

# **An experimental study of the solubility and speciation of tantalum in fluoride-bearing aqueous solutions at elevated temperature**

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## Abstract

The solubility of  $\text{Ta}_2\text{O}_5$  (solid) and the speciation of tantalum in HF-bearing aqueous solutions have been determined at temperatures of 100-250 °C and vapour-saturated water pressure. Tantalum is transported as the species  $\text{Ta}(\text{OH})_5^0$  at low HF concentration and pH ~1-3. At higher HF concentration, tantalum mobility is controlled by the species  $\text{TaF}_3(\text{OH})_3^-$  and  $\text{TaF}_5$ ; the presence of  $\text{TaF}_5^0$  is only evident at  $\leq 150$  °C. Equilibrium constants range from  $-17.4 \pm 0.45$  to  $-16.4 \pm 0.12$  for the formation of  $\text{Ta}(\text{OH})_5$  from crystalline  $\text{Ta}_2\text{O}_5$  and from  $-8.24 \pm 0.64$  to  $-8.55 \pm 0.68$  for the formation of  $\text{TaF}_3(\text{OH})_3^-$  at 100 and 250 °C, respectively. For  $\text{TaF}_5^0$ , they were determined to be 0.13 at 100 °C and -0.35 at 150 °C.

In many respects, the behaviour of tantalum in acidic fluoride-bearing solutions is similar to that of niobium. The solubility of  $\text{Ta}_2\text{O}_5$  (solid) is not dependent on HF concentration in fluoride-poor fluids, but rises rapidly at higher HF concentration. However, at the conditions of our experiments, namely a pH of ~2, temperature up to 250 °C, and a wide range of HF concentrations,  $\text{Ta}_2\text{O}_5$  (solid) solubility is almost invariably lower than that of  $\text{Nb}_2\text{O}_5$  (solid). Modelling of Nb and Ta leaching confirmed the preferential mobility of niobium under most conditions expected in natural fluoride-rich hydrothermal systems. This modelling also demonstrated that both niobium and tantalum are rapidly deposited upon removal of fluoride from an acidic brine. As a result of hydrothermal alteration, the Nb/Ta ratios of secondary minerals may increase relative to those of the primary mineral, or remain largely unaffected, depending on the pH of the fluid.

## 1. Introduction

Niobium and tantalum are considered geochemical twins, the aqueous behaviour of which is governed by their high charge (5+) and small radius (Pearson, 1963). Although they are immobile in most hydrothermal systems, reports of parts per million concentrations of niobium in fluid inclusions indicates that under some conditions at least, niobium may be mobilised hydrothermally (Rickers et al.,

2006). Further evidence of such mobility is provided by the Nechalacho alkaline igneous intrusion, in which the niobium and tantalum mineralisation, with rare exception, has a hydrothermal origin (Timofeev and Williams-Jones, 2015). Alkaline igneous systems of this kind, which contain appreciable concentrations of niobium and tantalum, are typically associated with fluoride alteration (e.g., Sheard et al., 2012). Insights into the conditions under which niobium is mobile were provided recently by the experimental study of Timofeev et al. (2015). This study investigated the solubility of Nb<sub>2</sub>O<sub>5</sub> (solid) in fluoride-bearing solutions and showed that the stability of niobium species increases exponentially with increasing HF concentration in the fluid. The study also emphasised the importance of acidity in promoting the mobility of niobium.

Because of the similarity of tantalum to niobium, the solubility and speciation of tantalum is predicted to be similar to that of niobium. Like Nb<sup>5+</sup>, Ta<sup>5+</sup> is a hard acid and should form strong complexes with the hard base, F<sup>-</sup> (Pearson, 1963; Williams-Jones and Migdisov 2014). The first indication that tantalum might behave differently from niobium in hydrothermal solutions was provided by Zarausky et al. (2010) who found that dissolution of columbite-(Mn) in a HF-bearing hydrothermal fluid at 400 °C and 100 Mpa yielded a concentration of tantalum that was an order of magnitude less than that of niobium. However, the results of these experiments are difficult to interpret because of the chemically complex nature of the solid and the lack of constraints placed on their experimental solution; the pH of the experimental solution and the stability constants of aqueous niobium and tantalum species were not evaluated. Nonetheless, their results indicate that the behaviour of tantalum in hydrothermal fluids may not mirror that of niobium, which is contrary to the conclusion of some studies of natural systems that the mobility of niobium and tantalum is roughly equal (e.g., Lumpkin and Ewing, 1992; Novák and Černý, 1998). They are also consistent with evidence from polyoxometalate studies that niobate and tantalate behaviour differs for some species, notably the hexaniobate and hexatantalte ions (Fullmer et al., 2014).

In this paper, we report the results of experiments conducted at 100, 150, 200, and 250 °C, and vapor-saturated water pressure designed to determine the solubility of Ta<sub>2</sub>O<sub>5</sub> (solid). The experiments were conducted at pH values of ~1 to 3 and HF concentrations from 10<sup>-5</sup> to 10<sup>0</sup> mol/kg. Results of these experiments are used to evaluate the speciation of tantalum at the conditions of interest, and determine formation constants for the dominant species. In conjunction with the results of Timofeev et al. (2015) on niobium solubility and speciation, we evaluate the potential of an ore-forming fluid to transport tantalum and niobium under hydrothermal conditions. We then evaluate the likelihood that differences in tantalum and niobium speciation will control the Nb/Ta ratios of secondary minerals.

## 2. Methods

### 2.1 Experimental technique

The experiments involved measuring the solubility of synthetic Ta<sub>2</sub>O<sub>5</sub> (solid) (99.99%, Alfa Aesar) in aqueous solutions of variable pH and HF concentration at temperatures of 100, 150, 200, and 250 °C, and vapor-saturated water pressure. The pH at the temperatures of interest ranged from 0.8 to 3.2, with most experiments being carried out at a pH of ~2.0; the HF concentration ranged from 10<sup>-5</sup> to 10<sup>0</sup> mol/kg. Experiments were performed in Teflon test tubes contained within titanium autoclaves (Fig. 1). Overall, the methodology employed in the experiments is similar to that of Migdisov and Williams-Jones (2007). The reader is therefore directed to this paper for information not covered in the text that follows.

Fluoride concentration was controlled by dissolving known amounts of NaF in nano-pure water. The pH of each solution was then reduced to the level of interest by adding an appropriate amount of trace metal grade HClO<sub>4</sub>. In order to maintain the predominance of ClO<sub>4</sub><sup>-</sup>, a non-complexing ligand, over HF as the background electrolyte, an amount of NaClO<sub>4</sub> approximately equal to that of NaF was added to each experimental solution containing more than 10<sup>-2</sup> m NaF. Experiments were initiated by placing

small sealed Teflon holders containing  $\text{Ta}_2\text{O}_5$  powder in Teflon test tubes, to which 20 ml of experimental solution was added. The Teflon test tubes were then placed in titanium autoclaves containing water (or solutions identical in composition to that used in the experiment) in order to balance pressures developed inside and outside the test tube, and heated in a Fisher Isotemp forced draft oven to the temperature of interest.

The time required to reach equilibrium was determined from a series of experiments of variable duration performed at 100 °C and 0.075 mol/kg HF. The duration of the experiments ranged from 1 to 9 days, with a steady state concentration, assumed to represent equilibrium, being reached after 6 days (Fig. 2). On the basis of the results from these kinetic experiments, all subsequent experiments were conducted for durations greater than six days. Heating, quenching and sampling of the autoclaves were carried out in less than an hour to minimize  $\text{Ta}_2\text{O}_5$  (solid) dissolution and precipitation before or after an experiment, respectively.

