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Johninnesite, $\text{Na}_2(\text{Mn}^{2+})_9(\text{Mg,Mn})_7(\text{AsO}_4)_2(\text{Si}_6\text{O}_{17})_2(\text{OH})_8$: a new occurrence in Val Ferrera (Graubünden, Switzerland)

by Joël Brugger^{1,2} and Peter Berlepsch¹

Abstract

The rare mineral johninnesite, $\text{Na}_2(\text{Mn}^{2+})_9(\text{Mg,Mn})_7(\text{AsO}_4)_2(\text{Si}_6\text{O}_{17})_2(\text{OH})_8$, has been discovered within a metamorphic Fe-Mn-deposit in Triassic marbles of the Schams nappes in Val Ferrera (Graubünden, Switzerland). To our knowledge, this is the second occurrence of this mineral, which was first described from Fe-Mn-ore lenses at the Kombat mine (Namibia). Johninnesite from Val Ferrera differs from the type material by its Fe and V contents, and by higher MgO contents which are correlated to lower MnO contents. IR and Raman spectra for this species are reported for the first time. Johninnesite is a product of the metamorphism of syn-genetic exhalative deposits, and the reason for the rarity can be ascribed to the geochemistry of the protolith. In particular, if the protolith is not depleted in aluminium, the widespread silico-arsenate ardennite will form instead of johninnesite.

Keywords: johninnesite, chemical analyses, arsenic, IR and Raman spectra, Val Ferrera, Switzerland.

Introduction

The rare mineral johninnesite has been described by DUNN et al. (1986) from the Kombat Mine (Namibia). This mine is located in dolostones of the Hüttenberg formation, the youngest formation of the Upper Proterozoic Otavi Group (Damara sequence, South-West Africa/Namibia; INNES and CHAPLIN, 1986). Johninnesite occurs in Fe-Mn-ore lenses embedded in feldspathic sandstones deposited near, or at the top of the Hüttenberg formation and subsequently transposed into the dolostones along steep folds. The Fe-Mn ores are layered and consist of magnetite, hausmannite, hematite, barite, calcite, tephroite, alleghanyite, pyrochroite. Their ore texture, mineralogy and geochemistry suggest that they are the metamorphosed equivalents of volcanic exhalative deposits.

The Hüttenberg formation underwent subgreenschist facies metamorphism. At the Kombat mine, ubiquitous rock alteration is linked to the deposition of various Cu, Pb, and Ag ores. The

temperature of the main mineralizing event has been measured from fluid inclusions as 200–280 °C (INNES and CHAPLIN, 1986).

The Fe-Mn ores of the Kombat mine are famous because they furnished a number of rare and unusual minerals, including Mn-bearing silicates such as leucophoenicite, glaucochroite, cuspidine, and ribbeite (type locality, PEACOR et al., 1987), vanadates such as kombatite (type locality, ROUSE et al., 1986), and arsenates such as sahlinite and johninnesite.

The structure of johninnesite was solved by GRICE and DUNN (1994), leading to the ideal structural formula $\text{Na}_2\text{Mn}_9(\text{Mg,Mn})_7(\text{AsO}_4)_2(\text{Si}_6\text{O}_{17})_2(\text{OH})_8$. The mineral is triclinic with space group P1. The johninnesite structure consists of sheets parallel to (100). GRICE and DUNN (1994) distinguish three distinct kinds of polyhedral sheets: (1) the tetrahedral layer (T) shares $[\text{Si}_6\text{O}_{17}]^{10-}$ rings and isolated $[\text{AsO}_4]^{3-}$ groups; (2) an edge sharing octahedral layer (O) with brucite-like geometry, 5/12 positions being occupied by Mn, 5/12 by (Mg,Mn) and the remaining two be-

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ing empty; (3) another octahedral layer (O') sharing Mn and Na polyhedra. The stacking order is TOTO'.

During the systematic study of the small Fe and Fe–Mn deposits of the Val Ferrera (Graubünden, Switzerland), johnninesite was found in abundance. As far as we know, Val Ferrera is the second locality for the mineral. This paper describes briefly the mineral assemblage and the geological context of this occurrence, discusses new chemical data on johnninesite (including johnninesite from the type locality), and gives some new spectroscopic data for this rare mineral species.

