

Gramaccioliite-(Y), a new mineral of the crichtonite group from Stura Valley, Piedmont, Italy

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Abstract: Gramaccioliite-(Y) is a new mineral within the crichtonite group. It was found in the gneiss of the Hercynian Massif of Argentera, at Sambuco (Stura Valley, Piedmont, Italy). It occurs as black lamellar mm-sized crystals. Associated minerals are quartz, albite, muscovite, anatase, brookite, rutile, fluorapatite, xenotime, pyrite, a mineral of the synchysite series, dessauite-(Y) and senaite. Optically, gramaccioliite-(Y) is opaque and shows very weak anisotropy and low birefractance; pleochroism is not observed. Chemical analysis carried out by means of EPM led to the following simplified formula: $(\text{Pb,Sr})(\text{Y,Mn})(\text{Ti,Fe})_{18}\text{Fe}_2\text{O}_{38}$. Gramaccioliite is trigonal, space group $R\bar{3}$, $a = 9.186(4)$ Å, $\alpha = 68.82(4)^\circ$. The strongest five reflections in the X-ray powder diffraction pattern [d in Å (hkl)] are: (3.002) (100) (300), (1.606) (95) (1.3.10), (2.892) (70) (116), (2.258) (70) (134), (1.809) (60) (318) (indices are referred to the hexagonal setting). The crystal structure of gramaccioliite-(Y) has been refined ($R = 0.086$) from single crystal X-ray diffraction data. The structure corresponds to that of the other members of the crichtonite group. During the study of gramaccioliite-(Y), a mineral described in literature as a Re-rich member of the crichtonite group from an unknown locality has been re-examined. New EPM data indicated the complete lack of rhenium in this mineral and allowed to correctly identify it as a second finding of gramaccioliite-(Y).

Key-words: gramaccioliite-(Y), new mineral, crichtonite group, Stura Valley, crystal structure, chemical analysis.

Introduction

The crichtonite group includes a series of complex titanium and iron oxides with the general chemical formula initially given as $\text{AM}_{21}\text{O}_{38}$ (Grey *et al.*, 1976). Later on, the formula was better re-written as $\text{X}^{\text{II}}\text{A}^{\text{VI}}\text{B}^{\text{VI}}\text{C}_{18}\text{T}_2\text{O}_{38}$ (Orlandi *et al.*, 1997), where major cations are: A = Sr, Pb, Ca, Na, K, REE, Ba, U; B = Mn, Y, REE, U, Zr; C = Ti, Fe^{3+} , Cr; and T = Fe^{3+} , Mg. Each species within the crichtonite group is characterized by a unique combination of dominant A and B cations. The minerals so far known within this group are crichtonite, senaite, davidite-(La), davidite-(Ce), davidite-(Y), lovingite, landauite, lindsayite, mathiasite, dessauite-(Y), and the new mineral "IMA 1998-070" (Table 1). With the only exception of crichtonite and senaite, which are known since almost a century, all these minerals were discovered in the last 30 years.

The new mineral which is being described in this paper was sampled several years ago. In a preliminary report (Piccoli, 1981) the mineral was identified as a member of the crichtonite group and named davidite, on the basis of a powder diffraction pattern and of a qualitative chemical analysis. A more detailed study confirmed that it is actually a new mineral species, which has Pb and Y as the dominant A and B cations, respectively.

The new mineral and its name, gramaccioliite-(Y), were approved by the IMA Commission on New Minerals and Mineral Names (ref. IMA 2001-034). The mineral was named after Carlo Maria Gramaccioli (b. 1935), professor of Physical Chemistry at the University of Milano and mineral collector, for his contribution to the lattice dynamics of minerals and to the systematic of Italian minerals. The type material is stored within the mineral collections of the Museo di Storia Naturale e del Territorio, Università di Pisa (catalogue no. 18299).

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Table 1. Minerals of the crichtonite group with dominating M0 and M1 cations.

Mineral	M0	M1
Crichtonite	Sr	Mn
Senaite	Pb	Mn
Lovingite	Ca	Zr
Landauite	Na	Mn
Davidite-(La)	REE	(REE, Y, U)
Davidite-(Ce)	REE	(REE, Y, U)
Davidite-(Y)	REE	(Y, REE, U)
Mathiasite	K	Zr
Dessauite-(Y)	Sr	Y
Lindsleyite	Ba	Zr
Gramaccioliite-(Y)	Pb	Y
IMA No. 1998-070 (approved in 2001)	Pb	(U ⁴⁺ , U ⁶⁺)



Fig. 1. Gramaccioliite-(Y): two tabular black metallic crystals (1.2 mm in diameter).

