

ACTINIDES IN GEOLOGY, ENERGY, AND THE ENVIRONMENT

Cabvinite, $\text{Th}_2\text{F}_7(\text{OH})\cdot 3\text{H}_2\text{O}$, the first natural actinide halide

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ABSTRACT

The new mineral species cabvinite, $\text{Th}_2\text{F}_7(\text{OH})\cdot 3\text{H}_2\text{O}$ (IMA 2016-011), has been discovered in the Mo-Bi ore deposit of Su Seinargiu, Sarroch, Cagliari, Sardinia, Italy. It occurs as white square prismatic crystals, up to 100 μm in length and 40 μm in thickness, associated with brookite and iron oxy-hydroxides in vugs of quartz veins. Electron microprobe analysis gave (mean of five spot analyses, in wt%): ThO_2 82.35, F 19.93, $\text{H}_2\text{O}_{\text{calc}}$ 10.21, sum 112.49, $\text{O}=\text{F}$ -8.40, total 104.09. On the basis of 2 Th atoms per formula unit, the empirical formula of cabvinite is $\text{Th}_2\text{F}_{6.7}(\text{OH})_{1.3}\cdot 3\text{H}_2\text{O}$. Main diffraction lines in the X-ray powder diffraction pattern are [d (Å) (relative visual intensity) hkl]: 8.02 (ms) 110; 3.975 (s) 121,211; 3.595 (m) 310,130; 2.832 (m) 400,321,231; 2.125 (m) 402; 2.056 (m) 332; and 2.004 (ms) 440,521,251. Cabvinite is tetragonal, space group $I4/m$, with $a = 11.3689(2)$, $c = 6.4175(1)$ Å, $V = 829.47(2)$ Å³, $Z = 4$. The crystal structure has been solved and refined to $R_1 = 0.021$ on the basis of 813 reflections with $F_o > 4\sigma(F_o)$. It consists of Th tricapped trigonal prisms, connected through corner-sharing, giving rise to a framework hosting [001] tunnels. Cabvinite is the first natural actinide halide, and the site of discovery appears to provide a natural laboratory for the study of Th mobility and sequestration.

Keywords: Cabvinite, halide, thorium, fluorine, crystal structure, Su Seinargiu, Sardinia, Italy

INTRODUCTION

Actinide mineralogy is an interesting research field, owing to several applications of Th and U in geoscience and their technological importance, related both to the nuclear power production and to the management of nuclear wastes. Whereas uranium forms more than 250 different mineral species, only a few minerals having Th as an essential component have been described (e.g., Hazen et al. 2009). In addition, these species belong to only some classes, i.e., oxides, carbonates, phosphates, and silicates (Table 1). Recently, advance in the knowledge of Th mineralogy has been achieved through the study of the mineral assemblages occurring at the small Mo-Bi prospect of Su Seinargiu, Sarroch, Cagliari, and Sardinia, Italy, with the description of the first natural thorium molybdates.

Su Seinargiu, with more than 60 different mineral species so far reported (Orlandi et al. 2015a) and 12 distinct Mo minerals described, can be considered as a reference locality to study Mo mineralogy. Indeed, among these 12 Mo minerals, 7 have their type locality at Su Seinargiu, i.e., the Bi-Mo oxides sardignaite, gelosaite, and mambertiite (Orlandi et al. 2010, 2011, 2015b), the REE molybdate tancaite-(Ce) (Bonaccorsi and Orlandi 2010), suseinargiuite, the Na-Bi analog of wulfenite (Orlandi et al. 2015c), and the two thorium molybdates ichnusaite, $\text{Th}(\text{MoO}_4)_2\cdot 3\text{H}_2\text{O}$, and nuragheite, $\text{Th}(\text{MoO}_4)_2\cdot \text{H}_2\text{O}$ (Orlandi et al. 2014, 2015d). The finding of the first two natural thorium molybdates focused our attention on Th minerals, with the identification of other phases (thorbastnäsite, thorite; Orlandi

et al. 2015a) and the first natural thorium halide, cabvinite, herewith described.

This new mineral species (IMA 2016-011) and its name were approved by the IMA-CNMNC. The holotype material of cabvinite is deposited in the mineralogical collections of the Museo di Storia Naturale, University of Pisa, Italy, under catalog number 19711. The name honors two Italian mineral collectors, Fernando Caboni (b. 1941) and Antonello Vinci (b. 1944), for their contribution to the knowledge of the Su Seinargiu mineralogy. Cabvinite is the acronym after their surnames, CABoni and VINci.

