Lead-antimony sulfosalts from Tuscany (Italy). VI. Pellouxite, ~ (Cu,Ag)₂Pb₂₁Sb₂₃S₅₅ClO, a new oxy-chloro-sulfosalt from Buca della Vena mine, Apuan Alps

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Abstract: Pellouxite, the second natural oxy-chloro-sulfosalt after pillaite, has been discovered in cavities of calcite veins in the small Fe-Ba deposit of Buca della Vena mine, Apuan Alps (Tuscany, Italy). The new mineral name honours professor Alberto Pelloux (1868-1948), curator of the mineralogical Museum at the University of Genova. Pellouxite occurs as black acicular flattened crystals with metallic lustre, up to 1 mm long and less than 0.05 mm thick. Main reflectance values [$\underline{\lambda}$ (nm), R_{air}/R_{oil} %]: 470, 38.3/23.8; 546, 37.3/22.4; 589, 36.9/21.5; 650, 35.2/19.6. It has monoclinic symmetry, space group C2/m, with a = 55.824(11), b = 4.0892(8), c = 24.128(5) Å, $\beta = 113.14(3)^{\circ}$ and V = 5065(2) Å³. The eight strongest lines of the X-ray powder diffraction pattern are [d(Å), I_{obs} (hkl)]: 4.002, 38 (60 \overline{o} , 40 \overline{o}); 3.878, 24 (20 \overline{o} , 11 $\overline{2}$); 3.562, 31 (804, 1202); 3.423, 100 (807, 160 $\overline{4}$, 40 $\overline{7}$); 3.009, 25 (80 $\overline{8}$, 912, 713); 2.948, 27 (131 $\overline{3}$,1111); 2.265, 19 (409); 2.048, 20 (020). Electron probe microanalysis gives (mean of 15 spots; wt.%, error σ): Pb 47.17(20), Sb 31.16(23), Cu 0.89(5), Ag 0.59(5), S 19.08(6), Cl 0.33(3), O 0.39(15), Total 99.60. The unit formula, on the basis of Pb + Sb = 22 at. according to the crystal structure study, is (Cu_{0.64}Ag_{0.25})Pb_{10.36}Sb_{11.64}S_{27.07}Cl_{0.42}O_{1.11} (Z = 4). Taking into account a 2b superstructure, the crystal chemical formula is (Cu,Ag_{0.25})Pb_{10.36}Sb_{11.64}S_{27.07}Cl_{0.42}O_{1.11} (Z = 4). Taking into account a 2b superstructure, the crystal chemical formula is (Cu,Ag_{0.25})Pb_{11.35}SclO (x = 0.12; d_{calc.} = 5.97 g/cm³), derived from the stoichiometric one (Cu,Ag_{0.2}Pb₂₁Sb₂₃S₅₅ClO. Pellouxite, structurally related to scainiite, is an expanded monoclinic derivative of synthetic hexagonal Ba₁₂Bi₂₄S₄₈. It belongs to the zinkenite group of lead sulfosalts with cyclically twinned structures and their derivatives. Like for pillaite, its formation is the result of a complex sulfide deposition

Key-words: pellouxite, new mineral, oxy-chloro-sulfide, sulfosalt, lead, antimony, Tuscany, Italy.

Introduction

Pellouxite is the seventh mineralogical species for which Buca della Vena mine in the Apuan Alps (Tuscany, Italy) is the type locality, after apuanite, versiliaite, stibivanite-2O, dessauite, scainiite and pillaite (Mellini *et al.*, 1979; Merlino *et al.*, 1989; Orlandi *et al.*, 1997, 1999, 2001). At Buca della Vena mine acicular lead-antimony sulfosalts are widely distributed (Orlandi & Checchi, 1986); within this group of minerals, zinkenite is the most common species, together with boulangerite, robinsonite, tintinaite, and, rarely, scainiite and pillaite. All these sulfosalts present very similar macroscopic features, and, at a first sight, these minerals are usually indistinguishable. For this reason a systematic study, collecting X-ray powder patterns with Gandolfi camera on single acicular crystals, was carried on hundreds of samples. This procedure permitted to identify recently pellouxite, as well as other probably new species still under study.