Occurrence

Numerous small Fe and Fe–Mn deposits (STUCKY, 1960) occur in the Triassic dolomite and calcite marbles of Val Ferrera (Graubünden, Switzerland), which belong to the para-autochthonous sedimentary cover of the Suretta nappe, to the Starlera nappe, and to the Schams nappes

(BAUDIN et al., 1995; SCHMID et al., in press). A syn-genetic exhalative origin has been proposed for these deposits (BRUGGER, 1996), which subsequently underwent a complex Tertiary metamorphism climaxing under greenschist to blueschist facies conditions (MARQUER et al., in press; SCHREURS, 1991).

So far, johnninesite has only been identified in a restricted area (about 10 m) of the Schmorrasgrat deposit in the Schams nappes. The host ore consists of hematite, jacobsite, quartz, dolomite, kutnohorite, and amphibole (magnesian riebeckite), which is often brecciated so that quartz and dolomite grains up to 2 cm are embedded in a black matrix of the ore minerals. Johnninesite may be the main component, with minor quartz and carbonate, in discordant veins up to 5 cm in width, or it may occur as an accessory in quartz, carbonate, manganberzeliite-palenzonaite veins. Rare associated minerals in both kinds of veins are walkkildellite, pink manganian biotite and fluoromérite (BRUGGER et al., 1997). Three johnninesite morphologies can be distinguished: (a) fi-



Fig. 1 Microphotograph of a johnninesite veinlet. j = johnninesite, r = roméite, d = dolomite (belongs to the veinlet), g = embedding ore, consisting mostly of dolomite, hematite, jacobsite, and manganian muscovite. Transmitted light, field of view 1.25×0.92 mm.

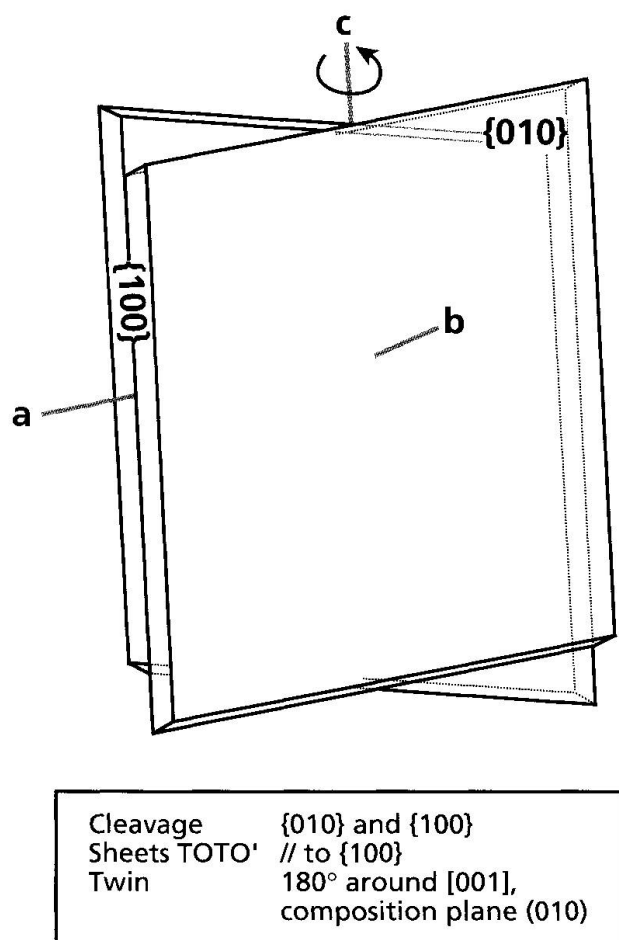


Fig. 2 Schematic view of a johninnesite crystal with a morphology of type (b). Polysynthetic twinning occurs by a 180° rotation around [001]. The dark/light gray bands represent the stacking of the polyhedral sheets which build the johninnesite structure.

brous crystals up to 4 cm in length, elongated perpendicular to the vein walls, which with quartz + carbonate grew synchronously to the opening of the fracture (Fig. 1); (b) rarely, similar veinlets contain prismatic crystals (about 2 mm × 1 mm × 0.3 mm; Fig. 2); and (c) small micaceous crystals (< 1 mm) which fill thin fractures over several cm².

Crystallography

Johninnesite from Val Ferrera originally was thought to be a yellow amphibole. A routine X-ray powder diagram was obtained with a Gandolfi camera, and a database check with the four strongest lines from the powder pattern unequivocally led to the triclinic mineral johninnesite. Powder data for johninnesite from the Kombat mine and from Val Ferrera are listed in table 1.

Tab. 1 Powder data for johninnesite from Val Ferrera and from the type locality.