OCCURRENCE AND MINERAL DESCRIPTION

Cabvinite was identified on only two small specimens from the Su Seinargiu prospect, Sarroch, Cagliari, Sardinia, Italy. The Mo-Bi mineralization is hosted within Variscan leucogranites (Caboi et al. 1978; Ghezzeo et al. 1981), and it is dated to 288.7 ± 0.5 Ma on the basis of the Re-Os age of molybdenite (Boni et al. 2003). Several Mo mineralizations are associated with Variscan leucogranites in Sardinia (Ghezzeo et al. 1981) and Su Seinargiu is one of the smallest prospects. Curiously, Caboi et al. (1978) stated that a peculiar feature of the Su Seinargiu Mo-Bi mineralization was related to the small number of different mineral species, with the mineral assemblage formed exclusively by quartz and molybdenite, with trace amounts of chalcocopyrite, pyrite, “wolframite,” and yellow ochres of Mo. On the contrary, a careful investigation of the Su Seinargiu mineralogy pointed out an outstanding mineral variety, with more than sixty different species, among which are unusual Bi-Mo-Th compounds (e.g., Orlandi et al. 2015a). The majority of these minerals seems to be related to the alteration (probably a low- T hydrothermal

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Special collection papers can be found online at <http://www.minsocam.org/MSA/AmMin/special-collections.html>.

TABLE 1. Minerals containing thorium as an essential component and chemical formulas after the IMA list (updated to September 2016) available at <http://nrmima.nrm.se/imalist.htm>

	Chemical formula	Type locality	Ref.
		Halides	
Cabvinite	Th ₂ F ₇ (OH)·3H ₂ O	Su Seinargiu, Sardinia, Italy	(1)
		Oxides	
Aspedamite	□ ₁₂ (Fe ³⁺ , Fe ²⁺) ₃ Nb ₄ [(Th(Nb, Fe ³⁺)) ₁₂ O ₄₂](H ₂ O, OH) ₁₂	Aspedammen, Østfold, Norway	(2)
Thorianite	ThO ₂	Balangoda, Ratnapura, Sri Lanka	(3)
Thorutite	(Th, U, Ca)Ti ₂ (O, OH) ₆	Severnyi area, Zardalek alkaline massif, Kyrgyzstan	(4)
		Carbonates	
Thorbasträsite	ThCa(CO ₃) ₂ F ₂ ·3H ₂ O	Pichikol' alkaline massif, Russia	(5)
Tuliokite	Na ₆ BaTh(CO ₃) ₆ ·6H ₂ O	Khibiny massif, Kola Peninsula, Russia	(6)
		Molybdates	
Ichnusaite	Th(MoO ₄) ₂ ·3H ₂ O	Su Seinargiu, Sardinia, Italy	(7)
Nuragheite	Th(MoO ₄) ₂ ·H ₂ O	Su Seinargiu, Sardinia, Italy	(8)
		Phosphates	
Althupite	AlTh(UO ₂) ₇ (PO ₄) ₄ (OH) ₅ ·15H ₂ O	Kobokobo pegmatite, Democratic Republic of Congo	(9)
Cheralite	CaTh(PO ₄) ₂	Kuttakuzhi, Kerala, India	(10)
Eylettersite	Th _{0.75} Al ₃ (PO ₄) ₂ (OH) ₆	Kobokobo pegmatite, Democratic Republic of Congo	(11)
Grayite	(Th, Pb, Ca)PO ₄ ·nH ₂ O	Gooddays mine, Mutoko Districk, Zimbabwe	(12)
		Silicates	
Ciprianiite	Ca ₄ (Th, REE) ₂ Al(B ₄ Si ₄ O ₂₂)(OH) ₂	Vetralla, Latium, Italy	(13)
Coutinhoite	Th ₂ Ba ₁₋₂ (UO ₂) ₂ Si ₂ O ₁₃ ·3H ₂ O	Urucum mine, Minas Gerais, Brazil	(14)
Ekanite	Ca ₂ ThSi ₆ O ₂₀	Ehiliyagoda, Ratnapura, Sri Lanka	(15)
Huttonite	ThSiO ₄	Gillespie's Beach, New Zealand	(16)
Steacyite	K _{0.3} (Na, Ca) ₂ ThSi ₆ O ₂₀	Mont Saint-Hilaire, Québec, Canada	(17)
Thorite	ThSiO ₄	Langesunds fjorden, Telemark, Norway	(18)
Thornasite	Na ₁₂ Th ₃ (Si ₆ O ₁₉) ₄ ·18H ₂ O	Mont Saint-Hilaire, Québec, Canada	(19)
Thorosteenstrupine	(Ca, Th, Mn) ₃ Si ₄ O ₁₁ F·6H ₂ O ^a	Chergilen REE occurrence, Russia	(20)
Turkestanite	(K, □)(Ca, Na) ₂ ThSi ₆ O ₂₀ ·nH ₂ O	Dzhelisu massif, Kyrgyzstan Darai-Pioz Glacier, Tadjikistan	(21)
Umbozerite	Na ₂ Sr ₄ ThSi ₆ (O, OH) ₂₄	Lovozero massif, Kola Peninsula, Russia	(22)

