American Mineralogist, Volume 68, pages 623–627, 1983

Chiavennite, $CaMnBe_2Si_5O_{13}(OH)_2 \cdot 2H_2O$, a new mineral from Chiavenna (Italy)

MIRELLA BONDI

Istituto di Mineralogia e Petrografia
dell'Università di Bologna
Piazza di Porta S. Donato 1, 40127 Bologna, Italy

WILLIAM L. GRIFFIN

Mineralogisk-Geologisk Museum
Universitetet i Oslo
Sars' Gate 1, Oslo 5, Norway

VITTORIO MATTIOLI

Via Keplero 5, 20126 Milano, Italy

AND ANNIBALE MOTTANA

Istituto di Mineralogia e Petrografia
dell'Università di Roma
Città Universitaria, 00185 Roma, Italy

Abstract

Chiavennite occurs as euhedral orange grains and as crusts coating beryl in the alpine pegmatites crossing the Chiavenna ultramafics in the Rhetic Alps of Italy. It is usually associated with bavenite and several other pegmatitic minerals. Chiavennite is optically biaxial, α =1.581(1) and γ = 1.600(1), faintly pleochroic from colorless or yellow (*X*) to yellow-orange (*Z*). The empirical formula derived from EDS microprobe analysis and separate analyses for BeO (optical spectrography) and H_2O (TGA) is $(Ca_{0.97}Na_{0.05})_{\Sigma 1.02}Mn_{0.97}(Be_{1.98}Al_{0.03})_{\Sigma 2.01}(Si_{4.65}Al_{0.35})_{\Sigma 5.00}O_{12.63}(OH)_{2.37} \cdot 2.16H_2O$ or ideally $CaMnBe_2Si_5O_{13}(OH)_2 \cdot 2H_2O$, as confirmed by the crystal structure determination. D(meas.) 2.64(1) g/cm^3, D(calc.) 2.657 g/cm^3. The mineral is orthorhombic, $P2_1ab$, with a = 8.729(5), b = 31.326(11), c = 4.903(2)Å, Z = 4. The most intense lines in the powder pattern (Gandolfi camera) are (as d, Å, I/I_0, hkl) 15.7(100)(020), 4.15(30)(041), 3.93(30)(080), 3.82(30)(240), 3.28(75)(201), 2.903(100)(251), 1.944 (30)(3.12.0). The genesis is related to late fluid activity within the pegmatite.

Introduction

The western margin of the alpine Val Masino-Val Bregaglia (= Bergell) composite pluton in the Rhetic Alps is crossed by swarms of pegmatites, related to the final crystallization stages of the pluton, and most likely to the emplacement of the San Fedelino (= Novate) granite body (Mottana *et al.*, 1978). These pegmatites are late-alpine in age (25–27 m.y., K–Ar on muscovite; Hanson *et al.*, 1966) and cross, completely undeformed, several units characterized by low pressure–high temperature metamorphism up to the sillimanite zone (Wenk *et al.*, 1974). The largest dikes occur on both sides of Valle di San Giacomo near the town of Chiavenna, Italy, and cross, subhorizontally, both the biotite–phengite–microcline augen gneisses of the "lower Corbet series" (Tambò nappe; Weber, 1966), and the Chiavenna mafic/ultramafic Complex (Schmutz, 1976), a metamorphosed slab of the oceanic crust separating the Tambò from the Adula mass.

These pegmatites show a zonal structure with grain size increasing from border to core and a concentration of large biotite flakes and small red garnet seams along the marginal zone. Although the mineral assemblage of the pegmatitic zone is in general rather uniform (albite + quartz + microcline perthite ± white mica) numerous accessory minerals have been found, such as bavenite, zircon, tourmaline (schorl), beryl (colorless or aquamarine), arsenopyrite, bismuthinite, bismutite, gahnite, py-

0003–004X/83/0506–0623$02.00

Fig. 1. Euhedral chiavennite crystal in vug. Maximum length 0.4 mm.

rite, pyrochlore, titanite, uraninite, aeschynite and laumontite. Recently one of us (V.M.) found orange crusts of unusual appearance coating beryl and usually accompanied by bavenite. Later, euhedral orange crystals, up to 0.4 mm in size, were also found in the same locality (Fig. 1). Examination showed this material to be a new mineral species here named chiavennite from the type locality Chiavenna, frazione Tanno, provincia Sondrio, region Lombardy, Italy.