Occurrence

Gramaccioliite-(Y) was found within quartz hydrothermal veins in a biotitic gneiss of the Hercynian Massif of Argentera (Maritime Alps), at Sambuco, close to Vinadio (CN), Stura Valley, Piedmont, Italy. For a detailed geological description of that locality the reader is referred to Piccoli (2002, and references therein). The paragenesis includes quartz, albite, muscovite, anatase, brookite, rutile, fluorapatite, xenotime, pyrite, a mineral similar to synchysite but not completely identified, and two other members of the crichtonite group, namely dessauite-(Y) and senaite. Sometimes domains of senaite coexist with gramaccioliite-(Y) within the same crystal.

Physical and optical properties

Gramaccioliite-(Y) occurs in thin lamellar crystals with hexagonal outline, up to 2-3 mm in length (Fig. 1). Crystals are black with a black streak, opaque and have metallic lustre. Cleavage was not observed, crystals are brittle and the fracture is conchoidal. Density was not measured owing to the scarcity of material. The calculated density is 4.66 g/cm³.

In reflected plane-polarized light the colour is black, the anisotropy is very weak. The bireflectance is low, pleochroism was not observed. Reflectance measurements for the four critical wavelengths are reported in Table 2.

Chemical data

The chemical composition of gramaccioliite-(Y) was obtained with electron probe microanalysis, using a JEOL

JXA-8600 instrument equipped with a Tracor Northern Series II system. The operating conditions were: accelerating voltage 20 kV, beam current 60 nA (monitored on a Faraday cup), diameter of the beam 1 μm, counting time 15 s for peak and 15 s for both left and right background. The following standards were used: metallic vanadium (V), metallic niobium (Nb), rutile (Ti), metallic rhenium (Re), monazite (Th, La, Ce, Nd), metallic uranium (U), hematite (Fe), YAG (Y), Cr-diopside (Ca), rhodonite (Mn), cuprite (Cu), willemite (Zn), celestine (Sr), benitoite (Ba), crocoite (Pb), sanidine (K). No other elements with Z > 9 were detected. H₂O and CO₂ were not determined directly, since the minerals of the crichtonite group are known to contain neither of two. The raw data were reduced using a Bence-Albee correction routine (Bence & Albee, 1968). The valence state of iron has been assumed as Fe³⁺, on the basis of the structural information and the electrostatic valence balance. This is in keeping to what is commonly observed in minerals of the crichtonite group, although the hypothesis that iron could occur, at least partially, as Fe²⁺ has been recently put forward (Zhang *et al.*, 1989). The chemical analysis (average of 10 points), the range, and the number of a.p.f.u. are given in Table 3. The resulting formula, based on 38 oxygens, is: (Pb_{0.61}Sr_{0.27}Ba_{0.02}U_{0.02})_{Σ=0.93} (Y_{0.49}Mn_{0.37}Ce_{0.08}Ca_{0.04}Nd_{0.02}La_{0.02})_{Σ=1.01} (Ti_{13.53}Fe_{5.49}Zn_{0.22}V_{0.04}Nb_{0.04})_{Σ=19.33} O₃₈. The simplified chemical formula may be written as (Pb,Sr)(Y,Mn)(Ti,Fe)₁₈Fe₂O₃₈, which may be assumed as the formal chemical formula for the new mineral.

X-ray diffraction study

The X-ray powder diffraction pattern of gramaccioliite-(Y) was recorded with a Gandolfi camera and is reported in Table 4. Intensities were estimated by measuring the area of the peaks in the digitalized pattern. The indexing is referred to the hexagonal cell, and the following unit-cell parameters were refined (in the hexagonal setting) from the

Table 2. Reflectance measurements (in air and oil) for the four critical wavelengths (standard: SiC).

	Air (%)	Oil (%)
470 nm	19.2	6.7
546 nm	17.9	5.9
589 nm	17.6	5.7
650 nm	17.4	5.8

Table 3. Electron microprobe analysis (average of 10 points) of gramaccioliite-(Y).

