

Deveroite-(Ce): a new REE-oxalate from Mount Cervandone, Devero Valley, Western-Central Alps, Italy

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[Received 25 July 2013; Accepted 19 September 2013; Associate Editor: A. Christy]

ABSTRACT

Deveroite-(Ce), ideally $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$, is a new mineral (IMA 2013-003) found in the alpine fissures of Mount Cervandone, overlooking the Devero Valley, Piedmont, Italy. It occurs as sprays of colourless elongated tabular, acicular prisms only on cervandonite-(Ce). It has a white streak, a vitreous lustre, is not fluorescent and has a hardness of 2–2.5 (Mohs' scale). The tenacity is brittle and the crystals have a perfect cleavage along {010}. The calculated density is 2.352 g/cm³. Deveroite-(Ce) is biaxial (–) with 2V of ~77°, is not pleochroic and the extinction angle ($\beta \wedge c$) is ~27°. No twinning was observed. Electron microprobe analyses gave the following chemical formula: $(\text{Ce}_{1.01}\text{Nd}_{0.33}\text{La}_{0.32}\text{Pr}_{0.11}\text{Y}_{0.11}\text{Sm}_{0.01}\text{Pb}_{0.04}\text{U}_{0.03}\text{Th}_{0.01}\text{Ca}_{0.04})_{2.01}(\text{C}_2\text{O}_4)_{2.99} \cdot 9.99\text{H}_2\text{O}$. Although synchrotron radiation was not used to solve the structure of devoite-(Ce) the extremely small size of the sample (13 $\mu\text{m} \times 3 \mu\text{m} \times 1 \mu\text{m}$) did not allow us to obtain reliable structural data. However, it was possible to determine the space group (monoclinic, $P2_1/c$) and the unit-cell parameters, which are: $a = 11.240(8) \text{ \AA}$, $b = 9.635(11) \text{ \AA}$, $c = 10.339(12) \text{ \AA}$, $\beta = 114.41(10)^\circ$, $V = 1019.6 \text{ \AA}^3$. The strongest lines in the powder diffraction pattern [d in $\text{Å}(hkl)$] are: 10.266(100)(100); 4.816(35.26)(211); 3.415(27.83)(300); 5.125(24.70)(200); and 4.988(22.98)(111). Deveroite-(Ce) is named in recognition of Devero valley and Devero Natural Park.

KEYWORDS: Deveroite-(Ce), new mineral, oxalate, Devero.

Introduction

MOUNT Cervandone (also named Cherbadung) overlooks the Devero Valley on the Italian side and the Wann Glacier on the Swiss side. It hosts mineral deposits which are among the most renowned in the Lepontine Alps. Six new REE-arsenates and REE-arsenites including asbesasite

(Graeser, 1966), cafarsite (Graeser, 1966), cervandonite-(Ce) (Armbruster *et al.*, 1988), fetiasite (Graeser *et al.*, 1994), gasparite-(Ce) (Graeser and Schwander, 1987) and paraniite-(Y) (Demartin *et al.*, 1994) were first described in these localities. Arsenates, sulfates and vanadates representing first occurrences at Wannigletscherand at Mount Cervandone were described also by Guastoni *et al.* (2006), and the crystal-chemistry of an arsenic-rich fergusonite-beta-(Y) was first characterized from a sample found at Mount Cervandone (Guastoni *et al.*, 2010).

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DOI: 10.1180/minmag.2013.077.7.11

In this study we describe a new mineral named *deveroite*-(Ce), ideally $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$, found at Mount Cervandone, Devero valley, Western-Central Alps, Italy. *Deveroite*-(Ce) was first identified in 2008 by Enzo Sartori and Vittorio Soldani, local collectors who collaborated with one of the authors (A.G.) and the Parco Veglia-Devero on the project of studying the mineralogy of Mount Cervandone.

Deveroite-(Ce) is the third natural oxalate found in the alpine fissures of Mount Cervandone after *moolooite*, $\text{Cu}(\text{C}_2\text{O}_4) \cdot n\text{H}_2\text{O}$ (Guastoni, 2009) and *lindbergite*, $\text{Mn}^{2+}(\text{C}_2\text{O}_4) \cdot 2\text{H}_2\text{O}$ (Albertini and Meisser, 2012). These minerals occur in Alpine fissures, crystallized by circulation of meteoric waters enriched with oxalic acid, similar to the mechanism reported by Krzemnicki (1996) for the formation of *wheddellite* in the Binntal region.

