ACTINIDES IN GEOLOGY, ENERGY, AND THE ENVIRONMENT

Nuragheite, Th(\text{MoO}_4)_2\cdot\text{H}_2\text{O}, the second natural thorium molybdate and its relationships to ichnusaitae and synthetic Th(\text{MoO}_4)_2†

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ABSTRACT

The new mineral species nuragheite, Th(\text{MoO}_4)_2\cdot\text{H}_2\text{O}, has been discovered in the Mo-Bi mineralization of Su Seinariu, Sarroch, Cagliari, Sardinia, Italy. It occurs as colorless thin \{100\} tabular crystals, up to 200 μm in length, associated with muscovite, xenotime-(Y), and ichnusaitae, Th(\text{MoO}_4)_2\cdot\text{H}_2\text{O}. Luster is pearly to adamantine; nuragheite is brittle, with a perfect \{100\} cleavage. Owing to the very small amount of available material and its intimate association with ichnusaitae, density and optical properties were not measured. Electron microprobe analysis gave (wt% = mean of six spot analyses): MoO\text{$_3$} 49.38, ThO\text{$_2$} 45.39, H\text{$_2$}O 5.23. On the basis of eight O atoms per formula unit and assuming one H\text{$_2$}O group, in agreement with the crystal structure data, the chemical formula of nuragheite is Th$_{100}$Mo$_{100}$O$_{300}$H$_2$O. Main diffraction lines, corresponding to multiple hk\text{i} indices, are \{d in Å (relative visual intensity)\}: 5.28 (m), 5.20 (m), 5.04 (m), 4.756 (m), 3.688 (m), 3.546 (vs), 3.177 (s), 3.024 (m). The crystal structure study gives a monoclinic unit cell, space group P2\text{$_1$/c}, with a = 7.358(2), b = 10.544(3), c = 9.489(2) Å, \(β = 91.88(2)°\), \(V = 735.8(2) Å^3\), Z = 4. The crystal structure has been solved and refined to a final \(R_1 = 0.078\) on the basis of 1342 “observed” reflections \(\{F_o > 4σ(F_o)\}\). It consists of \{100\} layers formed by ninefold-coordinated Th-centered polyhedra and Mo-centered tetrahedra. Its crystal structure is discussed in relation to that of ichnusaitae and that of synthetic orthorhombic Th(\text{MoO}_4)_2. The relationship between the progressive loss of water in the interlayer and the layer topology passing from ichnusaitae through nuragheite to synthetic (ThMo\text{$_2$}O$_4$)\text{$_2$} is examined. Nuragheite, the second thorium molybdate reported so far in nature, adds new data to the understanding of the crystal chemistry of actinide molybdates potentially forming during the alteration of spent nuclear fuel and influencing the release of radionuclides under repository conditions.

Keywords: Nuragheite, new mineral species, molybdate, thorium, crystal structure, OD structure, Su Seinariu, Sardinia, Italy

INTRODUCTION

The element thorium (\(Z = 90\)) was first discovered by the Swedish chemist J.J. Berzelius (1779–1848), who isolated it from a sample of the silicate mineral thorite, ThSiO$_4$, found in the Langesundfjord, Norway. Since then, only few minerals in which thorium is an essential component have been described owing to its geochemical behavior (e.g., Hazen et al. 2009). On the contrary, thorium occurs in solid solution in variable and usually small amounts in many rare-earth elements, zirconium, and uranium minerals, e.g., “monazite”, “xenotime”, zircon, and uraninite (Frodel 1958). Among the 22 known Th minerals, molybdates have been described only recently from the Mo-Bi mineralization of Su Seinariu, Sarroch, Cagliari, Sardinia, Italy. The preliminary screening with a scanning electron microscope of a set of specimens provided by the mineral collector Giuseppe Tanca allowed the identification of some crystals having Th and Mo as the only elements with \(Z > 9\). X-ray powder diffraction patterns indicated the existence of two different Th–Mo phases, usually occurring intimately intergrown. After the examination of several crystals, two pure grains were identified allowing the intensity data collections and the solution of their crystal structures. The two Th-Mo phases represent the first natural examples of such compounds; the very first one, ichnusaitae, Th(\text{MoO}_4)_2\cdot\text{H}_2\text{O}, has been described by Orlandi et al. (2014).

In this paper, we describe the second natural thorium molybdate, which was named nuragheite. The name is related to “nuraghe”, the main type of ancient megalithic building found in Sardinia, Italy. This kind of edifice is the symbol of Sardinia and its peculiar culture, the Nuragic civilization. The mineral and its name have been approved by the IMA-CNMNC, under the number 2013-088. The holotype specimen of nuragheite is deposited in the mineralogical collection of the Museo di Storia Naturale, Università di Pisa, via Roma 79, Calci, Pisa, Italy, under catalog number 19680.

OCCURRENCE AND MINERAL DESCRIPTION

Nuragheite was identified on specimens from the Su Seinariu prospect, Sarroch, Cagliari, Sardinia. The mineralization is composed by three vein systems, hosted in Varisic leucograni-