Oxide	Wt.%	Range	Cations (O = 38)
V ₂ O ₅	0.22	0.18-0.25	0.044
Nb ₂ O ₅	0.32	0.21-0.44	0.044
TiO ₂	59.47	57.75-61.21	13.525
ReO ₂	b.d.l.		-
ThO ₂	b.d.l.		-
UO ₂	0.33	0.19-0.65	0.022
Fe ₂ O ₃	24.14	22.90-25.61	5.494
Y ₂ O ₃	3.03	2.60-3.48	0.488
La ₂ O ₃	0.14	0.00-0.31	0.016
Ce ₂ O ₃	0.70	0.41-1.13	0.078
Nd ₂ O ₃	0.20	0.00-0.36	0.022
CaO	0.12	0.09-0.14	0.039
MnO	1.45	1.27-1.69	0.371
CuO	0.00	0.00-0.04	-
ZnO	0.99	0.90-1.05	0.221
SrO	1.56	1.23-1.82	0.274
BaO	0.19	0.00-0.26	0.023
PbO	7.53	6.26-8.36	0.613
K ₂ O	0.01	0.00-0.02	0.004
Total	100.40		

powder pattern: $a = 10.411(3)$, $c = 20.97(3)$ Å, $V = 1968.4$ Å³ ($Z = 3$).

The single-crystal study was referred to the rhombohedral cell, for the sake of consistency with the structural parameters available in literature for a number of minerals of the crichtonite group. A crystal fragment (dimensions *ca.* $0.5 \times 0.5 \times 0.05$ mm), previously tested by Weissenberg photographs, was used for the intensity data collection, which was carried out with a conventional Ital Structures four-circle diffractometer. Operating conditions were: 50 kV, 30 mA, graphite-monochromated MoK α radiation ($\lambda = 0.71069$ Å). The Laue group symmetry and the unit-cell metrics were consistent with those common to the whole crichtonite group. The unit-cell parameters (in the rhombohedral setting) obtained through least-squares fit of 2θ values of a set of 18 reflections accurately centered at the diffractometer were: $a = 9.186(4)$ Å, $\alpha = 68.82(4)^\circ$, $V = 649.8$ Å³ ($Z = 1$, space group $R\bar{3}$). A total of 3912 reflections were collected ($0 \leq h \leq 11$, $-11 \leq k \leq 11$, $-11 \leq l \leq 11$), which were reduced to a set of 1213 independent squared amplitude factors, after correction for Lorentz, polarization and absorption (the latter was accomplished on the basis of Ψ -scan measurements). Of the whole set of reflections, 750 were considered observed, having $F_o > 4\sigma(F_o)$, and were used in the least-squares refinement of the structure which was carried out with the SHELXL-93 program (Sheldrick, 1993). The starting fractional coordinates were those of davidite (Gatehouse *et al.*, 1979). The distribution of the different atomic species in the various independent sites was set up as to achieve the best agreement between chemical data and the number of electrons at each independent site, taking also into account the preference of some cations for specific sites, on the basis of the previous cases (a dozen refinements of minerals of the crichtonite group are available). The final occupancies represent the best compromise between chemical data and the quality of the

Table 4. X-ray powder pattern (Gandolfi camera, diameter 114.6 mm, Mn-filtered FeK α radiation) of gramaccioliite-(Y).

d_{obs}	d_{calc}	hkl	d_{obs}	d_{calc}	hkl
8.18	8.28	5 101	2.280	2.279	18 306
5.19	5.20	5 110	2.258	2.257	70 134
4.42	4.41	2 021	2.147	2.148	50 315
4.15	4.14	10 202	2.091	2.088	10 226
3.81	3.80	5 015	2.037	2.043	8 1.0.10
3.49	3.50	2 006	1.968	1.967	20 410
3.415	3.418	48 024	1.919	1.920	35 137
3.240	3.241	10 122	1.854	1.855	5 235
3.070	3.071	45 205	1.809	1.810	60 318
3.002	3.005	100 300	1.785	1.786	12 2.1.10
2.892	2.902	70 116	1.749	1.748	8 0.0.12
2.852	2.857	50 214	1.713	1.715	30 416
2.758	2.761	38 303	1.658	1.657	12 505 - 1.1.12
2.644	2.645	30 125	1.606	1.607	95 1.3.10
2.601	2.603	13 220	1.579	1.579	5 425
2.484	2.483	43 131	1.552	1.554	10 236
2.434	2.432	50 312 - 223	1.473	1.473	5 3.2.10
2.325	2.330	5 009	1.444	1.444	40 520

