*American Mineralogist, Volume 95, pages 537–544, 2010*

# Solubility of manganotantalite and manganocolumbite in pegmatitic melts

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## Abstract

Solubility experiments of $MnNb_2O_6$ and $MnTa_2O_6$ were conducted in two nominally dry to water-saturated pegmatitic melts with different amounts of Li, F, P, and B at 700 to 1000 °C and 200 MPa to determine the maximum concentrations of Nb and Ta in pegmatitic melts. The $Li_2O$, F, $B_2O_3$, and $P_2O_5$ contents in the melts were 1.16, 2.99, 1.78, and 1.55 wt% for melt composition PEG1 and 1.68, 5.46, 2.75, and 2.75 wt% for melt composition PEG2 and the resulting Al/(Na+K+Li) ratio for both melts is 0.92. The experimental data show that the solubility product of manganocolumbite increases by a factor of three upon increasing the water concentration from 0 to 4 wt%. Considering that pegmatitic melts at pressures above 50 to 100 MPa are hydrous (>4 wt% $H_2O$), the increase in solubility by this magnitude, over the stated range of water concentration, is not significant for pegmatites. The data also point out that the solubility of $MnNb_2O_6$ and $MnTa_2O_6$ is strongly temperature dependent, increasing by a factor of 50 for manganocolumbite and 15–20 for manganotantalite from 700 to 1000 °C under water-saturated conditions. The solubility also increases with increasing content of fluxing elements like Li, F, B, and P. In the pegmatite melt containing the highest amount of fluxing elements, the maximum concentrations of Ta and Nb are higher by nearly one order of magnitude when compared to a subaluminous rhyolitic melt.

**Keywords:** Pegmatitic melt, volatiles, solubility, columbite, tantalite

## Introduction

Niobium (Nb) and especially tantalum (Ta) are both key metals in high-technology industrial processes. Most of the world's tantalum is mined from rare-element pegmatites containing minerals from the columbite-tantalite group [$(Mn,Fe)(Nb,Ta)_2O_6$] or wodginite ($MnSnTa_2O_8$) (Fetherston 2004). Important parameters that still need to be constrained to understand Ta and Nb mineralization are the solubility of Ta and Nb oxides and their temperature of crystallization. Considering that columbite-tantalite is the most abundant group of Ta-Nb minerals, Linnen and Keppler (1997) and Linnen (1998) conducted high-pressure experiments in the temperature range 750–1035 °C to determine the solubility of the end-members manganotantalite ($MnTa_2O_6$) and manganocolumbite ($MnNb_2O_6$) in silicate melts. The results are extremely useful to constrain the possible amounts of Nb and Ta, which can be incorporated in Fe-free silicate melts. Linnen and Keppler (1997) demonstrated that peraluminous melts at 600 °C can contain up to 100 and 1400 ppm Nb and Ta, respectively. They showed that the solubility products of $MnTa_2O_6$ and $MnNb_2O_6$ are nearly identical in hydrous peralkaline melts, but that the solubility products of $MnNb_2O_6$ are smaller than those of $MnTa_2O_6$ in water-saturated metaluminous and peraluminous melts. Experiments on natural columbite-tantalite minerals in granitic melts were conducted by Borodulin et al. (2006). Their observations confirm the results from Linnen and Keppler (1997) in terms of the dependence of the solubility products on melt composition, temperature, and pressure. Keppler (1993) and Linnen (1998) also explored the individual effects of F and Li on the solubility of manganotantalite and manganocolumbite in a haplogranitic melt. To our knowledge, the solubility of columbite-tantalite has not been investigated in pegmatitic liquids that often contain high amounts of elements such as F, Li, B, and P, except for one abstract from Linnen (2006) who reports a $K_{sp}^{MnTa}$ value of $7.7 \times 10^{-3}$ $mol^2/kg^2$ for a melt with 4.4 wt% F, 2.25 wt% $B_2O_3$, 1.0 wt% $Li_2O$, and 1.7 wt% $P_2O_5$ at 800 °C and 200 MPa. Furthermore, pegmatitic melts are stable at very low temperatures and there are no solubility data below 750 °C. Considering that columbite-tantalite crystallize mainly from such volatile and fluxing element-rich systems, this study was conducted to provide experimental data on the influence of water and temperature on the solubility of manganocolumbite and manganotantalite in pegmatitic melts containing high amounts of Li, F, P, and B.

## Experimental methods

### Starting material

The solubility experiments have been conducted following the method described in detail by Linnen and Keppler (1997). Synthetic manganocolumbite or manganotantalite were equilibrated with a synthetic pegmatitic melt at different temperatures. Mn-Nb and Mn-Ta end-members were selected because significant $Mn^{3+}$ occurs only at very high $f_{O_2}$ (Kohn et al. 1990) and thus $f_{O_2}$ does not need to be carefully controlled. The oxygen fugacity in the used high-pressure autoclaves are about NNO (Ni-NiO) for cold-seal pressure vessels and MQF+4 (magnetite, quartz, fayalite) for internally heated pressure vessels (Berndt et al. 2005).

Crystals of $MnNb_2O_6$ and $MnTa_2O_6$ were synthesized hydrothermally by sealing 500 mg of a stoichiometric oxide mixture plus 50 mg of 5% HF solution in a noble metal capsule (length 40 mm, i.d. 4 mm, o.d. 4.4 mm). Synthesis conditions for $MnNb_2O_6$ were: 800 °C, 2 kbar, 10 days. The crystals are 5–100 μm in size and internally homogeneous (Fig. 1, top).

The experiments at such conditions were not successful for synthesizing large

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crystals of $MnTa_2O_6$. However, a synthesis at 1250 °C, 2 kbar, and 3 days yielded crystals with a size of 5–100 µm. The average Mn/Nb and Mn/Ta molar ratios (analyzed by electron microprobe) are 0.48 ± 0.02 and 0.49 ± 0.01, respectively, as expected for manganocolumbite or manganotantalite.