Despite the crystals being extremely thin and small (crystal sizes, $\leq 50 \mu\text{m} \times 5 \mu\text{m} \times 5 \mu\text{m}$), a combined single-crystal and powder X-ray diffraction (XRD) analysis allowed determination of space group and unit-cell parameters for *deveroite*-(Ce) which, together with the microprobe analysis, highlighted the crystal-chemical relations with its synthetic analogues Ce-oxalate, La-oxalate and Nd-oxalate.

Deveroite-(Ce) was approved by the IMA-Commission on New Minerals, Nomenclature and Classification (CNMNC) IMA2013-003. The mineral is named in recognition of the Devero valley and the Devero Natural Park where, for the past several years, a research project has been carried out and promoted by the Museum of Mineralogy of the University of Padova to study the mineralogy of this area of the Italian Alps. The holotype material is deposited in the mineralogical collection of the Museum of Mineralogy of the Department of Geosciences at the University of Padova (Italy), under catalogue number MMP M12148.

Occurrence

The area of Mount Cervandone includes steep rock walls and a talus field between the 'Bandiera' peak and 'Canalino Ferrari'. This area is characterized by swarms of sub-horizontal and parallel 'white' dykes with pegmatitic texture, which crop out for several metres along the central body of Mount Cervandone. These pegmatitic dykes, which cross cut the metamorphic rocks, are hosted by very fine-grained

two-mica leucocratic gneisses belonging to the 'Mount Leone-Arbola' nappe (Dal Piaz, 1975). These dykes are tens of centimetres thick, and tens of metres long, and are composed of coarse vitreous quartz, K-feldspar and greenish micas. Sporadic pegmatitic dykes contain fractured black tourmaline prisms and contorted mica flakes embedded in vitreous 'smoky' quartz, and exhibit boudinage-like textures. Locally the pegmatite dykes are cross cut by metre-long quartz veins up to several decimetres thick. The quartz veins are usually subvertical and discordant with respect to the foliation of the gneiss host rock and contain open fissures lined with quartz crystals, frequently containing Be-As-Y-REE minerals. In the pegmatite dykes, the Be, As, Y and REE minerals occur more frequently than in the quartz veins. The pegmatites show a strong NYF (niobium, yttrium, fluorine) geochemical signature, represented by the occurrence of a unique mineralogy that includes: *aeschynite*-(Y), *agardite*-(Y), Nb-rich anatase, arsenic-rich *fergusonite*-beta-(Y), *cervandonite*-(Ce), *chernovite*-(Y), *crichtonite-senaite*, *fluorite*, *gadolinite*-(Y), *monazite*-(Ce), *paraniite*-(Y), *synchysite*-(Ce), and *xenotime*-(Y) (Graeser and Stalder, 1976; Albertini, 1991; Graeser and Albertini, 1995).

It is evident that the formation of *deveroite*-(Ce) requires a source of oxalate, a source of REEs, and the presence of water as the fluid medium allowing REE and oxalate ions to form soluble REE-oxalate complexes (Gammons and Wood, 2000). A source of oxalate is provided by incomplete oxidation of organic material, such as decaying plant remains. In this case it is more likely that the source was crusty lichens, such as *Lecidea* *geographica*, which can survive at altitudes above 2500 m and is widespread at Mount Cervandone. Several examples of oxalate-rich minerals formed by lichens and fungi are reported in the literature: e.g. Russ *et al.* (1996) reported the formation of *whewellite*, a hydrated calcium oxalate, on limestones, whilst Chisholm *et al.* (1987) described the occurrence of *whewellite* and *moolooite*, a hydrated copper oxalate, within the medulla of four lichen species growing on copper bearing rocks. A source of REE is clearly provided by the hosting mineral, *cervandonite*-(Ce), an arsenosilicate with the formula $(\text{Ce}, \text{Nd}, \text{La})(\text{Fe}^{3+}, \text{Fe}^{2+}, \text{Ti}^{4+}, \text{Al})_3\text{O}_2(\text{Si}_2\text{O}_7)_{1-x}(\text{AsO}_3)_{1+x}(\text{OH})_{3x}$, (Demartin and Gramaccioli, 2008). *Deveroite*-(Ce) occurs only on crystals of *cervandonite*-(Ce). The partial

dissolution of cervandonite-(Ce) by reaction with aggressive meteoric waters enriched with oxalic acid (HC_2O_4^-)-liberated *LREE* and allowed the formation of deveroite-(Ce).

