

Medaite, $\text{Mn}_6[\text{VSi}_5\text{O}_{18}(\text{OH})]$, a new mineral and the first example of vanadatopentasilicate ion

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Abstract

Medaite occurs as small brown grains, intimately associate with tiragalloite, in veinlets cutting black, massive aggregates of braunite and quartz from an abandoned manganese mine at Molinello, near Chiavari, Liguria, Italy. The veinlets also contain quartz, manganese calcite, parsettensite and albite. Medaite is optically biaxial, positive, $\alpha = 1.77(1)$, $\beta = 1.78(1)$, $\gamma = 1.80(1)$, $2V_\gamma = 71^\circ$ (calc.), faintly pleochroic (dark to clear orange). The theoretical formula, derived from a crystal structure determination is $\text{Mn}_6[\text{VSi}_5\text{O}_{18}(\text{OH})]$, and the formula derived from microprobe analyses is $(\text{Mn}_{5.774}\text{Ca}_{0.190}\text{Fe}_{0.035})[(\text{V}_{0.815}\text{As}_{0.185})\text{Si}_5\text{O}_{18}(\text{OH})]$. Density (meas.) $3.70(5)$; (calc.) 3.750 g cm^{-3} . The crystals are monoclinic, $P2_1/n$, with $a = 6.712(1)$, $b = 28.948(8)$, $c = 7.578(2)\text{ \AA}$, $\beta = 95.4(2)^\circ$; the most intense lines in the powder pattern are (as d, I, hkl) $4.778(39)(101, 111)$; $3.259(100)(081, 220)$; $3.159(83)(052, 230)$; $3.097(70)(22\bar{1}, 132)$; $3.009(47)(23\bar{1}, 132)$; $2.941(68)(211, 091)$; $2.902(34)(142, 211)$; $2.785(47)(072, 25\bar{1})$; $2.613(69)(082, 20\bar{2}, 21\bar{2})$; $2.509(32)(013, 27\bar{1}, 261)$; $2.192(43)(30\bar{1}, 2.10.0, 31\bar{1})$; $1.660(29)(420, 1.12.3, 0.17.1)$. The most characteristic feature of the crystal structure is the presence of a vanadatopentasilicate ion $[\text{VSi}_5\text{O}_{18}(\text{OH})]^{12-}$ comprising six tetrahedra linked together to form a chain fragment. This new representative of heteropolysilicate ions is an extended relative of the arsenatotrisilicate ion $[\text{AsSi}_3\text{O}_{12}(\text{OH})]^{8-}$ found in tiragalloite, and is the longest ion allied to sorosilicates described so far. The name is in memory of Francesco Meda (1926–1977), a distinguished amateur mineralogist.

Introduction

A few years ago, the presence of new interesting minerals in the mines of Eastern Liguria, Italy, was pointed out (Cortesogno *et al.*, 1976, 1979; Gramaccioli *et al.*, 1979a). One of these new minerals, tiragalloite, has already been described (Gramaccioli *et al.*, 1980): its crystal structure shows the presence of an unusual "arsenatotrisilicate" ion $[\text{AsSi}_3\text{O}_{12}(\text{OH})]^{8-}$, the conformation of which resembles that of a tetrapolyphosphate (Gramaccioli *et al.*, 1979b, c). This ion can be considered to be an extension of the trisilicate ion $(\text{Si}_3\text{O}_{10})^{8-}$, to which a

further As-centered tetrahedron is added. Its presence, which reveals for the first time the existence in nature of non-isolated AsO_4 groups, points to extreme hydrolysis-preventing conditions.

On these grounds, the possibility of encountering some additional new minerals was considered to be quite likely, and attention was drawn to accompanying phases.

In several thin sections of rock containing tiragalloite, a dark orange to brown mineral was sometimes noticed (by A.M.). This mineral is often intimately intergrown with tiragalloite, and its optical properties do not agree with any common spe-

cies. The possibility of this being a darker variety of tiragalloite was ruled out, because no gradual transition between the darker mineral and the lighter orange tiragalloite was ever observed: on the contrary, sharp boundaries between these two phases were always evident, suggesting that they are discrete phases.