Two different pegmatitic starting glasses (PEG1 and PEG2) were prepared from a mixture of $SiO_2$, $Al_2O_3$, $Na_2CO_3$, $K_2CO_3$, $AlF_3$, $Li_2CO_3$, $(NH_4)H_2PO_4$, and $H_3BO_3$. The mixture for PEG1 was heated at 1200 °C in a furnace at 1 atm for 30 min. The quenched products contained mainly glass and some quartz. This material was ground and heated again at 1400 °C for 40 min to produce a pure glass. The mixture for PEG2 was heated at 1400 °C in a furnace at 1 atm for 40 min. Quartz was not detected in the run product and a second heating was not necessary. The major element compositions of the glasses were analyzed by electron microprobe. The lithium concentration was determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Additionally, Al-, Na-, and K-contents were measured for PEG2 with this method to check the analytical data obtained with the microprobe data set (Table 1). Boron and fluorine concentrations were analyzed commercially (Actlabs, Canada). The glass compositions PEG1 and PEG2 are given in Table 1. The molar ratios Al/(Na+K+Li) ($A.S.I._{Li}$) are 0.92. The Li-free ratios Al/(Na+K) (A.S.I.) are 1.13 and 1.26.

## Sample preparation

The synthesized glasses PEG1 and PEG2 were crushed and homogenized by grinding in an agate mortar. Approximately 30 mg of the glass powder and 3 mg of either $MnNb_2O_6$ or $MnTa_2O_6$ crystals were gently mixed, then loaded into Au or Au-Pd capsules (length 10 mm, i.d. 4 mm, o.d. 4.4 mm) with different amounts of water. The capsules were welded shut and checked for weight loss. They were placed in a drying oven at 110 °C, and then checked for weight loss again. For each glass composition 16 capsules were prepared, 8 with manganotantalite crystals and 8 with manganocolumbite crystals. The amount of added water was 0, 5, and 10 wt% $H_2O$ and the experimental conditions varied from water saturated to nearly dry (note that some water is always adsorbed on the surface of the glass powder). Indications for water saturation are the measured water concentrations (Table 2), which are always lower than the added amount of water by ~10 wt%.

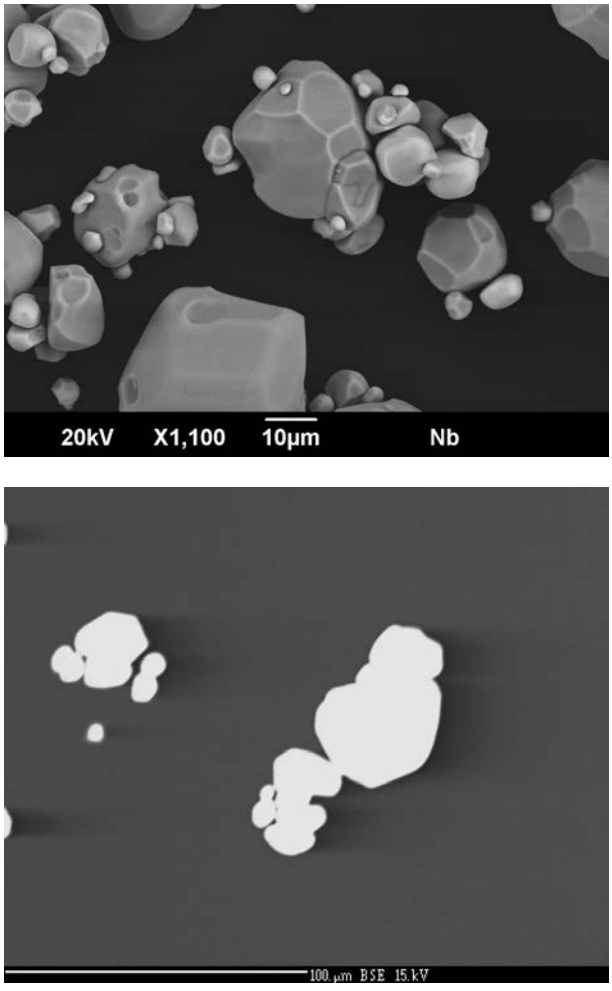



**Figure 1.** SEM image of manganocolumbite crystals used as starting materials (**top**) and BSE image of the run products using the example of experiment Ta15 (**bottom**).

## High-pressure equipment and experiments

Experiments were conducted in the range 700–1000 °C at 200 MPa. The experiments up to 800 °C were conducted in cold-seal pressure vessels (CSPV) with water as the pressure medium. For higher temperatures, internally heated pressure vessels (IHPV) with Ar as pressure medium were used. Temperatures were measured by using Ni-CrNi and $Pt\text{-}Pt_{90}Rh_{10}$ thermocouples, respectively. Quenching in both types of autoclaves was close to isobaric. In the CSPV, quenching was performed by removing the pressure vessel out of the furnace and using a compressed air flux around the vessel. The IHPV are equipped with a rapid quench design (Berndt et al. 2002) and quench rates are 150 to 200 °C/s. All capsules were weighted after the experiments to ensure that no leaks occurred during the experiments.

## Analytical methods

The compositions of the starting materials (PEG1, PEG2, and the synthesized crystals) as well as the compositions of the experimental products were determined using a Cameca SX-100 electron microprobe. A 15 keV accelerating voltage, 15 nA beam current, and a focused beam were used for measuring the composition of the synthetic crystals. The standards were $MnTiO_3$, Nb, and Ta and counting times ranged from 10 s (Mn) to 30 s (Nb, Ta). The starting glasses were measured using a 15 keV accelerating voltage, 4 nA beam current, and a beam diameter of 20 µm. The counting time ranged from 4 to 20 s. The respective standards were albite (Na), wollastonite (Si), corundum (Al), orthoclase (K), and apatite (P).

The concentrations of Mn, Nb, and Ta in the experimental products were determined using a 15 keV accelerating voltage, 10 nA beam current, a beam diameter of 20 µm, and with the PAP matrix correction (Pouchou and Pichoir 1991). For Nb and Ta, two spectrometers were used simultaneously to acquire a better counting statistic. The counting time for both elements was 120 s.

