

Tiragalloite, $Mn_4[AsSi_3O_{12}(OH)]$, a new mineral and the first example of arsenatotrisilicate

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Abstract

Tiragalloite occurs as small orange grains 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, manganiferous calcite, parsettensite, albite, and at least one other new mineral related to tiragalloite but containing essential vanadium instead of arsenic. Tiragalloite is optically biaxial, positive, $\alpha = 1.745(5)$, $\beta = 1.751(3)$, $\gamma = 1.760(5)$, $2V_\gamma = 38-46^\circ$, non-pleochroic. The theoretical formula, derived from crystal-structure determination, is $Mn_4[AsSi_3O_{12}(OH)]$, and the formula derived from 29 microprobe analyses is $(Mn_{3.909}Ca_{0.077}Fe_{0.013})[(As_{0.844}V_{0.116})Si_3O_{12}(OH)]$. Density (meas.) $3.84(6)$; (calc.) 3.829 g cm^{-3} . The crystals are monoclinic, $P2_1/n$, with $a = 6.66(1)$, $b = 19.92(2)$, $c = 7.67(1)\text{\AA}$, $\beta = 95.7(1)^\circ$; the most intense lines in the powder pattern are (as d , I , hkl) 6.299 (24) 110; 4.742 (60) 101,130; 3.267 (71) 210,032,122; 3.149 (50) 220; 3.042 (66) 061,151; 3.006 (100) 221,042,122; 2.496 (64) 062,171,013. In the crystal structure, the most characteristic feature is the presence of an arsenatotrisilicate ion $(AsSi_3O_{12}OH)^{8-}$, comprising four tetrahedra linked together to form a chain fragment. This new ion is an extension of the trisilicate $(Si_3O_{10})^{8-}$ ion with an additional As-centered tetrahedron linked to it. This example is the first of a new series of minerals. The name is for Paolo Tiragallo (b. 1905), a distinguished amateur mineralogist.

Introduction

The manganese mines in Eastern Liguria, Italy, are well known to mineralogists and mineral collectors for their wealth of fine specimens of colorful and interesting minerals, such as rhodonite, tizenite, parsettensite, and sursassite (Di Colbertaldo, 1970, p. 172-175; Cortesogno *et al.*, 1979). Recently, Mr. Mario Antofilli, an enthusiastic mineral collector from Genoa, gave the authors a few interesting samples which had been found several years ago in a manganese mine at Molinello, near Chiavari, Liguria. The mine is now abandoned.

A preliminary examination of the powder pattern,

and a microprobe analysis, indicated the possibility that this was a new species; however, more information was necessary (Gramaccioli *et al.*, 1979a). For this purpose, after much effort, a single crystal splinter was isolated from the matrix and an X-ray crystal structure analysis was completed (Gramaccioli *et al.*, 1979b). The crystal structure confirmed the nature of a new mineral, and this paper reports the full mineralogical data. We have named the new mineral tiragalloite in honor of Mr. Paolo Tiragallo, a distinguished amateur mineralogist and dean of the Mineral Collector Group in Liguria, an enthusiastic group of amateurs, whose activity led to the discovery of tiragalloite and other interesting species.

The mineral and the name have been approved by the IMA Commission on New Minerals and Mineral Names. Type material is preserved in the collections of the Institutes of Mineralogy at the University of Rome (Italy) and Oslo (Norway); a fine specimen, from which the analyzed samples have been derived, has been deposited at the City Museum of Natural History, Milan.

Occurrence

Tiragalloite occurs as small orange grains enclosed in brownish to orange veinlets, about one millimeter 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, tiragalloite practically never shows idiomorphic 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 small aggregates measuring up to 4–6 mm in diameter. The grains occasionally show an elongated shape. They are intimately associated with a number of other minerals, especially quartz, manganiferous calcite, parsettensite, and other new silicates related to tiragalloite but containing essential vanadium. For one of these, medaite, $\text{Mn}_6[\text{VSi}_5\text{O}_{18}(\text{OH})]$, we have solved the crystal structure and have found that it is related to tiragalloite. This name has also been approved by the IMA Commission on New Minerals and Mineral Names, and final refinement of the crystal structure is in progress. The association of all these minerals is often so intimate that considerable difficulty is encountered in obtaining X-ray diffraction powder patterns free from lines due to impurities (see below), and obtaining a pure crystal fragment for X-ray analysis has been difficult.

Only fresh unaltered boundaries between tiragalloite and the other minerals are observed, except against manganiferous calcite, where a fine spongy rim shows alteration of tiragalloite grains.

