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DELIENSITE, $Fe(UO_2)_2(SO_4)_2(OH)_2{\bullet}3H_2O$, A NEW FERROUS URANYL SULFATE HYDROXYL HYDRATE FROM MAS D'ALARY, LODÈVE, HÉRAULT, FRANCE

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ABSTRACT

Deliensite, ideally $Fe(UO_2)_2(SO_4)_2(OH)_2{\bullet}3H_2O$, is a new mineral species from the Mas d'Alary uranium deposit, in Lodève, Hérault, France. It occurs as submillimetric tabular crystals arranged in spherical aggregates, and is associated with uraninite, gypsum and pyrite. The crystals are pale yellow to grayish white in color with a vitreous luster, and nonfluorescent. D_{meas} 3.268 and D_{calc} 3.31 (empirical formula), 3.26 g/cm^3 (idealized formula); $H_{Mohs} = 2$. Optically biaxial negative, $2V = 73(2)°$, α 1.432(calc.), β 1.470(2) and γ 1.492(3) with optical orientation Y and Z in plane (100), and $Z \parallel$ elongation. The dispersion $r > v$ is weak, and the crystals are nonpleochroic. Deliensite is orthorhombic, space group *Pnnm* or *Pnn2*, with unit-cell parameters refined from powder data: a 15.908(5), b 16.274(3), c 6.903(1) Å, V 1787(1) Å^3, a:b:c: 0.9775:1:0.4242, $Z = 4$. The crystals show a tabular habit, tenacity is weak, and the {100} cleavage is perfect. The strongest ten reflections of the X-ray powder-diffraction pattern [d in (Å)(I)(hkl)] are: 7.95(81)(200), 5.90(100)(111), 4.26(31)(031), 4.20(37)(301), 3.94(71)(140), 3.45(67)(002), 3.165(50)(202), 2.893(41)(151), 2.596(70)(142) and 2.118(27)(033). Electron-microprobe and thermogravimetric analyses gave: FeO 7.42, UO_3 67.63, SO_3 17.37, H_2O 8.63, total 101.05 wt.%. The empirical formula (based on O = 13) is $Fe_{0.909}(UO_2)_{2.081}(SO_4)_{1.949}(OH)_{2.082}{\bullet}3.179\ H_2O$. Deliensite originates from the alteration of uraninite and primary sulfides, with a contribution from the host rocks. The mineral name honors Belgian mineralogist Michel Deliens. Holotype material is deposited in the mineralogical collection of the Royal Belgian Institute of Natural Sciences, Brussels, Belgium.

Keywords: deliensite, new mineral species, ferrous uranyl sulfate hydroxyl hydrate, Mas d'Alary, Lodève, Hérault, France.

SOMMAIRE

La deliensite, de formule idéale $Fe(UO_2)_2(SO_4)_2(OH)_2{\bullet}3H_2O$, est une nouvelle espèce minérale du gîte uranifère de Mas d'Alary, en Lodève, Hérault, France. Le minéral se présente en amas de cristaux tabulaires submillimétriques en agrégats sphérulitiques, associés à l'uraninite, au gypse et à la pyrite. La couleur des cristaux est jaune pâle à gris-blanc, avec un éclat vitreux; aucune fluorescence n'est développée en lumière ultra-violette. Le clivage {001} est bon. $D_{mes} = 3.268$ g/cm^3 et $D_{calc} = 3.31$ g/cm^3 (formule empirique), 3.26 g/cm^3 (formule idéale). $H_{Mohs} = 2$. Optiquement biaxe négative $2V = 73(2)°$, α 1.432(calc.), β 1.470(2) et γ 1.492 (2), avec orientation optique Y et Z dans le plan (100), et Z parallèle à l'allongement. La dispersion $r > v$ est faible, et les cristaux sont non pléochroïques. La deliensite est orthorhombique, groupe spatial *Pnnm* ou *Pnn2*, avec les paramètres réticulaires a 15.908(5), b 16.274(3) et c 6.903(1) Å, V 1787(1) Å^3, a:b:c 0.9775:1:0.4242, $Z = 4$. Les cristaux montrent un habitus tabulaire, la tenacité est faible, et le clivage {100} est parfait. Les dix raies les plus intenses [d(en Å)(I)(hkl)] sont: 7.95(81)(200), 5.90(100)(111), 4.26(31)(031), 4.20(37)(301), 3.94(71)(140), 3.45(67)(002), 3.165(50)(202), 2.893(41)(151), 2.596(70)(142), et 2.118(27)(033). Les analyses à la microsonde électronique et thermogravimétrique ont donné: FeO 7.42, UO_3 67.63, SO_3 17.37, H_2O 8.63, total 101.05% (en poids). La formule empirique (avec O = 13) est $Fe_{0.909}(UO_2)_{2.081}(SO_4)_{1.949}(OH)_{2.082}{\bullet}3.179\ H_2O$. Le minéral résulte de l'altération de l'uraninite et des sulfures primaires, en combinaison avec les éléments dérivés de la gangue du gîte uranifère. Le nom est à l'honneur de Michel Deliens, minéralogiste belge. Le minéral est conservé dans la collection minéralogique de l'Institut royal des Sciences naturelles de Belgique, à Bruxelles, Belgique.