At least one concentration profile was measured for each experimental product. At least six analyses were collected for each glass sample when the distribution of

**Table 1.** Analyses of the starting glasses PEG1 and PEG2

| Oxides | PEG1 (wt%) | PEG2 (wt%) |
|---|---|---|
| $SiO_2$ | 61.90 (0.34)* | 59.73 (0.13)* |
| $Al_2O_3$ | 20.05 (0.39)* | 19.56 (0.07)* |
| | | 19.75 (0.13)‡ |
| $Na_2O$ | 7.88 (0.45)* | 6.81 (0.15)* |
| | | 7.25 (0.10)‡ |
| $K_2O$ | 4.40 (0.07)* | 4.01 (0.17)* |
| | | 3.82 (0.02)‡ |
| F | 2.99 (0.01)† | 5.46 (0.01)† |
| $P_2O_5$ | 1.55 (0.21)* | 2.46 (0.21)* |
| $Li_2O$ | 1.162 (0.05)‡ | 1.68 (0.01)‡ |
| $B_2O_3$* | 1.78 (0.01)† | 2.75 (0.01)† |
| 2F=O | –1.23 | –2.30 |
| Total | 100.48 | 100.16 |

*Notes:* 1σ standard deviation is given in parentheses.
* The microprobe data are means of 10 measurements.
† Measured by Actlabs, Canada.
‡ Measured by ICP-OES analysis.

**Table 2.** Water solubility in pegmatitic melts (PEG1 and PEG2) at different temperatures

| *T* (°C) | PEG1 exp. | PEG1 $H_2O$ (wt%) | PEG2 exp. | PEG2 $H_2O$ (wt%) |
|---|---|---|---|---|
| 700 | Ta5 | 7.80 (0.06) | Nb13 | 8.18 (0.08) |
| 800 | Ta3 | 8.80 (0.07) | Ta11 | 9.06 (0.08) |
| 800 | Ta4 | 8.71 (0.05) | Ta12 | 10.03 (0.08) |
| 800 | Nb3 | 8.55 (0.06) | | |
| 800 | Nb4 | 8.58 (0.05) | Nb12 | 9.44 (0.07) |
| 1000 | Ta8 | 7.38 (0.05) | Ta16 | 8.54 (0.08) |
| 1000 | Nb7 | 7.21 (0.05) | Nb16 | 8.39 (0.06) |

Ta and Nb was homogeneous. In all measurements, the detection limits were 0.21 wt% for Na, 0.16 wt% for Si, 0.1 wt% for Al, 0.07 wt% for K, 0.04 wt% for Mn, 0.31 wt% for P, 0.05 wt% for Nb, and 0.15 wt% for Ta. The standard deviations of the Mn, Nb, and Ta concentrations are given in Table 3.

The Li-content in the starting glasses, as well as Al-, Na-, and K-contents in PEG2, were measured by inductively coupled plasma optical spectroscopy (ICP-OES) using a 1.2 kW plasma power, 15 L/min plasma flow, 1.5 L/min auxiliary flow, and 0.9 L/min nebulizer flow. The emission lines used were 236.705, 237.312, and 394.401 for Al; 766.491 and 769.897 for K; 323.263, 460.289, 610.365, and 670.783 for Li; and 330.237, 568.821, and 589.592 for Na. The uncertainties of the analyses were determined to be ±1σ. The standard deviations were ±0.13 wt% for Al, ±0.02 wt% for K, ±0.01 and ±0.05 wt% for Li and ±0.10 wt% for Na. Fluorine and B were analyzed commercially by Actlabs/Canada using ion selective electrode (ISE) for F and Promp Gamma Activation Analysis (PGNAA) for B.

The water contents of the quenched glasses were determined using "Karl-Fischer-Titration" (described by Behrens 1995) using glass chips of 15–20 mg. The maximal error is ±0.2 wt% $H_2O$. However, these water concentrations should be considered as rough estimations considering that most run products contain some residual crystals (leading to an underestimation of the water content) as well as small amounts of bubbles (leading to an overestimation of the water content).

## Results

All experimental products contained glass and crystals of either manganocolumbite or manganotantalite (Fig. 1, bottom). The experimental conditions and the MnO, $Ta_2O_5$, $Nb_2O_5$, and $H_2O$ concentrations of the glasses are given in Table 3.

The concentrations of MnO, $Nb_2O_5$, and $Ta_2O_5$ in glasses measured along diffusion profiles starting from the mineral interface are homogeneous (see standard deviations in Table 3), except for the experiment Ta6, performed at nearly dry conditions. In this experimental product, $Ta_2O_5$ concentrations decrease with increasing distance from the $MnTa_2O_6$ mineral/melt interface (Fig. 2), whereas the MnO concentrations are nearly constant. Therefore, the analytical data of this experiment is not used for the interpretations given below.

For most experiments, the molar Mn/Nb and Mn/Ta ratios are close or equal to the stoichiometric values of manganocolumbite and manganotantalite (average value is 0.51 for Mn/Nb and 0.5 for Mn/Ta; the problematic experiments are Nb14 and Ta14 conducted under nearly dry conditions). This indicates a stoichiometric dissolution of the crystals in the melt and the following dissolution reaction of manganocolumbite or manganotantalite can be written

$$MnNb_2O_6^{crystal} = MnO^{melt} + Nb_2O_5^{melt}$$
$$MnTa_2O_6^{crystal} = MnO^{melt} + Ta_2O_5^{melt}.$$

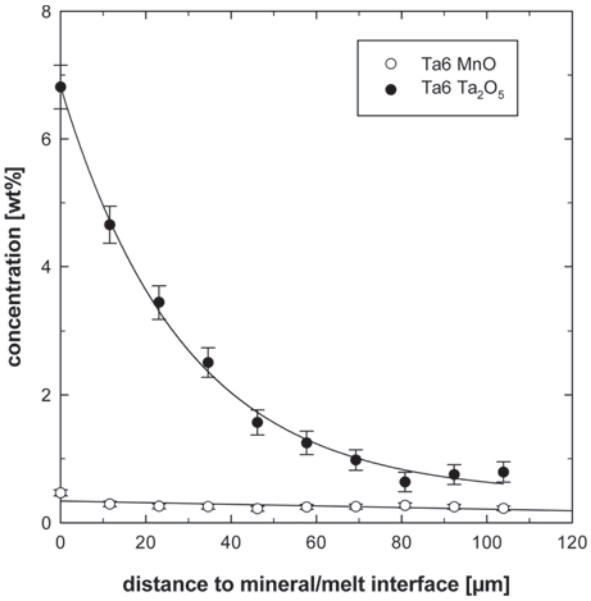
Therefore, the experimental results can also be expressed by the solubility products $K_{sp}^{MnNb}$ and $K_{sp}^{MnTa}$ (Table 3)

$$K_{sp}^{MnNb}\ \frac{mol^2}{kg^2} = X(MnO)\frac{mol}{kg} \cdot X(Nb_2O_5)\frac{mol}{kg}$$