Following completion of an experiment, the autoclave was quenched in cold water and the  $\text{Ta}_2\text{O}_5$ -bearing Teflon holder within the larger Teflon test tube was removed. The  $\text{Ta}_2\text{O}_5$  (solid) within the Teflon holder was analyzed by X-ray diffraction after completion of the experiments. No additional solids were detected, though we cannot entirely exclude the possibility of trace amounts of a solid tantalum fluoride phase being present in the experiments. A small aliquot of liquid (2 ml) was extracted from the Teflon test tube in order to measure the pH and fluoride concentration of the experimental solution. The pH (25 °C) of the latter was determined potentiometrically using a glass pH electrode. The acidity of the aliquot of experimental solution was then neutralized by adding 2 ml of TISAB II (Deionized water >84%, Sodium Acetate 8%, Sodium Chloride 6%, Acetic Acid 1%, CDTA <1%, Supplier: Thermo Fisher Scientific) solution and the fluoride concentration was measured using a Thermo Scientific Orion fluoride ion selective electrode. After removal of the above aliquot of liquid, one milliliter of TM grade HF was added to the Teflon test tube in order to dissolve any tantalum that may have precipitated on its walls during

quenching. The concentration of tantalum from the resulting solutions was measured using ICP-MS (UQAM, Montreal).

Of potential concern for the interpretation of the results of the experiments is the decomposition of perchlorate at the elevated temperature of the experiments. It is unlikely, however, that the effect of perchlorate decomposition was more than the experimental error of our experiments for the following reasons. 1) If perchlorate decomposition had significantly affected the results of our experiments, there would have been a steady deviation with time in the tantalum concentration determined in our kinetic runs from the equilibrium concentration. This was not the case. 2) Similar experiments performed in perchlorate-based solutions at the same temperatures to investigate the speciation of rare-earth elements and zirconium were not affected by the decomposition of perchlorate (Migdisov and Williams-Jones, 2007; Migdisov et al., 2009, 2011).

### 3. Results

#### 3.1 Identification of dissolved tantalum species

The results of the experiments performed at 100 to 250 °C, which are reported in Table 1, were used to identify the dissolved tantalum species. Two distinct trends are present in the data for all temperatures investigated (Fig. 3). At high HF activity, the logarithm of tantalum activity has a slope of ~3 with respect to the logarithm of HF activity. In addition, experiments performed at different pH conditions indicate that at 200 and 250 °C the logarithm of tantalum activity increases with increasing pH in the proportion 1:1 (Fig. 4c-d). The only tantalum species which can satisfy both of these relationships via its formation reaction is  $\text{TaF}_3(\text{OH})_3^-$ , which forms as follows:



At lower temperature, 100 and 150 °C, the dependence of the increase in the logarithm of tantalum activity with increasing pH decreases and approaches the proportion of ~1/2 at 100 °C (Fig. 4a-

b). Moreover, the slope in the logarithm of Ta activity versus HF activity at these temperatures exceeds 3 (Fig. 3a-b). By analogy with the Zr-bearing fluoride system within which species such as  $\text{Zr}(\text{OH})_3\text{F}^0$  and  $\text{Zr}(\text{OH})_2\text{F}_2^0$  predominate at  $>150^\circ\text{C}$ , but  $\text{ZrF}_5^-$  and  $\text{ZrF}_6^{2-}$  become increasingly abundant at  $<150^\circ\text{C}$  (Aja et al., 1995; Migdisov et al., 2011), we propose that this reflects the presence of a simple tantalum fluoride species, namely  $\text{TaF}_5^0$ , at lower temperature and pH:



The stability of this species is not pH dependent. As such, the slope of  $\sim 1/2$  in Ta-pH space represents the transition with decreasing pH from the predominance of  $\text{TaF}_3(\text{OH})_3^-$ , having a Ta-pH slope of 1, to the predominance of  $\text{TaF}_5^0$ , having a Ta-pH slope of 0. The predicted tantalum activity calculated using the formation constants for reactions (1), (2), (3) that are derived later show this gradual transition, and are in good agreement with our experimental data (Fig. 4). In addition, the expected slope relating changes in  $\text{TaF}_5$  activity to increasing HF activity is 5 ( $10\text{HF}^0:2\text{TaF}_5^0 \rightarrow 5:1$ ). This explains the increase in slope that we observe in the logarithm of tantalum activity with respect to HF activity at 100 and  $150^\circ\text{C}$ ;  $\text{TaF}_5^0$  becomes increasingly more abundant at higher HF activity at these temperatures (Fig. 3).

The trends in the data are strikingly different at lower HF concentration. The activity of tantalum is unaffected by HF activity at all temperatures, nor is it affected by the pH of the solution (Fig. 3, Fig. 5). These observations, coupled with the identification of niobium hydroxide species by Timofeev et al. (2015) at similar conditions, lead us to conclude that the predominant tantalum species at these lower HF concentrations is  $\text{Ta}(\text{OH})_5^0$ :



In order to calculate equilibrium constants for reactions (1), (2), and (3), it was necessary to use an activity model. The model used to calculate the activity of the dissolved species is presented in the next section and is the same as that used to determine the pH for each experiment.

### 3.2 Methods used in calculating ion activity

To calculate the activity of the ions, we used the extended Debye-Hückel equation (Helgeson et al., 1981):

$$\log \gamma_n = -\frac{A \cdot [z_n]^2 \cdot \sqrt{I}}{1 + B \cdot \bar{a} \cdot \sqrt{I}} + b_\gamma \cdot I \quad (4)$$

with A and B being the parameters of the Debye-Hückel equation,  $b_\gamma$  the extended parameter, which depends on the nature of the background electrolyte,  $\bar{a}$  the distance of closest approach, which is specific to the ion of interest,  $z$  the charge of the ion, and  $I$  the true ionic strength when all dissolved components are considered. The values of  $b_\gamma$ , the extended parameter, were taken from Migdisov and Williams-Jones (2007), who determined the best fit  $b_\gamma$  values for  $\text{ClO}_4^-$  in a chemically similar system. The distances of closest approach ( $\bar{a}$ ), were set at 9 Å for  $\text{H}^+$  (Kielland, 1937; Garrels and Christ, 1965), 3.5 Å for  $\text{F}^-$  and  $\text{OH}^-$  (Garrels and Christ 1965), 4 Å for  $\text{Na}^+$  (Garrels and Christ, 1965) and at 4.5 Å for  $\text{ClO}_4^-$  and  $\text{TaF}_3(\text{OH})_3^-$ . In order to calculate pH at the conditions of interest, it was assumed that  $\text{HClO}_4$  dissociates completely. The pH and activity of the dissolved species were refined iteratively for each experiment considering the following species:  $\text{H}^+/\text{OH}^-$ ,  $\text{Na}^+$ ,  $\text{HF}^0$ ,  $\text{ClO}_4^-$ ,  $\text{Ta}(\text{OH})_5^0$ ,  $\text{TaF}_5^0$ ,  $\text{TaF}_3(\text{OH})_3^-$ . The Haarr-Gallagher-Kell (Kestin et al., 1984) and Marshall and Franck (1981) models were used to determine the thermodynamic properties and dissociation constant of  $\text{H}_2\text{O}$  under our experimental conditions. Thermodynamic data for the aqueous species were obtained from Ryzhenko (1965), Ryzhenko et al. (1991), Johnson et al. (1992), Sverjensky et al. (1997), and Shock et al. (1997). With this activity model in hand, it was possible to calculate the equilibrium constants of reactions (1), (2) and (3).