The mineral has been approved by the Commission on New Minerals and Mineral Names, I.M.A., in September 1981, at the same time as another submitted material from Norway which proved to be indentical (Raade *et al.*, 1983, see following paper). Following the rule of priority the name chiavennite is to be used. The type material from Chiavenna is deposited in the collection of Museo di Mineralogia, Università di Roma, under specimen number 24342.

Physical properties

Chiavennite is pale orange-yellow in hand specimen, translucent, with a vitreous luster. Streak is white. Mohs' hardness is approximately 3. The crystals, although rare and minute, have a flat pseudohexagonal habit and show perfect "basal" cleavage.

The specific gravity, measured with a Westphal balance, is 2.64(1) g/cm^3. This value compares favorably with a calculated value of 2.657 g/cm^3 from unit-cell and chemical analysis data; for the theoretical composition the calculated value is 2.632 g/cm^3.

The mineral is insoluble in water, and in concentrated HCl, HNO_3 and H_2SO_4.

Chiavennite is optically biaxial, but the sign and 2*V* could not be obtained. The refractive indices measured at room temperature in white light are $\alpha = 1.581(1)$ and $\gamma = 1.600(1)$. The pleochroic scheme, determined on the same flakes used for the measurement of indices, is: *X* colorless to pale yellow, *Z* yellow-orange. In thin section the mineral is colorless to yellow and orange-yellow. A sharp zoning with deep orange colors is observed near the marginal part of crystals, possibly due to increased iron content (see below). By grinding, such a zoned material produces a pale ochre powder.

X-ray crystallography

The X-ray data have been obtained both by standard powder diffractometry on a slurry and by Gandolfi camera using a cluster of a few small grains. The observed *d*-

Table 1. X-ray powder diffraction data for chiavennite (Tanno, Chiavenna, Italy)

hkl[1]	d_{obs} (Å)[2]	I/I_o[2]	d_{calc} (Å)	d_{obs} (Å)[3]	I/I_o[3]
020	15.7	100bb	15.663	15.7	90
040	7.8	20	7.832	7.83	40
140	5.84	20	5.829	5.83	11
011	4.85	5	4.844	-	-
031	4.45	5	4.438	-	-
041	4.15	30	4.156	4.12	8
080	3.93	30b	3.916	3.93	100
240	3.82	30	3.812	3.81	10b
201	3.28	75	3.260	3.26	14
0.10.0	3.13	10	3.132	3.14	10
1.10.0	-	-	2.948	2.954	10
251,181	2.903	100	2.892,2.887	2.892	13
091	2.846	5	2.838	2.836	8
261	2.779	5	2.765	-	-
191	2.705	5	2.699	-	-
0.10.1	2.645	15	2.640	-	-
360,1.10.1	2.538	20	2.542,2.528	-	-
032	2.394	12	2.387	-	-
042	2.347	10	2.340	-	-
142	2.270	12	2.260	-	-
0.14.0,1.12.1	2.235	10	2.238,2.228	2.227	5
1.14.0	2.171	20	2.167	2.161	8
2.14.0	1.991	20	1.991	-	-
3.12.0	1.944	30	1.943	-	-
1.10.2	1.884	5	1.885	-	-
2.14.1	1.833	5	1.844	-	-
352,4.10.0	1.796	20	1.796,1.791	1.785	5
0.18.1	1.638	5	1.640	-	-

[1] indexed on the basis of the orthorhombic cell $\underline{a} = 8.729$ $\underline{b} = 31.326$, $\underline{c} = 4.903$ Å, $\underline{P2_1ab}$ (single crystal diffractometer, pers.comm.V. Tazzoli).