Mots-clés: deliensite, nouvelle espèce minérale, sulfate ferreux d'uranyle hydroxydé et hydraté, Mas d'Alary, Lodève, Hérault, France.

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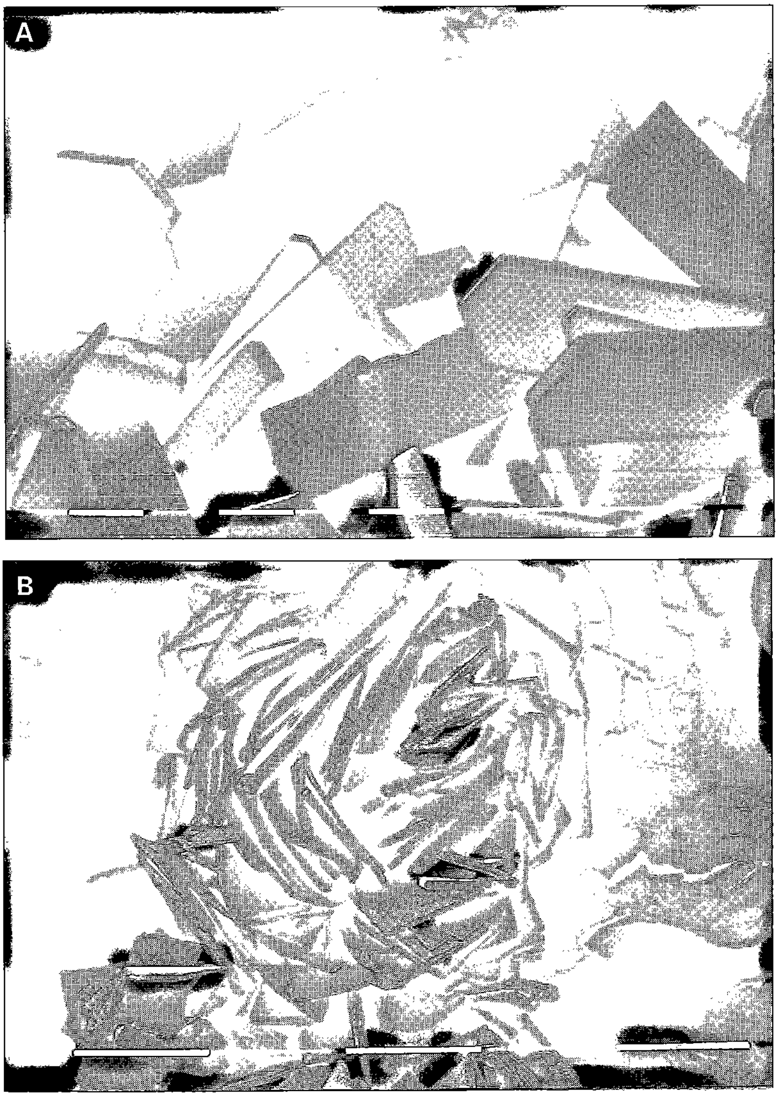

FIG. 1. A. Photomicrograph (scanning electron microscopy) of tabular crystals of deliensite (scale bar: 20 μm). B. Photomicrograph of spherical aggregate of deliensite crystals (scale bar: 10 μm).

