



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

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## Abstract

The solubility of Nb<sub>2</sub>O<sub>5</sub> and the speciation of niobium in HF-bearing aqueous solutions have been determined at temperatures of 150, 200, and 250 °C and saturated water pressure. At a pH of ~2 and at low HF concentration, niobium is transported primarily as the species Nb(OH)<sub>4</sub><sup>+</sup> and at high HF concentration, as the species NbF<sub>2</sub>(OH)<sub>3</sub><sup>o</sup>. Equilibrium constants for the formation of Nb(OH)<sub>4</sub><sup>+</sup> range from  $-11.23 \pm 0.26$  to  $-10.86 \pm 0.24$  and for the formation of NbF<sub>2</sub>(OH)<sub>3</sub><sup>o</sup> from  $-3.84 \pm 0.20$  to  $-5.08 \pm 0.42$ , at 150 and 250 °C.

The results of this study show that the solubility of Nb<sub>2</sub>O<sub>5</sub> (solid) in aqueous fluids increases with increasing HF concentration, but is not strongly affected by temperature. The influence of pH is variable; at low pH and HF concentration, a decrease in pH increases the solubility of Nb<sub>2</sub>O<sub>5</sub> (solid). At higher pH, the reverse may be true. Modeling of the transport and deposition of niobium suggests that simple mixing with a brine is not an effective method for removing niobium from solution. By contrast, interaction of an acidic fluid with carbonate rock results in a rapid reduction in the capacity of the fluid to mobilize niobium.

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## 1. INTRODUCTION

In most geological environments, niobium is highly immobile and, for this reason, is often used as a normalizing element in evaluations of mass-changes accompanying hydrothermal alteration (e.g., Maclean and Kranidotis, 1987; Christidis, 1998). However, in some settings, notably in hydrothermally altered alkaline igneous intrusions, the replacement of niobium-bearing minerals, such as pyrochlore and zircon, by secondary niobium

minerals, e.g., columbite and fergusonite-(Y), provides convincing evidence of niobium mobility, at least on a local scale (e.g., Sheard et al., 2012). In some cases, e.g., at Bayan Obo, China, the Nb mineralisation (aeschynite-(Ce)) may be entirely hydrothermal. Significantly, the Nb mineralisation there constitutes an economic resource of 1 million metric tons Nb hosted by dolomitic marbles (Smith and Henderson, 2000).

In principle, niobium as Nb<sup>5+</sup>, is a hard acid and should form strong complexes with hard bases (Pearson, 1963). As fluorine is commonly present in elevated concentrations in alkaline igneous complexes and as F<sup>-</sup> is a hard base, complexes involving fluoride could potentially explain the mobility of niobium in this environment. With this in mind, Zaraisky et al. (2010), measured the solubility of columbite-tantalite in fluoride-bearing aqueous solutions at temperatures up to 550 °C and pressures up to 100 MPa. They

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showed that the solubility of this phase does, indeed, increase sharply with increasing fluoride ion activity, and that the efficacy of fluoride in facilitating the transport of niobium is an order of magnitude greater than that of other ligands. However, they did not evaluate the aqueous niobium or tantalum speciation and thus did not determine stability constants that could be used to quantitatively evaluate niobium transport in hydrothermal fluids. The only experimental study that has quantitatively evaluated the stability of niobium species at elevated temperature is that of Peiffert et al. (2010), but this study was limited to an investigation of niobium hydroxide complexes at temperatures from 10 to 70 °C. Estimates of the stability constants of niobium hydroxide species at elevated temperature are also available from extrapolations of stability constants determined experimentally for these species at ambient temperature (Shock et al., 1997). These estimates should be treated with caution, however, as it is not uncommon for them to differ by many orders of magnitude from the stability constants determined experimentally at elevated temperature (e.g., Migdisov and Williams-Jones, 2007). According to Peiffert et al. (2010), pH is the main factor controlling niobium hydroxide species solubility in fluoride-free solutions, although it needs to be noted that this conclusion is strictly valid only for temperatures below 70 °C.