refinement. The refinement was completed with anisotropic displacement parameters for all cation sites and converged to the following values: $R1$ (conventional R factor) = 0.0861, $wR2$ (weighted R on squared F 's) = 0.2499, S (goodness of fit) = 1.137. Maximum and minimum heights in the final difference Fourier synthesis were $+7.62$ and -2.44 e/Å³, respectively. The rather high residual maxima could be related to the occurrence of additional sites with partial (5-10 %) occupancy, which was already noticed in other minerals of the group (mathiasite, dessauite-(Y), U-rich senaite). Armbruster & Kunz (1990) explained the occurrence of additional octahedral sites as the intergrowth of two strictly related structural units with a common packing of oxygens. In our case, however, the inclusion of these maxima as partially occupied by Fe³⁺ and Ti did not improve the refinement significantly; therefore, for the sake of simplicity, we preferred to leave them out in the last least-squares cycles.

The final fractional coordinates and isotropic displacement parameters are given in Table 5; the cation site occu-

Table 5. Final fractional coordinates and equivalent isotropic (U_{eq} for cations) or isotropic (U_{iso} , for oxygens) displacement parameters for gramaccioliite-(Y).

Site	x	y	z	U_{eq} or U_{iso}
M0	0.00000	0.00000	0.00000	0.0319(6)
M1	0.50000	0.50000	0.50000	0.0084(6)
M2	0.3096(2)	0.3096(2)	0.3096(2)	0.0120(7)
M3	0.3483(2)	0.1260(2)	0.0204(2)	0.0128(5)
M4	0.3088(3)	0.7192(3)	0.1480(3)	0.0109(5)
M5	0.4738(3)	0.0807(3)	0.6423(3)	0.0110(5)
O1	0.302(1)	0.629(1)	0.377(1)	0.014(2)
O2	0.150(1)	0.238(1)	0.937(1)	0.011(2)
O3	0.919(1)	0.461(1)	0.302(1)	0.009(2)
O4	0.144(1)	0.515(1)	0.991(1)	0.009(2)
O5	0.386(1)	0.487(1)	0.137(1)	0.007(2)
O6	0.705(1)	0.242(1)	0.070(1)	0.011(2)
O7	0.2149(8)	0.2149(8)	0.2149(8)	0.012(3)

Table 6. Site occupancy factors and anisotropic displacement parameters for cation sites.

Site	S.O.F.	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
M0	Pb _{0.60} Sr _{0.30} □ _{0.10}	0.0283(6)	0.0283(6)	0.0283(6)	-0.0035(4)	-0.0035(4)	-0.0035(4)
M1	Y _{0.48} Mn _{0.34} Ce _{0.12} U _{0.06}	0.0092(6)	0.0092(6)	0.0092(6)	-0.0033(4)	-0.0033(4)	-0.0033(4)
M2	Fe _{1.00}	0.0116(8)	0.0116(8)	0.0116(8)	-0.0027(5)	-0.0027(5)	-0.0027(5)
M3	Fe _{1.00}	0.0130(9)	0.0140(9)	0.0136(9)	-0.0058(7)	-0.0040(7)	-0.0035(7)
M4	Ti _{1.00}	0.0119(11)	0.0106(11)	0.0108(11)	-0.0048(8)	-0.0012(8)	-0.0035(8)
M5	Ti _{1.00}	0.0096(11)	0.0122(11)	0.0126(11)	-0.0047(8)	-0.0020(8)	-0.0038(8)

pancies and the anisotropic displacement parameters are given in Table 6; selected bond distances are given in Table 7.

Since the basic features of the structure of gramaccioliite-(Y) are identical to those of the other members of the crichtonite group, they will not be considered in detail here. The basic information provided in Tables 5-7 is enough to allow comparison with the other available refinements: crichtonite (Grey *et al.*, 1976), senaite (Grey & Lloyd, 1976), lovingite (Gatehouse *et al.*, 1978), landauite (Grey & Gatehouse, 1978), davidite-(La) (Gatehouse *et al.*, 1979), mathiasite (Gatehouse *et al.*, 1983; Lu & Peng, 1987; Zhang *et al.*, 1988), lindsleyite (Zhang *et al.*, 1988), U-rich senaite (Armbruster & Kunz, 1990), dessauite-(Y) (Orlandi *et al.*, 1997), synthetic Ca₂Zn₄Ti₁₆O₃₈ (Gatehouse & Grey, 1983), synthetic BaMn₃Ti₁₄⁴⁺Ti₃³⁺O₃₈ (Peterson & Grey, 1995).

