Balangeroite, a new fibrous silicate related to gageite from Balangero, Italy

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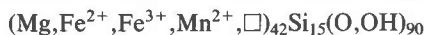*via S. Massimo 22, 10123 Torino, Italy*

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Abstract

Balangeroite occurs as brown asbestiform fibers in a paragenesis with long-fiber chrysotile, magnetite, and native Fe–Ni in the Balangero serpentinite (Lanzo Valley, Piedmont, Italy). It is orthorhombic with a 13.85(4), b 13.58(3), and c 9.65(3)Å; a sub-cell with $c' = c/3$ is strongly evident. The X-ray powder pattern demonstrates an isostructural relationship of the new mineral with gageite; the strongest reflections are: 9.59(40)(110), 6.77(80)(020), 3.378(45)(410), 3.278(40)(140), 2.714(100)(050,510), 2.674(75)(150,223), and 2.516(40)(250). The fibers are elongated parallel to [001], show one or more $\{hk0\}$ cleavages, and are usually intergrown with chrysotile. The refractive indexes are about the same, 1.680(5), both parallel and perpendicular to [001]; color is dark brown and yellow brown in these two directions, respectively. Chemical analysis gives a unit-cell content of

$$(Mg_{25.70}Fe^{2+}_{7.69}Fe^{3+}_{3.63}Mn^{2+}_{1.65}Al_{0.17}Ca_{0.07}Cr_{0.01}Ti_{0.01})_{\Sigma38.93}Si_{15.38}O_{53.66}(OH)_{35.92},$$

and the presence of a sub-cell with $c' = c/3$ suggests the formula

$$(Mg,Fe^{2+},Fe^{3+},Mn^{2+},\square)_{42}Si_{15}(O,OH)_{90}$$

with contents divisible by 3; a similar formula is probably also correct for the Mn–analogue, gageite. DTA, TGA, and high-temperature X-ray powder analyses show structural breakdown with a total weight loss of 9.4% and the appearance of olivine at 800°C. The infrared spectrum shows strong absorptions corresponding to vibrations in OH^- and $(SiO_4)^{4-}$ groups.

Introduction

Europe's most important chrysotile asbestos mine occurs in the Balangero serpentinite. This is a satellite body of the Lanzo Massif (Lanzo Valley, Piedmont, Italy), which is the largest ultramafic body of the Western Alps. A good reference list for the geology and petrology of the area is given by Compagnoni *et al.* (1980).

A recent specimen of a new mineral from the Balangero (or San Vittore) mine was brought to our attention by the mineral collector Enrico Beccuti in 1977, and other fresh samples were subsequently collected. It was eventually discovered that a large and relatively pure specimen had existed in the Turin University Mineralogy Institute's museum since 1925 with the inventory no. 14873 and label "fibrous serpentine (asbestos)—San Vittore, Balangero." The type material is now deposited in the museum.

To the workers of the mine the mineral was known as xylotile or metaxite. Stragiotti (1954) and Peretti and Zucchetti (1968) applied the term xylotile to a mineral from Balangero with "fibers which are several centimeters long, rigid, xyloid, yellow-brown and pleochroic." X-ray powder spectra (Table 1) and chemical compositions (Table 2) of xylotile and metaxite (Caillère, 1936), however, do not correspond to those of the new mineral. Metaxite is usually described as green and is regarded as a variety of antigorite or "serpentine," while xylotile is yellow-brown and is classed as a species by

Table 1. X-ray powder data. For balangeroite, data were obtained by diffractometry with $CuK\alpha$ radiation; indexes with $l \neq 3n$ are not considered because they are very weak.