### 3.3. Derivation of stability constants



The results of the experiments given in Table 1 were used to calculate equilibrium constants for the reactions presented in Equations (1), (2), and (3) by iteratively minimizing the error function U, which is given by the expression:

$$U = \sum_i \left( \frac{\log C_{Ta}^{Theo} - \log C_{Ta}^{Exp}}{\log C_{Ta}^{Exp}} \right)^2 \quad (5)$$

where  $i$  is the  $i$ th experimental point in the dataset,  $C_{Ta}^{Exp}$  is the concentration of Ta determined experimentally, and  $C_{Ta}^{Theo}$  is the concentration of Ta calculated theoretically using the starting compositions, the activity model, and the values of the formation constants, which were adjustable parameters in these iterations. The modeled system involved the same species as those considered in the calculation of ion activity. The error function, U, was minimized iteratively using the Nelder-Mead simplex search algorithm (Nelder and Mead, 1965; Dennis and Woods, 1987) for isothermal sets of solutions with the activity coefficients of the species and ionic strength recalculated after each iteration. Additional details on the methods of minimization can be found in Migdisov and Williams-Jones (2007) and Migdisov et al. (2009), which used the same data treatment method. The resulting equilibrium constants are reported in Table 2. Equilibrium constant uncertainties were calculated by propagating the error ( $1\sigma$ ) associated with tantalum species activity, normalized to the same HF concentration, using reactions (1), (2), and (3), and are also reported in Table 2. Uncertainties for the equilibrium constants associated with the species,  $TaF_5$  (Reaction 2), are not provided as the data were only sufficient to permit approximate values for these equilibrium constants to be determined.

## 4. Discussion

### 4.1 Comparison to previous studies

Results of previous studies that are directly comparable to the data presented in this paper are limited to those reported in the study of Zraisky et al. (2010). In their experiments Zraisky et al. (2010)

employed two starting solids; Ta<sub>2</sub>O<sub>5</sub> of greater than 99.99% purity, and a single crystal of columbite-tantalite from a quartz-amazonite-mica pegmatite. Whereas the solubility of Ta<sub>2</sub>O<sub>5</sub> (solid) determined by Zraisky et al. (2010) can be compared easily to that reported in this study, the activity of tantalum oxide within the columbite-(Mn) sample is uncertain and cannot be evaluated. Fortunately, electron microprobe analyses of this crystal suggest that it is relatively homogeneous. Thus, although the absolute solubility of the columbite-(Mn) may be difficult to interpret, relationships such as the change in solubility of the columbite-(Mn) with an increase in HF activity should be consistent with this study, at similar experimental conditions.

Two experiments were conducted by Zraisky et al. (2010) at HF concentrations ranging from 0.01 to ~1 molal HF. The first at 400 °C used columbite-(Mn) as the solid, and the second at 550 °C employed Ta<sub>2</sub>O<sub>5</sub> (solid). A pressure of 100 Mpa and a Co-CoO oxygen buffer were employed in both experiments. It was assumed that the solution descriptions of Zraisky et al. (2010) were complete despite their lack of detail. A 0.1 molal HF solution was therefore considered to have been prepared by the addition of an appropriate amount of trace metal grade hydrofluoric acid to nanopure water. Using these compositions, we calculated the pH and HF activity of each solution at the respective temperatures of the two experiments. We then assumed that the tantalum species, TaF<sub>3</sub>(OH)<sub>3</sub><sup>-</sup>, identified at higher HF concentrations in this study is also stable at the higher temperature and pH (~4) conditions of the experiments conducted by Zraisky et al. (2010). The concentrations of tantalum in solution determined by Zraisky et al. (2010) were accordingly adjusted to a pH of 2.0 using the stoichiometry of reaction (1). The results of these calculations are shown in Figure 6. A strong dependence of tantalum solubility with increasing HF concentration is observed at both 400 and 550 °C. The slope of ~3 of this dependence is identical to that observed by us at 100-250 °C, and would be the predicted slope, if our previous assumption about TaF<sub>3</sub>(OH)<sub>3</sub><sup>-</sup> being the dominant tantalum species at higher temperature is correct. In addition, the lower solubility of a tantalum solid at high temperature is consistent with the trends in the

stability of  $\text{TaF}_3(\text{OH})_3^-$  determined in this study. The concentration of  $\text{TaF}_3(\text{OH})_3^-$  reaches a maximum at  $\sim 150^\circ\text{C}$ , i.e., the concentration of this species is lower at higher and lower temperature (Table 2, Fig. 7). Therefore, consistent with this trend, the concentration of dissolved tantalum in equilibrium with columbite-(Mn) at  $400^\circ\text{C}$  should be less than that predicted by the best fit to our data for  $250^\circ\text{C}$ , which is what we observe (Fig. 6). If we extrapolate the results of this study to  $400^\circ\text{C}$ , the curve of best fit for this temperature lies just above and parallel to the data of Zraisky et al. (2010). This constitutes a remarkably high level of agreement, particularly considering that our study and that of Zraisky et al. (2010) employed different solids for this temperature.

At the lowest HF concentration considered by Zraisky et al. (2010), 0.01 m HF, at  $550^\circ\text{C}$ , the solubility of  $\text{Ta}_2\text{O}_5$  (solid) is higher than would be expected solely from the presence of  $\text{TaF}_3(\text{OH})_3^-$ . This could be due to the transition to the predominance field of  $\text{Ta}(\text{OH})_5^0$ , which we predict to be increasingly stable at elevated temperature.

#### 4.2 Differences in the behaviour of tantalum and niobium

Tantalum-bearing minerals, such as the columbite and pyrochlore group minerals, commonly contain appreciable quantities of niobium. Therefore, a scenario favourable for the transport of tantalum, such as the interaction of an acidic fluoride-bearing solution at elevated temperature with a tantalum-bearing rock, might also be favorable for the transport of niobium. After this interaction, however, the relative proportions of niobium and tantalum in the rock might have changed significantly. The results of this study and those for niobium in similarly acidic, fluoride-bearing solutions reported by Timofeev et al. (2015) allow us to assess the relative behaviour of these two metals during fluid-rock interaction.

At low HF activity ( $< \sim 10^{-3}$ ) and a pH of 2, the solubility  $\text{Nb}_2\text{O}_5$  (solid) is independent of HF activity but at higher HF activity the logarithm of the solubility of  $\text{Nb}_2\text{O}_5$  (solid) increases at a rate of

approximately twice that of the logarithm of HF activity (Timofeev et al., 2015). By contrast, the solubility of Ta<sub>2</sub>O<sub>5</sub> (solid) is lower and begins rising at a much higher HF activity (10<sup>-2</sup>). The rate of increase in the solubility of Ta<sub>2</sub>O<sub>5</sub> (solid) with increasing HF activity, however, is higher, i.e., the logarithm of aTa/aHF is ~3 (Fig. 7). If the data for niobium are extended to higher HF activity, it can be seen that, despite the greater rate of increase in the solubility of Ta<sub>2</sub>O<sub>5</sub> (solid) with increasing HF activity, Ta<sub>2</sub>O<sub>5</sub> (solid) solubility does not exceed that for Nb<sub>2</sub>O<sub>5</sub> (solid) until a HF activity of ~0.25 or concentration of ~5,000 ppm is reached. Although such a high fluoride concentration has been reported for a natural system (Banks et al., 1994, reported HF concentrations for hypersaline fluids in the Capitan Pluton, New Mexico, USA, ranging between ~500-5000 ppm), HF concentrations in most naturally occurring fluids are likely to be significantly lower; they are buffered to low values by the precipitation of very weakly soluble minerals, such as fluorite and topaz.