Notes: (1) This work; (2) Cooper et al. 2012; (3) Dunstan 1904; (4) Gotman and Khapaev 1958; (5) Pavlenko et al. 1965; (6) Yakovenchuk et al. 1990; (7) Orlandi et al. 2014; (8) Orlandi et al. 2015d; (9) Piret and Deliens 1987; (10) Bowie and Horne 1953; (11) van Wambeke 1972; (12) Bowie 1957; (13) Della Ventura et al. 2002; (14) Atencio et al. 2004; (15) Anderson et al. 1961; (16) Pabst and Hutton 1951; (17) Perrault and Szymański 1982; (18) Gahn et al. 1817; (19) Ansell and Chao 1987; (20) Kupriyanova et al. 1962; (21) Pautov et al. 1997; (22) Es'kova et al. 1974.

^aThe chemical formula of thorosteenstrupine could be Na₀₋₅Ca₁₋₃(Th, REE)₆(Mn, Fe, Al, Ti)₄₋₅(Si₆O₁₈)₂[(Si, P)O₄]₆(OH, F, O)_x·nH₂O (Pekov et al. 1997).

alteration) of the Mo-Bi ores.

Cabvinite occurs as white square prismatic crystals, elongated on [001], up to 100 μm in length and 40 μm in thickness (Fig. 1). It is transparent, with a vitreous luster. Streak is white. Cabvinite is brittle; scanning electron microscope images suggest the occurrence of a {001} cleavage or parting. Owing to the very small amount of available material and its small size, micro-indentation hardness, density, as well as optical properties, were not measured. On the basis of the ideal formula, the calculated density is 5.35 g/cm³. The mean refractive index of cabvinite, obtained from the Gladstone-Dale relationship (Mandarino 1979, 1981) using the ideal formula and the calculated density, is 1.838.

Cabvinite occurs in small vugs of quartz veins associated with brookite and iron oxy-hydroxides ("limonite").

CHEMICAL DATA AND MICRO-RAMAN SPECTROMETRY

Preliminary chemical analyses of cabvinite performed through energy dispersive spectrometry showed Th and F as the only elements with *Z* > 8. Quantitative data were obtained through wavelength-dispersive spectrometry (WDS mode) with a Superprobe JEOL JXA8200 electron microprobe at the "Eugen F. Stumpfl" Laboratory, Leoben University, Austria, using the following analytical conditions: accelerating voltage 15 kV, beam current 10 nA, nominal beam diameter 1 μm. The peak and backgrounds counting times were 20 and 10 s, respectively. The following diffracting crystals were selected: PETH for Th and TAP for F. Standards (element, emission line) were: thorianite (ThMα) and fluorite (FKα). The ZAF routine was applied for the correction of recorded raw data. Five spot analyses were performed on a polished grain that was found to

be homogeneous. Direct H₂O determination was not performed owing to the scarcity of available material but its occurrence was first suggested by the structural study and then confirmed by micro-Raman spectrometry (see below). Chemical data are given in Table 2; the chemical formula, based on 2 Th atoms per formula unit (apfu), assuming 3 H₂O groups and (OH+F) = 8 apfu, is Th₂F_{6.7}(OH)_{1.3}·3H₂O. The ideal formula of cabvinite is Th₂F₇(OH)·3H₂O, corresponding to (in wt%) ThO₂ 79.04, H₂O 9.44, F 19.90, O(≡F) –8.38, sum 100.00.

