



# Molybdenum isotope fractionation during acid leaching of a granitic uranium ore

Valérie Migeon<sup>a,b</sup>, Bernard Bourdon<sup>a,\*</sup>, Eric Pili<sup>b</sup>, Caroline Fitoussi<sup>a</sup>

<sup>a</sup> *Laboratoire de Géologie de Lyon (LGL-TPE), ENS Lyon, CNRS and Université Claude Bernard de Lyon, 46 allée d'Italie, 69364 Lyon Cedex 7, France*

<sup>b</sup> *CEA, DAM, DIF, F-91297 Arpajon, France*

Received 16 June 2017; accepted in revised form 3 April 2018; Available online 12 April 2018

## Abstract

As an attempt to prevent illicit trafficking of nuclear materials, it is critical to identify the origin and transformation of uranium materials from the nuclear fuel cycle based on chemical and isotope tracers. The potential of molybdenum (Mo) isotopes as tracers is considered in this study. We focused on leaching, the first industrial process used to release uranium from ores, which is also known to extract Mo depending on chemical conditions. Batch experiments were performed in the laboratory with pH ranging from 0.3 to 5.5 in sulfuric acid. In order to span a large range in uranium and molybdenum yields, oxidizers such as nitric acid, hydrogen peroxide and manganese dioxide were also added. An enrichment in heavy Mo isotopes is produced in the solution during leaching of a granitic uranium ore, when Mo recovery is not quantitative. At least two Mo reservoirs were identified in the ore: ~40% as Mo oxides soluble in water or sulfuric acid, and ~40% of Mo hosted in sulfides soluble in nitric acid or hydrogen peroxide. At pH > 1.8, adsorption and/or precipitation processes induce a decrease in Mo yields with time correlated with large Mo isotope fractionations. Quantitative models were used to evaluate the relative importance of the processes involved in Mo isotope fractionation: dissolution, adsorption, desorption, precipitation, polymerization and depolymerization. Model best fits are obtained when combining the effects of dissolution/precipitation, and adsorption/desorption onto secondary minerals. These processes are inferred to produce an equilibrium isotope fractionation, with an enrichment in heavy Mo isotopes in the liquid phase and in light isotopes in the solid phase. Quantification of Mo isotope fractionation resulting from uranium leaching is thus a promising tool to trace the origin and transformation of nuclear materials. Our observations of Mo leaching are also consistent with observations of natural Mo isotope fractionation taking place during chemical weathering in terrestrial environments where the role of secondary processes such as adsorption is significant. © 2018 Elsevier Ltd. All rights reserved.

**Keywords:** Molybdenum isotopes; Granite; Acid leaching; Isotope fractionation; Nuclear forensics

## 1. INTRODUCTION

In the nuclear fuel cycle, several wet or dry processes are used to concentrate and purify uranium from other elements contained in uranium ores (Seidel, 1993). Molybdenum (Mo) is an impurity difficult to separate from

uranium (Stone, 2006), due to similarities in their chemical properties (Dean et al., 1997; Morford and Emerson, 1999; Zheng et al., 2000; Adelson et al., 2001; Chaillou et al., 2002; Sundby et al., 2004). The large range of <sup>98</sup>Mo/<sup>95</sup>Mo isotope ratios measured in uranium ore concentrates suggests that Mo isotopes have a potential for identifying the origin and transformation of uranium in the nuclear fuel cycle (Migeon et al., 2015), in the framework of efforts to prevent illicit trafficking. The ability to trace the removal of Mo in the purification of uranium is also of

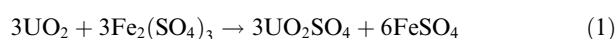
\* Corresponding author.

E-mail addresses: [bernard.bourdon@ens-lyon.fr](mailto:bernard.bourdon@ens-lyon.fr) (B. Bourdon), [eric.pili@cea.fr](mailto:eric.pili@cea.fr) (E. Pili), [caroline.fitoussi@ens-lyon.fr](mailto:caroline.fitoussi@ens-lyon.fr) (C. Fitoussi).

interest in order to improve this key industrial process in the production of commercially acceptable uranium ore concentrates.