In order to evaluate the effect of an acidic, fluoride-bearing solution on a niobium- and tantalum-bearing host rock, we modelled the progressive flushing of 50 grams of host rock containing 25 grams each of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> with a brine containing 50, 500, or 5000 ppm HF in addition to 1.5m NaCl, 0.5m KCl, and 0.01m HCl, at 150 °C. The niobium and tantalum oxides were chosen due to the absence of thermodynamic data for niobium and tantalum minerals. Their thermodynamic data were obtained from Jacob et al. (2010) and Jacob et al. (2009), respectively. It should be noted that separate minerals may control the relative solubility of niobium and tantalum in natural systems, thereby making the use of niobium and tantalum oxides in the model a necessary, but potentially important simplification. Thermodynamic data for the other minerals were obtained from Holland and Powell (1998) and Robie and Hemingway (1995). Thermodynamic data for the aqueous species not considered in this study were obtained from Johnson et al. (1992), Shock et al. (1997), Sverjensky et al. (1997), and Timofeev et al. (2015). Extended parameters for NaCl in the Debye-Hückel equation were taken from Oelkers and Helgeson (1991).

The results of this model are shown in Figure 8. The quantity of brine (containing 50 ppm HF) needed to leach significant niobium from the original host rock exceeds a million liters. After interaction of this amount of fluid with the rock, the content of tantalum was effectively unchanged. Increasing the HF concentration to 500 ppm resulted in a two orders of magnitude reduction in the amount of brine necessary to remove significant niobium. However, tantalum is difficult to mobilize, and approximately one and a half order of magnitude more solution was required to leach tantalum in a proportion similar to that of niobium. In our most HF-rich example, a brine containing 5,000 ppm HF is able to efficiently leach both niobium and tantalum after interacting with less than a thousand liters of brine. Nevertheless, more niobium is mobilized than tantalum in this fluoride-rich solution, albeit by a small margin.

It should be noted that the data for tantalum collected in this study was to a higher HF activity ( $\log a_{\text{HF}} \sim -0.4$ ) than that for niobium ( $\log a_{\text{HF}} \sim -2$ ) collected by Timofeev et al. (2015). Thus, it is plausible that at higher HF activity than considered by Timofeev et al. (2015), the dependence of niobium solubility on HF activity increases from a logarithmic slope of 2 to a slope of 3. Such an increase is suggested by the observation that concentrations of niobium and tantalum in equilibrium with columbite-(Mn) at 400 °C have similar dependencies on HF activity (Zaraisky et al., 2010). If the logarithm of the slope of Nb solubility over HF activity were to approach that for tantalum at high HF activity, transport of niobium would predominate relative to that of tantalum under almost any fluoride activity at acidic conditions. However, Zaraisky et al. (2010) recognised a logarithmic molal Nb/HF slope of 2 for their columbite-(Mn) solubility data, which is consistent with the neutral  $\text{NbF}_2(\text{OH})_3^0$  species identified by Timofeev et al. (2015). In order to achieve a logarithmic slope of 3, a pH dependence similar to that suggested for the species  $\text{TaF}_3(\text{OH})_3^-$  in this study would have to be present for a negatively charged niobium hydroxyl-fluoride species.

If previously collected niobium speciation data are accurate to higher fluoride activity, pH could play an important role in niobium-tantalum fractionation. The species,  $\text{TaF}_3(\text{OH})_3^-$ , is more stable at a higher pH, whereas the stability of  $\text{NbF}_2(\text{OH})_3^0$  is pH-independent (Timofeev et al., 2015). Therefore, the HF activity at which tantalum species are more abundant than their niobium counterparts would decrease considerably at elevated pH (e.g., 3-4 versus the value of ~2 employed in this study). During fluid-rock interaction, however, although interaction of an acidic fluid with a calcium-bearing rock will lead to an increase in its pH, the associated precipitation of fluorite and decrease in HF activity will result in the deposition of  $\text{Ta}_2\text{O}_5$  (solid) (Fig. 9). Thus, despite a delay in the deposition of  $\text{Ta}_2\text{O}_5$  relative to  $\text{Nb}_2\text{O}_5$  because of the increase in pH, niobium species will remain more abundant in solution until the concentration of all niobium and tantalum species fall below that of  $\text{Ta}(\text{OH})_5^0$ , the stability of which is independent of pH and HF activity.

#### 4.3 Applications to natural systems

Niobium-tantalum fractionation can occur not only during hydrothermal alteration of a host rock, but also during subsequent events that result in the precipitation of niobium-tantalum bearing minerals. To assess this latter possibility, we modelled two scenarios identical to those used by Timofeev et al. (2015) to evaluate the hydrothermal deposition of niobium in natural systems. Both scenarios were evaluated at 150 °C and saturated water pressure. In the first scenario, one liter of an acidic (~pH 2.1) fluid with 500 ppm HF, 1.5m NaCl, 0.5m KCl, and 0.01m HCl, which was saturated with respect to  $\text{Nb}_2\text{O}_5$  (solid) and  $\text{Ta}_2\text{O}_5$  (solid), was mixed iteratively with 1mL aliquots of a brine containing 0.75m NaCl, 0.25m KCl, and 1m  $\text{CaCl}_2$  until a 1:1 fluid ratio was reached (Fig. 9a). The starting concentration of HF corresponds to that measured in fluid inclusions in the Capitan Pluton (Banks et al., 1994). In the second scenario, an acidic fluid identical to that used in the first model was reacted iteratively with 10 mg aliquots of calcite, representing a limestone or marble, until one liter of acidic solution had reacted with

2 grams of calcite (Fig. 9b). Thermodynamic data for the minerals and aqueous species involved in this model are identical to those employed for the previous model addressing Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> dissolution.

By incorporating the data of this study, these models demonstrate the behaviour of tantalum relative to niobium. Increases in pH in the first fluid mixing scenario are relatively minor and as such, although concentrations of NbF<sub>2</sub>(OH)<sub>3</sub><sup>0</sup> and TaF<sub>3</sub>(OH)<sub>3</sub><sup>-</sup> decrease with progressive mixing and fluorite deposition, both niobium and tantalum remain in solution. This decrease would be progressively minimized with fluid mixing models incorporating lesser amount of calcium; fluorite would not precipitate and most of the niobium and tantalum would remain in the fluid. By contrast, interaction of the acidic brine with calcite (model 2) results in a large increase in pH, deposition of considerable amounts of fluorite, and a rapid decrease in the concentration of the aqueous species of both niobium and tantalum. From this perspective, the behaviour of niobium and tantalum appears to be quite similar and the conclusions of Timofeev et al. (2015) validated; the neutralization of an acidic brine by limestone or marble is a far more effective method for limiting the mobility of niobium and tantalum than mixing with another brine. There is one notable difference in behaviour of the two metals in the second model. As TaF<sub>3</sub>(OH)<sub>3</sub><sup>-</sup> is a pH-dependent species, the initially rapid rise in pH offsets the decrease in HF activity caused by fluorite precipitation and results in an initial suppression of Ta<sub>2</sub>O<sub>5</sub> (solid) precipitation relative to that of Nb<sub>2</sub>O<sub>5</sub> (solid). This interpretation is predicated on the assumption that the niobium hydroxyl-fluoride species is neutrally charged. A negatively charged niobium hydroxyl-fluoride species would eliminate this small depositional gap. However, this small difference is potentially significant in interactions involving large amounts of fluid with wall rocks containing relatively minor volumetric proportions of a Ca-bearing mineral (e.g., calcite). A hydrothermal fluid interacting with small amounts of calcite would precipitate niobium-bearing minerals and in the process become progressively enriched in tantalum relative to niobium. Further along the fluid pathway and following additional neutralization, tantalum would be deposited. As a result, domains distinctly enriched in niobium and

374 tantalum may form upstream and downstream in the fluid conduit, respectively. Such domains would be  
375 difficult to identify in natural environments, however, as the proportion of calcite required for such a  
376 scenario has a very restricted range.