Physical properties

Tiragalloite is orange to yellow in thin section. Hand specimens of the mineral are decidedly orange, sometimes with a tendency towards brownish (in the latter case, some intergrowth with similar species containing vanadium occurs, and the brown color might not be actually due to the tiragalloite). The mineral has a subadamantine luster. It is transparent in thin section and translucent in small splinters.

There is a good cleavage along {100} and a distinct parting normal to the elongation.

The density, measured by flotation in dilute Clerici solution at room temperature, is $3.84 \pm 0.06 \text{ g cm}^{-3}$. This value compares favorably with a calculated value of 3.829 g cm^{-3} from unit-cell and chemical analysis data; for the pure end member (*i.e.* with no substitution for As and Mn) the calculated value is 3.860 g cm^{-3} .

Tiragalloite is only slightly soluble in HNO_3 , giving the solution a light pink color, and insoluble in HCl or H_2SO_4 .

Tiragalloite is biaxial, positive, with $2V_\gamma = 38\text{--}46^\circ$; these values for the axial angle have been obtained from measurements on the universal stage (6 determinations with the stage in orthoscopic setting). The indices of refraction are: $\alpha = 1.745 \pm 0.005$, $\beta = 1.751 \pm 0.003$, $\gamma = 1.760 \pm 0.005$; these have been measured in white light, using small flakes oriented for β on the universal stage. From this value and the measured birefringence (obtained from a thin section, using a Berek compensator) α and γ have been obtained.

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 pole is $5\text{--}6^\circ$; the elongation is positive.

No pleochroism 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 axial dispersion is inclined, in agreement with the monoclinic symmetry.

The geometric mean of the refraction indices, 1.752, is in substantial agreement with the calculated value (1.763) 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 tiragalloite are $a = 6.66(1)$, $b = 19.92(2)$, $c = 7.67(1)\text{\AA}$, $\beta = 95.7(1)^\circ$. These data have been determined and refined from 60 reflections given by a single crystal, mounted on a Syntex P1 automatic diffractometer, with 2θ around 50° , using $\text{MoK}\alpha$ radiation ($\lambda = 0.7107\text{\AA}$). 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 indicated unambiguously. 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 0.049 for 1777 independent reflections; the procedure and the results have been reported elsewhere (Gramaccioli *et al.*, 1979b). The most interesting feature is the presence of an arsenatotrisilicate ion ($\text{AsSi}_3\text{O}_{12}\text{OH}$)⁸⁻ composed of four tetrahedra linked together to form a chain fragment. This new ion is an extension of the trisilicate (Si_3O_{10})⁸⁻ ion with an additional AsO_4 tetrahedron. This example is the first of a new series of minerals allied to sorosilicates, where the length of the chain fragments is considerably extended. Curiously enough, there are other atoms besides Si at the center of the tetrahedra; such tetrahedra are found only at one extremity of the chain fragment. The new mineral medaite represents a second example of these ions [*i.e.* a vanadopentasilicate ($\text{VSi}_5\text{O}_{18}\text{OH}$)¹²⁻ with five SiO_4 tetrahedra joined together into a chain fragment, plus an additional tetrahedron with central vanadium, in part replaced by As]. In the crystal structure of these minerals, there are a series of hydrogen bonds linking the chain fragments to each other (from end to end), and this may be an essential stabilizing factor for this kind of species.

X-ray powder diffraction data are reported in Table 1. The indices in Table 1 have been assigned on the basis of comparison with single-crystal data, and when a peak is a superposition of several reflections, only the three most intense peaks (if more than 5 percent of the total) are listed, in order of importance. In such cases, the recalculated distance in the third column is a weighted average of these peaks. In view of the large absorption factor, the agreement between observed and calculated data must be considered satisfactory. Note that, with complex structures of low symmetry such as the present case, only a procedure of this kind can insure correct indexing.

In all the powder patterns obtained thus far, moderately strong lines at 12.440 and 2.93–2.95 Å are present. The single exception is the pattern obtained from a Gandolfi camera, which does not show the line at 12.440 Å; even in this pattern, however, the line at 2.93 Å persists. They are surely due to the presence of impurities, such as parsettensite (Mn-stilp-

nomelane) and manganian calcite, because they do not match any significantly strong reflection recalculated from single-crystal data.

Crystal chemistry

Electron-microprobe analyses were made 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 Geologisk Museum, Oslo. The analyses are based on metal standards (for As, V, Fe, Mn), wollastonite (for Ca), and quartz (for Si). Twenty-one spot analyses were completed on one grain, and 8 additional analyses were made of randomly chosen spots on as many grains in the same thin section. The results (Table 2) show within-grain variation to be as large as inter-grain variation.