**Table 3.** Experimental results of $MnNb_2O_6$ and $MnTa_2O_6$ dissolution experiments in PEG1 and PEG2

| PEG1 | $H_2O$* (wt%) | $T$ (°C) | $P$ (bar) | Time (days) | MnO† (wt%) | $Nb_2O_5$† (wt%) | $K_{sp} \times 10^{-4}$ ($mol^2/kg^2$) | log $K_{sp}$‡ ($mol^2/kg^2$) | Mn/Nb§ |
|---|---|---|---|---|---|---|---|---|---|
| Nb1 | 4.72 (0.05) | 800 | 2000 | 4 | 0.19 (0.01) | 0.63 (0.02) | 6.22 | –3.21 (0.04) | 0.55 |
| Nb2 | 4.67 (0.04) | 800 | 2000 | 8 | 0.18 (0.01) | 0.61 (0.03) | 5.90 | –3.23 (0.07) | 0.56 |
| Nb3 | 8.55 (0.06) | 800 | 2000 | 4 | 0.21 (0.01) | 0.65 (0.02) | 7.06 | –3.15 (0.03) | 0.60 |
| Nb4 | 8.58 (0.05) | 800 | 2000 | 8 | 0.19 (0.01) | 0.64 (0.02) | 6.39 | –3.19 (0.05) | 0.56 |
| Nb5 | n.a. | 1000 | 2045 | 3 | 0.34 (0.02) | 1.67 (0.18) | 30.36 | –2.52 (0.08) | 0.38 |
| Nb6 | 4.60 (0.05) | 1000 | 2045 | 3 | 0.62 (0.01) | 2.44 (0.03) | 80.80 | –2.09 (0.02) | 0.48 |
| Nb7 | 7.21 (0.05) | 1000 | 2045 | 3 | 0.66 (0.01) | 2.65 (0.04) | 92.53 | –2.03 (0.01) | 0.47 |
| PEG1 | | | | | | $Ta_2O_5$† | | | Mn/Ta§ |
| Ta1 | 4.21 (0.05) | 800 | 2000 | 4 | 0.28 (0.02) | 1.86 (0.21) | 16.84 | –2.77 (0.08) | 0.47 |
| Ta2 | 4.84 (0.05) | 800 | 2000 | 8 | 0.31 (0.02) | 1.92 (0.22) | 18.88 | –2.72 (0.07) | 0.50 |
| Ta3 | 8.80 (0.07) | 800 | 2000 | 4 | 0.27 (0.02) | 1.74 (0.09) | 14.87 | –2.83 (0.06) | 0.48 |
| Ta4 | 8.71 (0.05) | 800 | 2000 | 8 | 0.28 (0.01) | 1.74 (0.11) | 15.49 | –2.81 (0.05) | 0.50 |
| Ta5 | 7.80 (0.06) | 700 | 2000 | 11 | 0.16 (0.01) | 0.94 (0.08) | 4.89 | –3.31 (0.07) | 0.54 |
| Ta6 | n.a. | 1000 | 2000 | 3 | | | | | |
| Ta7 | 4.49 (0.04) | 1000 | 2000 | 3 | 0.70 (0.03) | 4.75 (0.11) | 106.73 | –1.97 (0.03) | 0.46 |
| Ta8 | 7.38 (0.05) | 1000 | 2000 | 3 | 0.61 (0.01) | 4.04 (0.36) | 78.97 | –2.10 (0.06) | 0.47 |
| PEG2 | | | | | | $Nb_2O_5$† | | | Mn/Nb§ |
| Nb9 | 5.14 (0.09) | 800 | 2000 | 4 | 0.22 (0.03) | 0.80 (0.02) | 9.56 | –3.02 (0.06) | 0.52 |
| Nb10 | 6.86 (0.09) | 800 | 2000 | 8 | 0.21 (0.02) | 0.79 (0.02) | 8.80 | –3.06 (0.06) | 0.49 |
| Nb11 | n.d. | 800 | 2000 | 4 | 0.23 (0.02) | 0.81 (0.02) | 10.04 | –3.00 (0.05) | 0.54 |
| Nb12 | 9.44 (0.07) | 800 | 2000 | 8 | 0.22 (0.02) | 0.78 (0.03) | 9.11 | –3.04 (0.06) | 0.52 |
| Nb13 | 8.18 (0.08) | 700 | 2000 | 11 | 0.12 (0.01) | 0.38 (0.03) | 2.34 | –3.63 (0.08) | 0.56 |
| Nb14 | n.a. | 1000 | 2039 | 3 | 0.43 (0.01) | 2.87 (0.26) | 65.58 | –2.18 (0.05) | 0.28 |
| Nb15 | 4.87 (0.06) | 1000 | 2039 | 3 | 0.76 (0.04) | 3.02 (0.07) | 121.08 | –1.92 (0.03) | 0.47 |
| Nb16 | 8.39 (0.06) | 1000 | 2039 | 3 | 0.68 (0.07) | 3.10 (0.11) | 111.82 | –1.95 (0.06) | 0.41 |
| PEG2 | | | | | | $Ta_2O_5$† | | | Mn/Ta§ |
| Ta9 | 4.83 (0.10) | 800 | 2000 | 4 | 0.32 (0.02) | 2.21 (0.06) | 22.80 | –2.64 (0.04) | 0.45 |
| Ta10 | 4.80 (0.06) | 800 | 2000 | 8 | 0.36 (0.01) | 2.37 (0.07) | 27.19 | –2.57 (0.02) | 0.47 |
| Ta11 | 9.06 (0.08) | 800 | 2000 | 4 | 0.29 (0.01) | 1.90 (0.08) | 17.32 | –2.76 (0.03) | 0.47 |
| Ta12 | 10.03 (0.08) | 800 | 2000 | 8 | 0.32 (0.02) | 1.80 (0.06) | 18.42 | –2.73 (0.04) | 0.56 |
| Ta13 | n.d. | 700 | 2000 | 11 | 0.16 (0.02) | 1.09 (0.04) | 5.73 | –3.24 (0.06) | 0.47 |
| Ta14 | n.a. | 1000 | 2000 | 3 | 0.62 (0.02) | 6.06 (0.51) | 119.07 | –1.92 (0.05) | 0.32 |
| Ta15 | 4.97 (0.05) | 1000 | 2000 | 3 | 0.84 (0.02) | 5.72 (0.06) | 153.70 | –1.81 (0.02) | 0.46 |
| Ta16 | 8.54 (0.08) | 1000 | 2000 | 3 | 0.76 (0.02) | 5.07 (0.16) | 122.41 | –1.91 (0.03) | 0.46 |