377         The results of the above models suggest that niobium and tantalum do not behave in an identical  
378 fashion in hydrothermal fluids. If these two metals are leached from a host rock, a much lower fluid/rock  
379 ratio is required to mobilize niobium than is the case for tantalum. Once the chemistry of the fluid is  
380 altered such that the pH increases or HF activity decreases both niobium and tantalum precipitate. In  
381 rare cases deposition of tantalum may be temporarily suppressed.

382         Niobium- and tantalum-bearing pegmatites that have experienced hydrothermal alteration  
383 commonly demonstrate evidence of niobium and tantalum mobilization. For example, fine-grained  
384 secondary muscovite containing ~50 ppm Ta and ~25 ppm Nb in the Tanco pegmatite is interpreted to  
385 have crystallized from Ta-bearing aqueous fluids during a late hydrothermal event (Van Lichtenvelde et  
386 al. 2008). In another example, Rickers et al. (2006) reported the occurrence of early fluid inclusions in  
387 the Variscan Ehrenfriedersdorf complex that contain up to 29 ppm Nb; Ta was not analyzed.

388         Pegmatites that have been hydrothermally altered may retain their primary Nb/Ta ratios or have  
389 quite different ratios of these metals. In the Moose II LCT (Li-Cs-Ta) pegmatite in the Northwest  
390 Territories, Canada, the secondary muscovite is enriched in niobium and depleted in tantalum relative to  
391 the primary muscovite (Anderson et al., 2013). Furthermore, overgrowths of columbite-(Fe) on primary  
392 columbite-(Fe) crystals in the Moose II pegmatite are commonly Nb-rich. Based on these observations,  
393 Anderson et al. (2013) concluded that the pegmatite had been enriched in Nb by a F- and Nb-rich fluid.  
394 Indeed, the behaviour of Nb and Ta in this pegmatite is entirely consistent with the results of this study.  
395 In other settings Nb/Ta ratios may remain largely unaffected by hydrothermal alteration. For example,  
396 secondary tantalum oxide phases in the Moldanubicum granitic pegmatites, Czech Republic, have similar  
397 Nb/Ta ratios to their primary counterparts (Novák and Černý, 1998). In the Tanco pegmatite, the Nb/Ta



ratios of the primary and secondary muscovite grains also do not differ greatly (Van Lichtenvelde et al., 2008). Two factors may be responsible for Nb/Ta ratios remaining unaffected. The first is the pH of the hydrothermal fluid. As mentioned previously, the solubility of tantalum in HF-rich systems increases with increasing pH. Therefore, the Nb/Ta ratios of the secondary minerals could reflect the pH of the altering hydrothermal fluid. Hydrothermal alteration of the Moose II pegmatite may have occurred at a lower pH than the Tanco pegmatite, but this is not known as the pH of the altering fluid in these systems was not constrained. Alternatively, the kinetics of Nb-Ta bearing mineral dissolution may be such that the hydrothermal fluid does not achieve Nb-Ta saturation and the results of this study are not applicable. However, kinetic runs performed in this study and by Timofeev et al. (2015) suggest that Nb<sub>2</sub>O<sub>5</sub> (solid) dissolution is faster than that of Ta<sub>2</sub>O<sub>5</sub> (solid). As a result, we propose that pH, in addition to HF activity, may play a role in determining the Nb/Ta ratios of secondary minerals.

## 5. Conclusions

The results of this study show that transport of tantalum in fluoride-bearing hydrothermal fluids is controlled by Ta(OH)<sub>5</sub><sup>0</sup> at low fluoride concentration, and TaF<sub>3</sub>(OH)<sub>3</sub><sup>-</sup> and TaF<sub>5</sub><sup>0</sup>, at high fluoride concentration. Dissolved tantalum concentration rises rapidly at >10<sup>-2</sup> HF mol/kg. Niobium is more soluble than tantalum in acidic hydrothermal fluids, except for those containing extremely high concentrations of fluoride, explaining why niobium is commonly mobilized preferentially from niobium-tantalum-bearing rocks. At higher pH, tantalum concentrations may approach those of niobium in hydrothermal fluids, which could explain why Nb/Ta ratios of secondary minerals remain unchanged from those of the primary minerals in some hydrothermally altered rocks.

## Acknowledgements

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507 Table 1. Compositions of the experimental solutions (mol/kg).

T(°C)	$\Sigma\text{ClO}_4$	$\text{Na}^+/\text{HF}^0, 10^{-2}$	$\text{Ta}, 10^{-8}$	pH (25 °C)	T(°C)	$\Sigma\text{ClO}_4$	$\text{Na}^+/\text{HF}^0, 10^{-2}$	$\text{Ta}, 10^{-8}$	pH (25 °C)
100	0.036	1.20	1.81	1.67	↓	0.028	0.0463	0.179	1.61
↓	0.024	0.572	0.47	1.78	↓	0.059	0.0437	0.432	1.29
↓	0.0153	0.108	0.199	1.89	↓	0.14	0.0414	0.183	0.92
↓	0.0149	0.0549	0.177	1.89	↓	0.338	7.3	188	1.7
↓	0.0127	0.0103	0.138	1.94	↓	0.27	7.65	314	1.95
↓	0.0127	0.00523	0.385	1.94	↓	0.218	7.62	553	2.2
↓	0.0107	0.00158	0.144	2.01	↓	0.191	7.71	938	2.4
↓	1.685	88.4	256000	2.7	150	0.207	7.56	1070	2.52
↓	1.28	75.5	209000	2.69	200	0.0303	0.915	1.10	1.72
↓	0.92	45.8	54500	2.66	↓	0.0212	0.492	1.00	1.83
↓	0.37	19.8	8240	2.64	↓	0.0149	0.0981	1.40	1.9
↓	0.151	8.22	418	2.55	↓	0.0141	0.0613	1.13	1.91
↓	0.099	5.22	177	2.44	↓	0.0108	0.0115	0.411	2.01
↓	0.0412	1.89	32.3	2.25	↓	0.011	0.00753	0.665	2
↓	0.342	7.32	260	1.69	↓	0.0107	0.00223	0.473	2.01
↓	0.266	7.47	382	1.96	↓	1.35	54.4	449000	2.83
↓	0.218	7.69	449	2.2	↓	1.02	48.3	399000	2.8
↓	0.19	7.56	591	2.4	↓	0.828	36.7	133000	2.72
↓	0.208	7.53	726	2.51	↓	0.362	19.1	22600	2.67
↓	0.165	7.56	1060	2.6	↓	0.145	7.67	538	2.57
↓	0.207	7.44	693	2.51	↓	0.0898	4.56	119	2.43
↓	0.207	7.47	674	2.51	↓	0.0423	1.87	14.6	2.22
↓	0.208	7.56	798	2.51	↓	0.00116	0.0549	0.495	3.08
↓	0.029	1.04	2.02	1.77	↓	0.00226	0.0494	0.425	2.74
↓	0.0203	0.525	0.504	1.86	↓	0.00515	0.0432	0.547	2.35
↓	0.013	0.0991	0.438	1.96	↓	0.0104	0.052	0.856	2.04
↓	0.0125	0.0524	0.381	1.96	↓	0.03	0.0419	0.617	1.64
↓	0.0105	0.00979	0.211	2.02	↓	0.06	0.0369	0.639	1.29
↓	0.0102	0.00516	0.311	2.03	↓	0.13	0.0355	0.434	0.94
↓	0.0102	0.00107	0.204	2.03	↓	0.20	8.16	348	2.38
↓	0.0325	1.15	1.65	1.72	↓	0.21	7.94	929	2.52
↓	0.0234	0.584	0.528	1.8	↓	0.17	8.36	2150	2.59
↓	0.015	0.112	0.414	1.9	200	0.17	8.03	3770	2.64
↓	0.0132	0.0572	0.391	1.94	250	0.0332	1.05	0.546	1.69
↓	0.0116	0.0105	0.270	1.98	↓	0.0252	0.60	1.08	1.76
↓	0.0124	0.00577	0.307	1.95	↓	0.0173	0.132	0.618	1.84
↓	0.0115	0.00107	0.244	1.98	↓	0.0167	0.0708	0.757	1.84
↓	0.873	42.4	208000	2.71	↓	0.0128	0.0154	0.548	1.94
↓	0.358	18.0	18100	2.65	↓	0.0119	0.0122	0.701	1.97
↓	0.122	6.07	784	2.71	↓	0.0126	0.00506	0.680	1.94
↓	0.039	1.81	25.9	2.3	↓	0.648	28.9	113000	2.68
↓	1.60	74.6	558000	2.69	↓	0.541	24.2	64400	2.61
↓	1.16	59.3	448000	2.7	↓	0.226	10.7	469	2.38
↓	0.87	37.9	207000	2.65	↓	0.179	8.46	334	2.47
↓	0.35	16.8	20900	2.65	↓	0.132	5.79	84.8	2.48
↓	0.14	7.03	759	2.55	↓	0.0526	2.35	8.86	2.17
↓	0.09	4.31	209	2.46	↓	0.295	8.92	54.2	1.9
↓	0.04	1.70	24.0	2.29	↓	0.241	9.21	153	2.14
↓	0.00112	0.0481	0.186	3.08	↓	0.208	8.71	240	2.33
↓	0.0024	0.0483	0.202	2.71	↓	0.218	8.46	311	2.49
↓	0.0048	0.046	0.219	2.38	250	0.174	8.43	3060	2.61
↓	0.0104	0.0483	0.221	2.04					

