  for a given melt composition. Based on the differences in the activity coefficients of Nb and Ta in melts, the progressive crystallization of a subaluminous or peraluminous granite suite or the fractional crystallization of columbite-tantalite can result in a decrease in whole-rock or mineral Nb/Ta ratios. Similarly, the Zr/Hf ratio in whole-rock or zircon-hafnon can decrease with progressive crystallization, although the solubilities of these minerals are much lower, so there is less of a problem in explaining their occurrence as magmatic minerals.

## Introduction

Mineral deposits of Sn, Nb, Ta, Zr and Hf are potentially magmatic in origin, i.e., the ore minerals crystallize directly from silicate melt. The interpretation of a magmatic origin is commonly based on textural evidence, but in order to evaluate this hypothesis the solubilities of ore minerals in silicate melts of appropriate composition must be known. Therefore systematic experimental studies were undertaken to determine the controls on the solubilities of cassiterite ( $\text{SnO}_2$ ), manganocolumbite ( $\text{MnNb}_2\text{O}_6$ ), manganotantalite ( $\text{MnTa}_2\text{O}_6$ ), zircon ( $\text{ZrSiO}_4$ ) and hafnon ( $\text{HfSiO}_4$ ) in granitic melts. Melt composition and temperature were the two principle parameters investigated, since these exert a major control on ore mineral solubility. In addition, cassiterite solubility was determined as a function of the redox state of the melt since tin can be either  $2^+$  or  $4^+$  at geologically relevant conditions.

## Experimental Equipment and Method

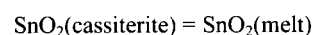
All starting materials were synthesized, except for zircon. Granitic glasses or gels have molar  $\text{Al}/(\text{Na}+\text{K})$  ratios (hereafter referred to as A.S.I.) of 0.64, 0.83, 0.94, 1.02, 1.13 and 1.22 and the subaluminous (A.S.I. 1.02) composition corresponds to the 2 kbar water-saturated haplogranite minimum. In the cassiterite

dissolution experiments a diffusion profile technique was used to obtain solubility in order to avoid the problem of Sn alloying with the Au or Pt capsules. Only one temperature and pressure was investigated (850°C and 2 kbar). These experiments were conducted largely using an internally-heated pressure vessel at Orléans, France. This vessel was equipped with a Shaw membrane to allow the measurement of the  $\text{H}_2$  fugacities ( $f_{\text{H}_2}$ ) of different  $\text{H}_2/\text{Ar}$  mixtures that were used as a pressure medium. Other redox conditions were obtained using different intrinsic  $f_{\text{H}_2}$  of Ar-pressurized cold seal pressure vessels at Orléans, France, as well as  $\text{H}_2\text{O}$ -pressurized cold seal pressure vessels at Bayreuth, Germany. The experiments were run in two stages. In the first stage  $\text{H}_2\text{O}$ -saturated glasses were prepared by sealing ~100-200 mg of gel in an Au capsule together with an appropriate amount of water. The  $f_{\text{H}_2}$  of the experiment was measured at this time, and since the melts were  $\text{H}_2\text{O}$ -saturated, the  $f_{\text{H}_2\text{O}}$  is known and the  $f_{\text{O}_2}$  can be calculated. In the second stage a single cassiterite crystal was placed in the middle of a Au capsule, surrounded by crushed  $\text{H}_2\text{O}$ -saturated glass, arc-welded shut, then put at the same P-T- $f_{\text{H}_2}$  conditions as the first stage for ~6 hours to allow Sn to diffuse into the melt. The experiment was then quenched and a diffusion profile away from the cassiterite crystal in the granitic glass was measured by electron microprobe. Cassiterite solubilities were then calculated by inverting the error function of diffusion from an infinite planar source. Further details on the experimental equipment and method can be found in Linnen et al. (1996).