INTRODUCTION

Deliensite, ideally $Fe(UO_2)_2(SO_4)_2(OH)_2•3H_2O$, is a new ferrous uranyl sulfate hydroxyl hydrate from Mas d'Alary, Lodève, Hérault, France, collected in 1994. Iron-, lead- and zinc-bearing sulfides are associated with the uranium mineralization. Uraninite and coffinite occur as stratiform horizons, as banded lens-like masses, and seldom as veins. The exceptionally high concentration of uranium within the deposits of Lodève can only be explained by volcanic activity. The geology and metallogenesis of these deposits were extensively described by Deliens *et al.* (1992). The alteration of the primary ore leads to the formation of a plethora of secondary uranium minerals. The abundance of secondary uranium minerals is primarily due to the diversity of primary sulfides that are associated with uraninite. From this locality, four new uranium-bearing species have been described: metalodèvite (Agrinier *et al.* 1972), fontanite (Deliens & Piret 1992), seelite (Bariand *et al.* 1993) and rabejacite (Deliens & Piret 1993). The discovery specimen of deliensite was collected and given to the authors by Jean Claude Leydet, member of "Association française de microminéralogie". The mineral and the mineral name (IMA number 96–013) were approved by the Commission on New Minerals and Mineral Names, IMA. The type specimen of deliensite is stored as RC 4718 in the mineralogical collection of the Royal Belgian Institute of Natural Sciences, Brussels, Belgium. The mineral name honors Michel Deliens (b. 1939), head of the division of mineralogy at the Royal Belgian Institute of Natural Sciences, Brussels, Belgium, who has been involved in the description of twenty-five new uranium-bearing minerals.

MORPHOLOGY, PHYSICAL PROPERTIES AND OCCURRENCE

Deliensite occurs as pale yellow to grayish white microtabular crystals arranged in spherical aggregates up to 4 mm in diameter. The crystals have a mean length of 0.35 mm and a width of 0.06–0.15 mm. The mineral is transparent to translucent, with a vitreous luster and white streak. It is nonfluorescent. The Mohs hardness is 2, the tenacity, weak, and the {100} cleavage, perfect. Many crystals are twinned with parting along (010). The SEM photomicrograph (Fig. 1A) shows crystals with a tabular habit and a pronounced elongation on [001]. Figure 1B shows the spherical aggregates of the crystals. The density measured by flotation in heavy liquids (methylene iodide + toluene) at 25°C is 3.268(7) g/cm^3. The calculated density is 3.31 g/cm^3 if based on the empirical formula, and 3.26 g/cm^3 if based on the idealized formula. The mineral is readily soluble in dilute HCl.

Deliensite was found in the oxidation zone of the Mas d'Alary uranium deposit, Lodève, Hérault, France. It is found in close association with uraninite, gypsum and granular pyrite.

OPTICAL CHARACTERISTICS

The mineral is biaxial negative, with a measured $2V$ value of 73(2)° (Tobi method). The indices of refraction were determined at 589 nm: α 1.432(calc.), β 1.470(2) and γ 1.492(2). The dispersion ($r > v$) is weak, and the crystals are nonpleochroic. The optical orientation is such that Y and Z are located in the plane (100), and Z parallel to elongation (Fig. 2).

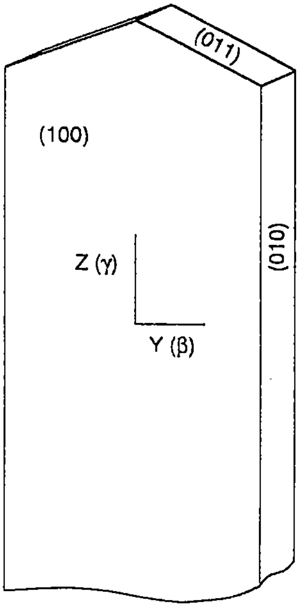

FIG. 2. Optical orientation of the vibration directions in deliensite.

X-RAY CRYSTALLOGRAPHY

The X-ray powder-diffraction data were recorded with a Guinier–Hägg camera using monochromated CuKα_1 radiation (λ 1.5406 Å). Synthetic fluorphlogopite (SRM–675) was used as a calibrant for the lower-2θ values, and silicon powder (SRM–460) was used for the higher-2θ values. The relative intensities of the diffraction lines were measured with a Carl-Zeiss Jena MD–100 microdensitometer. The pattern is unique, and could not be matched with any phase in the ICDD Powder Diffraction File. Single crystals of deliensite were examined using Weissenberg methods employing Ni-filtered Cu radiation. Film data of the 0, 1 and 2 levels for a crystal mounted along the c axis indicate orthorhombic symmetry. Systematic absences give the permissible space-groups *Pnnm* (58) or *Pnn2* (34). The refined unit-cell parameters: a 15.908(5), b 16.274(3), c 6.903(1) Å, V 1787(1) Å^3, a:b:c 0.9775:1:0.4242, $Z = 4$, are based on the d-values of 34 X-ray powder-diffraction lines. The indexing of the powder-diffraction lines is conformable with the single-crystal Weissenberg data. The program PIRUM (Werner 1969) was used for unit-cell refinement. Figure of merit values are M(20) = 16, F(20) = 19(0.008140,132). A fully indexed powder-diffraction pattern is given in Table 1.