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514 Table 2: Equilibrium constants and their associated uncertainty for the Ta<sub>2</sub>O<sub>5</sub> dissolution reactions, (1), (2), and (3).  
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T(°C)	100	150	200	250
Ta <sub>2</sub> O <sub>5</sub> <sup>cryst</sup> + 5H <sub>2</sub> O = 2Ta(OH) <sub>5</sub> <sup>°</sup>	-17.4 ± 0.45	-17.1 ± 0.32	-16.4 ± 0.36	-16.4 ± 0.12
Ta <sub>2</sub> O <sub>5</sub> <sup>cryst</sup> + 6HF <sup>0</sup> + H <sub>2</sub> O = 2TaF <sub>3</sub> (OH) <sub>3</sub> <sup>-</sup> + 2H <sup>+</sup>	-8.24 ± 0.64	-7.45 ± 0.65	-8.60 ± 0.64	-8.55 ± 0.68
Ta <sub>2</sub> O <sub>5</sub> <sup>cryst</sup> + 10HF <sup>0</sup> = 2TaF <sub>5</sub> <sup>°</sup> + 5H <sub>2</sub> O	~ 0.13	~ -0.35	-	-

- Fig. 1. A schematic drawing illustrating the experimental set-up. \*H<sub>2</sub>O surrounding the Teflon test tube was replaced by the experimental solution in a small number of experiments.
- Fig. 2. Results from a series of experiments illustrating the solubility of Ta<sub>2</sub>O<sub>5</sub> (solid) as a function of time in an aqueous solution at 100 °C containing 0.075 mol/kg HF. The data suggest that equilibrium (dashed line) was attained after 6 days.
- Fig. 3. The solubility of Ta<sub>2</sub>O<sub>5</sub> (solid), normalized to a pH of 2.0 on the basis of reactions (1), (2), and (3), as a function of the concentration of HF at (a) 100 °C (b), 150 °C, (c), 200 °C, and (d) 250 °C. The dashed lines indicate the solubility of Ta<sub>2</sub>O<sub>5</sub> (solid) calculated from the values of log K for reactions (1), (2), and (3) at each respective temperature. Results from the pH dependence experiments illustrated in Figure 4 are also shown, but have not been normalized to a pH of 2. The results of kinetic run experiments of duration of 6 days or more are included in the data set for 100 °C.
- Fig. 4. The solubility of Ta<sub>2</sub>O<sub>5</sub> (solid) as a function of pH at 100 °C (a), 150 °C (b), 200 °C (c), and 250 °C (d) for solutions containing > 0.075 mol/kg HF. The dashed lines indicate the solubility of Ta<sub>2</sub>O<sub>5</sub> (solid) calculated from the values of log K for reactions (1), (2), and (3) at each respective temperature.
- Fig. 5. The solubility of Ta<sub>2</sub>O<sub>5</sub> (solid) as a function of pH at 150 and 200 °C in solutions containing ~5×10<sup>-4</sup> mol/kg HF. The dashed lines represent best fits to the data calculated from the log K value of reaction (1).
- Fig. 6. Tantalum concentrations in equilibrium with columbite-(Mn) at 400 °C and Ta<sub>2</sub>O<sub>5</sub> at 550 °C calculated using data obtained by Zarausky et al. (2010). The best fit of the solubility data obtained at 250 °C in this study and extrapolated to 400 °C are shown for reference.
- Fig. 7. The activity of Ta in equilibrium with Ta<sub>2</sub>O<sub>5</sub> (solid) determined in this study at 100-250 °C compared to the activity of Nb in equilibrium with Nb<sub>2</sub>O<sub>5</sub> (solid) as determined by Timofeev et al. (2015) at 150 °C.
- Fig. 8. Amounts of Nb<sub>2</sub>O<sub>5</sub> and Ta<sub>2</sub>O<sub>5</sub> remaining from a sample initially containing 25 grams of each oxide following progressive flushing of the sample with brine containing 50, 500, or 5000 ppm HF in addition to 1.5m NaCl, 0.5m KCl, and 0.01m HCl, at 150 °C.
- Fig. 9. The instantaneous concentrations of aqueous species and cumulative concentrations of precipitated solids at 150 °C in a niobium- and tantalum-saturated fluid containing 500 ppm HF, 1.5m NaCl, 0.5m KCl, and 0.01m HCl (a) during progressive mixing with a brine containing 0.75m NaCl, 0.25m KCl, and 1m CaCl<sub>2</sub>, and (b) during progressive interaction with calcite (representing limestone or marble).