The Nb-Ta-Zr-Hf solubility experiments were carried out at Bayreuth, Germany, using Ar-pressurized TZM pressure vessels and  $\text{H}_2\text{O}$ -pressurized cold seal pressure vessels. A mixture of ~10:1  $\text{H}_2\text{O}$ -saturated granitic glass or gel and crystals (columbite, tantalite, zircon or hafnon) were sealed in Au or Pt capsules, then experiments were conducted at 2kbar and 1035° to 750°C, typically for 2-4 weeks. After the experiments were quenched the glasses were analysed by electron microprobe. Reversal experiments, where equilibrium was approached by crystal growth resulting from decreasing temperature, were conducted to demonstrate that the experimental run times were sufficiently long to produce equilibrium values. The peralkaline to peraluminous haplo-granitic glasses from above were used as starting materials. Additional experiments examined the effects of Li and Li+F on solubility. In these experiments the lithium and fluorine contents in subaluminous granite melts varied, but the  $\text{Al}/(\text{Li}+\text{Na}+\text{K})$  ratio was kept constant at 1.0. Further details on the experimental equipment and method can be found in Linnen and Kepler (1997) and Linnen (1998).

## Results of Cassiterite Solubility Experiments

The results of the cassiterite solubility experiments are summarized in Figures 1 and 2. If tin enters the silicate melt in the  $4^+$  valance, then cassiterite solubility should be independent of oxygen fugacity ( $f_{\text{O}_2}$ ). This is the reaction:



However, if tin enters the silicate melt in the  $2^+$  valance, then log cassiterite solubility should have a negative dependence on log

$f_{O_2}$ , with a slope of  $-0.5$ , defined by the reaction:

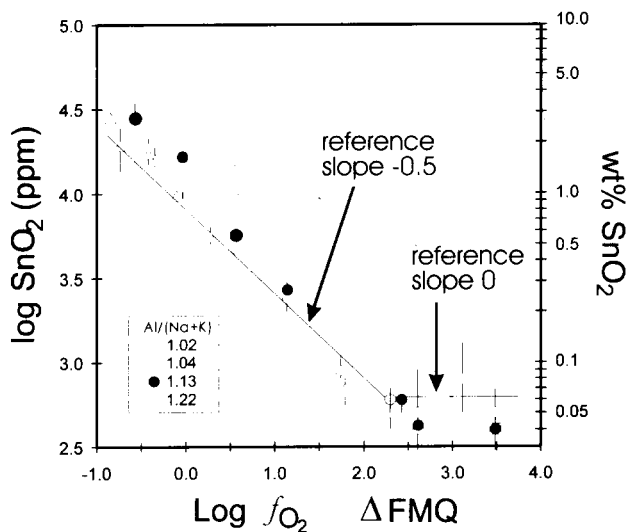
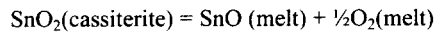


Figure 1. Cassiterite solubility in  $\text{H}_2\text{O}$ -saturated subaluminous to peraluminous granite melts at  $850^\circ\text{C}$  and 2 kbar (after Linnen et al., 1996).

On Figure 1 it is clear that cassiterite solubilities in subaluminous and peraluminous melts at  $\log f_{O_2}$  conditions greater than  $\sim\text{FMQ}+2.5$  are nearly independent of  $f_{O_2}$ . Thus tin is dominantly quadrivalent in the melt. Cassiterite solubilities are also low,  $\sim 700$  ppm  $\text{SnO}_2$ . Note that these experiments were conducted at  $850^\circ\text{C}$  and 2 kbar. Cassiterite solubility will decrease with decreasing temperature. At lower  $\log f_{O_2}$  conditions,  $\log \text{SnO}_2$  solubility increases dramatically, at a slope of roughly  $-0.5$ , to several wt% at  $\text{FMQ}-0.5$ , indicating  $\text{Sn}^{2+}$  is predominant in the melt. As alkalis are added to the melt, cassiterite solubility increases (Figure 2), with up to 10 wt%  $\text{SnO}_2$  required for cassiterite saturation in a peralkaline granite at  $850^\circ\text{C}$  and 2 kbar.

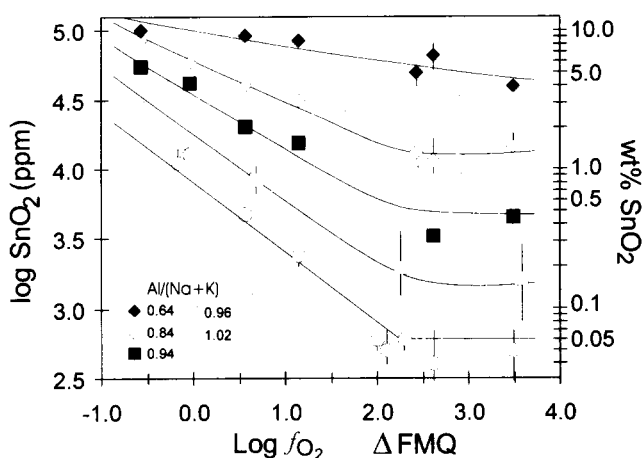


Figure 2. Cassiterite solubility in  $\text{H}_2\text{O}$ -saturated peralkaline to subaluminous granite melts at  $850^\circ\text{C}$  and 2 kbar (after Linnen et al., 1996).