Balangeroite				Gageite[a]		Metaxite[b]		Xylotile[b]	
I_o	d_o (Å)	hkl	d_c (Å)	I_o	d_o (Å)	I_o	d_o (Å)	I_o	d_o (Å)
40	9.59	110	9.70	3	9.70	vs	8.16	w	4.37
80	6.77	020	6.79	10	6.87	s	6.92	w	3.81
30	3.405	040	3.395	2	6.14	w	4.72	w	3.38
45	3.378	410	3.355	6	3.44	w	4.37	w	3.12
40	3.278	140	3.297	4	3.34	vs	3.81	w	2.70
35	3.198	003	3.217	6	3.25	s	3.58	w	2.53
30	3.030	240	3.048	4	3.08	w	2.96	w	2.43
100	2.714	050;510	2.716;2.714	8	2.758	vs	2.53	w	2.30
75	2.674	223;150	2.680;2.665	8	2.707	s	2.43	w	2.08
5	2.613	033	2.622	3	2.659	w	2.09	w	1.94
5	2.578	133	2.576	5	2.614	w	1.97	w	1.73
30	2.536	520	2.565	6	2.556	w	1.73	w	1.53
40	2.516	250	2.528	2	2.481	s	1.53	w	1.35
5	2.442	233;440	2.452;2.424	1	2.365	vs	1.31	w	1.29
25	2.324	413	2.322	3	2.307	w	1.05	w	1.20
10	2.274	610	2.276	3	2.244	w	1.00	w	1.02
5	2.243	423	2.226	3	2.176	w	0.91		
20	2.138	450	2.137	4	2.151	w	0.89		
25	2.123	503	2.099	3	2.103				
10	2.023	360;523	2.032;2.005	3	2.081				
15	1.927	443;170	1.936;1.921	1	2.056				
15	1.863	270	1.868	3	2.015				
5	1.688	703;180	1.685;1.685	3	1.952				
5	1.656	073;553	1.661;1.661	2	1.894				
10	1.595	106;016;380	1.598;1.597;1.593	3	1.863				
5	1.523	803;480	1.524;1.524	3	1.802				
15	1.494	473;183	1.498;1.493	6	1.674				
5	1.475	236	1.480	2	1.627				
5	1.443	146;833;663	1.446;1.445;1.444	2	1.617				
5	1.358	526;256;763	1.363;1.357;1.352	4	1.587				
				3	1.554				
				6	1.518				

[a] Moore (1968)

[b] Caillère (1936)

vs = very strong

s = strong

w = weak

Table 2. Chemical analyses of balangeroite and related compounds

	1		2	3	4
MgO	30.35	34.15	31.81	13.93	37.68
FeO	21.43	27.95	16.95[a]	0.60	1.69
Fe_2O_3	—		8.89[a]	18.30	2.94
MnO	2.93	3.92	3.59	0.17	—
Cr_2O_3	0	0.13	0.03	—	—
CaO	0	0.16	0.13	0.76	2.09
TiO_2	0	0.05	0.03	0.04	—
SiO_2	24.41	29.36	28.37	46.65	42.15
Al_2O_3	0	1.50	0.27	0.66	0.79
H_2O	—		9.93[b]	19.17	13.04
Total			100.00	100.28	100.38

1. *Balangeroite* - Min/max % weights for 16 electron microprobe analyses. Standards: olivine, garnet and two pyroxenes.

2. *Balangeroite* - Average % weight.

3. *Xylotile* - Average of 4 analyses by Caillère (1936).

4. *Metaxite* - Average of 4 analyses by Caillère (1936); this author's analysis No. 12 is excluded because of its large Al_2O_3 content.

[a] A ratio $Fe^{2+}/Fe^{3+} = 2.12$ has been deduced from wet analyses.

[b] Difference to 100% (see text).

Long fiber asbestos veins containing balangeroite developed early in the Balangero serpentinite evolution, as indicated by the presence of chrysotile corroded by metamorphic olivine which, in turn, has been partially transformed into antigorite by later shear movements along the original veins (Compagnoni *et al.*, 1980). Balangeroite also has been identified in thin sections of rocks from the Lanzo Massif as a pseudomorph after orthopyroxenes. It is probably an uncommon, but not rare, serpentinite mineral.

Physical and crystallographic properties

Balangeroite is found as brown, rigid and brittle xyloid fibers that are either loose, or compact when in large quantities, and may run several centimeters in the [001] direction. They have a vitreous-greasy luster and are only transparent in thin section. Even fibers with a very small cross-section are composite (Fig. 1) and usually intergrown with chrysotile; one or more {*hk*0} cleavages are very good. The physical aspect of the material makes optical measurements difficult and imprecise. The mineral is definitely anisotropic and shows distinct pleochroism, being dark brown and yellow brown parallel and perpendicular to [001] respectively. By comparison with gageite (see below), balangeroite should be biaxial, but, because of its texture, only one refractive index value, 1.680(5), has been observed perpendic-

Caillère (1936). Both display optical properties close to those of the serpentine minerals and a xyloid aspect (Caillère, 1936).

The new mineral, balangeroite, is named after the locality where it was discovered. The name and the species have been approved by the I.M.A. Commission on New Minerals and Mineral Names.