The new mineral species and name were approved by the IMA-CNMMN (vote n° 2001-033). The name honours the late professor Alberto Pelloux (Crema 1868 -Bordighera 1947), curator of the mineralogical Museum at the University of Genova. President of the "Società Geologica Italiana", he was a skilful studious and personal systematic collector of minerals from Tuscany. His collection is now preserved at the Mineralogical Museum of the "Dipartimento geomineralogico" of Bari University.

1. Occurrence and geological setting

The small Ba and Fe-oxide deposit of Buca della Vena is located near the small village of Ponte Stazzemese (Lucca) in the Apuan Alps (Benvenuti *et al.*, 1986); it was

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Fig. 1. SEM image of millimetric fibres and laths of pellouxite.

exploited for barite and iron oxides up to 1988, and consists mainly of a fine-grained mixture of barite and iron oxides (magnetite and hematite), with minor pyrite.

The mineralization is hosted within two carbonate lenses of dolomite limestones of Upper Triassic (Grezzoni) and marbles, interbedded with lenses of phyllites. As also reported in the first description of the occurrences of scainiite and pillaite (Orlandi *et al.*, 1999 and 2001), the ore body and the hosted rocks present evident deformation features, which have been referred to a first compressive tectonic phase dating back 26 m.y. (Kligfield *et al.*, 1986). Measured homogenization temperatures in beryl crystals present in the ore body ranged from 250°C to 340°C (Duchi *et al.*, 1993), in good agreement with the metamorphic grade of the area referred to the greenschist facies (Di Pisa *et al.*, 1985), as well as fluid inclusion studies related

Table 1. Pellouxite: reflectance data (random section) from 400 to 800 nm in air (R_{air}) and oil (R_{oil}).

λ(nm)) R _{air}	R _{oil}	λ(nm)	R _{air}	R _{oil}
400	40.5	25.9	600	36.2	21.2
420	40.7	24.2	620	35.8	20.7
440	39.4	23.8	640	35.3	19.9
460	38.8	24.3	650	35.2	19.6
470	38.3	23.8	660	35.2	19.8
480	38.9	23.6	680	34.1	19.6
500	38.2	23.0	700	33.6	19.3
520	38.3	22.9	720	33.6	18.0
540	37.4	22.6	740	32.5	17.9
546	37.3	22.4	760	32.1	17.1
560	37.4	22.1	780	30.9	16.3
580	37.0	21.4	800	30.0	16.0
589	36.9	21.5			

Polishing method: 600/1200 mesh carborundum (paper); 6, 3, 1 and $^{1}/_{4}$ diamond on cloth; final buffing with Cr₂O₃ on cloth. LEICA DMR microscope with objectives FLUOTAR 20x/0.50 POL (air) and OEL 50x/0.85 (oil). Microscope photometer: Leica MPV-SP, monochromator resolution: $\lambda = 2$ nm. Standard: SiC (NPL n°50).

to the last fault movement of the Apuan Alps (Hodgkins & Stewart, 1994).

Like scainiite and pillaite, pellouxite occurs in tardive extentional calcite veins that cut the Ba-Fe ore body, as well as the phyllites and the dolomitic limestones. In these calcite veins, pellouxite is associated with many other leadantimony acicular sulfosalts as referred in the introduction. Other sulfides and sulfosalts associated with pellouxite are tetrahedrite, bournonite, sphalerite, cinnabar, galena, andorite, chalcostibite and gersdorffite.

2. Mineralogical characterization

2.1 Appearance and physical properties

Pellouxite occurs as black acicular crystals with [010] elongation, and flattened on (100); they are up to 1 mm long and less than 0.05 mm thick (Fig. 1). Lozenge-shaped sections of the fibres are visible in polished sections. The mineral is brittle (with flexible fibres), and presents a good cleavage parallel to the elongation, which would correspond to $\{201\}$ according to the crystal structure (Palvadeau *et al.*, 2004). Density and hardness were not determined owing to the small size of the crystals; the calculated density is 5.97 g/cm³ for Z = 4, on the basis of the structural formula (see § 2.4).

Megascopically, pellouxite is opaque with a black metallic lustre, and a brown streak. In reflected light, it is weakly bireflectant (white to white-grey); with crossed polars, anisotropy is distinct, without polarization colours (like zinkenite), nor twinning. Red internal reflections are frequent at the grain edges and defects, but not within the crystals. Table 1 gives the reflectance values in air and oil from 400 to 800 nm for a random section of a fibre, with the polarization direction perpendicular to the elongation. The *R* values for the four basic COM wavelengths are (λ (nm), R_{air}/R_{oil} %): 470, 38.3/23.8; 546, 37.3/22.4; 589, 36.9/21.5; 650, 35.2/19.6. Figure 2 represents the two reflectance curves in air and oil; they are very close to the minimum curves obtained on zinkenite by Criddle & Stanley (1993).