It is also apparent from Figure 2 that the break in slope is progressively less pronounced as the melt becomes increasingly more alkaline. The progressive flattening of the cassiterite solubility curves indicates that at fixed  $f_{O_2}$  conditions, the  $\text{Sn}^{4+}/\text{Sn}^{2+}$  ratio increases with melt alkalinity.

These solubility studies have several important implications. One is that tin can potentially be a petrogenetic indicator of redox changes.  $\text{Sn}^{4+}$  easily substitutes for  $\text{Ti}^{4+}$  in Ti-Fe oxides, whereas  $\text{Sn}^{2+}$  should not. Abrupt changes in  $f_{O_2}$  may therefore be reflected by changes in whole-rock tin abundances. Cassiterite saturation can occur in oxidized subaluminous to peraluminous melts that contain on the order of 700 ppm  $\text{SnO}_2$  at  $850^\circ\text{C}$  and 2 kbar. Solubilities will be even lower at lower temperature (Štemprók, 1990). However, tin deposits are typically associated with reduced peraluminous granites. The fact that these granites are reduced is important. In oxidized granitic melts tin is likely to be compatible or only mildly incompatible. This is because  $\text{Sn}^{4+}$  substitutes for  $\text{Ti}^{4+}$  in particular in magnetite. In reduced granites the modal abundances of oxides are usually much lower compared to oxidized granites. Because tin in the melt has a  $2^+$  valence it will not partition as strongly into these oxides. Therefore tin is more incompatible in reduced peraluminous granitic melts and with fractional crystallization the tin concentration in residual melts will rise. A late-stage oxidation of an evolved melt will thus be an effective crystallization mechanism for magmatic cassiterite in peraluminous granites and pegmatites. By contrast, peralkaline granites and pegmatites require almost an order of magnitude more  $\text{SnO}_2$  for cassiterite saturation. A higher  $\text{Sn}^{4+}/\text{Sn}^{2+}$  ratio in the melts should also lead to a greater depletion of tin caused by crystallization of Ti phases. Consequently, magmatic cassiterite is much less likely in peralkaline systems.

#### Results of Columbite-Tantalite Solubility Experiments

The results of columbite and tantalite solubility experiments in  $\text{H}_2\text{O}$ -saturated Li-F-free haplogranitic melts at  $800^\circ\text{C}$  and 2 kbar are shown in Figures 3 and 4, respectively. Because solubilities are dependent on  $\text{MnO}$  contents, as well as  $\text{Nb}_2\text{O}_5$  and  $\text{Ta}_2\text{O}_5$  contents, the solubilities are reported as molar solubility products, and have units of  $\text{mol}^2/\text{kg}^2$ . Equilibrium was approached by dissolution and crystallization. In addition, in order to test for Henry's law behaviour (does the solubility product remain constant for different abundances of Mn, Nb and Ta), a series of dissolution experiments were conducted where glasses were doped with  $\text{MnO}$ ,  $\text{Nb}_2\text{O}_5$  or  $\text{Ta}_2\text{O}_5$ . The excellent agreement between the different types of experiments implies that equilibrium had been attained, and that the melt activity coefficients of Mn, Nb and Ta are constant, at fixed melt composition, P and T.

A comparison of Figures 3 and 4 shows that the molar solubility products of columbite and tantalite are nearly identical in peralkaline melts. With increasing A.S.I. (note that the A.S.I. is modified to take into account the effects of Mn on melt structure) both solubilities decrease, but not to the same degree; at an A.S.I.  $>1.0$  tantalite is roughly three times more soluble than columbite. If the two solubility products are divided the effect of Mn cancels and the number is proportional to the Nb/Ta activity ratio in the melt. The data thus imply that the activity coefficient of  $\text{Ta}_2\text{O}_5$  in a peraluminous melt is lower than that of  $\text{Nb}_2\text{O}_5$ , and with crystal fractionation the whole-rock Nb/Ta ratio of the residual melt should decrease. Similarly, the Nb/Ta ratio of

a columbite-tantalite crystallization sequence should decrease with fractionation.