A re-examination of an ill-characterized mineral

Sarp *et al.* (1981) described a "strange" mineral as a rhenium-rich member of the crichtonite-senaite group. The mineral was found in a sample of unknown origin during re-examination of the mineral collections at the Natural History Museum, Geneva (Switzerland). A powder (Gandolfi) and single-crystal (precession and Weissenberg) X-ray diffraction study led to unambiguously ascribe the mineral to the crichtonite group. However, some oddities were observed in its chemical composition (microprobe analyses). These oddities were not only related to the unusual amount of rhenium, but also to the high (Pb+Sr) sum, *ca.* 1.70 a.p.f.u.. In fact, in the crichtonite-type struc-

ture, both atoms are likely to occupy the M0 site, and this should imply a (Pb+Sr) sum not exceeding 1 a.p.f.u., and even less, since the M0 site is often not fully occupied.

We obtained from the authors a small sample of the originally studied material, and we carried out new electron probe chemical analysis together with those of gramaccioliite-(Y), for comparative purposes, and with the aim to clarify its real nature and its place within the crichtonite group. The analyses are reported in Table 8. The standards used were the same already listed for gramaccioliite.

The results are surprising. In fact, rhenium is not present in the mineral, and the new data gave a total of 0.88 cations per formula unit which can enter the M0 site (Pb+Sr+U+Ba), well within the normal range for crichtonite-group minerals. The original analysis by Sarp *et al.* (1981) was for some reason wrong, and the claimed rhenium-rich member of the crichtonite group actually does not exist.

The recalculation of the chemical formula gives (Pb_{0.44}Sr_{0.37}U_{0.06}Ba_{0.02})_{Σ=0.88} (Y_{0.48}Mn_{0.30}Ce_{0.13}La_{0.08}Ca_{0.02})_{Σ=1.01} (Ti_{12.80}Fe_{6.52}Zn_{0.17}V_{0.06}Nb_{0.02})_{Σ=19.55} O₃₈, and indicates that, being Pb and Y the dominant cations in M0 and M1 sites, respectively, the mineral studied by Sarp *et al.* (1981) is nothing but gramaccioliite-(Y). That sample,

Table 7. Selected bond distances (Å) in gramaccioliite-(Y).

M0-O2	2.774(10) x 6	M4-O2	1.872(10)
M0-O6	2.852(9) x 6	M4-O3	1.932(9)
M1-O1	2.225(10) x 6	M4-O1	1.950(10)
M2-O5	1.950(9) x 3	M4-O6	1.951(10)
M2-O7	1.978(18)	M4-O5	2.020(9)
		M4-O6	2.078(9)
M3-O4	1.955(9)	M5-O4	1.862(10)
M3-O3	1.995(9)	M5-O1	1.876(10)
M3-O4	2.011(9)	M5-O3	1.933(9)
M3-O2	2.014(9)	M5-O5	2.001(9)
M3-O7	2.027(9)	M5-O6	2.020(9)
M3-O2	2.088(10)	M5-O5	2.185(9)

Table 8. Electron microprobe analysis (average of 10 points) of the mineral originally studied by Sarp *et al.* (1981).

Oxide	Wt. %	Range	Cations (O = 38)
V ₂ O ₅	0.27	0.24-0.30	0.055
Nb ₂ O ₅	0.12	0.08-0.14	0.017
TiO ₂	55.65	54.63-56.08	12.795
ReO ₂	b.d.l.		-
ThO ₂	b.d.l.		-
UO ₂	0.92	0.63-1.18	0.063
Fe ₂ O ₃	28.32	28.15-28.41	6.516
Y ₂ O ₃	2.93	2.71-3.09	0.477
La ₂ O ₃	0.70	0.60-0.77	0.079
Ce ₂ O ₃	1.18	1.05-1.31	0.132
Nd ₂ O ₃	0.03	0.00-0.11	0.003
CaO	0.07	0.06-0.09	0.023
MnO	1.14	1.11-1.25	0.295
CuO	0.01	0.00-0.06	0.002
ZnO	0.74	0.72-0.79	0.167
SrO	2.00	1.86-2.11	0.374
BaO	0.17	0.10-0.28	0.020
PbO	5.31	5.11-5.49	0.437
K ₂ O	0.00	0.00-0.02	-
Total	99.56		

however, was never proposed for approval as a valid mineralogical species, and therefore gramaccioliite-(Y) from Sambuco di Vinadio, Stura Valley, Piedmont, Italy has to be considered the holotype. In the light of the new chemical data, the Swiss museum sample can now be considered another gramaccioliite-(Y) from an unspecified occurrence.

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