Physical and optical properties

Deveroite-(Ce) occurs as sprays of colourless, elongated, tabular or acicular prisms (Figs 1, 2, 3) only on cervandonite-(Ce). The mineral exhibits euhedral morphology and shows no inclusions of, or intergrowths with, other minerals. The maximum size available of single crystals suitable for single-crystal study was 15 μm . However, scanning electron microscope images show that deveroite-(Ce) can reach a maximum size of $\sim 50 \mu\text{m}$.

Deveroite-(Ce) is associated with agardite-(Ce), asbecasite, cafarsite, K-feldspar, muscovite, quartz. It has a white streak, a vitreous lustre, is not fluorescent, and neither pleochroism nor twinning was observed. Due to the extremely limited thickness of the crystals, any possible attempt at micro-indentation on such thin crystals could only provide unreliable data. The tenacity is brittle and the crystals have a perfect cleavage along $\{010\}$. Due to the small grain size, it was impossible to measure the density, therefore we report only the value of 2.352 g/cm^3 calculated using the empirical formula and single-crystal unit-cell data. Optically, deveroite-(Ce) is biaxial (-). Due to the crystal size of deveroite-(Ce), it was impossible to obtain the refractive indexes for the new mineral. However, we report those available for synthetic $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$



FIG. 1. Holotype of deveroite-(Ce): platy, acicular, prismatic, colourless crystals of deveroite-(Ce) on a black aggregate of cervandonite-(Ce). The field of view is 1.35 mm wide.

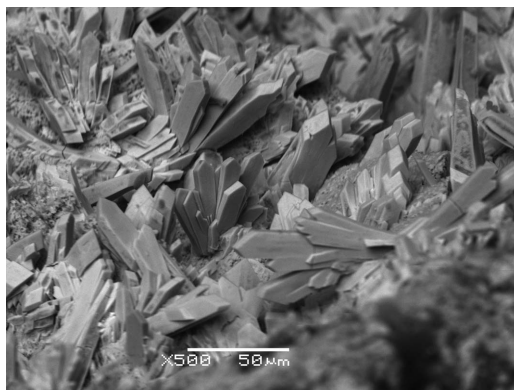


FIG. 2. Backscattered SEM image of the holotype of deveroite-(Ce) showing the morphology of the crystal aggregates.

oxalate, which are: $\alpha = 1.473$, $\beta = 1.548$, and $\gamma = 1.601$. These refractive indexes should be very similar to those of deveroite-(Ce), based on the similarity found for the other optical properties: (1) the measured extinction angle $\beta^{\wedge}c$ is 27° in the direction $+a$ for deveroite-(Ce), practically identical to the 26.5° angle for synthetic $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ (Fig. 4); (2) the $2V$ (77°) is



FIG. 3. Extremely thin and small crystals of deveroite-(Ce) from the holotype (top of the figure). The crystal was used to obtain the optical properties and the single-crystal data by synchrotron radiation

identical to that of $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$. The Gladstone-Dale compatibility using the calculated density is rated as superior.

Experimental methods

Electron microprobe analysis

Microprobe analyses (EMPA) were performed on the crystal fragment used for the synchrotron radiation measurement at the Dipartimento di Scienze Geologiche e Geotecnologie, Università di Milano-Bicocca. The chemical composition was determined using a SEM Tescan VEGA TS 5136 XM equipped with energy-dispersive analysis (EDS) by means of a standardized EDAX GENESIS 4000 XMS electron microprobe. Major and minor elements were determined at 20 kV accelerating voltage and 190 pA (in a Faraday cup), spot size 250 nm, 100 s as counting time, and working distance 23 mm. For the EDS analyses the following lines were used: CaK, LaL, CeL, PrL, NdL, YL, SmM, PbM, ThM

and UM. The crystal fragment was found to be homogeneous within analytical error. Na, K, Gd, Tb, Dy, Ho, Er, Tm and Yb were below the detection limit (of 0.1 wt.%). The mean analytical results (11 analyses) are given in Table 1. The empirical formula (based on 22 O atoms per formula unit (a.p.f.u.)) obtained from the EMPA analyses is (with H_2O and C_2O_3 calculated by stoichiometry): $(\text{Ce}_{1.01}\text{Nd}_{0.33}\text{La}_{0.32}\text{Pr}_{0.11}\text{Y}_{0.11}\text{Sm}_{0.01}\text{Pb}_{0.04}\text{U}_{0.03}\text{Th}_{0.01}\text{Ca}_{0.04})_{2.01}(\text{C}_2\text{O}_4)_{2.99} \cdot 9.99\text{H}_2\text{O}$. The ideal formula is $\text{Ce}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$, which requires Ce_2O_3 45.35, C_2O_3 29.80, H_2O 24.85, total 100.00 wt.%.