Val Ferrera ¹		Kombat Mine ²		
d_{obs}	I_{obs}	d_{calc}	d_{obs}	I_{obs}
10.08	20	9.83		
9.67	30	9.71	9.8	60
			7.8	2
			7.3	5
5.93	20	5.928	5.99	40
5.90	25			
5.193	< 10	5.197	5.26	10
4.859	< 10	4.855	4.91	10
			4.39	10
			4.24	2
4.046	< 10	4.042	4.06	30
3.862	25	3.863	3.89	30
3.659	10	3.666	3.67	30
3.451	10	3.451	3.48	30
3.351	20	3.358	3.38	40
3.257	20	3.276		
3.213	50	3.237	3.23	60
3.037	10	3.037	3.05	10
2.945	20	2.955	2.965	20
2.853	20	2.852	2.892	20
2.829	20	2.828	2.842	20
2.667	100	2.662	2.676	100
2.620	< 10	2.621	2.63	2
2.561	20	2.561	2.571	10
2.474	30	2.462	2.479	40
2.429	20	2.429	2.436	30
2.352	30	2.351	2.354	20
			2.288	10
2.222	30	2.222	2.228	20
2.182	20	2.182	2.19	10
2.139	20	2.139	2.147	5
2.035	20	2.035	2.044	20
1.859	30	1.859	1.866	30
1.791	20	1.792	1.796	20
1.723	10	1.723	1.726	10
1.695	10	1.695	1.701	10
1.623	10	1.623	1.623	2
1.604	50	1.604	1.606	30
1.538	50	1.538	1.539	40
			1.498	2
1.438	< 10	1.439	1.441	10
			1.427	5
1.398	< 10	1.398	1.402	2
1.380	< 10	1.381	1.386	2
1.362	30	1.362	1.365	5

¹ G683, Schmorrasgrat; Gandolfi camera 114.6 mm diameter, Mn-filtered FeK_α radiation ($\lambda = 1.93728 \text{ \AA}$); I_{obs} : visually estimated intensities; d_{calc} : theoretical d-values for the cell obtained by least-squares refinement of G683 (program Appleman, APPLEMAN and EVANS, 1973).

² DUNN et al. (1986): 4 d_{obs} with $I_{\text{obs}} = 1$ are not listed.

The unit cell parameters (Tab. 2) were derived by least-squares refinement using the powder data and compared to the data reported by DUNN

Tab. 2 Cell parameters for johnninesite from Val Ferrera and from the type locality.

	Val Ferrera	Kombat mine
a [Å]	10.48(1)	10.44(2)
b [Å]	11.01(1)	11.064(6)
c [Å]	9.58(1)	9.62(1)
α [°]	107.02(2)	107.43(7)
β [°]	82.54(2)	82.7(1)
γ [°]	112.03(1)	111.61(1)

et al. (1986). Taking into account the variation in chemical composition, the refined unit cells are in good agreement.

The same twinning as reported by DUNN et al. (1986) and GRICE and DUNN (1994) was observed on a precession film showing the (100) plane of the reciprocal lattice of johnninesite from Val Ferrera (Fig. 2). This film also displayed weak reflections which could be related to a super structure.

Chemistry

Chemical analyses were performed on a JEOL JXA-8600 electron microprobe operated at 15 kV and 10 nA with a focused electron beam scanning a surface of about 20 μm^2 . The following stan-

dards, lines, and analysator crystals were used: adamite: As L_{α} /TAP; V_2O_5 : V K_{α} /LiF; albite: Si K_{α} /TAP; spessartine: Mn K_{α} /LiF; graffonite: Fe K_{α} /LiF; olivine: Mg K_{α} /TAP; albite: Na K_{α} /TAP; wollastonite: Ca K_{α} /TAP; celestite: Sr K_{α} /PET; galena: Pb L_{α} /PET.

This analytical procedure yields satisfactory results for minerals such as amphiboles, medaite or ardennite. However, the johnninesite analyses (Tab. 3) are characterized, relative to the theoretical formula, by an excess silicon content which correlates mainly with deficiencies of the (Mg+Mn) values. The use of different standards (e.g., marokite for Mn, sillimanite or jadeite for Si) could not eliminate this non-stoichiometry.

The comparison of the analyses of johnninesite from the Kombat mine and from Val Ferrera obtained under similar analytical conditions shows that:

(1) At Val Ferrera it contains small but significant amounts of Fe.

(2) It also has a significant V content, which is negatively correlated to the As content; V therefore enters the johnninesite structure along the As_{-1}V exchange vector (Fig. 3a).

(3) Johnninesite from Val Ferrera usually has a higher MgO content which correlates with a lower MnO content (Fig. 3b).

Tab. 3 Chemical data for johnninesite (all values in weight-%).