Paragenesis

Balangeroite occurs as brown asbestiform fibers in a paragenesis with long-fiber slip chrysotile, magnetite, and native Fe–Ni; it is relatively abundant in the schistose serpentinite at the contact with the unproductive Balangero serpentinite. Other associated minerals are metamorphic olivine, chlorite, Ti–clinohumite, diopside, antigorite, and opaque ores; calcite, aragonite, opal, chalcedony, and clays are usually found in the serpentinite fractures.
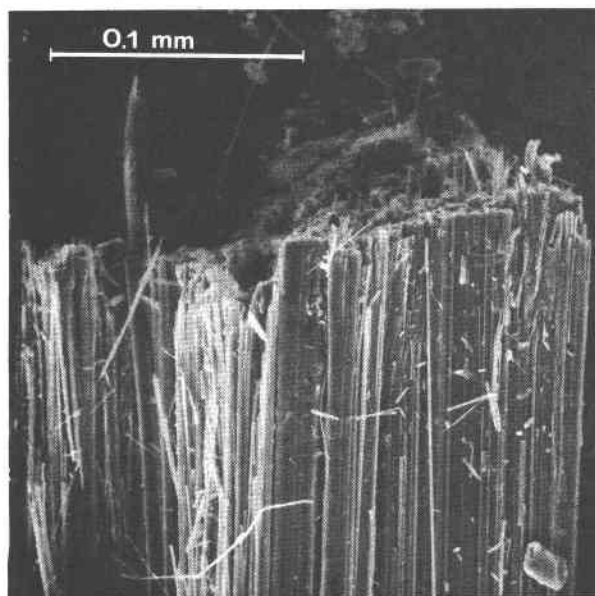

Fig. 1. SEM view of a typical fiber of balangeroite.

ular to [001]; practically the same value has been found in the elongation direction. A density of 2.98(3) g/cm^3 was measured with a torsion balance.

The [001] rotation X-ray photographs give c 9.65(3)Å (Cu$K\alpha$ radiation) and reveal the presence of a pseudo cell with $c' = c/3$; in fact, the first layer line is very weak and the second absent. Only continuous lines appear on the Weissenberg photographs, showing that there is rotational disorder about the elongation direction. The X-ray powder pattern (Table 1) indicates that balangeroite is iso-structural with gageite (Moore, 1968); by least-squares refinement the following cell was obtained: a 13.85(4), b 13.58(3), and c 9.65(3)Å. The value of c is trebled with respect to gageite, for which, however, weak streaks on c-axis rotation photographs were ignored (Moore, 1968). The unit cell has been confirmed by electron diffraction.

Thermal and infrared study

The continuous X-ray powder pattern between 20 and 900°C recorded for balangeroite with a high temperature Guinier-Lenné camera (Cu$K\alpha$ radiation) displays a sudden shrinkage (about 1%) of the cell parameters at 300°C; structural collapse occurs at 650°C, and at 800°C olivine appears.

The TGA curve (Fig. 2) shows a step between 580 and 750°C corresponding to 6.4% weight loss; slopes between 50 and 580°C and between 750 and 1000°C account for 1.6 and 1.4% weight loss respectively. The DTA curve is characterized by endo- and exothermic reactions at 620 and 700°C, in that order.

The major effects thus revealed are interpreted as breakdown of the crystal structure with the contemporaneous loss of the water, followed by the crystallization of at least one new phase. The presence
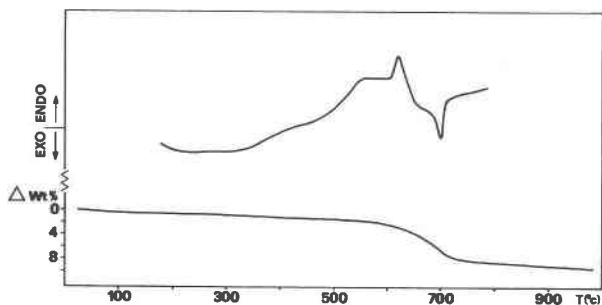

Fig. 2. DTA (top) and TGA (bottom) curves in Ar atmosphere; 10 mg of balangeroite with 20 and 10°C/min speed, respectively.

of water is proved by the large IR absorption around 3500 cm^{-1} (Fig. 3). The high temperature of dehydration suggests that there exists more OH$^-$ than H$_2$O in the structure. The minor thermal effects are not so easily interpreted. Shrinkage of the cell and other TGA and DTA reactions noted before breakdown are probably due to minor structural changes (including some earlier loss of water) related to the atomic disorder that can be deduced for balangeroite from Moore's (1969) structural model for isostructural gageite.