X-ray diffraction

A single crystal of deveeroite-(Ce) $13 \mu\text{m} \times 3 \mu\text{m} \times 1 \mu\text{m}$ in size was analysed by XRD at Diamond Light Source Ltd. in the extreme-conditions beamline (I15). The experiment was performed using a fully focused beam of $\lambda = 0.20675 \text{ \AA}$, as calibrated by diffraction from a

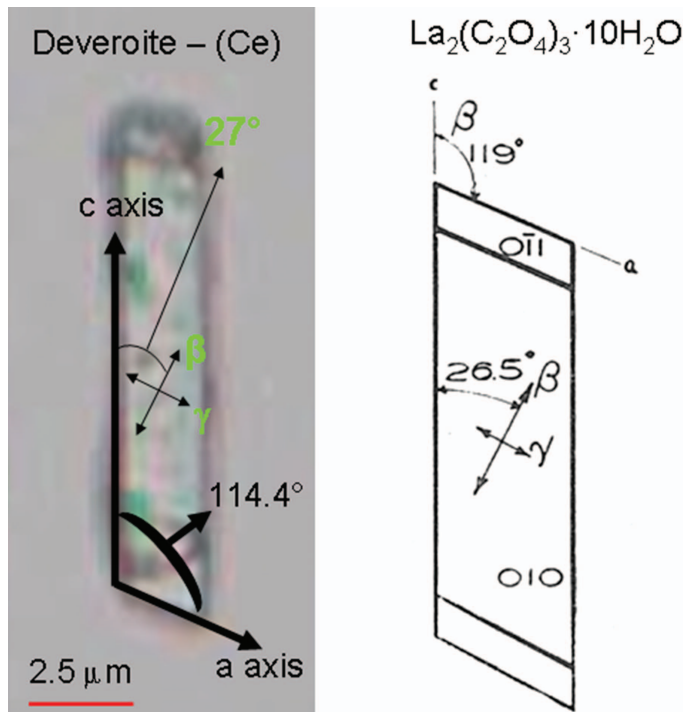


FIG. 4. Comparison between deveeroite-(Ce) and La-oxalate $[\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}]$ (Gilpin and McCrone, 1952) in order to show their similar optical properties. The image of deveeroite-(Ce) on the left is an insert from Fig. 3, whereas on the right side we show part of a drawing from fig. 1 of Gilpin and McCrone (1952) relative to the synthetic $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ oxalate.

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TABLE 1. Chemical data for deveeroite-(Ce).

Constituent	Wt.%	Range	SD	Probe standard
CaO	0.34	0.25–0.44	0.06	Almandine garnet
C ₂ O ₃ *	29.7			
Y ₂ O ₃	1.66	1.19–2.04	0.33	Yttrium garnet
La ₂ O ₃	7.29	6.60–8.40	0.53	Monazite-(Ce)
Ce ₂ O ₃	22.8	22.03–24.28	0.81	Monazite-(Ce)
Pr ₂ O ₃	2.53	2.10–2.88	0.23	Monazite-(Ce)
Nd ₂ O ₃	7.53	7.14–7.90	0.29	Monazite-(Ce)
Sm ₂ O ₃	0.24	0.13–0.43	0.09	Monazite-(Ce)
PbO ₂	1.24	1.42–2.53	0.17	Galena
ThO ₂	0.29	0.22–0.35	0.04	Uraninite
UO ₂	1.05	0.86–1.19	0.11	Uraninite
H ₂ O*	24.8			
Total	99.47			

* Calculated from stoichiometry.

NIST ruby sphere. A 20 μm circular pinhole defined the beam size and shape. The crystal was mounted with a MiTeGen micro-loop on the diffractometer, data were then collected with an Atlas CCD detector (Agilent technologies) scanning φ and ω with a width of 1° . The φ scan was performed in the range from -60° to $+120^\circ$ at a $\kappa = -137.75^\circ$, $\omega = 56^\circ$ while the ω scan was performed from 15 to 95° at $\varphi = 98.00^\circ$ and $\kappa = -134.75^\circ$. Data were then treated with the *Crysalis* software package. Although the extremely small size of the sample did not allow us to refine the structural data, it was possible to obtain the unit-cell parameters $a = 11.240(8)$ \AA , $b = 9.635(11)$ \AA , $c = 10.339(12)$ \AA , $\beta = 114.41(10)^\circ$, $V = 1019.6$ \AA^3 and the space group was assigned as monoclinic $P2_1/c$ based on the systematic absences.