At the same time, a series of microprobe analyses on tiragalloite-containing specimens, carried out by one of us (W.L.G.), revealed the presence of another mineral accompanying tiragalloite. This mineral, whose composition was different from any known species, was characterized by the presence of substantial quantities of vanadium and a lower arsenic content than for tiragalloite. The silicon content (see Table 2) was definitely higher than the average value (32.38%) found by us for tiragalloite (Gramaccioli *et al.*, 1980), ruling out the possibility of dealing with the corresponding vanadium-bearing equivalent. Instead, the presence of a new mineral allied to tiragalloite, but with a longer silicate chain fragment, and containing V instead of As, was considered to be likely.

After much effort, a single monocrystalline splinter of the dark mineral was isolated from the matrix. A preliminary measurement of the unit-cell parameters showed a marked similarity to those of tiragalloite, a , c , and β being almost identical for these two minerals, and the b axis being nearly exactly 1.5 times greater than for tiragalloite. Soon after, the solution of the crystal structure confirmed the results obtained from microprobe analysis, and showed that it is indeed a new mineral. This paper reports the complete mineralogical data.

We have named the new mineral medaite in memory of Dr. Francesco Meda from Turin, a distinguished amateur mineralogist who died in 1977, and whose enthusiastic activity as a teacher has contributed to making mineralogy popular in Italy. The mineral and the name have been approved by the IMA Commission on New Minerals and Mineral Names. Type material has been deposited in the collections of the Institute of Mineralogy of Milan University, and of the Mineralogy Museums of the Universities of Rome (Italy), and Oslo (Norway), under the same label as tiragalloite.

Occurrence

Medaite occurs as a rare associate of tiragalloite in an abandoned manganese mine at Molinello near Chiavari, Liguria, not far from Gambatesa, where Mn-mining is still active, and other interesting min-

erals are also found (Cortesogno *et al.*, 1979; Basso *et al.*, 1979; Palenzona, 1980). It appears as small brown grains embedded in brownish veinlets, a few millimeters thick, cutting a black Mn ore made up mainly of quartz and braunite, with traces of serpentine. In these veins, which have almost no cavities, medaite never occurs as euhedral crystals. The grains, measuring up to 1.5 mm in length but usually much smaller (0.2–0.4 mm) are either isolated, surrounded nearly invariably by quartz, or grouped together into aggregates measuring up to 7–10 mm in diameter; only fresh, unaltered boundaries between medaite and quartz are observed. Some grains occasionally show an elongated shape, and a good cleavage along one direction. Medaite is usually embedded in quartz, or associated with manganiferous calcite and tiragalloite; it often occurs as regularly oriented lamellae in tiragalloite, suggesting syntaxial growth. These lamellae show sharp boundaries when they are observed in thin section. The association of all these minerals is often so intimate, that no reliable diffraction pattern has been obtained so far for medaite, and even for tiragalloite all diffraction patterns contain moderately strong lines due to impurities (Gramaccioli *et al.*, 1980). For these reasons, obtaining a pure crystal fragment for X-ray analysis has been very difficult.

Physical properties

Hand specimens of the mineral are brownish-red. The mineral has a subadamantine luster. It is transparent in thin sections and translucent in small splinters. There is a good {100} cleavage and a distinct parting normal to the elongation. Medaite is dark orange to brownish in thin section; it is markedly darker than tiragalloite.

The density, measured by flotation in a dilute Clerici solution at room temperature is 3.70 ± 0.05 g cm⁻³. This value compares favorably with a calculated value of 3.750 g cm⁻³ from unit-cell and chemical analysis data. For the pure end-member (*i.e.*, with no substitution for V and Mn) the calculated value is 3.743 g cm⁻³. The mineral is insoluble in water, HCl, and HNO₃.

