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Study of the alteration products of a natural uraninite by Raman spectroscopy

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ABSTRACT

Uraninite is a mineral considered as an analogue of the spent fuel, and the study of its alteration products has been used to predict the secondary phases produced during the fuel storage under specific environmental conditions. In this work, we study by Raman spectroscopy the alteration by weathering of the primary uraninite from the uranium deposit of Sierra Albarrana. The identification of the different secondary phases is based on the analysis of the symmetrical stretching vibration of the uranyl group (UO_2^{2+}), which allows the identification of individual uranyl phases and can be used as a fingerprint. Additionally, we show in this work a new approach to perform a semi-quantitative analysis of these uranium minerals by means of Raman spectroscopy. From this analysis we found the next sequence of alteration products: rutherfordine in contact with the uraninite core, then a mixture of uranyl silicates: soddyite, uranophane alpha and kasolite. Soddyite prevails in the inner part while uranophane alpha predominates in the outer part of the sample, and kasolite appears intermittently (1.0–3.3 mm; 4.6–7.1 mm and 8.8–10 mm).

1. Introduction

High-level nuclear waste, such as irradiated UO_2 (spent fuel) will be disposed in an underground repository. It is expected that the spent fuel will be exposed to groundwater after storage times of the order of some thousand years, when the containers surrounding the waste may be breached. Identification of the reaction products generated by the interaction of the waste form with water is required to characterize the repository performance [1].

All scenarios describing the spent fuel–groundwater contact require extrapolations to the far future of a complex system, whose components are not all well-defined. It is expected that the conditions in a spent fuel deep geological disposal will be reducing. Nevertheless, the amount of oxidizing species near the spent fuel surface will increase due to the radiolysis of water caused by the ionizing radiation associated with the fuel [2], which is dominated at the predicted time of the breached containers by the α-decay [3,4]. In particular, only those radiolysis products, which are formed in the water layer near the fuel surface, i.e. within <50 μm of the fuel surface, are effective in causing the fuel oxidation [5]. Therefore, both dissolution and precipitation processes under this conditions will affect the overall behavior of the fuel matrix. Depending of the surface/volume ratio, secondary phases will appear on the spent fuel surface as alteration products [6].

Different approaches can be done in order to study the dissolution/precipitation processes of spent nuclear fuel (SF) and understand the potential migration of uranium under repository conditions during millions of years. On one hand, the use of mathematical models [7,8] allows predicts SF behavior in the long-term at the expected conditions. These theoretical methods require the knowledge of physico-chemical parameters. These must be obtained experimentally in laboratory assays for SF analogues, such as uranium dioxide UO_2 [9,10] or SIMFUEL [11,12]. On the other hand, the studies of natural analogues have been very successful, to understand different aspects of the SF corrosion processes at longer storage times [13–24].

The uraninite is known as the natural analogue of the SF, and studies about its dissolution [13,14] and its corrosion [15,16] at different conditions have been performed for decades. The consideration of this mineral as an analogue of the SF is mainly due to two reasons: (1) uraninite is a non-stoichiometric compound with a chemical composition very similar to that of spent fuel ($UO_2 > 95\%$) [17,18], although natural uraninite contains variable quantities of radiogenic lead which could generate secondary U–Pb phases after alteration; (2) both materials have a cubic fluorite structure, (space group Fm3m). Studies of different uraninites have been widely performed. Some studies [19–22] have shown the

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temporal sequence of the alteration products of natural uraninites at different geochemical conditions. The general trend of this sequence was previously recognized by Frondel [23,24] and it is still widely accepted as: (1) uranium oxides, (2) uranyl oxyhydroxides and (3) uranyl silicates; and the specific alteration products depend on local conditions.

Characterization of the alteration products of natural uraninites has been conventionally done by the combination of different techniques: optical petrography (OP) [19], scanning electron microscopy/energy-dispersive X-ray analysis (SEM/EDS) [19–22] and electron microprobe analysis (EMPA) [19–21]. There are nowadays other techniques that can provide a complete information by themselves, without using complementary techniques, such as Raman spectroscopy.

The advantages of the Raman spectroscopy are as follow: (1) the samples do not require any special preparation, so possible alterations due to these previous steps are avoided by using this technique; (2) this technique allows the analysis of very small samples with little background interference [25–27]. However, knowledge of Raman spectra of uranyl-based minerals is still rather limited except the effort of Frost et al. and Amme et al. [28,36,37].

This work focuses on the complete identification by Raman spectroscopy of the supergenic uranyl phases produced by alteration of a natural analogue of the spent fuel: the uraninite from Sierra Albarrana (Spain). To the best of our knowledge this is the first study of uraninite and its associated secondary uranium minerals from the uranium deposit of Sierra Albarrana, and it has been shown that the complete characterization of uranium secondary phases is possible using only one characterization technique. Emphasis on the development of a new approach, the semi-quantitative analysis of these uranium minerals by Raman spectroscopy has been done.