In order to confirm our results further, X-ray powder diffraction (XRPD) measurement was performed on a number of (15–20) crystals. The XRPD data were recorded on a PANalytical θ - θ diffractometer equipped with long fine focus Cu X-ray tube operating at 40 kV and 40 mA, focusing crystal mirror (W/Si), capillary spinner and a solid state detector (PIXCel). The detector active length (aperture) is 3.347° , and this enables signal collection over a large angular range at the same time, reducing the total time of the scan. The scan was performed over the range 5 – $70^\circ 2\theta$ with an integrated step size of $0.026^\circ 2\theta$ and a total time for data acquisition of ~ 68 h (angular speed $0.00028^\circ/\text{s}$). This corresponds to a scan with a

virtual counting statistic of 24000 s/step. The program *High Score Plus* (PANalytical) was used for phase identification and to perform Le Bail structureless whole-pattern fitting (Le Bail *et al.*, 1988). A pseudo-Voigt function was employed for the profile shapes. Refined parameters were scale zero-shift, background, lattice constants, and profile parameters (Gaussian and Lorentzian coefficients). The Le Bail fit gave the following agreement indices: $R_p = 12.39\%$, $R_{wp} = 15.40\%$ and $R_{Bragg} = 5.48\%$. The list of d spacings obtained by XRPD for deveeroite-(Ce) from the Le Bail refinement are reported together with the observed data from simple profile fitting in Table 2. The unit-cell parameters obtained by XRPD refinement are: $a = 11.2725(9)$ \AA , $b = 9.6109(9)$ \AA , $c = 10.346(1)$ \AA , $\beta = 114.539(7)^\circ$, $V = 1019.621$ \AA^3 . The unit-cell data from powder diffraction are in perfect agreement with those obtained by single-crystal XRD.

Results and discussion

The first attempt to identify deveeroite-(Ce) by powder XRD failed, as we realized that the new mineral did not have any natural analogue. Extending the search to the synthetic crystalline compounds, we found a good match of space-group symmetry and unit-cell parameters between deveeroite-(Ce) and three synthetic analogues: $\text{Ce}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4\text{H}_2\text{O}$ and the isostructural $\text{Nd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ (Ollendorff *et al.*, 1969), and $\text{La}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4\text{H}_2\text{O}$ (Gilpin and McCrone,

TABLE 2. List of d spacings obtained by XRPD for deveeroite-(Ce).

$h k l$	d_{calc} (Å)	I_{rel}
1 0 0	10.2543	100
1 1 0	7.0124	8
0 1 $\bar{1}$	6.7243	8
1 1 $\bar{1}$	6.5910	22
1 0 $\bar{2}$	5.1670	11
2 0 0	5.1272	29
1 1 1	4.9855	40
2 1 $\bar{1}$	4.8256	41
0 2 0	4.8054	42
0 0 2	4.7057	2
2 1 0	4.5237	9
1 2 0	4.3513	7
3 0 $\bar{2}$	3.5554	3
1 2 $\bar{2}$	3.5188	6
3 0 0	3.4181	27
2 2 $\bar{2}$	3.2955	3
3 1 0	3.2205	4
1 3 0	3.0579	10
0 3 $\bar{1}$	3.0327	2
2 2 1	3.0172	5
0 1 3	2.9823	4
2 0 2	2.9157	4
3 1 $\bar{3}$	2.8710	4
3 2 0	2.7854	5
3 1 1	2.7366	14
4 1 $\bar{1}$	2.6740	10
2 3 $\bar{2}$	2.6153	6
1 1 3	2.6014	6
2 2 2	2.4928	4
4 2 $\bar{3}$	2.2716	2
1 2 4	2.2415	4
2 1 3	2.2243	8
4 1 1	2.1889	7
0 4 $\bar{2}$	2.1399	2
4 2 4	2.0481	17
3 3 4	1.9597	3
5 2 0	1.8863	4
1 4 3	1.7956	3
5 3 4	1.7058	2
7 2 $\bar{3}$	1.5247	2

1952; Huang *et al.*, 1991) (Table 3) with analogous stoichiometries but different 9-fold coordinated cations. The close structural relationship with these phases is confirmed by the relationship between unit-cell volume and composition. As shown in Fig. 5, the change in composition, represented in terms of ionic radius, is significantly related to the increase in the unit-cell volume. This is consistent with the