CHEMICAL COMPOSITION

Crystals of deliensite were chemically analyzed with a Cameca SX–50 electron microprobe, utilizing a beam size of 2 μm, an operating voltage of 15 kV, and a beam current of 20 nA. Except for the major components, no peaks of elements with an atomic number of 6 or greater were significantly above the detection limit, indicating that deliensite is essentially a pure Fe–U–S phase. The following standards were used: hematite (Fe), synthetic uraninite (U) and barite (S). The H_2O content was determined thermogravimetri-

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR DELIENSITE

hkl	d_{obs} (Å)	d_{calc} (Å)	*I*	*hkl*	d_{obs} (Å)	d_{calc} (Å)	*I*
200	7.95	7.954	81	701	2.158	2.159	8
011	6.34	6.355	15	033	2.118	2.118	27
111	5.90	5.901	100	262	2.061	2.060	10
031	4.26	4.265	31	233	2.046	2.047	9
301	4.20	4.205	37	080	2.033	2.034	11
040	4.06	4.068	13	180	2.019	2.018	9
140	3.94	3.942	71	053	1.878	1.879	9
002	3.45	3.451	67	153	1.865	1.866	20
202	3.165	3.166	50	443	1.789	1.789	9
051	2.942	2.944	21	091	1.749	1.749	19
151	2.893	2.895	41	760	1.741	1.742	12
441	2.629	2.630	16	004	1.725	1.726	22
142	2.596	2.597	70	291	1.707	1.708	19
161	2.492	2.493	9	204	1.686	1.687	14
342	2.357	2.358	15	144	1.580	1.581	24
113	2.255	2.255	21	155	1.266	1.267	10
171	2.182	2.182	10	674	1.228	1.228	11

cally. A thermogravimetric analysis (TGA) revealed a total loss of 8.63 wt.%. Five electron-microprobe analyses, carried out on each of four different crystals, yield (in wt.%) FeO 7.42(5.70–8.36), UO_3 67.63(65.42–69.88), and SO_3 17.37(16.71–18.20); with the 8.63% H_2O, the total is 101.05 wt.%. Fe^{3+} could not be detected by microchemical tests using KCNS on separate crystals. This does not preclude that some crystals of deliensite may be partially oxidized. The oxide formula calculated on the basis of 13 O atoms is: 0.909 FeO•2.081 UO_3•1.949 SO_3•4.220 H_2O. The empirical formula, taking into account electroneutrality, is: $Fe_{0.909}(UO_2)_{2.081}(SO_4)_{1.949}(OH)_{2.082}$•$3.179H_2O$. The ideal formula is $Fe(UO_2)_2(SO_4)_2(OH)_2$•$3H_2O$. Calculations of the Gladstone–Dale relationship, using the constants of Mandarino (1981), yield a compatiblity index of 0.072, which indicates fair agreement between physical and chemical data using the measured density.

THERMAL STABILITY

The thermal stability of deliensite was studied with a thermogravimetric analyzer TGA 2950, TA Instruments, utilizing a heating rate of 5°C/min and a constant N_2-flow of 50 mL/min. The TGA curve (Fig. 3) shows that dehydration and dehydroxylation do not take place in distinct steps; instead, over an interval between 110 and 500°C, the dehydration is complete, and corresponds to a loss of 8.63 wt.% H_2O. Between 500 and 800°C, decomposition of the sulfate group takes place and corresponds to a loss of 17.87 wt.%, which is in excellent agreement with the averaged value of 17.37 wt.% SO_3 obtained by electron-microprobe analyses.

TABLE 2. INFRARED-ABSORPTION BANDS OBSERVED IN DELIENSITE

Wavenumber (cm^{-1})	Assignment*	Wavenumber (cm^{-1})	Assignment*
3409 (s,b)	$\nu_1 H_2O$	933 (m)	ν_2 UO_2
1629 (m)	δ H_2O	854-813 (w)	ν_1 UO_2
1120, 1081 (s)	ν_3 SO_4	593 (w)	ν_4 SO_4

Symbols: s: strong, m: medium, w: weak, b: broad. * Moenke (1962, 1966).