In uranium ore samples, uranium (U) concentrations vary from a few hundred  $\mu\text{g/g}$  to 20 wt.% and molybdenum concentrations vary from a few  $\text{ng/g}$  to more than 0.5 wt.% (Gupta, 1992), with U/Mo ratios ranging between  $1 \times 10^{-3}$  and 1 (Wagani, 2007; CETAMA, 2011). Uranium-bearing minerals are mainly U(IV) compounds such as uraninite ( $\text{UO}_2$ ), pitchblende (colloform  $\text{UO}_2$ ) and coffinite ( $\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$ ), Finch and Murakami, 1999; Hazen et al., 2009) and less frequently U(VI) compounds such as hydroxide, silicate, phosphate, vanadate, arsenate, carbonate, sulfate and molybdate minerals. Molybdenum-bearing minerals are sulfides (e.g. molybdenite:  $\text{MoS}_2$ , jordisite: amorphous  $\text{MoS}_2$ ), oxides (molybdite:  $\text{MoO}_3$ , ilsemannite:  $\text{Mo}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ ), molybdates (ferrimolybdite:  $\text{Fe}_2(\text{MoO}_4)_3 \cdot n\text{H}_2\text{O}$ , powellite:  $\text{CaMoO}_4$ , wulfenite:  $\text{PbMoO}_4$ ). Mo substitutes to iron in the pyrite structure. It can also be associated with uraninite or adsorbed to Fe and Mn oxides contained in U ores (Barling and Anbar, 2004; Wasylenki et al., 2008, 2011; Goldberg et al., 2009a, 2012).

In the nuclear fuel cycle, leaching of uranium ore is the first important step for concentrating uranium in solution before further purification. Numerous studies have been dedicated to the optimization of this process (Eary and Cathles, 1983; Vetter et al., 1989; Roodt and Sandenbergh, 2003; Balasubrahmanyam et al., 2007; Lottering et al., 2008; Guettaf et al., 2009; Roshani and Mirjalili, 2009; Venter and Boylett, 2009; Tamrakar et al., 2010; Ram et al., 2013; Kim et al., 2014; Gadja et al., 2015). Acid or alkaline leaching methods are used depending on the composition of the gangue, reagent availability, uranium extraction efficiency and energy consumption (Seidel, 1993). Acid leaching with sulfuric acid is commonly used in a majority of uranium mills because of the wide availability of this acid and its low cost. In an industrial context, acid leaching of uranium ore slurry is carried out at ambient pressure, at temperatures ranging between 30 and 65 °C and over less than 8 h. Sulfuric acid is added with a proportion of 10–100 g/kg of ore, ultimately resulting in a free acid concentration between 2 and 10 g/L (Seidel, 1993). The oxidative dissolution of U(IV) to the hexavalent form is promoted by excess ferric ions in solution (1–2 g/L, Burkin, 1980; Seidel, 1993). Iron is naturally released from the ore or added during the leaching process. Re-oxidation of  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$  is obtained by adding oxidizers such as  $\text{MnO}_2$ ,  $\text{NaClO}_3$ ,  $\text{H}_2\text{O}_2$ ,  $\text{HNO}_3$  (Michel, 1987, 1997; Seidel, 1993). In this context, the complete reaction of uraninite or pitchblende oxidative dissolution can be written as:



The pH must range between 1.5 and 2 in order to prevent precipitation of uranium and iron, as well as other ions. Uranium recovery is generally between 85 and 97% (Michel, 1997). In oxidizing conditions, U(VI) is in the uranyl form ( $\text{UO}_2^{2+}$ ) and in sulfuric acid it forms a uranyl sulfate complex  $\text{UO}_2(\text{SO}_4)_3^{4-}$  at  $\text{pH} < 4$  (Seidel, 1993).  $\text{Fe}^{3+}$  is significantly soluble only at  $\text{pH} < 2.5$ . A higher pH can lead to the precipitation of iron hydroxides ( $\text{Fe}(\text{OH})_3$ ) or

schwertmannite ( $\text{Fe}_8\text{O}_8(\text{OH})_{8-2x}(\text{SO}_4)_x$ ) in the presence of sulfates (Yu et al., 1999; Majzlan et al., 2004).