Compositional data

In addition to wet chemical and X-ray fluorescence analysis, electron microprobe analysis was performed; the common intergrowth with chrysotile suggested that the latter would provide better chemical resolution (Table 2). These results also showed some variability due to submicroscopic intergrowths or zoning. A ratio $Fe^{2+}/Fe^{3+} = 2.12$ was deduced from wet chemical analyses; average weight loss after calcination at 1000°C was 9.5%. This was attributed to H$_2$O, though total H$_2$O was taken as the difference from 100% of the microprobe results due to the more probable presence of impurities in analyses involving larger quantities of material and the possible oxidation of Fe^{2+} under heating. The following empirical formula for the unit cell was obtained on the basis of the known volume and density:

$$(Mg_{25.70}Fe^{2+}_{7.69}Fe^{3+}_{3.63}Mn^{2+}_{1.65}Al_{0.17}Ca_{0.07}Cr_{0.01}$$

$$Ti_{0.01})_{\Sigma 38.93}Si_{15.38}O_{53.66}(OH)_{35.92}.$$

After normalization to 15 Si in the unit cell, as discussed below, $D_{calc} = 2.904$ g/cm^3 was obtained with M.W. = 3174.24. The measured specific refractive energy is 0.228, and 0.223 and 0.220 are calculated with Larsen and Berman's (1934) and Mandarino's (1976) refractivities, respectively. This agreement is "excellent" on Mandarino's (1981) scale.

Crystal chemistry

Moore's (1969) structural model for gageite is based on a unit cell with $c' = 3.279(3)$Å and space group *Pnnm;* streaks requiring a trebled c were ignored. The chemical formula proposed was $M^{2+}_7O(OH)_8(Si_2O_6)$ ($Z = 2$) instead of M^{2+}_7 (OH)$_6$(Si$_3$O$_{10}$) given previously by the same author
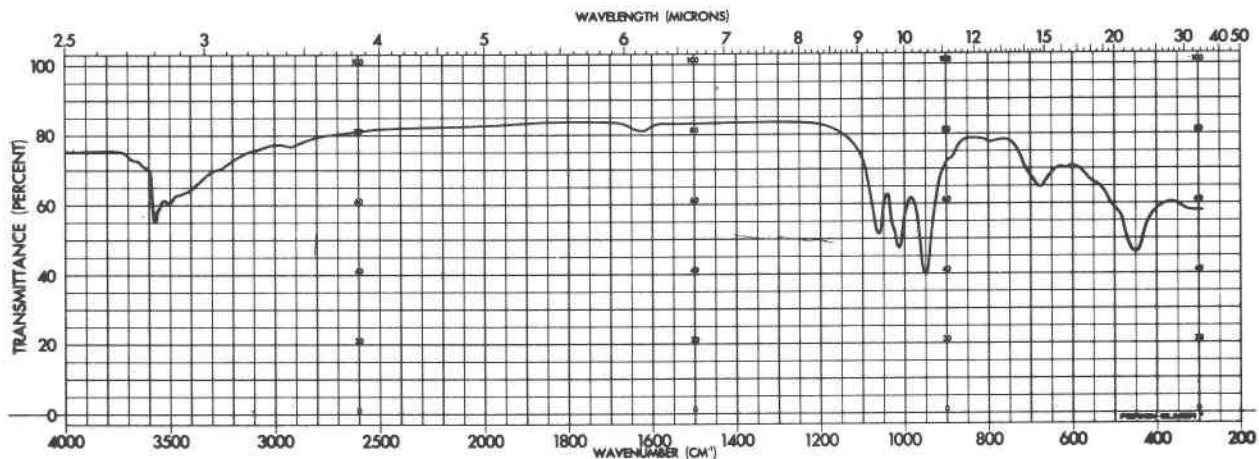
Fig. 3. Infrared spectrum of balangeroite (KBr disk).

(Moore, 1968). New chemical analyses have suggested $(Mn_{28}Mg_{10}Zn_2)_{\Sigma40}Si_{15}O_{50}(OH)_{40}$, with one unit formula in the trebled cell (Dunn, 1979).

Whereas Moore's (1969) model surely needs adjustments in the silicon tetrahedra, the octahedral framework seems reasonable; therefore, 42 octahedral cations should be present in the real cell. To account for the sub-cell with $c' = c/3$ it seems reasonable, even if not strictly necessary for all atoms, to postulate any atomic multiplicity in the cell as a multiple of 3 and write the corresponding chemical formula $(Mg,Fe^{2+},Fe^{3+},Mn^{2+},\square)_{42}Si_{15}(O,OH)_{90}$, where $\square$ represents vacancies. Such a formula with vacancies and an indefinite O/OH ratio would reconcile Moore's model with the presence of trivalent cations and some variation in the water content. Some H_2O could be present in the structural "pipes" instead of the disordered Si-tetrahedra and account for loss of weight at low temperature. Different occupation of the cation sites, partial order of the tetrahedra, and the possible presence of H_2O in the pipes could cause the breakdown of the higher symmetry with $c' = c/3$ which is required to a first approximation by the octahedral framework.

Balangeroite, with the abundances of its cations decreasing in the order shown above, represents the Mg-dominant analog of gageite, its Mn^{2+}-dominant member. Nearly pure Mn^{2+} members have recently been found in various parts of Japan (A. Kato, personal communication), and other members of the series are probably present in Nature.

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