Unpolarized micro-Raman spectra were collected on an unpolished sample of cabvinite in nearly backscattered geometry with a Jobin-Yvon Horiba XploRA Plus apparatus, equipped with a motorized x-y stage and an Olympus BX41 microscope with a 10× objective. The Raman spectra were excited using a 532 nm line of a solid-state laser attenuated to 50%. The minimum lateral and depth resolution was set to a few micrometers. The system was calibrated using the 520.6 cm⁻¹ Raman band of silicon before each experimental session. Spectra were collected through multiple acquisitions with single counting times of 60 s. Backscattered radiation was analyzed with a 1200 mm⁻¹ grating monochromator. Peak deconvolution was performed using the software Fityk (Wojdyr 2010). The Raman spectrum of cabvinite shows few bands, located below 600 cm⁻¹, as usual for several fluorides (e.g., Li₃ThF₇; Oliveira et al. 1999). Relatively strong bands occur at 113, 209, 342, and 461 cm⁻¹ (Fig. 2a), which could be interpreted as lattice vibrations or Th–F modes. A strong and broad band occur in the region between 3000 and 3800 cm⁻¹ (Fig. 2b), which could be attributed to the O–H stretching vibrations. The deconvolution of such a band indicated the occurrence of two main bands at 3257 and 3407 cm⁻¹. By using

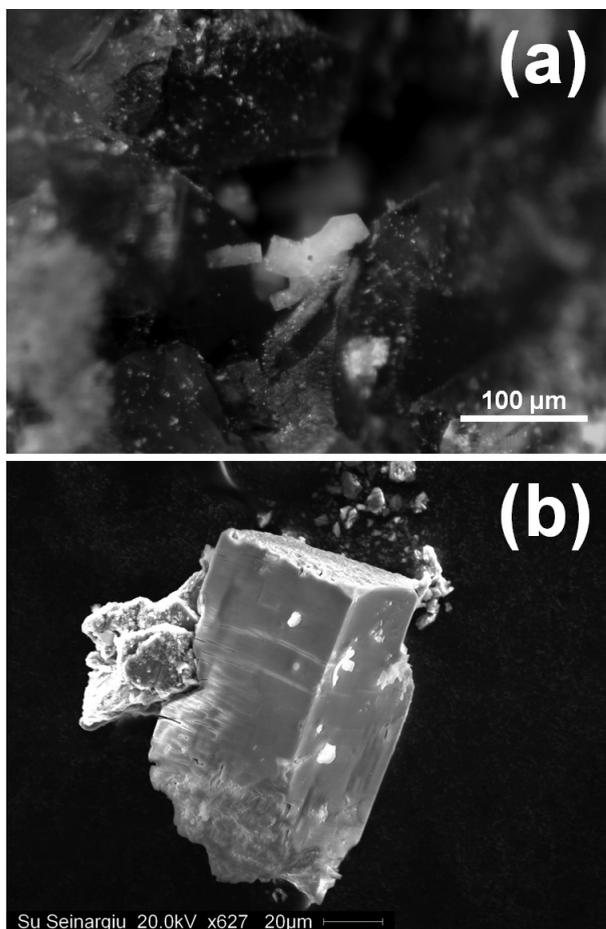


FIGURE 1. Cabvinite, white prismatic crystals, up to 100 μm , with iron oxides in a cavity of a quartz vein (a); SEM image of the crystal used for the crystallographic study (b), showing the prismatic habit and the occurrence of a $\{001\}$ cleavage or parting. Holotype material. Collection of Museo di Storia Naturale of the Pisa University, catalog number 19711.

the relationship between O–H stretching frequencies and O \cdots O distances proposed by Libowitzky (1999), these Raman bands could correspond to hydrogen bonds having O \cdots O distances of 2.72 and 2.80 \AA , respectively.

X-RAY CRYSTALLOGRAPHY AND STRUCTURE REFINEMENT

X-ray powder diffraction pattern of cabvinite was collected using a 114.6 mm diameter Gandolfi camera and Ni-filtered $\text{CuK}\alpha$ radiation. The observed X-ray powder diffraction pattern, as well as the calculated one, is given in Supplementary¹ Table S1. Unit-cell parameters, refined using UnitCell (Holland and Redfern 1997) on the basis of 15 unequivocally indexed reflections, are $a = 11.370(1)$, $c = 6.424(1)$ \AA , $V = 830.5(1)$ \AA^3 .