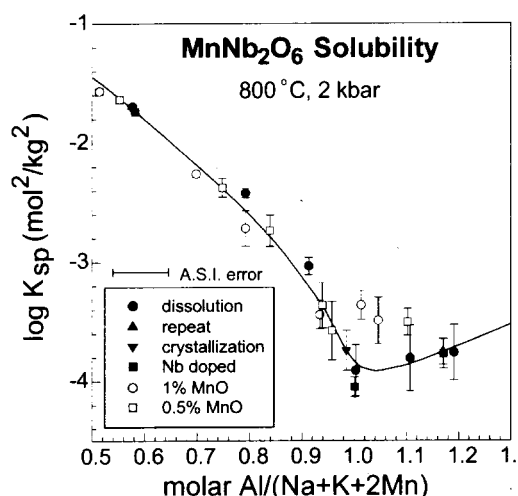


Figure 3. Columbite solubility in  $H_2O$ -saturated peralkaline to peraluminous granite melts at  $800^\circ C$  and 2kbar (after Linnen and Keppler, 1997).

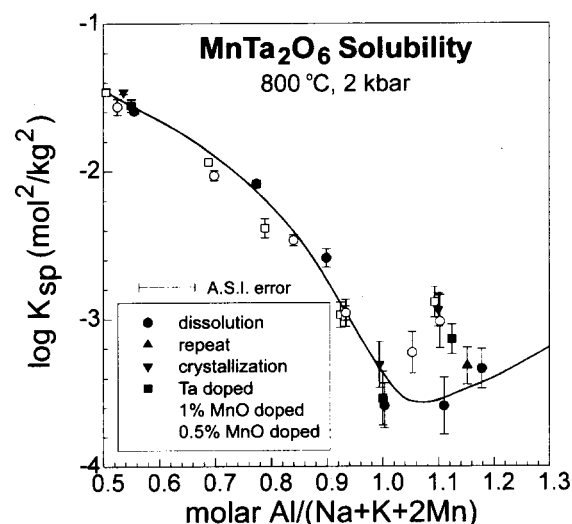


Figure 4. Tantalite solubility in  $H_2O$ -saturated peralkaline to peraluminous granite melts at  $800^\circ C$  and 2kbar (after Linnen and Keppler, 1997).

Additional questions of importance are: How much Nb or Ta are required for melts to be columbite or tantalite saturation, and are these abundances reasonable, i.e., do the experiments support the interpretation that some columbite-tantalite mineralization is magmatic in origin. It is difficult to envision columbite-tantalite saturation in strongly peralkaline granites. Assuming equimolar proportions of MnO (or FeO) and  $Nb_2O_5$  or  $Ta_2O_5$ , several wt%  $Nb_2O_5$  or  $Ta_2O_5$  are required for columbite-tantalite saturation. This is true even if experimental solubility products are extrapolated to lower temperature, e.g.,  $600^\circ C$ . If the solubility

products from subaluminous and peraluminous melts are extrapolated to  $600^\circ C$  and 0.05 wt% MnO, a reasonable value, is used then columbite and tantalite saturation are estimated at 70-100 ppm, or 500-1400 ppm Ta, respectively. While the Nb value is reasonable for a highly evolved granitic liquid, the Ta value is unreasonable high. A likely explanation is that the Fe content of the melt has been ignored. Divalent Fe behaves similarly to Mn and if an MnO+FeO concentration of 0.5 wt% is assumed, the amount of Nb or Ta required for columbite-tantalite saturation is reduced by an order of magnitude. The latter values for Ta are similar to the concentrations observed in glasses or melt inclusions from highly evolved granitic/rhyolitic liquids. However the effects of Li and F on solubility have been ignored. Therefore the effect of Li on columbite-tantalite solubility was determined (Fig. 5), and combined with the previous work by Keppler (1993), who determined the influence of fluorine on columbite-tantalite solubility.