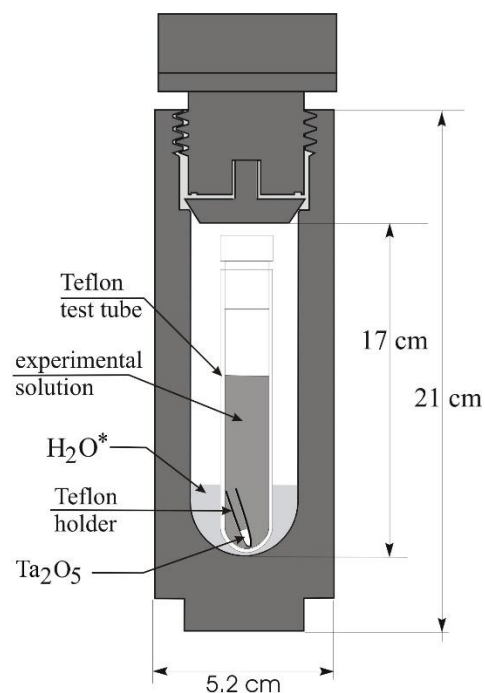


Figure 1

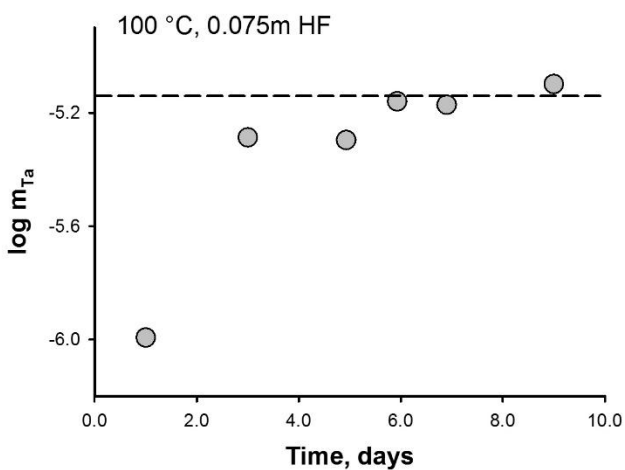


Figure 2

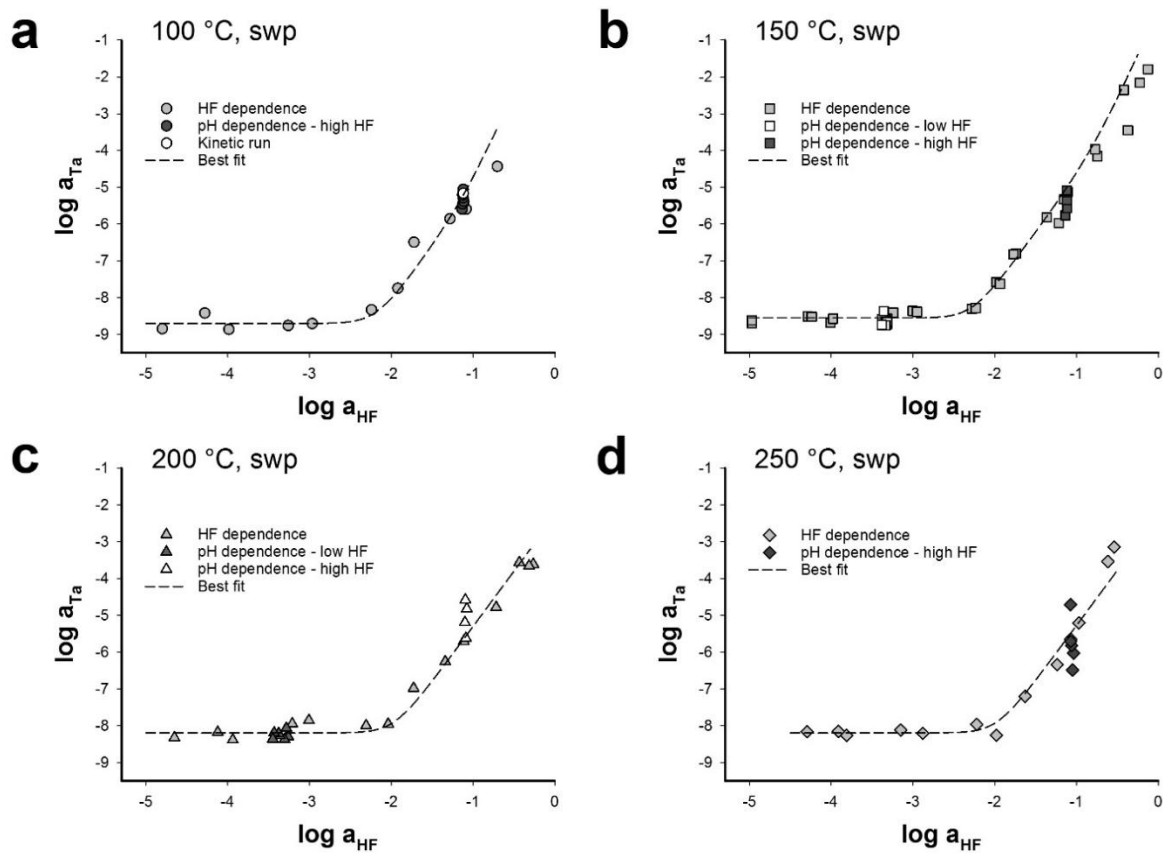


Figure 3



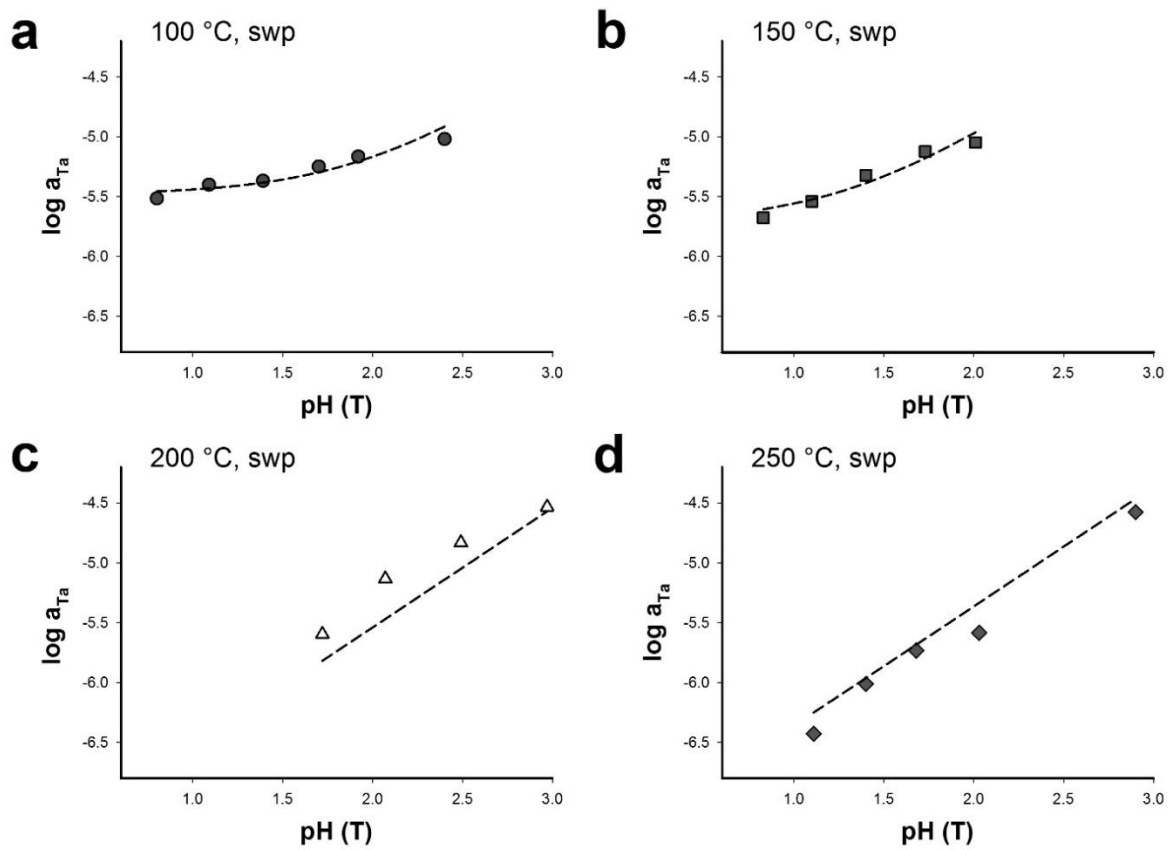


Figure 4

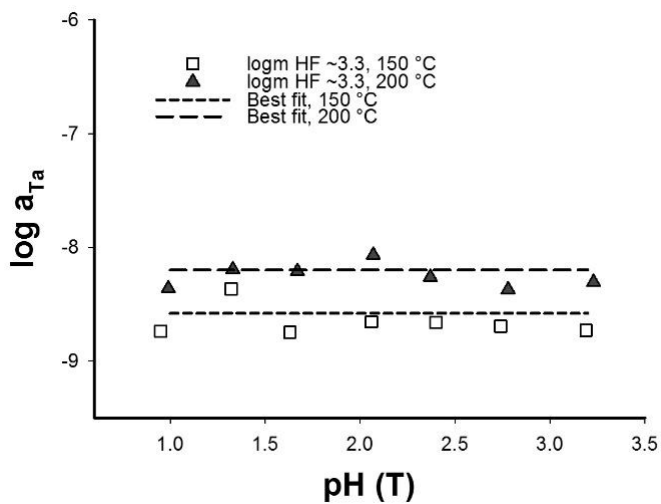


Figure 5