Medaite is biaxial, positive, with $2V_{\gamma} = 71^{\circ}$. This value for the axial angle has been calculated; no direct measurement was possible, because of very strong absorption. The indices of refraction are: $\alpha = 1.77 \pm 0.02$, $\beta = 1.78 \pm 0.01$, $\gamma = 1.80 \pm 0.02$. These have been measured in white light, using small flakes oriented for β on the universal stage. α and γ

have been obtained from this value and the measured birefringence (obtained from a thin section, using a Berek compensator).

The orientation of the indicatrix is approximately parallel to the crystallographic axes, with $a \approx \alpha$, $b = \beta$, $c \approx \gamma$. The angle between α and the cleavage normal is 3° ; the elongation is positive.

A faint pleochroism from dark to lighter orange has been observed. In some cases, twinning has been detected under the microscope; it is symmetric, with the twin plane coincident with the cleavage plane.

The geometric mean of the refractive indices, 1.783, is in substantial agreement with the value (1.805) calculated according to the Gladstone–Dale rule, using the new constants proposed by Mandarino (1976). There is consequently good agreement between data from X-ray crystallography, chemical analysis, and optical measurements.

X-ray data

The unit-cell dimensions of medaite are $a = 6.712(1)$, $b = 28.948(8)$, $c = 7.578(2)\text{\AA}$, $\beta = 95.4(2)^\circ$. These data have been determined and refined from data for 28 reflections, obtained with a single crystal mounted on a Syntex P1 automatic diffractometer, with 2θ approximately 50° , and using $\text{MoK}\alpha$ radiation ($\lambda = 0.7017\text{\AA}$). For this refinement a least-squares procedure was followed, and the standard deviations reported above are derived from the residuals and the inverse matrix of the normal equations.

From the Laue symmetry of the reciprocal lattice ($2/m$), and extinctions ($0k0: k = 2n + 1$ and $h0l: h + l = 2n + 1$) $P2_1/n$ symmetry is unambiguously indicated. This symmetry has been confirmed by solving the crystal structure. The number of formula units per cell is 4, and all the atoms are in general positions.

The crystal structure has been solved and refined to an R index of 0.059 for 3350 independent reflections; the procedure and the results have been reported elsewhere (Gramaccioli *et al.*, 1981). The most interesting feature is the presence of a vanadotopentasilicate ion $[\text{VSi}_5\text{O}_{18}(\text{OH})]^{12-}$, composed of six tetrahedra linked together to form a chain fragment. This new ion and the corresponding arsenatotrisilicate ion $[\text{AsSi}_3\text{O}_{12}(\text{OH})]^{8-}$ in tiragalloite are the only representatives known thus far for heteropolysilicate ions. The conformation of the vanadotopentasilicate ion can be derived from the corresponding ion in tiragalloite, by repeating the last

two Si-centered tetrahedra (compare Fig. 1 in Gramaccioli *et al.*, 1979b with the corresponding figure in Gramaccioli *et al.*, 1981). In view of this analogy, the close relationships between the two minerals are clear, and the mutual substitution of As and V is to be expected.

This new ion in medaite considerably extends the field of sorosilicates, because it shows the existence in nature of long, unbranched polynuclear ions intermediate between $(\text{X}_2\text{O}_7)^{n-}$, and infinite $(\text{XO}_3)^{\infty-}$. Whereas these extremes are well represented by several common sorosilicates and inosilicates, respectively, there is a substantial gap between them. Trisilicates are rare, and no linear tetra- or pentasilicates have been described up to the present time among minerals. Tiragalloite and medaite thus have structures with the longest known chains of this type.

It might be interesting to know whether the existence of a VO_4 or AsO_4 tetrahedron joined to the chain fragment is an essential factor for the stability of such long ions, and thus acts to prevent the formation of the much more common inosilicate structures. The presence of a series of hydrogen bonds linking the chain fragments to each other (from end to end) also may be an essential stabilizing factor for this kind of structure.