[2] Gandolfi camera (114.6 mm diameter, Mn-filtered Fe-target, 120 hr) on three grains analyzed by microprobe.

[3] diffractometer pattern (Ni-filtered Cu-target, 1/2°2θ min^{-1}) on powder analyzed for H_2O and BeO.

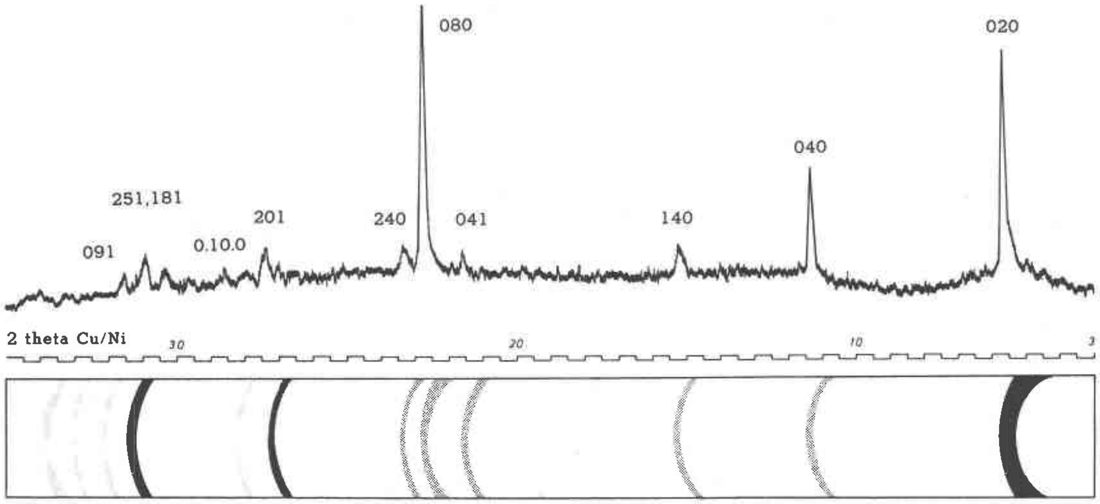

Fig. 2. Diffractometer trace on powdered material (above) and intensities of the lines observed in the Gandolfi film on the grains (below).

values and the relative intensities of the peaks, measured graphically on the diffractometer tracing and visually estimated in the film, are listed in Table 1 and shown in Figure 2. Due to the pronounced preferred orientation of chiavennite cleavage flakes, the two sets of intensities compare rather poorly: in particular in the diffractometer pattern some reflections are enhanced as can usually be seen in layer silicates. The X-ray structure determination of chiavennite, currently under way by V. Tazzoli *et al.*, showed it to be orthorhombic, space group $P2_1ab$ (systematic absences $h0l$: $h = 2n + 1$ and $hk0$: $k = 2n + 1$). A least squares technique applied to the diffraction angles of 25 strong reflections, measured by means of an automated single-crystal diffractometer, provided the refined cell parameters $a = 8.729(5)$, $b = 31.326(11)$, $c = 4.903(2)$Å. The indices in Table 1 were assigned accordingly.

Chemical composition

Electron microprobe analyses were carried out using a LINK system model 860 energy-dispersive analyzer, with on-line matrix corrections by the ZAF-4 program, fitted on the ARL-EMX probe of the Mineralogisk-Geologisk Museum, Oslo. The analyses are based on the following standards: Mn metal, Al_2O_3, wollastonite (for Ca and Si), and jadeite (for Na).

Four spot analyses on three grains (the same used for the Gandolfi powder pattern) were performed. The initial results are given in Table 2 column 1. No other elements within the sensitivity of the EDS microprobe could be detected: Fe, in particular, is absent in these grains.