2.2 X-ray data

Rotation, Weissenberg and precession photographs indicated that pellouxite is monoclinic, space group C2/m. The unit-cell parameters obtained through the crystal structure study with a STOE image plate X-ray diffractometer are a = 55.824(11), b = 4.0892(8), c = 24.128(5) Å; $\beta =$ 113.14(3)°; V = 5065(2) Å³. A rotation photograph around b elongation shows a very weak diffuse line between the zero and first layer lines indicative of a 2b superstructure.

A first X-ray powder diffraction pattern of pellouxite was collected from a single crystal with a Gandolfi camera of 114.6 mm in diameter and CuK α radiation, giving about twenty visible diffraction lines. Finally, a detailed X-ray powder diffraction pattern (Table 2) was obtained with an INEL X-ray Position Sensitive Detector after crushing numerous fibres extracted from the same sample used for



Rair

Roil

λ (nm)



0-

(%) 25 25

T	. d	d.u.	La	h	k	1	I	. d		л-гау І	/ po h	wu k	l	I	d	d	Lui	h	k	11	[d	d.u.	La	h	k	1
- mea o	s. ∝meas.	• calc.	-calc.		0	$\frac{1}{2}$	-meas	s. a meas.	• calc.	-calc.	12	<u> </u>	2	-meas.	• meas.	• calc.	-calc	10	0	<u>_</u>	meas	1 0617	• calc.	-calc	 	1	0
	7.94	7 1008	4	4	0	5	22	5.202	3 1836	24	11	1	$\frac{3}{2}$	9	2.071	2.0089	3 7	10	1	7	0	1.901/	1.9591	4	23	1	$\frac{0}{0}$
12	6.86	6 8402	4	8	0	$\frac{1}{2}$			3 1430	3	11	1	$\frac{2}{3}$		2.037	2.0340	5	15	1	$\frac{7}{5}$	7	1 9466	1.9303	4	$\frac{21}{23}$	1	$\frac{1}{8}$
7	6.02	6.0267	2	4	0	$\frac{2}{4}$	17	3.123	3.1208	5	8	0	5	4	2.604	2.5970	4	3	1	7	,	1.9400	1.9440	3	10	0	9
13	4.120	4.1123	11	8	0	3	1,	0.120	3.1186	0	5	1	$\frac{1}{5}$	7	2.568	2.5639	5	11	1	$\frac{1}{7}$			1.9367	3	25	1	$\overline{\overline{6}}$
		4.0316	4	1	1	1	12	3.078	3.0755	11	11	1	0			2.5192	3	15	1	1	8	1.9259	1.9237	10	11	1	0
		4.0177	8	6	0	6			3.0747	7	18	0	$\overline{4}$			2.4947	4	13	1	7			1.9223	5	25	1	$\overline{2}$
38	4.002	3.9955	16	4	0	6	13	3.051	3.0497	15	1	1	$\overline{5}$	5	2.469	2.4651	6	1	1	7			1.8996	8	15	1	11
		3.9928	1	6	0	4			3.0449	10	<u>11</u>	1	$\overline{4}$	5	2.383	2.3854	4	<u>19</u>	1	3	5	1.8972	1.8950	5	<u>23</u>	1	1
		3.9871	6	1	1	1	25	3.009	3.0132	12	8	0	8			2.3656	7	<u>19</u>	1	$\overline{2}$	4	1.8831	1.8824	3	<u>24</u>	0	11
7	3.931	3.9236	6	<u>12</u>	0	1			3.0003	19	9	1	2	5	2.356	2.3536	7	7	1	6	4	1.8586	1.8604	3	<u>21</u>	1	3
24	3.878	3.881 7	12	2	0	6			2.9992	6	7	1	3	5	2.346	2.3428	4	<u>13</u>	1	8	5	1.8361	1.8366	6	<u>11</u>	1	8
		3.8653	4	1	1	$\overline{2}$			2.9602	6	<u>13</u>	1	2	4	2.332	2.3270	4	1	1	8			1.8333	3	<u>28</u>	0	0