X-ray powder diffraction data are reported in Table 1. In the absence of a reliable powder diffrac-

Table 1. X-ray powder diffraction data for medaite

d	I	hkl	d	I	hkl
6.510	23	110	2.227	7	063, 30 $\bar{7}$
6.070	8	120	2.192	43	30 $\bar{7}$, 2, 10, 0, 31 $\bar{7}$
5.221	12	041	2.173	11	330, 30 $\bar{7}$, 0, 11, 2
4.778	39	101, 111	2.133	13	1, 10, 2, 340, 2, 10, $\bar{7}$
4.064	7	061	2.066	26	2, 11, $\bar{7}$, 1, 13, 1, 1, 11, 2
3.321	27	210, 12 $\bar{2}$, 042	1.999	15	1 $\bar{7}$ 3, 31 $\bar{2}$, 36 $\bar{7}$
3.259	100	081, 220	1.851	16	034, 36 $\bar{2}$, 2, 10, 2
3.159	83	052, 230	1.804	7	3 $\bar{7}$ 2, 381, 1, 15, $\bar{7}$
3.097	70	22 $\bar{7}$	1.770	7	15 $\bar{4}$, 2, 11, 2, 2, 12, $\bar{2}$
3.009	47	23 $\bar{7}$, 132	1.759	15	0, 16, 1, 352, 124
2.941	68	211, 091	1.720	8	144, 362, 33 $\bar{3}$
2.902	34	142, 211	1.703	22	2, 10, $\bar{5}$, 224
2.822	11	231, 072	1.667	15	410, 2, 15, 0, 420
2.785	47	072, 25 $\bar{7}$	1.660	29	420, 1, 12, 3, 0, 17, 1
2.747	27	19 $\bar{7}$, 072	1.634	9	3, 11, 1
2.703	13	0, 10, 1	1.605	11	1, 17, 1, 0, 18, 0, 450
2.613	69	082, 20 $\bar{2}$, 21 $\bar{2}$	1.575	25	333, 383, 3, 12, 1
2.533	29	1, 10, $\bar{7}$, 261, 23 $\bar{2}$	1.499	7	3, 10, $\bar{5}$, 264
2.509	32	013, 27 $\bar{7}$, 261	1.458	8	3, 11, $\bar{5}$, 3, 15, 0, 432
2.485	15	023, 18 $\bar{2}$, 0, 11, 1	1.434	8	165, 2, 18, $\bar{7}$, 452
2.447	21	092	1.427	8	135, 2, 17, $\bar{2}$, 393
2.423	11	11 $\bar{3}$, 092, 271	1.413	17	462, 145, 2, 18, 1
2.381	10	182, 28 $\bar{7}$, 043	1.401	8	4, 10, 1, 155
2.317	27	290, 232	1.372	7	2, 18, $\bar{2}$, 4, 11, 1, 2, 16, $\bar{5}$
2.298	18	0, 10, 2, 290			

tion pattern, the reported values have been recalculated from single-crystal data, using a program written by one of us (C.M.G.). Here, a procedure similar to the one described by Borg and Smith (1969) has been adopted, assuming a Lorentzian shape for profiles, with $\omega = 0.1^\circ$ at $2\theta = 40^\circ$. When a certain peak is a superposition of several reflections, only the three most intense contributions (if more than 5% of the total) are listed, in order of importance. In such cases, the recalculated spacing in the first column is a weighted average of these reflections. Apart from the theoretical soundness of such a procedure, and the excellent agreement between observed and calculated patterns shown in Borg and Smith's work, the very satisfactory agreement that we obtained for tiragalloite (Gramaccioli *et al.*, 1980) indicates the reliability of this method. Note also that with complex structures of low symmetry such as the present one, only a procedure of this kind can insure a correct indexing.