During acid leaching of uranium and subsequent purification steps, molybdenum when present is actively eliminated and it can be extracted as a by-product (Ajuria, 1990; Seidel, 1993). In dilute sulfuric acid, only oxidized molybdenum minerals are expected to dissolve, whereas the addition of an oxidizer should lead to the dissolution of sulfides such as molybdenite and jordisite (Gupta, 1992). At the pH conditions used for uranium extraction,  $\text{pH} < 2.5$ , molybdic acid ( $\text{H}_2\text{MoO}_4$  or  $\text{MoO}_3 \cdot 2\text{H}_2\text{O}$ ) and cations ( $\text{MoO}_2^{2+}$  and more complex ones) are the main species in solution (Betenekov et al., 2016). At pH ranging from 2.5 to 6.5, the dominant species are  $\text{HMoO}_4^-$  and polyanions such as  $\text{Mo}_6\text{O}_{13}^{3-}$  or  $\text{Mo}_6\text{O}_{20}^{4-}$ , for Mo concentrations  $> 0.03$  mM. At higher pH, only molybdate anions ( $\text{MoO}_4^{2-}$ ) are present (Gupta, 1992; Takeno, 2005). When iron and molybdenum coexist in a sulfate bearing solution, precipitation of ferrimolybdate ( $\text{Fe}_2(\text{MoO}_4)_3 \cdot n\text{H}_2\text{O}$ ) could possibly occur at a pH around 3.5 (Gupta, 1992). At higher pH, iron hydroxides or schwertmannite can precipitate and molybdate anions can be adsorbed onto newly formed mineral phases (Yu et al., 1999; Majzlan et al., 2004; Antelo et al., 2012). Other precipitates, such as sodium molybdate ( $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ), calcium molybdate ( $\text{CaMoO}_4$ ), aluminium molybdate ( $\text{Al}_2(\text{MoO}_4)_3$ ) or lead molybdate ( $\text{PbMoO}_4$ ) could form in these conditions (Gupta, 1992; Barling and Anbar, 2004).

Previous laboratory experiments of molybdenum leaching from magmatic rocks have led to contradictory results regarding the Mo isotope composition of the leach solution. Siebert et al. (2003) suggested that no Mo isotope fractionation takes place during 24 h-long leaching of granitic rocks with cold 0.05 M HCl. The Mo isotope composition of leachates was indistinguishable from that of the granite. In contrast, Voegelin et al. (2012) performed leaching experiments on granite, basalt and orthogneiss, with nitric acid (0.3 and 2 M) to avoid secondary mineral formation and adsorption on Fe-Mn (oxyhydr)oxides. These authors reported enrichment in heavy Mo isotopes in the leaching solution. In addition, formation of secondary minerals in the leach solution could lead to Mo isotope fractionation because fractionation takes place during adsorption of dissolved Mo onto Fe and Mn hydroxides (Siebert et al., 2003; Barling and Anbar, 2004; Wasylenki et al., 2006, 2008; Goldberg et al., 2009b).

The aim of this study was to quantify the isotope fractionation of molybdenum during acid leaching of a granitic uranium ore under various experimental conditions. Dilute sulfuric acid was used as the leaching solution, and the influence of various oxidizing agents, such as  $\text{MnO}_2$ ,  $\text{HNO}_3$  and  $\text{H}_2\text{O}_2$  was tested.

## 2. EXPERIMENTAL PROCEDURE

### 2.1. Starting material

For this study, a uranium ore standard reference, MIN D, was purchased from CETAMA (CETAMA, 2011). This powder has a particle size of 40  $\mu\text{m}$ . According to its

Download English Version:

<https://daneshyari.com/en/article/8910745>

Download Persian Version:

<https://daneshyari.com/article/8910745>

[Daneshyari.com](https://daneshyari.com)