2. Materials and methods

2.1. Mineral sample and geological setting

The sample studied is a “uraninite + gummite” from Sierra Albarrana (Córdoba, Spain), kindly provided by the Museum of Natural Sciences of Alava (Vitoria, Spain). It has been collected during the uranium extractive activity in 1960.

The sample structure corresponds to the ideal gummite occurrence [23,24] (see Fig. 1a): a veined central core black to brownish black and yellow to orange or greenish yellow surrounding zone, vitreous to dull or earthy, formed by several supergenic minerals.

The uranium-rare earth mineralization at Sierra Albarrana (Cordoba, Spain) [29] is distributed in a complex pegmatite field of granitic composition. The pegmatites are not related with plutonic bodies and are syn-metamorphic and formed by anatexis associated to medium to high grade metamorphism during Variscan. The pegmatite field is hosted by the Cambrian quartzite and gneiss of the metamorphic nucleus of the Albarrana formation [30]. The pegmatite forms irregular bodies and veins parallel to the Variscan structures. The pegmatite mineralogy is controlled by the metamorphic grade and the accessory minerals include uraninite, thorite, brannerite, beryl, schorl , rutile, ilmenite, allanite–(Ce), zircon, monazite–(Ce), xenotime, columbite–tantalite, chrysoberyl and Fe–Mn–Mg–Caphosphates [31,32]. From a geochemical point of view, the uraninite-gummite samples studied in this work belong to a pegmatite of the Muscovite-rare element class in the Cherny classification [33] and the type “Dieresis” in the classification of Gonzalez del Tánago [34], hosted by rich biotitic-muscovitic gneisses. This type of pegmatite was worked for the extraction of uranium.

2.2. Preparation of the sample

The sample studied in this work was obtained from the Mineralogy collection of the Natural Sciences Museum of Alava (MCNA, Vitoria, Spain). The sample is from the *Dieresis* uranium mine (Sierra Albarrana, Córdoba, Spain).

The sample was cut using a diamond saw and polished. The thick polished sections obtained were subjected to spectroscopic analysis.

2.3. SEM–EDS

A polished section of the sample was analyzed under a Jeol 5600-LV scanning electron microscope equipped with an Oxford Industries INCA X-sight energy dispersive X-ray spectrometer. Backscattered electron images and energy dispersive spectra were obtained on the sample mounted on Al stubs and without coating ($V = 20$ kV $I = 85$ μA, electron beam diameter 1 μm).

2.4. Raman spectroscopy technique

The Raman spectroscopy was carried out using a Horiba LabRam HR evolution spectrometer (Jobin Yvon Technology). A red laser of HeNe with a wavelength of 632.81 nm and an operation power of 20 mW was used as the excitation source. The laser was focused onto the sample using 20× objective at the confocal microscope BX4 with confocal 800 mm; the scatter light was collected with the same objective and then dispersed with a Jobin-Yvon spectrometer (600 gooves/mm), and detected with a peltier cooled CCD detector (256 × 1024 pix.). The spectral resolution was about 1 cm^{-1} per pixel.

2.5. Raman mapping procedure

The surface of the sample was analyzed by acquiring 100 spectra in different points separated 100 μm from each other. The first one corresponds to the center of the sample and the rest were located on a line going from the center of the sample outwards, (see Fig. 1a and b). In Fig. 1 we have indicated the position at the sample in which the spectra were taken. As it can be seen, we have divided the sample in eight regions for further analysis. The choice of the different region lengths was performed by visual analysis. Regions 1, 2 and 3 correspond to zones of different darkness near to the core of the sample, whereas zone 4, 5, 6, 7 and 8 correspond to different yellow tones of the sample, and are separated by veins.

The protocol used is a combination of the line-mapping and step-by-step procedures, as described below: The sample is placed in the motorized x–y stage under the microscope objective and focused on the center. Then, a line-mapping is performed using the automatized line-scanning tool. This tool allows the acquisition of a complete Raman spectrum at different points on a line by automatically moving the stage in one or two directions (x–y).

The microscope objective used in this work, with a magnification of 20×, allows the visualization of a maximum area of 500 μm × 70 μm (Fig. 1c). Therefore, in order to analyze the whole sample (10 mm) 20 lines with 5 equidistant points each have been measured. This was performed with the step-by-step procedure, in which the motorized stage is moved 500 μm (the line-mapping length) in the x direction to allow the analysis of the next part of the sample.

The acquisition time for each spectrum was ∼100 s on an extended shift of 100–1200 cm^{-1}. During the start of all Raman scan, a cosmic ray subtraction is automatically carried out to count any radioactive interference from the atmosphere or the sample. All spectra were re-calibrated daily with the emission lines of a Ne lamp. Spectra manipulation such as baseline adjustment,