The ideal formula of tiragalloite as derived from crystal structure analysis is $\text{Mn}_4[\text{AsSi}_3\text{O}_{12}(\text{OH})]$. The collected data are accurate enough to detect and locate the hydrogen atom, and the presence and nature of water in the mineral is therefore completely clarified. If partial substitution of Mn by Ca and Fe and of As by V is assumed on the basis of the analytical results, then from the experimental ratios Mn/Ca, Mn/Fe and As/V a formula such as $(\text{Mn}_{3.909}\text{Ca}_{0.077}\text{Fe}_{0.013})[(\text{As}_{0.844}\text{V}_{0.116})\text{Si}_3\text{O}_{12}(\text{OH})]$ can be deduced. Unless otherwise specified, the physical properties reported here for the new mineral are calculated from this formula.

The agreement between the analyzed composition and that derived from X-ray data is quite satisfactory. A still better agreement might be obtained if one assumes partial replacement of (As,V) by Si, since the analytical data are relatively too high in Si and too low in As or V. However, there are three good reasons for considering such replacement to be unlikely: (1) the final difference Fourier does not show any evidence of substitution of As atoms by much lighter atoms (Gramaccioli *et al.*, 1979b); (2) the As–O and Si–O bond length averages in tiragalloite (1.693 and 1.627 Å, respectively) are in close agreement with the average values (1.686 and 1.623 Å, respectively) reported by Ferraris (1970) and Smith and Bailey (1963) for arsenates and metasilicates with no substitution of As for Si; the partial substitution of vanadium for arsenic should not affect these considerations, since the As–O and V–O bond lengths are very similar; (3) there is apparently no way to reestablish charge balance, unless some oxygen around As is replaced by OH or F, or some

Table 1. X-ray powder diffraction data for tiragalloite

(1)			(2)			(3)			(1)			(2)			(3)		
d	I		d	I		d	I		d	I		d	I		d	I	
6.298	14					6.299	24		110			2.189	21		2.183	28	30 $\bar{1}$,310
4.979	18	4.97 m	4.991	16					031,040			2.157	22		2.160	11	320,270
4.779	21	4.77 m	4.742	60					101,130						2.112	13	27 $\bar{1}$,172
			4.114	7					13 $\bar{1}$			2.062	21		2.074	16	143,082
3.514	34	3.53 m	3.523	30					051,022						2.008	10	191,18 $\bar{2}$,063
			3.43 w	16					150,141			1.993	10*		1.991	17	280,31 $\bar{2}$
3.258	100	3.28 s	3.267	71					210,032,12 $\bar{2}$			1.975	8*		1.979	7	153
3.151	73	3.15 s	3.149	50					220			1.853	16		1.852	11	34 $\bar{2}$,024,19 $\bar{2}$
3.118	25		3.115	27					21 $\bar{1}$			1.822	10		1.825	10	272,36 $\bar{1}$,312
3.034	72	3.03 m	3.042	66					061,151			1.756	28		1.761	16	0.11.1,044
3.003	72	3.00 s	3.006	100					22 $\bar{1}$,042,12 $\bar{2}$			1.742	11*		1.744	11	14 $\bar{4}$,124,1.11.0
2.889	31	2.89 s	2.904	43					211			1.718	10*		1.721	10	342,32 $\bar{3}$,253
2.846	30	2.85 w	2.845	35					132,23 $\bar{1}$						1.709	12	134,2.10.0,1.11. $\bar{1}$
2.782	40	2.78 w	2.804	24					16 $\bar{1}$						1.692	18	27 $\bar{3}$
2.736	54	2.74 s	2.738	39					052			1.691	18		1.688	22	1.11.1,183,2.10. $\bar{1}$
2.695	31		2.685	14					231						1.674	9	371
2.657	25		2.663	24					071,24 $\bar{1}$			1.659	40		1.661	14	400,0.12.0,263
2.608	65	2.60 w	2.606	49					21 $\bar{2}$,20 $\bar{2}$,152			1.654	27		1.653	16	410,34 $\bar{3}$
2.529	29	2.53 w	2.530	21					241,22 $\bar{2}$						1.621	22	0.12.1,24 $\bar{4}$,292
2.499	45											1.605	21		1.590	16	193,381
2.489	58	2.49 s	2.496	64					062,17 $\bar{1}$,013			1.413	17 (?)				
			2.472	14					25 $\bar{1}$,152			1.408	18		1.409	21	135,442,392
2.440	29		2.437	20					023,10 $\bar{3}$,171						1.386	9	471,145,373
			2.348	18					260,033						1.379	11	452,480,2.13. $\bar{1}$
			2.316	11					222,24 $\bar{2}$						1.297	11	32 $\bar{5}$,354,1.15.0
2.296	17		2.272	16					072,113,103								

1) Diffraction pattern obtained from a powdered sample, using Cu K_{α} radiation.