The addition of 2 wt%  $Li_2O$  increases columbite and tantalite solubilities by a factor of ~2-3. Linnen (1998) combined this data with that of Keppler (1993) to predict whether melts, with the compositions of natural glasses and melt inclusions, should be saturated with respect to columbite and tantalite. The calculation was made assuming that FeO could be treated as equivalent to MnO and that the effects of  $Li_2O$  and F are additive. These calculations suggested that at  $600^\circ C$  natural Li-F-rich melt might be saturated with columbite but are not saturated with tantalite. Therefore, a model is proposed where Nb and in particular Ta are retained in melts with high Li-F concentrations. The crystallization of a  $Li\pm F$  phase lowers the columbite and tantalite solubility products and causes their crystallization. This explains why tantalum mineralization is invariably associated with lithium. An alternate, less favoured explanation is that tantalite crystallization occurs at much lower temperatures.

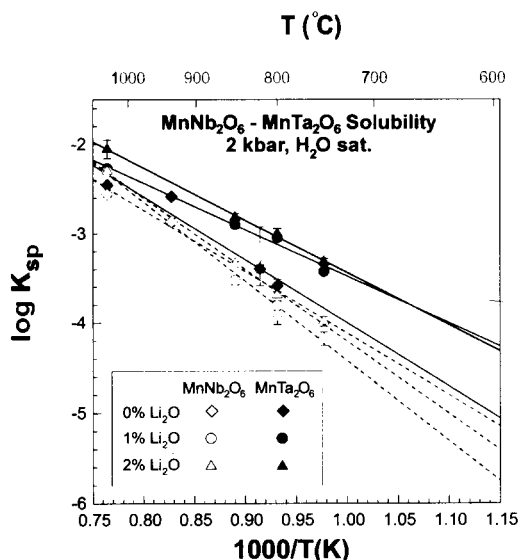


Figure 5. Temperature dependence of columbite and tantalite solubilities in subaluminous (A.S.I.=1.0) granitic melts with different concentrations of  $Li_2O$  (after Linnen, 1998).

## Results of Zircon-Hafnon Solubility Experiments

The results of zircon and hafnon solubility experiments in  $H_2O$ -saturated Li-F-free haplogranitic melts at  $800^\circ C$  and 2 kbar are shown in Figure 5. The solubility of zircon in  $H_2O$ -saturated subaluminous granite melt at  $800^\circ C$  and 2 kbar is  $< 100$  ppm Zr, so, in contrast to tantalum crystallization, there is no problem in attaining high enough concentrations of Zr in the melt for zircon saturation. However, it is questionable as to why there are changes in Zr/Hf ratios in zircons, or during the evolution of a granitic suite. Experiments were conducted at  $1035^\circ C$  in order to be able to use an electron microprobe to determine Zr concentrations in glasses. The results are remarkably similar to the columbite-tantalite study. Zircon and hafnon solubilities range from several wt%  $ZrO_2$  and  $HfO_2$  in the peralkaline liquids to several thousand ppm in the subaluminous and peraluminous liquids. Like columbite-tantalite, the division of the molar solubilities is proportional to the melt activity coefficient ratio. This division is shown by Figure 6. The interpretation of this diagram is thus also similar: with crystal fractionation the whole-rock Zr/Hf ratio of the residual melt should decrease. Similarly, the Zr/Hf ratio of a zircon-hafnon crystallization sequence should decrease with fractionation. These results indicate that the elevated Hf contents in highly evolved granites and pegmatites is thus a consequence of fractionation, and it is not necessary to invoke fluid metasomatism.

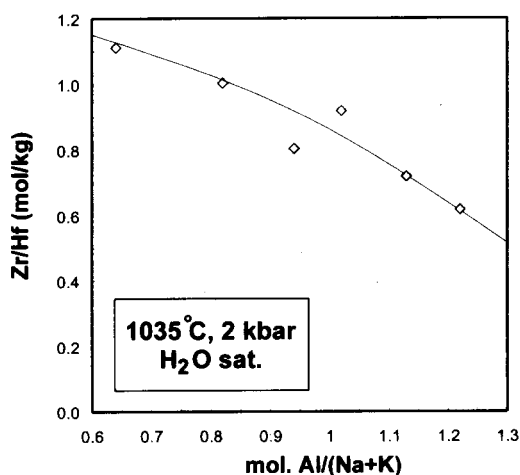


Figure 6 Molar ratio of zircon to hafnon solubility in  $H_2O$ -saturated peralkaline to peraluminous granite melt at  $1035^\circ C$  and 2 kbar.

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