		3.8574	8	3	1	2			2.9564	5	1	1	5	6	2.288	2.2866	8	<u>19</u>	1	6			1.8201	4	4	2	6
		3.8541	5	3	1	1	27	2.948	2.9449	7	<u>13</u>	1	3	7	2.276	2.2763	8	5	1	7	4	1.8136	1.8108	3	<u>26</u>	0	11
		3.8385	6	5	1	1			2.9445	31	<u>11</u>	1	1			2.2728	3	<u>24</u>	0	$\overline{2}$			1.8108	5	<u>23</u>	1	10
		3.8281	3	<u>14</u>	0	4			2.9412	11	5	1	4	19	2.265	2.2619	7	4	0	9			1.8003	5	9	1	12
16	3.800	3.7989	14	5	1	0			2.9236	16	<u>13</u>	1	1			2.2301	4	<u>17</u>	1	2	3	1.7890	1.7874	5	<u>17</u>	1	6
		3.7884	3	<u>10</u>	0	6	14	2.888	2.8835	5	<u>12</u>	0	4	14	2.228	2.2266	4	<u>21</u>	1	4			1.7731	4	8	2	4
13	3.767	3.7658	3	5	1	2			2.8801	7	<u>13</u>	1	4			2.2256	6	<u>18</u>	0	10	4	1.7709	1.7718	5	<u>12</u>	2	2
		3.7620	4	4	0	5	18	2.861	2.8672	8	<u>14</u>	0	3			2.2253	4	<u>11</u>	1	9			1.7682	5	<u>27</u>	1	1
		3.6570	3	5	1	1			2.8566	27	7	1	6			2.2251	4	<u>21</u>	1	3			1.7666	4	5	1	12
15	3.648	3.6444	19	3	1	3	10	2.848	2.8405	11	<u>13</u>	1	0	6	2.216	2.2110	8	<u>19</u>	1	7	8	1.7566	1.7557	6	8	2	7
		3.6397	5	3	1	2			2.8126	4	9	1	6	5	2.196	2.1940	4	<u>13</u>	1	9			1.7549	17	<u>16</u>	2	4
8	3.610	3.6070	5	<u>14</u>	0	5			2.7839	4	<u>11</u>	1	2	9	2.141	2.1389	10	<u>24</u>	0	0			1.7528	4	4	2	7
31	3.562	3.5607	16	8	0	4	18	2.781	2.7824	15	1	1	6			2.0993	5	5	1	8	3	1.7423	1.7428	3	<u>32</u>	0	6
		3.5504	16	<u>12</u>	0	2			2.7749	15	<u>13</u>	1	5	3	2.094	2.0923	6	<u>17</u>	1	9	4	1.7250	1.7226	7	<u>12</u>	2	3
		3.4881	4	7	1	3			2.7711	10	7	1	4	12	2.077	2.0755	4	2	0	11	5	1.7109	1.7101	6	<u>32</u>	0	8
7	3.474	3.4670	4	<u>16</u>	0	2	9	2.750	2.7480	5	<u>15</u>	1	3			2.0533	5	<u>24</u>	0	1	4	1.7050	1.7021	2	8	0	14
		3.4263	23	8	0	7			2.7461	9	<u>15</u>	1	2	20	2.048	2.0446	47	0	2	0	4	1.6948	1.6954	3	<u>22</u>	0	6
100	3.423	3.4202	61	<u>16</u>	0	4			2.7361	5	<u>20</u>	0	5	12	2.018	2.0171	6	<u>20</u>	0	11			1.6919	3	8	2	8
		3.4043	16	4	0	7	8	2.705	2.7030	7	<u>15</u>	1	1			2.0119	4	7	1	8	4	1.6865	1.6851	2	<u>24</u>	0	5
8	3.382	3.3818	5	3	1	4			2.6984	7	5	1	5	8	1.970	1.9693	3	<u>28</u>	0	3	3	1.6673	1.6647	3	<u>14</u>	2	3
		3.3711	6	5	1	4	9	2.687	2.6808	4	8	0	9			1.9679	3	6	0	10	6	1.5944	1.5937	2	<u>18</u>	0	15
L 10	3 3 1 1	3 3078	5	2	0	7																					

Operating conditions: INEL Position Sensitive Detector; $CuK\alpha I$ ($\lambda = 1.540598$ Å); generator power 30 mA x 40 kV; calibration with Na₂Ca₃Al₂F₁₄; 2θ range $2^{\circ} \le 2\theta \le 120^{\circ}$; exposure time ≈ 60 h. Indexed with a = 55.824, b = 4.0892, c = 24.128 Å, and $\beta = 113.14^{\circ}$.

