ACTINIDES IN GEOLOGY, ENERGY, AND THE ENVIRONMENT

Ichnusaite, Th(MoO₄)₂·3H₂O, the first natural thorium molybdate: Occurrence, description, and crystal structure†

PAOLO ORLANDI¹², CRISTIAN BIAGIONI¹*, LUCA BINDI³ AND FABRIZIO NESTOLA⁴

¹Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, I-56126 Pisa, Italy
²Istituto di Geoscienze e Georisorse, CNR, Via Moruzzi 1, I-56124 Pisa, Italy
³Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Via G. La Pira, I-50121 Firenze, Italy
⁴Dipartimento di Geoscienze, Università di Padova, Via Gradenigo, 6, I-35131 Padova, Italy

ABSTRACT

The new mineral species ichnusaite, Th(MoO₄)₂·3H₂O, has been discovered in the Mo-Bi mineralization of Su Seinargiu, Sarroch, Cagliari, Sardinia, Italy. It occurs as colorless thin {100} tabular crystals, up to 200 µm in length, associated with muscovite, xenotime-(Y), and nauragheite, Th(MoO₄)₂·H₂O. Luster is pearly adamantine. Ichnusaite is brittle, with a perfect {100} cleavage. Owing to the very small quantity of available material and its intimate association with nauragheite, density and optical properties could not be measured. Electron microprobe analysis gave (mean of 4 spot analyses in wt%): MoO₄, 47.86(1.43), ThO₂, 43.40(79), total 91.26(87). On the basis of 8 O atoms per formula unit and assuming 3 H₂O groups, in agreement with the crystal structure data, the chemical formula of ichnusaite is Th₀.⁰⁹Mo₂.⁰⁶Oₓ·3H₂O. Main diffraction lines, corresponding to multiple hkl indices, are [d(Å), relative visual intensity]: 5.66 (m), 3.930 (m), 3.479 (s), 3.257 (s), 3.074 (m). Ichnusaite is monoclinic, space group P2₁/c, with a = 9.6797(12), b = 10.3771(13), c = 9.3782(12) Å, β = 90.00(1)°, V = 942.0(2) Å³, Z = 4. The crystal structure has been solved and refined to a final R₁ = 0.051 on the basis of 2008 observed reflections [with F̅o > 4σ(Fo)]. It consists of electron-neutral [Th(MoO₄)₂(H₂O)₃]⁺ (100) sheets of polymerized ThO₂(H₂O)₆ and MoO₄ polyhedra; successive sheets, stacked along [100], are connected through hydrogen bonds. Ichnusaite brings new understanding about the crystal chemistry of actinide molybdates, that may form during the alteration of spent nuclear fuel and influence the release of radionuclides under repository conditions.

Keywords: Ichnusaite, new mineral species, molybdate, thorium, crystal structure, Su Seinargiu, Sardinia, Italy

INTRODUCTION

Thorium (Z = 90) is an actinide element found in the bulk silicate Earth with the estimated average concentration of ~0.06 ppm (Plant et al. 1999); even if it is about three times more abundant than uranium, only 22 mineral species containing Th as an essential component are known (Table 1), compared to more than 200 uranium mineral species. This difference is discussed by Hazen et al. (2009) and related to three main aspects: (1) Th occurs only as Th⁴⁺ and it does not have an analog of (UO₂)⁴⁻ ion, not forming isomorphs of the numerous uranyl compounds; (2) the half-life of ²³²Th (the most abundant isotope of Th) is ~14 billion years so that thorium minerals do not show extensive degree of radiation damage and chemical alteration; and (3) Th-compounds are relatively insoluble, and Th⁴⁺ is mobilized under much more restricted chemical-physical conditions than U⁴⁺, not being complexed by chloride or carbonate (as occurs for U⁴⁺) but only forming F-complexes. Thorium occurs as a minor component in rare-earth element phosphates (e.g., monazite, xenotime) and as a trace element in apatite-group minerals (Luo et al. 2011); owing to its occurrence in these common rock-accessory phases, Th minerals can be used as geochronometers for dating through the U-Th-Pb and (U,Th)/He methods.

During a routine check of mineral samples from Su Seinargiu (Sardinia, Italy) through qualitative EDS chemical analyses, some crystals were identified containing only Th and Mo. Up to now, natural thorium molybdates were unknown and consequently X-ray diffraction studies were performed to completely characterize this new compound. X-ray powder diffraction patterns collected through a Gandolphi camera revealed the presence of two different Th-Mo phases. Single-crystal X-ray diffraction studies showed that these two phases commonly form intimate intergrowths, making difficult their mineralogical study. Through the examination of several crystals, two pure grains of both phases were identified, allowing the intensity data collection and solution of the two crystal structures. The two Th-Mo phases, differing in their hydration states, were proposed as new minerals.

In this paper, we describe the first of these two natural thorium molybdates, which was named ichnusaite (pronounced iknusa-iit). The name is from the old Greek name of Sardinia, ἰχνουσα, ichnusa. The mineral and its name have been approved by the CNMNC-IMA under the number 2013-087. The holotype specimen of ichnusaite is deposited in the mineral-

---

* E-mail: biagioni@dst.unipi.it
† Special collection papers can be found on GSW at http://ammin.geoscienceworld.org/site/misc/specialissuelestlist.xhtml.