2) Diffraction pattern obtained from a single grain, using Fe K_{α} radiation, and a Gandolfi camera.

3) Recalculated diffraction pattern from single-crystal data, assuming Cu K_{α} radiation and a resolving power of 0.1° in θ angles, using a program written by C.M.G.

* Reflections marked with an asterisk are relative to another nearly identical powder pattern, obtained using a Niskanen specimen holder instead of a Schliephake specimen holder.

The symbols *s*, *m*, and *w* for the intensity refer to strong, medium, and weak, respectively.

vacancies are present. However, if some OH replaces oxygen, some variation in bond length should appear, and this is not observed. A Si-F bond is unlikely in non-fumarolic minerals. The energy of formation of oxygen vacancies in structures of this kind is usually so high as to preclude them in substantial number.

For all these reasons, we believe that no substantial replacement of (As,V) by Si occurs in tiragalloite, and some overestimation of silicon and underestimation of arsenic (and vanadium?) has occurred in the chemical analysis. Note, however, that these over- or underestimates are well within the limits of a

reasonable uncertainty even in the best analytical results of this kind.

Conditions of formation

Tiragalloite is the only known example of a mineral containing non-isolated AsO_4 groups; no such examples are known in nature even for phosphates, with the possible exception of kehoeite (McConnell, 1964). This probably depends on the ease of hydrolysis of polyphosphate or polyarsenate ions relative to complex silicates, polyarsenates being even more unstable than polyphosphates (Emeleus and Sharpe, 1978, p. 314-315). The conditions nearly universally

Table 2. Electron microprobe analyses for tiragalloite. All results are in weight percent

	On 1 grain (n spot=21)		On 8 grains (n spot=8)		Average (σ)	Theoretical (1-2)	
SiO ₂	32.27	(31.85-33.36)	32.68	(31.94-33.28)	32.38±0.19	30.86	30.66
FeO	0.14	(0.00-0.38)	0.25	(0.00-0.54)	0.17±0.05	0.16	-
MnO	48.47	(47.83-49.58)	48.01	(47.36-48.71)	48.34±0.21	47.49	48.26
CaO	0.79	(0.63-1.02)	0.66	(0.42-0.79)	0.75±0.06	0.74	-
As ₂ O ₅	16.00	(15.06-17.28)	16.27	(15.76-16.84)	16.07±0.12	17.40	19.54
V ₂ O ₅	1.73	(1.17-2.26)	1.53	(1.19-1.82)	1.67±0.09	1.81	-
H ₂ O						1.54	1.53
Total	99.39		99.40		99.38	100.00	100.00

The theoretical results are relative to calculated formula (1), or to the As-rich end member (2), respectively.

encountered in the earth's crust apparently favor the existence of crystal structures with isolated AsO₄ or PO₄ groups.

Consequently, the physicochemical conditions leading to formation of tiragalloite must be quite exceptional (the mineral is rare, even at Molinello), and they should especially disfavor hydrolysis. Such requirements point to relatively low temperatures and high concentrations in solution (or, in other words, relatively low fugacity of water). The low temperature is indirectly confirmed by the absence of mutual substitution between As and Si, which might be important in other arsenate-silicate minerals but is probably insignificant for tiragalloite.

There are, of course, several stabilizing factors besides the network of hydrogen bonds. The presence of vanadium might be important, since this element is even more likely than As or P to form complex ions by joining up VO₄ tetrahedra. Such ions can also be found in nature [*i.e.* in the mineral chervetite, Pb₂V₂O₇, described by Bariand *et al.* (1963) and Kawahara (1967)]. From this point of view, it might be interesting to know whether the pure As-containing tiragalloite is stable enough to be found in nature. Another favorable condition can be recognized by considering that the AsO₄ group is linked to an SiO₄, instead of to another AsO₄ tetrahedron, thereby forming an intermediate structure between complex arsenates (unstable in nature) and complex silicates (very stable in natural conditions). The difficulty for the AsO₄ group to link with the other tetrahedra is shown by its presence at one extremity, rather than in the middle of the chain segment (a similar situation occurs in medaite).

Ardennite is another manganese silicate occasionally present in some alpine and subalpine deposits.

It also contains Ca, Mg, Al, and essential As and V, the last two elements substituting for each other. In its crystal structure a trisilicate group (Si₃O₁₀)⁸⁻ is present, together with isolated (As,V)O₄ and SiO₄ tetrahedra (Donnay and Allmann, 1968); water is present in amounts around 5 percent.

In view of the similarity in crystal structures and chemical composition, it might be inferred that these two minerals can be formed in lieu of one another, the determining factor very probably being connected with conditions which favor or disfavor hydrolysis.

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