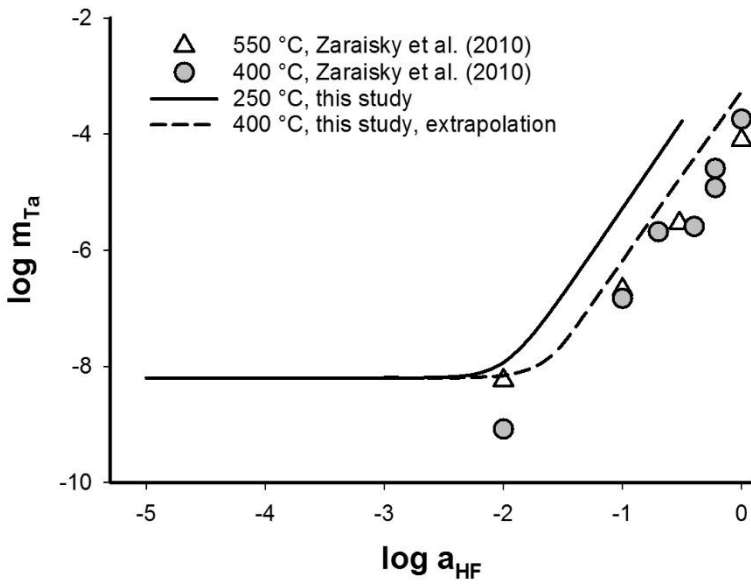


Figure 6

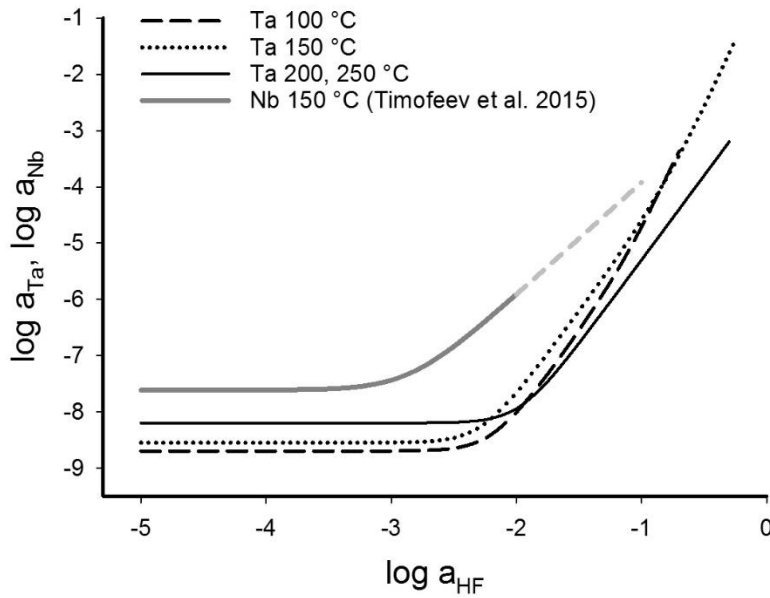


Figure 7

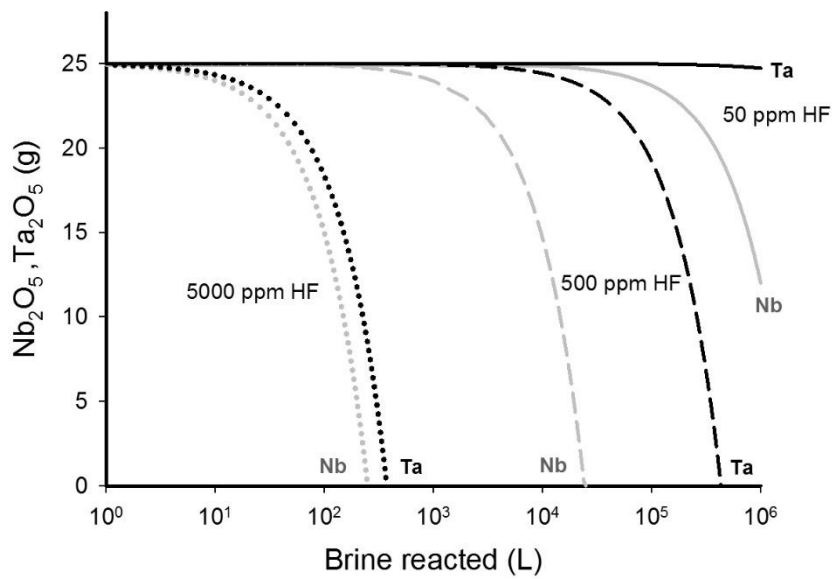
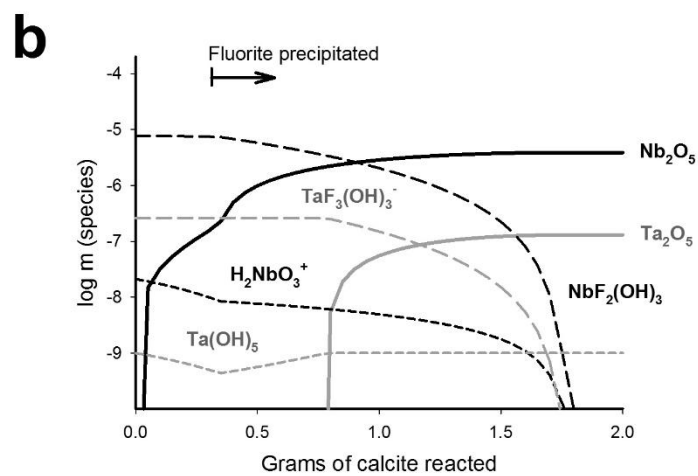
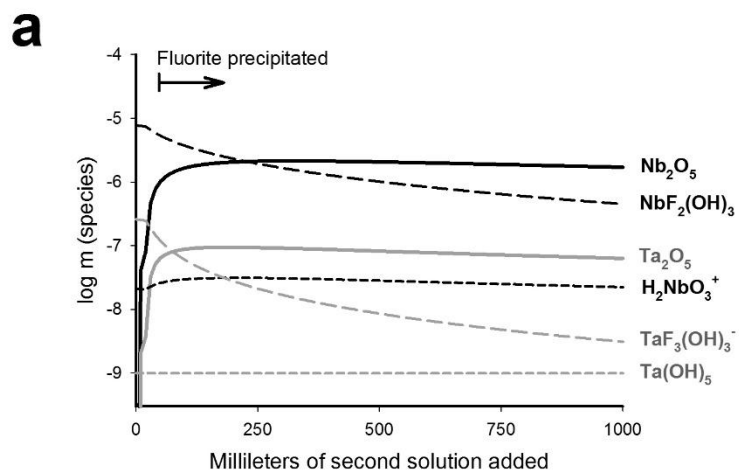


Figure 8



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617 Figure 9