

ACTINIDES IN GEOLOGY, ENERGY, AND THE ENVIRONMENT

**Ichnusaite,  $\text{Th}(\text{MoO}_4)_2 \cdot 3\text{H}_2\text{O}$ , the first natural thorium molybdate: Occurrence, description, and crystal structure†**

**PAOLO ORLANDI<sup>1,2</sup>, CRISTIAN BIAGIONI<sup>1,\*</sup>, LUCA BINDI<sup>3</sup> AND FABRIZIO NESTOLA<sup>4</sup>**

<sup>1</sup>Dipartimento di Scienze della Terra, Università di Pisa, Via S. Maria 53, I-56126 Pisa, Italy

<sup>2</sup>Istituto di Geoscienze e Georisorse, CNR, Via Moruzzi 1, I-56124 Pisa, Italy

<sup>3</sup>Dipartimento di Scienze della Terra, Università degli Studi di Firenze, Via G. La Pira, 4, I-50121 Firenze, Italy

<sup>4</sup>Dipartimento di Geoscienze, Università di Padova, Via Gradenigo, 6, I-35131 Padova, Italy

**ABSTRACT**

The new mineral species ichnusaite,  $\text{Th}(\text{MoO}_4)_2 \cdot 3\text{H}_2\text{O}$ , 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  $\mu\text{m}$  in length, associated with muscovite, xenotime-(Y), and nuragheite,  $\text{Th}(\text{MoO}_4)_2 \cdot \text{H}_2\text{O}$ . 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 nuragheite, density and optical properties could not be measured. Electron microprobe analysis gave (mean of 4 spot analyses in wt%):  $\text{MoO}_3$  47.86(1.43),  $\text{ThO}_2$  43.40(79), total 91.26(87). On the basis of 8 O atoms per formula unit and assuming 3  $\text{H}_2\text{O}$  groups, in agreement with the crystal structure data, the chemical formula of ichnusaite is  $\text{Th}_{0.99}\text{Mo}_{2.01}\text{O}_8 \cdot 3\text{H}_2\text{O}$ . Main diffraction lines, corresponding to multiple  $hkl$  indices, are [ $d(\text{\AA})$ , relative visual intensity]: 5.66 (m), 3.930 (m), 3.479 (s), 3.257 (s), 3.074 (m). Ichnusaite is monoclinic, space group  $P2_1/c$ , with  $a = 9.6797(12)$ ,  $b = 10.3771(13)$ ,  $c = 9.3782(12)$   $\text{\AA}$ ,  $\beta = 90.00(1)^\circ$ ,  $V = 942.0(2)$   $\text{\AA}^3$ ,  $Z = 4$ . The crystal structure has been solved and refined to a final  $R_1 = 0.051$  on the basis of 2008 observed reflections [with  $F_o > 4\sigma(F_o)$ ]. It consists of electroneutral  $[\text{Th}(\text{MoO}_4)_2(\text{H}_2\text{O})_2]^0$  (100) sheets of polymerized  $\text{ThO}_7(\text{H}_2\text{O})_2$  and  $\text{MoO}_4$  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