Water was determined by TG analysis on a separate 10.68 mg aliquot of another specimen from the same outcrop. The total weight loss on heating is 11.3% (Fig. 3) and occurs in two steps: a continuous and steady loss up to 640–650°C (corresponding to a 6.75 wt.% of mostly H_2O) followed by a quick loss continuing up to 1000°C (corresponding to a 4.5–4.6 wt.% loss due mostly to OH). The presence of both OH and H_2O is confirmed by the infrared spectrum (Fig. 4).

The broad bands at 3500–3400 cm^{-1} are due to adsorbed water, and the sharp band at 1640 cm^{-1} to water bending vibrations. The band at 3590 cm^{-1} is attributed to the stretching vibrations of structural OH. Hydroxyl is confirmed also by the sharp absorption at 680 cm^{-1} to be assigned to its vibrational motions. Other stretching bands for hydroxyl of lower energy mode are present in the 2900 and 2300 cm^{-1} regions.

Table 2. Chemical analysis of chiavennite (Tanno, Chiavenna, Italy)

	1 (wt.%)	range	2 (wt.%)		3	
SiO_2	49.84	(49.39-50.53)	52.5	Si	4.654	5.00
Al_2O_3	3.24	(2.96- 3.38)	3.6	Al^{IV}	0.346	
				Al^{VI}	0.030	2.01
BeO	n.d.		9.3	Be	1.981	
MnO	11.10	(10.98-11.20)	12.9	Mn	0.969	
CaO	9.77	(9.51-10.02)	10.2	Ca	0.969	1.02
Na_2O	0.29	(0.15- 0.46)	0.3	Na	0.052	
H_2O	n.d.		11.3			
Total			100.1			

n.d. = not determined
1. Microprobe analysis for elements heavier than 11: initial results, uncorrected for H_2O and BeO.
2. Preferred combined analysis, with the previous microprobe data recalculated using the α-factors of Albee and Ray (1970) for BeO and H_2O. Be determined spectrographically; H_2O by TGA.
3. Number of atoms on the basis of nine cations.

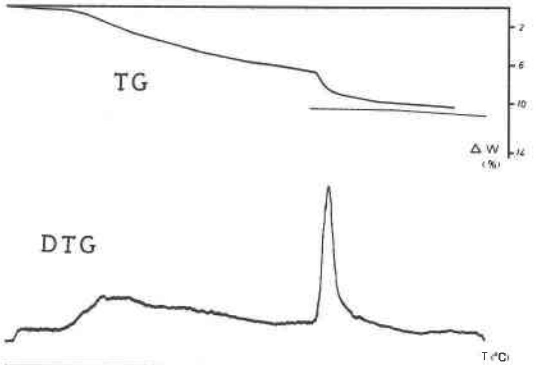

Fig. 3. Thermal behavior of chiavennite in air (Analyzer Dupont 951, prog. rate 20°C/min, time constant 1 sec).

The IR spectrum of chiavennite is particularly complex in the region from 1200 to 200 cm^{-1}. A complete assignment has not been attempted, in view of the as yet insufficient structural information. However, the major absorption bands for complex silicate ions and for berillates can be easily recognized. The overall IR spectrum of chiavennite resembles that of bavenite, but it is considerably more complex in detail.

A portion of the sample used for TG and IR determinations was checked by qualitative spectrographic analysis using the Hilger E-478 quartz spectrograph. The major components were found to be Be, Si, Al, Mn, and Ca; Mg and Fe are present in traces, and B, Li, and P are absent.

A quantitative spectrographic determination for Be and Fe was performed on the same material, using an especially developed method and synthetic mixes as standards. Spectrographically pure reagents in the required amounts were added with graphite and $SrCO_3$ as diluents (G. Bocchi, pers. comm.). The total BeO content is 9.3±0.2 wt.%; that of FeO is 1.80±0.10 wt.%. Since the microprobe analysis of the grains used for the X-ray work had shown no Fe, slight chemical differences between the two samples studied is to be inferred. Such a compositional difference is irrelevant as far as the Be content is concerned, but it points out that Fe, although not essential to the chiavennite formula, is significant as a possible substitute for Mn (up to almost 20% by weight). The observed variations in the physical properties, and particularly in the color of chiavennite, thus find their explanation.