Single-crystal X-ray diffraction data were collected using a Bruker Smart Breeze diffractometer equipped with an air-cooled CCD area detector. Graphite-monochromatized $\text{MoK}\alpha$ radiation

was used. The detector-to-crystal distance was 50 mm; 1455 frames were collected using ω and ϕ scan modes, in 0.5° slices, with an exposure time of 25 s per frame. Data were integrated and corrected for Lorentz-polarization, background, and absorption, using the package of software Apex2 (Bruker AXS 2004). The statistical tests on the distribution of $|E|$ values ($|E^2 - 1| = 0.840$) indicated the possible presence of an inversion center. The unit-cell parameters of cabvinite are similar to those of synthetic $\text{Th}_2\text{F}_7(\text{AuF}_4)$ (Schmidt and Müller 1999), i.e., $a = 11.306(1)$, $c = 6.313(1)$ \AA , $V = 807.0(1)$ \AA^3 , space group $I4/mcm$, to be compared with those observed in cabvinite, i.e., $a = 11.3689(2)$, $c = 6.4175(1)$ \AA , $V = 829.47(2)$ \AA^3 . Consequently, the crystal structure of cabvinite was initially refined using SHELXL-2014 (Sheldrick 2015) starting from the atomic coordinates of the synthetic compound. The site labeled Au in the crystal structure of synthetic $\text{Th}_2\text{F}_7(\text{AuF}_4)$ was found to be completely empty. The refinement converged to $R_1 = 0.052$, giving reasonable Th– ϕ ($\phi = \text{F}, \text{O}$) distances. However, a maximum residual of about $5.5 e/\text{\AA}^3$ was unexplained, being located at 1.50 \AA from one anion position. In addition, some weak reflections did not match the chosen space group symmetry. Therefore, the crystal structure was solved by direct methods using SHELXS-97 (Sheldrick 2008) in the space group $I4/m$, assuming the occurrence of a $\{100\}$ twin plane. The crystal structure solution allowed the identification of one Th position and five anion sites. Curves for neutral atoms were taken from the *International Tables for Crystallography* (Wilson 1992). An anisotropic model for all atom positions but one (the only exception being represented by $\text{Ow}5$) achieved a final $R_1 = 0.0209$ on the basis of 813 reflections with $F_o > 4\sigma(F_o)$. Twin ratio is 0.49(1), likely indicating a perfect merohedral twinning. Details of the selected crystal, data collection, and refinement are given in Table 3. The CIF is available as supplementary material¹.

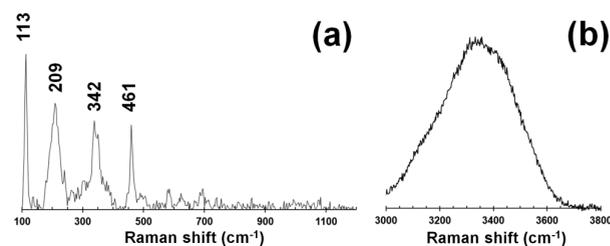


FIGURE 2. Micro-Raman spectrum of cabvinite, in the regions 100–1200 cm^{-1} (a) and 3000–3800 cm^{-1} (b).

TABLE 2. Electron-microprobe data (mean of 5 spot analyses, in wt%) of cabvinite and atoms per formula unit (apfu), on the basis of 2 Th apfu

Oxide	wt%	Range	e.s.d.
ThO_2	82.35	81.71–83.40	0.67
F	19.93	18.16–22.03	1.72
H_2O	10.21	9.08–11.18	0.95
Sum	112.49	111.60–113.02	0.55
$\text{O}=\text{F}$	–8.40		
Total	104.09		
Element	apfu	Range	e.s.d.
Th	2.00	–	–
F	6.73	6.12–7.48	0.63
OH	1.27	0.52–1.88	0.63
H_2O	3.00	–	–

¹Deposit item AM-17-76013, Supplementary Table S1. Deposit items are free to all readers and found on the MSA web site, via the specific issue's Table of Contents (go to http://www.minsocam.org/MSA/AmMin/TOC/2017/Jul2017_data/Jul2017_data.html)

TABLE 3. Crystal data and summary of parameters describing data collection and refinement for cabvinitite