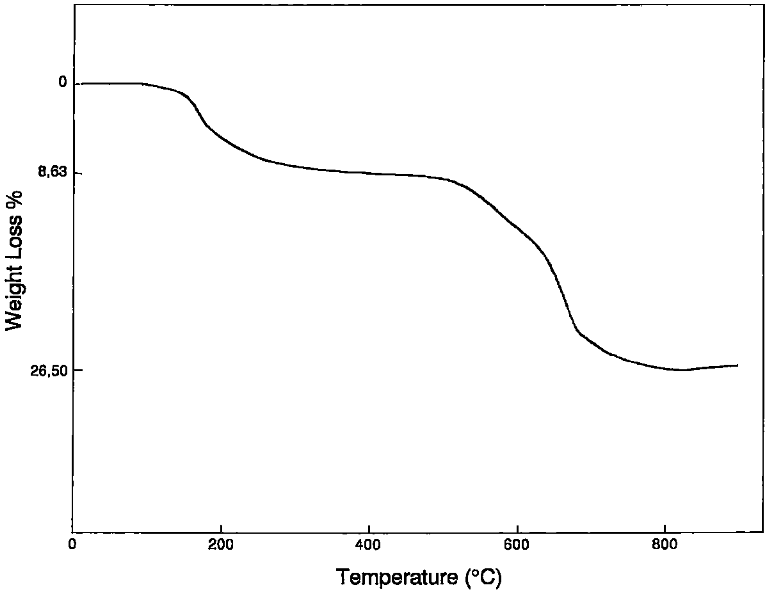

FIG. 3. Thermogravimetric curve of deliensite.

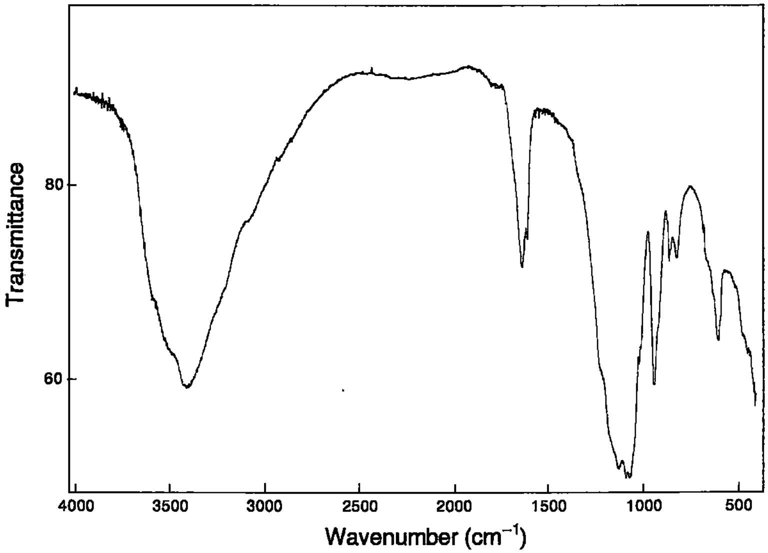

FIG. 4. Fourier-transform infrared-absorption spectrum of deliensite from 400 to 4000 cm^{-1}.

INFRARED SPECTROSCOPY

The infrared spectrum was recorded using the KBr dispersion technique (1 mg sample and 300 mg KBr) with an Ati-Mattson Genesis Fourier transform infrared spectrometer, which covers the range 400–4000 cm^{-1}. The infrared spectrum (Fig. 4) is characterized by the vibrations of H_2O molecules, OH, UO_2 and SO_4 groups. The absorption bands at 3409 and 1629 cm^{-1} are due to H_2O stretching vibrations and deformation modes, respectively (Moenke 1962, 1966). The assignment of the absorption bands is summarized in Table 2.

RELATIONSHIP TO OTHER SPECIES

After rabejacite, deliensite is the second uranyl sulfate to be found at Mas d'Alary. Like most uranyl sulfates, deliensite occurs as a microcrystalline crust on the surface of samples. It differs from rabejacite, $Ca(UO_2)_4(SO_4)_2(OH)_6 \bullet 6 H_2O$, which also occurs in the same area, by the grayish white color of the flakes and by its vitreous luster. The X-ray powder-diffraction pattern is also characteristic and cannot be confused with that of any other known species.

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