On the basis of the data obtained for light elements, the microprobe analysis was recalculated using the empirical α-factors of Albee and Ray (1970). The results are given in Table 2, column 2. The empirical formula, calculated on the basis of a total cation content of 9 is: $(Ca_{0.97}Na_{0.05})_{\Sigma 1.02}Mn_{0.97}(Be_{1.98}Al_{0.03})_{\Sigma 2.01}$ $(Si_{4.65}Al_{0.35})_{\Sigma 5.00}$ $O_{12.63}(OH)_{2.37}\cdot 2.16H_2O$. The empirical formula is in good agreement with the theoretical formula $CaMnBe_2Si_5O_{13}(OH)_2\cdot 2H_2O$ inferred from the crystal structure determination (V. Tazzoli *et al.*, personal communication). The small substitution of Al for Si is normal in complex silicates, as is the substitution of Fe^{2+} and Mg for Mn suggested by the spectrographic analysis.

Conditions of formation

Chiavennite is a late phase produced by the migration of fluid through the pegmatite, leading to reaction with preexisting beryl crystals. Chiavennite forms crusts over beryl as well as occasional pseudomorphs (hexagonal prisms consisting now of chiavennite + bavenite). Bavenite, $Ca_4Al_2Be_2[(OH)_2Si_9O_{26}]$, is always present together with chiavennite as the alteration product of beryl. The

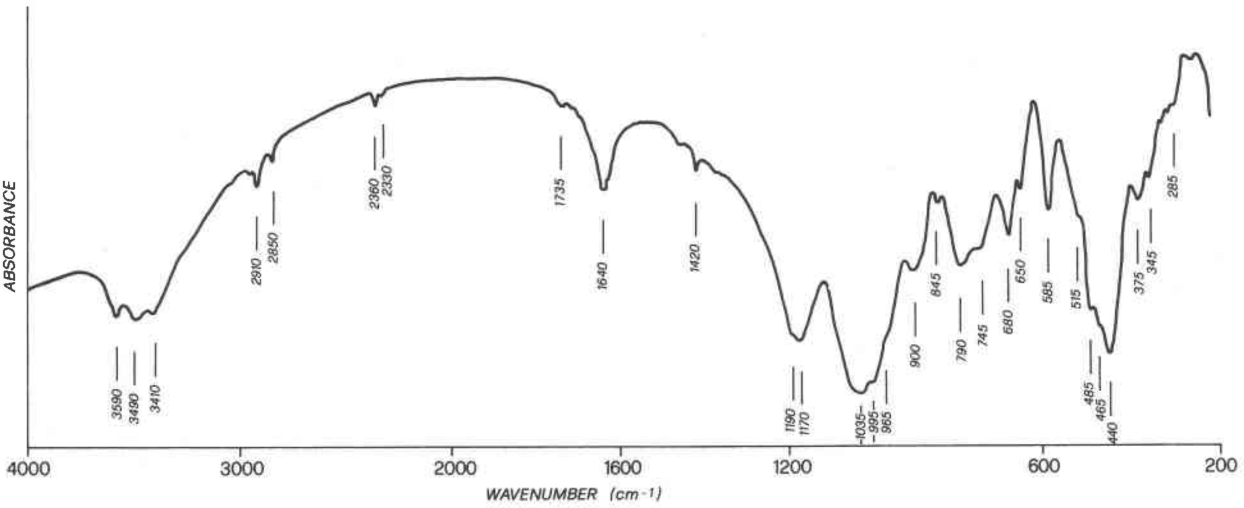

Fig. 4. The infrared spectrum of chiavennite (Perkin-Elmer mod. 580/B IR spectrograph, sample weight 0.7 mg, 1:110 CsBr disk, scan time 10 min).

fluids therefore must have been particularly rich in Ca (in excess of Mn) while Al and Si are probably derived directly from the decomposition of beryl. The presence of these elements in the fluids may be related to a late stage or serpentinization of the ultramafic rocks into which pegmatites are intruded.