Crystal data	
SREF formula	Th ₂ F ₇ (OH)·3H ₂ O
Crystal size (mm)	0.095 × 0.040 × 0.040
Cell setting, space group	Tetragonal, I4/m
a, c (Å)	11.3689(2), 6.4175(1)
V (Å ³)	829.47(2)
Z	4
Data collection and refinement	
Radiation, wavelength (Å)	MoKα, 0.71073
Temperature (K)	293
Detector-to-sample distance (mm)	50
Maximum observed 2θ (°)	71.64
Measured reflections	2605
Unique reflections	825
Reflections F _o > 4σ(F _o)	813
R _{int} after absorption correction	0.0159
R _i	0.0167
Range of h, k, l	-16 ≤ h ≤ 16 -17 ≤ k ≤ 8 -8 ≤ l ≤ 9
R _i [F _o > 4σ(F _o)]	0.0209
R _i (all data)	0.0213
wR ₂ (on F _o ²)	0.0677
Goof	1.041
Number of l.s. parameters	36
Maximum and minimum residual	3.21 (at 0.50 Å from O5) -1.86 (at 0.29 Å from Th)

CRYSTAL STRUCTURE DESCRIPTION

Atom coordinates, site occupancies, and displacement parameters are reported in Table 4, whereas selected bond distances and bond-valence sums (BVS, in valence unit, v.u.), calculated using the bond parameters of Brese and O'Keeffe (1991), are given in Table 5.

The crystal structure of cabvinitite (Fig. 3) has one symmetrically unique cation site and five anion positions. Thorium occurs in a tricapped trigonal prismatic coordination, forming a ThF₇(OH)_{0.5}(H₂O)_{1.5} polyhedron. Th–φ distances range between 2.318 (Th–F1) and 2.585 Å (Th–Ow5), with average bond distance of 2.385 Å. Its BVS is 4.09 v.u., in agreement with the formal charge of Th, i.e., +4. Thorium-centered polyhedra are connected through corner-sharing, giving rise to a framework hosting [001] tunnels. Fluorine is hosted at the F1, F2, and F3 sites, whereas O4 and Ow5 are mixed (OH, H₂O) and pure H₂O sites, respectively. The anion sites F1, F2, and F3 are twofold coordinated by Th, and have BVS of 1.02, 0.94, and 0.96 v.u., respectively, in agreement with their occupancy by fluorine anions. Atoms hosted at O4 and Ow5 sites are undersaturated with respect to the bond-valence requirements, with BVS of 0.42 and 0.32 v.u., respectively.

Figure 4 shows an hypothetical hydrogen bond system involving O4 and Ow5 sites. Short O···O distances are represented by O4···O4 and Ow5···Ow5 distances, i.e., 2.66(1) and 2.73(2) Å, respectively, lying in the (001) plane; along c, the O4···Ow5 distance is relatively long, i.e., 3.29(1) Å. By using the relationship of Ferraris and Ivaldi (1988), the bond strengths of the O4···O4, Ow5···Ow5, and O4···Ow5 distances are 0.26, 0.22, and 0.09 v.u., respectively. In the model proposed in Figure 4, the O4 site could be occupied by OH⁻ or H₂O groups. In the first case (1), O4 is acceptor of two hydrogen bonds from two symmetry-related O4 and from an H₂O group hosted at the Ow5 site along +c; moreover, the OH⁻ group is donor in a long O4···Ow5 bond along -c. In this configuration, the BVS at the O4 site is

TABLE 4. Site occupancies, atomic coordinates, and isotropic (e) or equivalent isotropic displacement parameters (in Å²) for cabvinitite

Site	Wyckoff position	Occupancy	x/a	y/b	z/c	U _{eq/iso}
Th	8h	Th _{1.00}	0.14040(3)	0.35220(3)	0	0.0065(1)
F1	4c	F _{1.00}	0	1/2	0	0.020(1)
F2	16i	F _{1.00}	-0.0015(6)	0.3112(3)	0.2508(6)	0.022(1)
F3	8f	F _{1.00}	1/4	1/4	1/4	0.034(2)
O4	8h	(OH) _{0.50} (H ₂ O) _{0.50}	0.0891(7)	0.1394(8)	0	0.030(2)
Ow5	8h	H ₂ O	0.363(2)	0.400(5)	0	0.064(2) ^a