Crystal chemistry

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. The system is mounted on an ARL-EMX probe at Mineralogisk-Geologisk Museum, Oslo. The analyses were based on metal standards (for As, V, Fe, Mn), wollastonite (for Ca) and quartz (for Si). Two spot analyses were completed on one grain, and 5 additional analyses were made of randomly chosen spots on as many grains in the same thin section. The results (Table 2) show a marked constancy in composition.

The ideal formula of medaite, as derived from

Table 2. Analytical results for medaite (in weight percent)

	Experimental (variability range)	Experimental (average)	Theoretical (actual formula)	Theoretical (ideal formula)
SiO ₂	37.25-39.01	38.09	36.29	36.36
MnO	49.13-51.13	49.94	49.50	51.53
FeO	0.05- 0.64	0.31	0.30	-
CaO	1.13- 1.46	1.30	1.29	-
As ₂ O ₅	2.01- 2.32	2.11	2.57	-
V ₂ O ₅	7.09- 7.90	7.44	8.96	11.01
H ₂ O*			1.09	1.09
Total		99.19	100.00	100.00

* Water inferred from crystal structure determination

crystal structure analysis is Mn₆[VSi₅O₁₈(OH)]. The intensity data are accurate enough to have led to the location of the hydrogen atom, which is shown to be a component of the hydroxyl group.

If partial substitution of Mn by Ca and Fe, and of V by As is assumed on the basis of the analytical results, then from the experimental ratios Mn/Ca, Mn/Fe and V/As, an actual formula (Mn_{5.774}Ca_{0.190}Fe_{0.035})[(V_{0.815}As_{0.185})Si₅O₁₈(OH)] can be deduced (Table 2). Unless otherwise specified, the physical properties reported here for the new mineral are recalculated from this formula.

The agreement between the analyzed composition and that derived from X-ray data is quite satisfactory. As for tiragalloite, a still better agreement might be obtained if one assumes partial replacement of (V,As) by Si, since the analysis is high in Si and low in V or As with respect to the formula determined by structure analysis. However, for the same reasons we had considered for tiragalloite (Gramaccioli *et al.*, 1980), and in obvious analogy with this mineral, we believe that no substantial replacement of (V,As) by Si occurs in medaite, and some overestimation of silicon and underestimation of V and As has occurred in the chemical analysis. These over- or underestimations are within the limits of a reasonable uncertainty in analytical results of this kind.

Conditions of formation

Since medaite and tiragalloite are found together in apparent textural equilibrium, and considering the close structural and chemical relationships between these two minerals, it is reasonable to assume they were formed at the same time and under the same conditions. The practically constant V/As ratios observed in the various grains of these minerals which have been analyzed, and the marked difference between the ratio in tiragalloite and the corresponding one in medaite suggest thermodynamic equilibrium between the two minerals, with a different distribution of the two elements in the two phases.

The very presence of tiragalloite, which is the only known example of a mineral containing non-isolated AsO₄ groups, implies extreme hydrolysis-preventing physico-chemical conditions, which are very rarely encountered in nature. These conditions probably involve low temperature and relatively high concentration in solution (Gramaccioli *et al.*, 1980). As in tiragalloite, the (V,As)O₄ groups in medaite are not found linked together, but they are

linked to the polysilicate chain fragment at one extremity. A discussion and a possible explanation for this situation has already been given by us (Gramaccioli *et al.*, 1980).

However, the presence of a member of his series with prevailing vanadium and a longer chain fragment seems to suggest a few additional details, which might be quite important. For example, polyvanadates are easily formed under artificial or natural conditions, and no extreme hydrolysis-preventing conditions appear to be necessary, although the structure of most natural products (minerals) does not involve linking-up of VO_4 tetrahedra, but rather other types of coordination around this metal.

Why have no polyvanadates of the more "common" type formed under these conditions? It would seem that the stabilizing effect due to the particular kind of structure (involving coordination around Mn, and hydrogen bonding: see Gramaccioli *et al.*, 1981) must be significant. The essential stability of this kind of structure is confirmed by its existence in two minerals containing ions which, although similar, are considerably different in length.

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