In this paper, we report results of a series of experiments designed to determine the solubility of Nb<sub>2</sub>O<sub>5</sub> (solid) in aqueous solutions as a function of fluoride activity and pH at temperatures of 150, 200, and 250 °C, and vapor-saturated water pressure. The results of these experiments, which are reported below, are used to evaluate the speciation of niobium at the conditions of interest, and determine formation constants for the dominant species. Based on the latter, we assess the capacity of a circulating, fluoride-bearing, hydrothermal fluid to mobilize niobium.

## 2. METHODS

### 2.1. Experimental technique

Our experiments involved measuring the solubility of synthetic Nb<sub>2</sub>O<sub>5</sub> (solid) (99.99%, Alfa Aesar) in aqueous solutions of variable pH and HF concentration at temperatures of 150, 200, and 250 °C, and vapor-saturated water pressure. The pH at the temperatures of interest ranged from 1.6 to 3.1, with most experiments being carried out at a pH between 2 and 2.4, and the HF concentration ranged from 10<sup>-5</sup> to 10<sup>-2</sup> mol/kg. The experiments were performed in Teflon test tubes contained within titanium autoclaves (Fig. 1). The overall 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.

The concentration of fluoride in the experimental solutions was controlled by dissolving known amounts of NaF in nano-pure water. The pH of each solution was then lowered to the level of interest by adding an appropriate amount of TM grade HClO<sub>4</sub>. At the beginning of each experiment, small Teflon holders containing Nb<sub>2</sub>O<sub>5</sub> powder

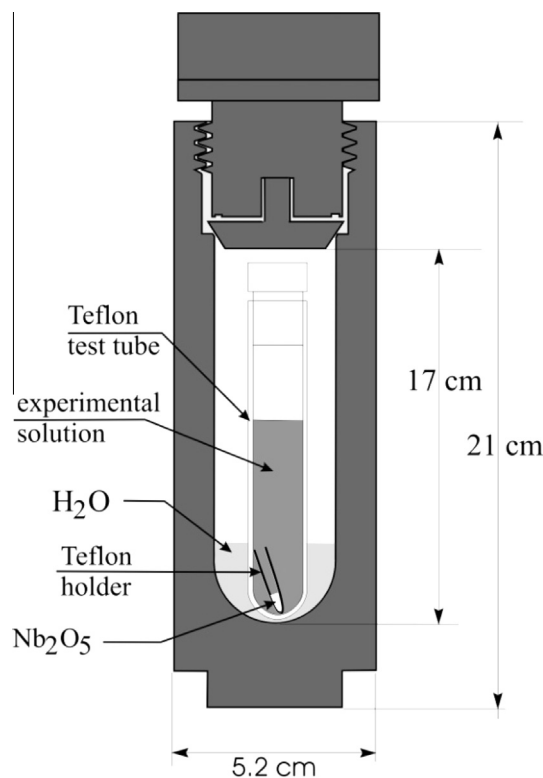


Fig. 1. A schematic drawing illustrating the experimental set-up.

were placed in a Teflon test tube, to which between 17 and 20 ml of experimental solution was added depending on the size of the test tube used in the experiment. The Teflon test tubes were then placed in titanium autoclaves containing nano-pure water in order to balance pressures developed inside and outside the test tube, and heated in a Fisher Isotemp forced draft oven where they were left to equilibrate at the temperature of interest. The time required to reach equilibrium was determined from a series of experiments of variable duration performed at 150 °C. The duration of the experiments ranged from 1 to 12 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. The reproducibility of the experiments with durations >6 days was  $\sim\pm 10\%$ . Heating, quenching and sampling of the autoclaves were carried out in less than an hour to minimize Nb<sub>2</sub>O<sub>5</sub> (solid) dissolution and precipitation before or after an experiment, respectively.

Following completion of an experiment, the autoclave was quenched in cold water and the Nb<sub>2</sub>O<sub>5</sub>-bearing Teflon holder within the larger Teflon test tube was removed. The Nb<sub>2</sub>O<sub>5</sub> (solid) within the Teflon holder was analyzed by X-ray diffraction after conclusion of the experiments. No additional solids were detected. A small aliquot (3 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 experimental solution was determined from this aliquot potentiometrically using a glass pH

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