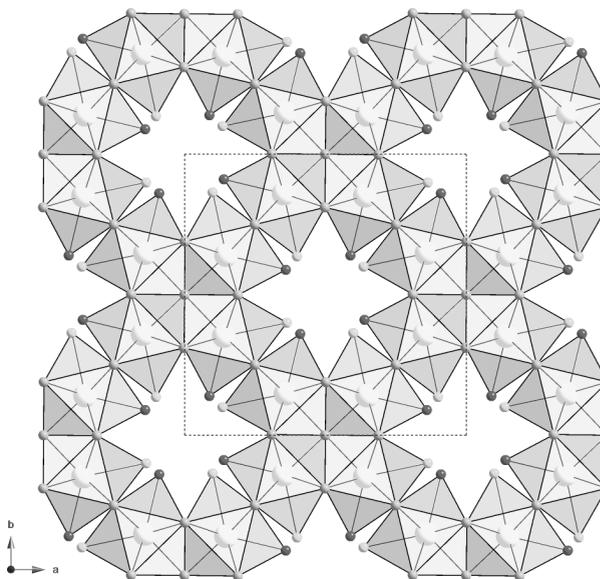
Note: U_{eq/iso} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 5. Selected bond distances (in angstroms) and bond-valence balance (in v.u.) for cabvinitite

Th			Th	Σ _{anions}
-F1	2.3177(2)			
-F2	2.326(5) × 2	F1	^{2x} →0.51	1.02
-F3	2.3402(2) × 2	F2	0.50 ^{ix2} , 0.44 ^{ix2}	0.94
-F2	2.372(5) × 2	F3	^{2x} →0.48 ^{ix2}	0.96
-O4	2.489(9)	O4	0.42	0.94 ⁱ , -0.01 ⁱⁱ
-Ow5	2.585(15)	O5	0.32	0.32 ⁱⁱⁱ , 0.23 ^{iv}
		Σ _{cation}	4.09	

Note: Left and right superscripts indicate the number of bonds for each anion and cation, respectively. Superscripts i, ii, iii, and iv refer to the possible hydrogen bond schemes involving O4 and Ow5 described in the text.

0.94 v.u. In the second case (2), O4 is donor in two hydrogen bonds with symmetry-related O4 (hosting OH⁻ groups) and it is acceptor of an hydrogen bond from Ow5; its BVS is -0.01 v.u. Ow5 is acceptor and donor of hydrogen bonds with symmetry-related Ow5 sites within the (001) plane; in addition, it could be acceptor and donor with OH⁻ groups hosted at O4 belonging to consecutive planes along c (case 3) or it could be donor with H₂O groups hosted at O4 (case 4). In the first case, its BVS is 0.32 v.u., whereas in the second case the BVS is 0.23 v.u. The relatively high BVS at Ow5 site could be a consequence of the inaccuracy of the location of this oxygen atom, in agreement with its relatively high displacement parameter.

**FIGURE 3.** Crystal structure of cabvinitite, as seen down c. Symbols: light gray polyhedra = Th site. Circles: gray = F sites; dark gray = O4 site; light gray = Ow5 site.

The crystal-chemical formula of cabvinite, derived from the crystal structure study, is $\text{Th}_2\text{F}_7(\text{OH}) \cdot 3\text{H}_2\text{O}$ ($Z = 4$).

DISCUSSION

Cabvinite is the first thorium halide known in nature. It belongs to the 03.D group of the Strunz and Nickel classification, i.e., oxyhalides, hydroxyhalides, and related double halides (Strunz and Nickel 2001), being a hydrated thorium hydroxyfluoride. The only other mineral containing Th and F as essential components is the fluorocarbonate thorbastnäsité, described by Pavlenko et al. (1965) from Eastern Siberia, Russia. Unfortunately, its crystal structure has not been solved yet. On the contrary, several thorium fluorides have been synthesized. Some of them are microporous compounds, with a Th–F framework forming channels hosting alkali metals (e.g., $\text{CsTh}_6\text{F}_{25}$, $\text{NaTh}_3\text{F}_{13}$, $\text{CsTh}_3\text{F}_{13}$, $\text{RbTh}_3\text{F}_{13}$; Underwood et al. 2011, 2012). Following the IUPAC recommendations (Rouquérol et al. 1994), cabvinite can be described as a microporous compound too. As described above, Schmidt and Müller (1999) obtained synthetic $\text{Th}_2\text{F}_7(\text{AuF}_4)$, that can be derived from cabvinite through the substitution $\square + [(\text{OH})^- + 3\text{H}_2\text{O}] = \text{Au}^{3+} + 4\text{F}^-$, with Au^{3+} being host within the channels. The unit-cell volume of cabvinite is larger than that of the synthetic compound, i.e., 829.5 vs. 807.0 Å³, respectively, corresponding to $\Delta V = +2.8\%$. The expansion of the unit-cell volume of cabvinite is in line with the empty nature of the Au site occurring in the [001] tunnels of the synthetic compound. In cabvinite, tunnels host the H atoms of OH[−] and H₂O

groups. In addition to the thorium synthetic compound, Schmidt and Müller (2004) were able to obtain the U isotope $\text{U}_2\text{F}_7[\text{AuF}_4]$.