Table 3. Electron-probe microanalysis of pellouxite. Ideal formula according to the crystal structure study (Palvadeau *et al.*, 2004): $(Cu_{0.68}Ag_{0.26})Pb_{10.44}Sb_{11.56}S_{27.5}Cl_{0.5}O_{0.5}$.

Elem	ients (w	t. %)						
No (anal. nb.)	Pb	Sb	Cu	Ag	S	Cl	0	Total
1a (5)	47.22	31.18	0.89	0.54	19.13	0.32	0.20	99.49
1b (4)	46.91	31.03	0.89	0.58	19.03	0.37	0.34	99.15
2 (3)	47.18	31.47	0.94	0.58	19.12	0.31	0.48	100.08
1a' (3)	47.39	30.95	0.82	0.65	19.02	0.30	0.55	99.68
Mean	47.17	31.16	0.89	0.59	19.08	0.33	0.39	99.60
σ	0.20	0.23	0.05	0.05	0.06	0.03	0.15	0.39
Ideal formula	47.55	30.94	0.95	0.61	19.38	0.39	0.18	100
Atomic ratio (Pb + Sb = 22 at.)	I							Ev*
Mean analysis	10.36	11.64	0.64	0.25	27.07	0.42	1.11	- 2.5%
Ideal formula	10.44	11.56	0.68	0.26	27.50	0.50	0.50	

* relative error on the valency balance.

electron probe microanalysis as well as for crystal structure study. The powder was put into a 0.30 mm diameter Lindemann capillary, and the X-ray diffraction pattern was recorded within the interval $2^{\circ} \le 2 \ \theta \le 120^{\circ}$, according to the procedure defined by Deniard *et al.* (1991). All 70 measured diffraction lines correspond to the main ones given by the simulation of the powder diagram from the crystal structure (FULLPROF program), and no extra line due to impurities was noted.

The relative intensities of the main measured lines do not fit exactly those of the calculated ones, that is due, on the one hand, to the preferential orientation of some fibres within the powder, sub-parallell to the axis of the capillary and, on the other hand, to the omission of numerous calculated lines with weak intensity. The unit-cell parameters calculated from the powder diagram do not present any significant difference from those given by the crystal structure study.

2.3 Chemical analysis

Qualitative SEM-EDS chemical analysis of pellouxite showed major lead, antimony and sulfur, with minor copper, silver and chlorine, and without any significant amount of other element with Z > 11. The electron-probe microanalysis of four distinct areas, corresponding to a total of 15 spot analyses, is given in Table 3. Operating conditions were as follows: 20 kV (10 kV for oxygen), 20 nA, standards (element, *emission line*, counting time for one spot analysis): PbS (PbM α , 20 s), pyrite (FeK α , 20 s; SK α , 10 s), stibnite (SbL α , 10 s), Cu metal (CuK α , 20 s), Ag metal (AgL α , 10 s), vanadinite (ClK α , 20 s), cassiterite (OK α , 30 s).

Dadsonite, which contains a small amount of Cl (0.36 wt.%; Moëlo, 1979), was used as a secondary standard for this element. It was also possible to ascertain that the Pb/Sb atomic ratio of pellouxite is close, but significantly lower, to that of dadsonite (0.89 against 0.92). As a small oxidation film is always present at the surface of polished sections of Pb or Sb sulfides and sulfosalts, the oxygen content in pellouxite has been corrected basically by comparison with the analyses of galena, stibnite, robin-

sonite and dadsonite: about 0.33 wt. % oxygen has been subtracted. Nevertheless, one must point that the relative error on the oxygen content is very high, and the presence of this element in this sulfosalt was ascertained only on the basis of the crystal structure study (see discussion in Palvadeau *et al.*, 2004).

On the basis of these structural data, and considering a total of 22 atoms for Pb and Sb, the chemical formula of pellouxite is $(Cu_{0.64}Ag_{0.25})Pb_{10.36}Sb_{11.64}S_{27.07}Cl_{0.42}O_{1.11}$ (*Z* = 4). This formula has been taken as a basis for the crystal structure study and the following crystal chemical interpretation.