*Notes:* n.d. = not determined. n.a. = no water added.
* $H_2O$-content measured by KFT.
† Means of at least 6 measurements.
‡ $K_{sp}$ solubility product.
§ Mn/Nb molar ratio.



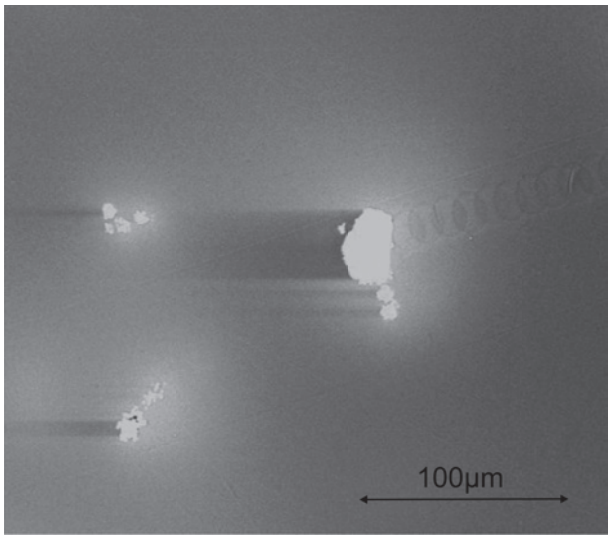




**FIGURE 2.** BSE image (**right**) and concentration profiles of MnO and $Ta_2O_5$ in wt% (**left**) from experiment Ta6.

$$K_{sp}^{MnTa}\ \frac{mol^2}{kg^2} = X(MnO)\frac{mol}{kg} \cdot X(Ta_2O_5)\frac{mol}{kg}$$

where the superscript $X(\cdots)$ represents the molar concentrations of MnO, $Nb_2O_5$, and $Ta_2O_5$, respectively. The error on the solubility products given in Table 3 has been calculated taking into account the standard deviation of the MnO, $Ta_2O_5$, and $Nb_2O_5$ concentrations. The experiments at 800 °C were conducted at the same $P$-$T$-$X_{H_2O}$ conditions for different run durations (4 and 8 days, Table 3). The calculated $K_{sp}$ from these experiments are indistinguishable within the stated uncertainties. Nevertheless, the data obtained after 8 days were used to calculate the solubility products in the following discussion, considering that equilibrium is better approached in products from experiments with long run duration.

In the experiments Nb14 and Ta14 conducted under nearly dry conditions, the dissolution mechanism may have differed from the equation given above because the Mn/Nb ratio is significantly lower than that of manganocolumbite and manganotantalite, respectively. This could be due to the formation of an undetected new crystalline phase (incongruent dissolution). Therefore, the analytical data of these experiments might be critical.

### Temperature dependence

Figure 3 shows the temperature dependence of $K_{sp}^{MnNb}$ and $K_{sp}^{MnTa}$ in the water-saturated pegmatitic melt PEG1 with A.S.I.$_{Li}$ 0.92 and a total content of Li, F, P, and B of 4.55 wt% as well as in the water-saturated pegmatitic melt PEG2 with A.S.I.$_{Li}$ 0.92 and a total content of Li, F, P, and B of 7.83 wt%. The logarithmic value of the solubility products of manganocolumbite and manganotantalite both show a linear relationship with $1/T$. The solubility product for manganotantalite increases by a factor of 15 to 25 ($4.9 \times 10^{-4}$ to $79.0 \times 10^{-4}$ mol$^2$/kg$^2$ in PEG1 and $5.7 \times 10^{-4}$ to $122.4 \times 10^{-4}$ mol$^2$/kg$^2$ in PEG2) from 700 to 1000 °C and the solubility product of manganocolumbite increases by a factor of roughly 50 ($2.3 \times 10^{-4}$ to $112 \times 10^{-4}$ mol$^2$/kg$^2$ in PEG2) over the same temperature range. The slopes of the interpolated linear trends for manganotantalite are nearly identical for PEG1 and PEG2 within the error and are about –5.2 for manganotantalite and about –7.5 for manganocolumbite. Thus, the effect of temperature on the solubility of manganocolumbite and manganotantalite in PEG1 and PEG2 is similar, but the solubility products are higher in PEG2 (with the highest concentrations

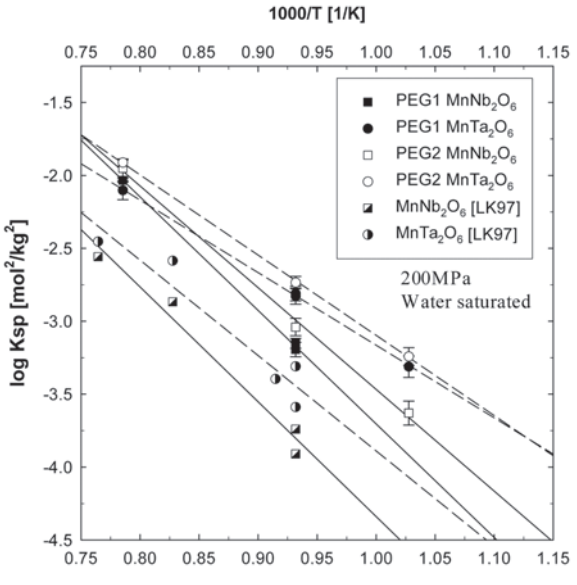



**FIGURE 3.** The effect of temperature on manganocolumbite and manganotantalite solubility in water-saturated pegmatitic (PEG1 and PEG2) and granitic melts at 200 MPa. Data for granitic melts [LK97] from Linnen and Keppler (1997).

of Li, F, P, and B) by a factor of 1.5 for manganotantalite and manganocolumbite, respectively.