Cabvinite is likely the product of the alteration of the primary Mo–Bi ore at Su Seiniargiu; the source of thorium is not well-known but other secondary Th minerals like ichnusaite, nuragheite, and thorbastnäsité seem to be related to the same hydrothermal alteration event. Orlandi et al. (2014) observed the presence of corroded crystals of xenotime-(Y) in the same kind of occurrence of ichnusaite, suggesting that the dissolution of xenotime-(Y) could be the source of Th. Finally, the presence of F in the hydrothermal fluids could have favored the solubility and mobility of Th (e.g., Langmuir and Herman 1980; Wood and Ricketts 2000).

IMPLICATIONS

The study of the small Su Seiniargiu Mo–Bi mineralization provided the mineral systematics of three very rare Th compounds, i.e., the two thorium molybdates ichnusaite and nuragheite and the thorium fluoride cabvinite. Ichnusaite was cited by Hazen and Ausubel (2016) as an example of rarity in the mineral kingdom. Cabvinite is a further notable example of such a rarity, being the first thorium halide yet described. Following Hazen and Ausubel (2016), rarity can be due to (1) restricted phase stability in *P–T–X* space, (2) incorporation of rare combinations of elements, (3) degradation under ambient conditions, and (4) negative sampling biases. The *P–T–X* conditions governing the crystallization of cabvinite are not known. Notwithstanding the well-known role played by F in favoring Th mobility (e.g., Langmuir and Herman 1980), no Th fluorides had been found before this study. Consequently, the crystallizing conditions occurring at Su Seiniargiu are clearly unusual; the locality seems to be a natural laboratory for Th mobility, and late-stage crystallization of Th fluorides, fluorocarbonates, and molybdates. Taking into account the restricted conditions favoring Th mobilization, a careful study of the fluid-rock interactions occurring at Su Seiniargiu is mandatory, to achieve a better knowledge of Th geochemistry and its potential dispersion in the environment. In addition to peculiar geochemical conditions required for its crystallization, cabvinite could have been overlooked owing to its appearance similar to that of other common species (e.g., baryte).

Finally, cabvinite represents a new structure type among natural compounds and brings new data to the understanding of actinide mineralogy, thus confirming the central role played by rare minerals to advances in crystal chemistry.

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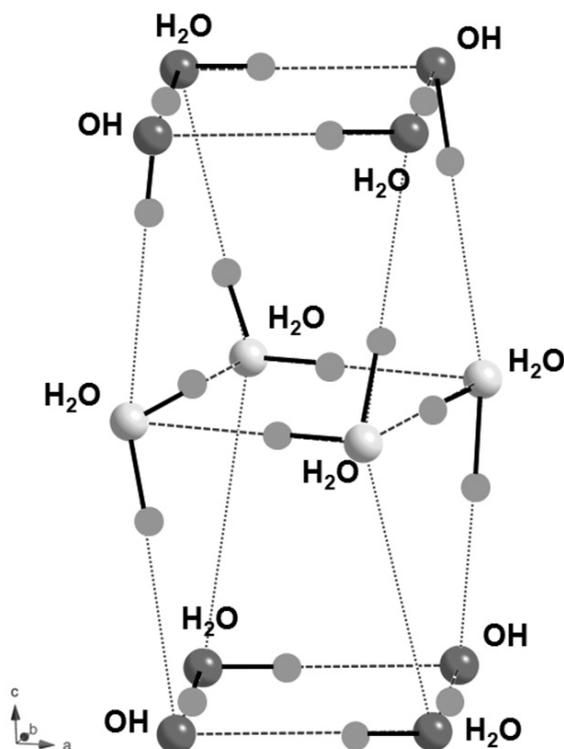


FIGURE 4. Hypothetical hydrogen bond system in cabvinite. Circles: dark gray = O4 site; light gray = Ow5 site. Gray circles represent the hypothetical positions of H atoms.

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