The geological history and evolution of the Chiavenna ultramafics is rather complex (Schmutz, 1976). They started as mantle-derived peridotites intruded as a cold slab into the oceanic sequence separating the paleo-Adula from the paleo-Tambò continental masses. They were then retrograded to serpentinites, probably in the oceanic environment, but recrystallized to an anhydrous assemblage consisting mostly of olivine crystals with granoblastic polygonal texture ("olivinite") during the Lepontine thermal maximum (38±3 m.y.) of the Alpine metamorphism.

The olivinite now shows an incipient transformation to serpentinite (post-Lepontine), particularly along shear-planes and zones that include small rodingite bands. We suggest that the migration of $Ca+Mn+H_2O$ fluids into the pegmatites, obviously later than their emplacement at 25–27 m.y., may be simultaneous with the formation of these rodingites. Therefore it may indicate a very final alpine mineralization phase related to the overall uplift of the area.

The beryl pseudomorphs are composed of bavenite as the inner core and of chiavennite as the outer layer. This suggests that the chiavennite formed even later than bavenite as the last phase of the entire paragenetic evolution. This is in full agreement with the low temperature formation of chiavennite as implied from the high content of molecular water in this phase.

Acknowledgments

Our best thanks are due to G. Bocchi for the careful spectrographic determination of BeO, to L. Poppi, for TG analysis, and to V. Tazzoli, Istituto di Mineralogia, University of Pavia, Italy, for the crystal structure determination. Dr. Akira Kato, chairman of the Commission on New Minerals and Mineral Names, I.M.A., tactfully handled the case and offered valuable advice. The manuscript was reviewed by R. Mezzetti, L. Morten, G. Raade, and M. Fornaseri and benefited by the careful editing of M. Ross. Financial support was given by the Italian National Research Council, under grants CT80.02608.05 (Rome) and CT80.01022.05 (Bologna).

References

Albee, A. L. and Ray, L. (1970) Correction factors for electron-probe microanalysis of silicates, oxides, carbonates, phosphates and sulphates. Analytical Chemistry, 42, 1408–1414.

Hanson, G. N., El Tahlawi, M. R., and Weber, W. (1966) K–Ar and Rb–Sr ages of pegmatites in the South Central Alps. Earth and Planetary Science Letters, 1, 407–413.

Mottana, Annibale, Morten, Lauro, and Brunfelt, A. O. (1978) Distribuzione delle Terre Rare nel Massiccio Val Masino-Val Bregaglia (Alpi Centrali). Rendiconti della Società Italiana di Mineralogia e Petrologia 34, 485–497.

Raade, G. Åmli, Reidar, MLadeck, M. H., Din V. K., Larsen, A. O. and Åsheim, Arne (1983) Chiavennite from syenite pegmatites in the Oslo Region, Norway, American Mineralogist, 68, 628–633.

Schmutz, H. J. (1976) Der Mafitit-Ultramafitit-Komplex zwischen Chiavenna und Val Bondasca. Beiträge für geologische Karte der Schweiz. Neue Folge. 149, 1–73.

Weber, Werner (1966) Zür Geologie zwischen Chiavenna und Mesocco. Promotionsarbeit Nr. 3808 Eidgenossische Technische Hochschule, Zürich, 1–248.

Wenk, H. R., Wenk, Eduard, and Wallace, J. H. (1974) Metamorphic mineral assemblages in pelitic rocks of the Bergell Alps. Schweizerische Mineralogische und Petrographische Mitteilungen, 54, 507–554.

Manuscript received, February 10, 1982;
accepted for publication, November 4, 1982.