### Dependence on water content

The data set from the experiments conducted at 1000 °C is used to show the dependence of $K_{sp}^{MnNb}$ and $K_{sp}^{MnTa}$ on the water content of the melt (Fig. 4). The solubility products of manganocolumbite and manganotantalite both increase with increasing water content in the melt. However, a significant influence of water is only detectable for $K_{sp}^{MnNb}$ between nominally dry glasses and glasses containing 4 wt% $H_2O$ with an increase by a factor of 3 ($30 \times 10^{-4}$ to $93 \times 10^{-4}$ mol$^2$/kg$^2$) for PEG1. For $K_{sp}^{MnTa}$, the values are nearly identical within the calculated uncertainty. Furthermore, it can be noted that the influence of water is more pronounced for PEG1 than for PEG2 in the range 0–4 wt% $H_2O$ in the melt. As already mentioned above, the data set in Figure 4 confirms the higher solubility products of PEG2 compared with PEG1.

## Discussion

### Attainment of equilibrium and diffusivity of Nb and Ta

Two main observations are required to demonstrate equilibrium conditions in our experiments. First, the experimental duration must be long enough to allow complete diffusion of the elements comprising manganocolumbite and manganotantalite throughout the melt. Except for experiment Ta6, a homogeneous distribution of Mn, Ta, and Nb was observed in all glasses. In addition, the experiments at 800 °C were conducted at the same $P$-$T$-$X_{H_2O}$ conditions for different run durations (4 and 8 days, Table 3) and the calculated solubility products are identical within error. Experiment Ta6 was conducted at nominally dry conditions and the diffusivity of cations is significantly lower in such melts compared to hydrous melts (Koepke and Behrens 2001). Second, the calculation of the solubility products is only valid if manganocolumbite and manganotantalite are stable phases at the investigated conditions. This can be tested by the molar Mn/Nb and Mn/Ta ratios in the melts. The ratios are close or equal to those in manganocolumbite and manganotantalite (taking the uncertainty into account) in most experiments, which is evidence for equilibrium between melt and these solid phases. However, the analysis of the products of experiments Nb14 and Ta14 clearly indicates that the dissolution reaction formulated above is not valid. The low non-stoichiometric Mn/Nb ratio suggests either that a Mn-bearing phase may have crystallized in the charge or that Mn diffusivity is faster than the dissolution rate of the manganocolumbite crystal (Zhang et al. 1989). Since no additional phase was identified in the products, the second hypothesis is preferred.

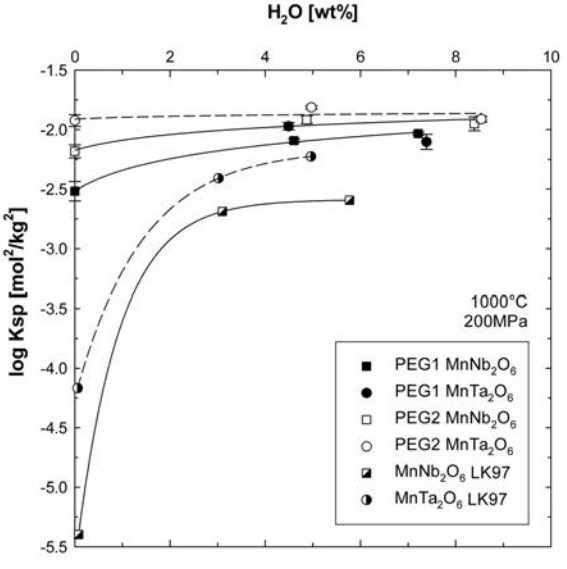



**Figure 4.** The effect of water content on manganocolumbite and manganotantalite solubility in pegmatitic (PEG1 and PEG2) and granitic melts at 1000 °C and 200 MPa. Data for granitic melts [LK97] from Linnen and Keppler (1997). These experiments were conducted at 1035 °C.

It is interesting to note that comparison of experiments Ta6 and Nb5, both conducted for the same duration at 1000 °C, indicate that the diffusivity of Ta is lower than that of Nb in the pegmatite melt (homogeneous distribution of Nb in experiment Nb5; heterogeneous distribution of Ta in experiment Ta6; Fig. 2). The diffusivity of high field strength elements is expected to decrease with increasing charge (Jambon 1982). Koepke and Behrens (2001) investigated the diffusivity of Nb, Zr, and Hf in andesitic melts and also noted that this rule was not confirmed for Nb (slightly higher diffusivity of Nb compared to Zr and Hf). A possible explanation could be the formation of $Nb^{5+}$ as well as $Nb^{3+}$ due to slight differences in electronegativity when compared to Ta. This would explain a different geochemical behavior (Wolff 1984). However, we are not aware of any spectroscopic data of this element that supports the presence of $Nb^{3+}$ (Piilonen et al. 2006).

Comparison of experiments Ta6 and Ta14 conducted with compositions PEG1 and PEG2 also confirms the effect of fluxing elements on the diffusivity of high field strength elements described by London (1987). In experiment Ta6, a significant decrease of the $Ta_2O_5$ concentrations with increasing distance to the mineral-melt interface could be observed, whereas experiment Ta14 shows a nearly constant distribution of $Ta_2O_5$ in the melt that indicates a higher diffusivity of Ta in composition PEG2 with the highest amount of Li, F, P, and B. Nevertheless, the high standard deviation also indicates that in this experiment the distribution might be affected by the diffusivity of Ta. This observation shows that the diffusivities of high field strength elements in pegmatite melts are needed to constrain the conditions at which crystallization of Ta- and Nb-bearing minerals may occur according to the "boundary layers model" described by London (2005).