2.4. Crystal chemistry

The detailed presentation of the crystal structure is given in a separate paper (Palvadeau *et al.*, 2004). Figure 3 presents the projection along *b* of the crystal structure of pellouxite (half of the unit cell). Among cations, there are 9 pure Pb positions, 10 pure Sb positions, and 3 Pb/Sb and one Cu/Ag pairs (*i.e.* split mixed site); among anions, there are 27 pure S sites, one oxygen site (half-filled) and one Cl/S pair.

The weak 2*b* superstructure is likely indicative of an ordering along *b* of Pb/Sb, O/vacancy and Cl/S pairs, in each case with the 0.50/0.50 s.o.f. ratio. One exception is due to vacancies (~ 6 % according to EPMA) on the Cu/Ag pair, which have been correlated to the Sb excess of the neighbouring Pb/Sb pair, according to the substitution: Pb²⁺ + (Cu, Ag)⁺ \rightarrow Sb³⁺ + vacancy. Doubling the unit formula yields the structural formula (Cu,Ag)_{2-x}Pb_{21-x} Sb_{23+x}S₅₅ClO (*x* = 0.12, and *Z* = 2 (or 4 for the supercell)), directly derived from the ideal stoichiometric one (Cu,Ag)₂Pb₂₁Sb₂₃S₅₅ClO.

One can verify (Table 3) the good agreement between measured and ideal weight concentrations for all elements, taking into account that the error σ on measured weight percentages is a part of the total error, restricted to counting statistic. The main difference concerns the oxygen percentage (0.18 wt. % calc. against 0.39(15) meas.), which is not really significant, due to the problem of oxidation film. The ideal Pb/Sb ratio (0.903) is close to the



Fig. 3. Projection along *b* of the crystal structure of pellouxite [~ $(a/2 \ge c)$ unit cell]. All empty circles in the upper left part correspond to one formula unit. Black and grey circles in the other part represent *y* atomic coordinates equal (or close) to 0 or 0.5, respectively.

measured one (0.890), and significantly below that of dadsonite (0.920) used as an internal standard.

Pellouxite is structurally related to scainiite, $Pb_{14}Sb_{30}S_{54}O_5$ (Moëlo *et al.*, 2000). It is an expanded monoclinic derivative of synthetic hexagonal $Ba_{12}Bi_{24}S_{48}$, belonging to the zinkenite group of lead sulfosalts with cyclically twinned structures and analogues (Makovicky, 1985).

3. Paragenetic considerations and conclusion

Together with the presence of scainiite and pillaite (Orlandi *et al.*, 1999, 2001), the discovery of the new mineral pellouxite at Buca della Vena mine confirms that this deposit acts like a natural laboratory for the crystallization of very complex sulfosalts, due to specific thermochemical conditions. As pointed before (Orlandi *et al.*, 2001), the massive iron ore constituting the host rock has simultaneously controlled fO_2 and fS_2 during the formation of the late sulfosalt bearing veinlets, due to the intimate association of pyrite + hematite + magnetite in the wallrock.

According to fluid inclusion studies in Apuan Alps (Hodgkins & Stewart, 1994), as well as in neighbouring hydrothermal deposits within the Carrara marble (Costagliola *et al.*, 1999), a high chlorinity of late hydrothermal solutions, due to the leaching of Triassic formations, is very probable at Buca della Vena too, and would have favoured the formation of chlorosulfosalts, pillaite and pellouxite.

Due to the erratic distribution of late sulfosalt veinlets within the Fe-Ba ore, small local changes in the thermochemical conditions as well as Pb/Sb ratio or minor metal content (Cu, Ag...) were sufficient to induce the formation of distinct sulfosalts from place to place. The study of new samples, which is under way, indicates the presence of other new sulfosalts in this deposit. Acknowledgements: We sincerely thank Profs. Drs. S. Graeser (Natural History Museum, Basel) and E. Makovicky (Geological Institute, University of Copenhagen) for their careful reading of the manuscript. We also thank Luigi Pierotti, Ugo Quilici, Moreno Romani and Stefano Conforti who kindly provided the samples for our study. C. Deudon (LCS-IMN, Nantes) kindly recorded the INEL X-ray powder diagram.

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