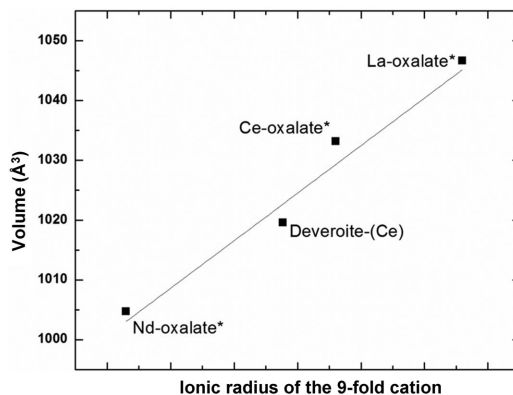


FIG. 5. Unit-cell volume of synthetic oxalates and deveeroite-(Ce) vs. the average ionic radius of the 9-fold coordinated cations.

idea that, assuming constant volume for both the (C_2O_4) and H_2O groups, the unit-cell volume for these oxalates is controlled by the size of the 9-fold coordinated cations (i.e. Ce, Nd, La) only. However, given that structural data are also lacking for the synthetic compounds, the details of the structural role of H_2O and its effect on overall volume cannot be unravelled.

Conclusions

Deveeroite-(Ce) is the natural hydrated REE-bearing analogue of the La, Ce and Nd synthetic oxalate compounds. It is likely that it formed by circulation of meteoric waters at low temperatures, between 20 and 30°C, temperatures that occur during the summer at the altitude of the type locality in the Italian Alps. Further natural sulfate-oxalates of the REE, coskrenite-(Ce) (Peacor *et al.*, 1999) levinsonite-(Y) and zughun-stite-(Ce) (Rouse *et al.*, 2001), seem to be formed under the same conditions.

With respect to the other two oxalates found at Mount Cervandone, moolooite and lindbergite, deveeroite-(Ce) seems to be more stable. Lindbergite, monoclinic $Mn(C_2O_4) \cdot 2H_2O$, is itself a secondary phase that is formed by rapid dehydration on exposure of the very unstable, unnamed orthorhombic $Mn(C_2O_4) \cdot 2H_2O$ (Atencio *et al.*, 2004).

Given the organic anion, large water content and probable thermal instability of deveeroite-(Ce), there is unlikely to be any direct genetic relationship with Alpine hydrothermal fluids. Deveeroite-(Ce) is likely to have formed very

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TABLE 3. Selected crystallographic data for synthetic REE oxalates.

Formula	Deveroite-(Ce) Ce ₂ (C ₂ O ₄) ₃ ·10H ₂ O	Ce-oxalate (synthetic) [Ce ₂ (C ₂ O ₄) ₃ (H ₂ O) ₆ ·4H ₂ O	La-oxalate (synthetic) [La ₂ (C ₂ O ₄) ₃ (H ₂ O) ₆ ·4H ₂ O	Nd-oxalate (synthetic) Nd ₂ (C ₂ O ₄) ₃ ·10H ₂ O
Cell data				
<i>a</i> (Å)	11.2725(9)	11.347	11.382(6)	11.192
<i>b</i> (Å)	9.6109(9)	9.630	9.624(5)	9.612
<i>c</i> (Å)	10.346(1)	10.392	10.502(8)	10.257
β (°)	114.539(7)	114.52	114.52(4)	114.42
<i>V</i> (Å ³)	1019.64	1033.14	1046.65	1004.71
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> ₂ / <i>c</i>	<i>P</i> ₂ / <i>c</i>	<i>P</i> ₂ / <i>c</i>	<i>P</i> ₂ / <i>c</i>
References	This study	Ollendorf <i>et al.</i> (1969)	Huang <i>et al.</i> (1991)	Ollendorf <i>et al.</i> (1969)

recently at near-surface conditions, from LREE released by very local dissolution of cervandonite-(Ce), which have been chelated and transported as oxalate complexes (Hofmann and Bernasconi, 1998; Gammons and Wood, 2000). The oxalate, in turn, is probably derived from organic material such as lichens.

Acknowledgements

The authors thank Domenico Forloni who donated the specimen shown in Fig. 1 used to obtain all the relevant data of this study and Enrico Bonacina who photographed the specimen. The work was supported by “Progetto d’Ateneo of University of Padova” to FN. The Principal Editor, Peter Williams, an anonymous referee and Stuart Mills are thanked for their helpful comments, which improved the manuscript.

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