### Dependence of the solubility of $MnNb_2O_6$ and $MnTa_2O_6$ on the concentrations of fluxing elements

Figure 5 shows the evolution of the solubility product of manganocolumbite and manganotantalite as a function of the total concentration of Li, F, P, and B in the melt at 800 °C, 200 MPa, and water-saturated conditions. As described above, the solubility of manganocolumbite and manganotantalite is clearly influenced by the concentration of Li, F, P, and B in the melt and

increases with increasing contents of these elements, at least in the temperature range 800–1000 °C (Fig. 3). It has to be noted that data used for a composition free of Li, F, P, and B (data shown in Figs. 3 and 5) were determined for a haplogranite composition investigated by Linnen and Keppler (1997). This composition [Al/(Na+K) = 1] does not have the same proportions of Na, K, Al, and Si as the PEG1 [Al/(Na+K) = 1.13; Al/(Na+K+Li) = 0.92] or PEG2 [Al/(Na+K) = 1.26; Al/(Na+K+Li) = 0.92] compositions and, assuming that Li has at least the same effect as K or Na, the solubility product of a Li-, F-, P-, and B-free PEG composition should be slightly higher (Linnen and Keppler 1997). However, the comparison of haplogranitic melts with different amounts of Li and a constant A.S.I. shows that Li apparently has a larger effect on manganocolumbite and manganotantalite solubility than Na or K (Linnen 1998). Structural explanations for the increase in solubility of manganocolumbite and manganotantalite in Li- and F-bearing melts are given by Keppler (1993) and Linnen (1998). The experiments conducted by Linnen (1998) showed that the effects of Li and F can be considered to be additive (Linnen 1998). However, our data set does not allow us to discuss whether the same observation can be expected for B and P. Assuming that effects of Li and F are additive in our compositions and that the difference in major element concentration between the compositions PEG1 and PEG2 and that investigated by Linnen (1998) does not affect significantly the solubility products, it can be noted that B and P should also lead to an increase of the solubility product. On the basis of the available data, this increase is expected to be moderate. For example, Linnen (1998) determined a solubility product $K_{sp}^{MnTa}$ of 15.0 (±1) × $10^{-4}$ $mol^2/kg^2$ for a composition containing 2 wt% $Li_2O$ and 4.75 wt% F at 800 °C and 200 MPa.

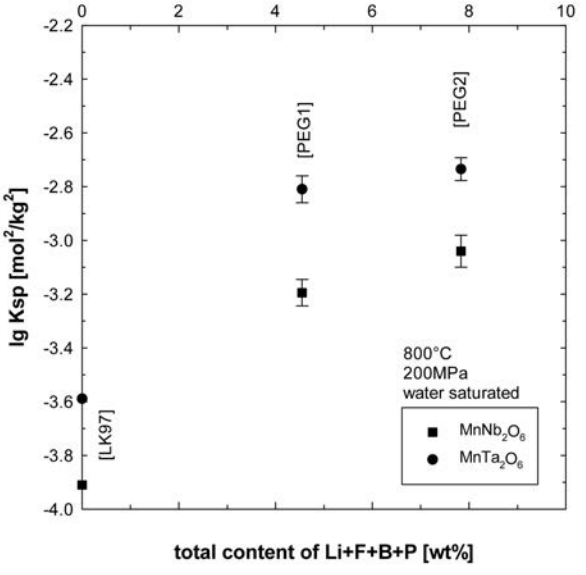



**FIGURE 5.** The effect of volatiles except of water on manganocolumbite and manganotantalite solubility at 800 °C, 200 MPa, and water-saturated conditions. [LK97] data for a melt free of Li, F, B, and F from Linen and Keppler (1997).

At the same conditions, $K_{sp}^{MnTa}$ in composition PEG2 containing 1.68 wt% $Li_2O$ and 4.64 wt% F was found to be in the range of 18.4 (±1.8) × $10^{-4}$ $mol^2/kg^2$. Wolf and London (1993) suggested that phosphorous, but not boron may also increase the solubility of columbite. According to this observation, the effect described above would be attributed to the influence of P only. However, systematic experiments demonstrating this hypothesis have not been performed.

### Water in pegmatite melts and effect of water on the solubility of $MnNb_2O_6$ and $MnTa_2O_6$

The data of this study show that water does not significantly affect the solubility of manganocolumbite and manganotantalite at 1000 °C for water concentrations varying from ~4 wt% to water-saturated conditions (~7.3 wt% $H_2O$ for PEG 1 and ~8.5 wt% $H_2O$ for PEG 2; Table 2). Figure 4 shows that increasing water content may slightly increase $K_{sp}^{MnNb}$ and $K_{sp}^{MnTa}$ in melts containing < ~4 wt% water and that the effect of water may be slightly more significant for $K_{sp}^{MnNb}$ than for $K_{sp}^{MnTa}$. The explanation requires detailed additional work to clarify if water (through exchange reactions with alkalis, London 2008) or redox or acid-base state of the melt may be responsible for such behavior. Our results on pegmatite melts are also compared to the data obtained by Linnen and Keppler (1997) for a Li-, F-, B-, and P-free haplogranite melt (Figs. 3 and 5). In their study, water was found to increase markedly $K_{sp}^{MnNb}$ and $K_{sp}^{MnTa}$ for melts containing 0 to 3 wt% $H_2O$. Additional experiments from Linnen (2005), conducted at 2 kbar and 1035 °C, show a significant influence of water only up to 2 wt% $H_2O$ in the melt. Obviously, the high concentrations of fluxing elements like Li, F, B, and P in compositions PEG1 and PEG2 explain the small effect of water observed in these melts. Thus, in a first approach, at least Li and F have qualitatively the same influence on $K_{sp}^{MnNb}$ and $K_{sp}^{MnTa}$ as water.

Since water, as well as fluorine, depolymerize the melt structure, the observed effect of F is not surprising and this indicates that non-bridging oxygen atoms could form complexes with HFS elements like Nb and Ta (Keppler 1993; Farges et al. 2006; Piilonen et al. 2006). The difference in Nb and Ta concentrations of melts saturated with manganocolumbite and manganotantalite could be related to a preferential bonding of Ta with non-bridging oxygen atoms. However, a higher Ta concentration is also observed in fully polymerized melts (subaluminous melts without volatiles and non-bridging oxygen atoms; Linnen and Keppler 1997). Differences in the solution behavior of these elements may therefore be attributed to differences in electronegativity (1.6 for Nb, 1.5 for Ta, Greenwood and Earnshaw 1984) or to differences in the charge density distribution of the d-orbitals (Linnen and Keppler 1997). The effect of Li is more difficult to assess and detailed studies investigating the effect of the alkalis Li, Na, and K on the solubility of manganocolumbite and manganotantalite in subaluminous, peraluminous, and peralkaline melts need to be conducted to quantify the role of alkali exchange and of excess alkalis. The analytical data given in Table 2 also confirm that the solubility of water in pegmatite melts is significantly higher than that in rhyolitic melts and that volatiles, such as F and B, increase water solubility (e.g., Holtz et al. 1993).

It is emphasized that the data in Table 2 were obtained from the analysis of glass (~15–20 mg) by Karl Fischer titration.

Since the experimental glasses always exhibit small amounts of bubbles, the water contents given in Table 2 may be slightly higher than the water solubility. However, the presence of bubbles cannot explain the systematic variations in Table 3. The PEG2 melts may contain up to 9.5 (±0.8) wt% $H_2O$ at 800 °C and 200 MPa, whereas a maximum of ~6 wt% water can be incorporated in a rhyolitic melt at the same pressure and temperature (e.g., Liu et al. 2005). It is interesting to note that a significant temperature dependence of water is observed in compositions PEG1 and PEG2. This temperature dependence appears to be complex, considering that the highest values are observed at 800 °C (for both compositions) and lower values are observed at 700 and 1000 °C and may be of importance for interpreting second boiling processes in pegmatites.

**Implication for natural systems**

Natural pegmatitic melts crystallize at temperatures below the experimental temperatures in this study. However, assuming the linear dependence observed in Figure 3, the results can be extrapolated to 600 °C, a typical temperature at which pegmatites crystallize. In addition, pegmatite melts are expected to be rich in water and volatiles, implying that our data for water-rich melts (>4 wt% $H_2O$) are geologically relevant. The calculated values from the linear equation defined for $K_{sp}^{MnNb}$ and $K_{sp}^{MnTa}$ (water-saturated conditions) at 600 °C are $1.46 \times 10^{-5}$ and $1.29 \times 10^{-4}$ mol$^2$/kg$^2$ in PEG1 and $3.31 \times 10^{-5}$ and $1.27 \times 10^{-4}$ mol$^2$/kg$^2$ in PEG2, respectively. Based on these values and using a concentration of 0.05 wt% MnO in the melt, a value that is realistic for rare metal pegmatite melts (Linnen 1998) 400 to 900 ppm Nb and ~6500 ppm Ta are required for manganocolumbite and manganotantalite saturation in the pegmatitic melts PEG1 and PEG2, respectively. Although, the data set in this work indicates a higher Ta value in PEG2 when compared to PEG1 in the temperature range from 700 to 1000 °C, the similar estimated values of ~6500 ppm for Ta in both pegmatitic melts at 600 °C might be related to the uncertainties of the calculated regression lines. The extrapolated data for a water-saturated granitic melt (A.S.I. = 1.0) obtained by Linnen and Keppler (1997) at 600 °C are 70 and 500 ppm for Nb and Ta, respectively. Thus, variations by a factor of ~10 may be expected between F-, Li-, B-, and P-free and a typical F-, Li-, B-, and P-bearing pegmatite melts (assuming water-saturated conditions).

The maximum Ta and Nb concentrations calculated above for rare metal pegmatite melts are high but if higher MnO contents are used, lower Nb and Ta concentrations are required for saturation. Assuming that FeO plays the same role as MnO (Fe and Mn are incorporated in natural columbite and tantalite), and considering that FeO+MnO can reach up to 0.5 wt% or greater in pegmatite melts (Linnen and Keppler 1997), the maximum Nb and Ta contents in pegmatite melts could be an order of magnitude lower. Furthermore, Nb and Ta concentrations in natural melts can also be controlled by other minerals such as pyrochlore (microlite), and in this case, the concentrations of Nb and Ta necessary to crystallize manganocolumbite or manganotantalite may not be reached. To understand the behavior of Nb and Ta in pegmatitic systems, future studies need to focus on the solubility of other Nb- and Ta-bearing systems and on the Fe end-members of the columbite-tantalite group in pegmatite melts. Considering that there is a complete solid solution between manganocolumbite and manganotantalite, the solubility of minerals with intermediate compositions needs to be investigated. However, dissolution experiments are expected to be difficult since solid-state diffusion would be required to attain equilibrium between melt and intermediate minerals. Finally, the behavior of the Fe end-members of the columbite-tantalite group is poorly known. The only data we are aware of are from Linnen and Cuney (2005) who showed that the solubilities are an order of magnitude higher than those of the Mn end-members at the same conditions.

The results confirm that the solubility of manganotantalite is higher than that of manganocolumbite in silicate melts. The temperature dependence of the solubility products $K_{sp}^{MnNb}$ and $K_{sp}^{MnTa}$ in pegmatite melts is identical within uncertainty to that of rhyolitic melts. The concentrations of Li, F, P, and B present in typical pegmatite melts may increase the solubility of manganotantalite and manganocolumbite by a factor of 10 when compared to rhyolitic melts.

The experimental data shows that the amount of water influences the manganotantalite and manganocolumbite solubility only at low $H_2O$ contents, and especially in melts free of fluxing elements (Li, F, P, and B). Considering that pegmatitic melts have high water concentrations, the influence of the water content on the solubility of manganocolumbite and manganotantalite is expected to be negligible at pressures above 50 to 100 MPa (conditions at which water solubility is >4 wt% $H_2O$). Thus, the crystallization of manganocolumbite and manganotantalite in pegmatite melts via the boundary layer model proposed by London (2005) is not expected to be controlled by changing water contents but rather by variations in concentrations of other elements such as F and Li.

## Acknowledgments

This research was supported by the German Science Foundation (DFG Ho1337/20). We thank O. Diedrich for preparing the samples and thin sections, Wanja Dziony for help with the electron microprobe analyses as well as Renat Almeev, Sarah Cichy, Jan Schüssler, and Sara Fanara for help with the high-pressure facilities, the ICP-OES and the KFT. The manuscript also benefitted from reviews by P. Candela and D. London.

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Manuscript received November 24, 2008
Manuscript accepted October 26, 2009
Manuscript handled by Charles Lesher