	σ^1	A	B	range	C	range
SiO_2	0.21	35.5	35.68	35.35–36.06	36.34	35.66– 37.35
As_2O_5	0.18	10.6	9.43	9.01– 9.87	8.59	6.63– 9.81
V_2O_5	0.10		0.13	< 0.10– 0.18	0.81	0.30– 1.34
MnO	0.41	40.7	39.04	38.25–39.97	37.91	35.97– 39.95
FeO	0.05	0.1	< 0.05	< 0.05– 0.13	0.20	< 0.05– 1.86
MgO	0.10	8.2	7.12	6.92– 7.24	8.43	7.26– 9.30
CaO	0.05		< 0.05	–	0.13	< 0.05– 0.68
Na_2O	0.07	3.1	2.94	2.85– 3.02	2.84	2.64– 2.99
H_2O^2		3.51 ³	3.38	3.39– 3.43	3.47	3.42– 3.53
Sum		101.71	97.75	96.95–98.18	98.72	97.72–100.29

PbO: up to 0.15(5) wt% in Val Ferrera; < 0.05 wt% in the Kombat mine.

Ideal formula (GRICE and DUNN, 1994): $\text{Na}_2\text{Mn}_9(\text{Mg},\text{Mn})_7(\text{AsO}_4)_2(\text{Si}_6\text{O}_{17})_2(\text{OH})_8$

Empirical formulas:

A: $\text{Na}_{2.05}\text{Mn}_{9.00}(\text{Mg}_{4.18}\text{Mn}_{2.78}\text{Fe}_{0.03})_{6.99}\text{As}_{1.89}\text{Si}_{12.13}\text{O}_{42}(\text{OH})_8$

B: $\text{Na}_{2.01}\text{Mn}_{9.00}(\text{Mg}_{3.74}\text{Mn}_{2.66}\text{Fe}_{0.01})_{6.41}(\text{As}_{1.74}\text{V}_{0.03})_{1.77}\text{Si}_{12.58}\text{O}_{42}(\text{OH})_8$

C: $\text{Na}_{1.90}\text{Mn}_{9.00}(\text{Mg}_{4.35}\text{Mn}_{2.11}\text{Fe}_{0.06})_{6.52}(\text{As}_{1.55}\text{V}_{0.19})_{1.74}\text{Si}_{12.57}\text{O}_{42}(\text{OH})_8$

A Type locality, DUNN et al. (1986).

B Type locality, this paper; mean of 6 analyses.

C Schmorrasgrat, Graubünden, Switzerland; mean of 16 analyses.

¹ error on counting statistics; for trace elements, this corresponds to the detection limit.

² calculated with respect to the ideal formula.

Normalization on 50 oxygens per formula unit (including 8 hydroxyl groups).

³ the value measured by DUNN et al. (1986) was 2.6 wt% H_2O .

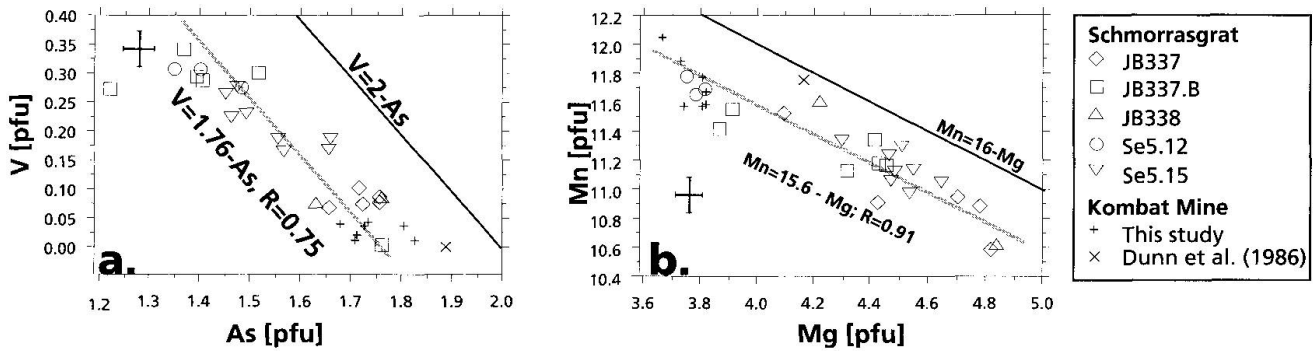


Fig. 3 Chemical variation of johninnesite (normalized EMP data). 1- σ errors from the counting statistics are plotted.

Infrared and Raman spectroscopy

Fourier transform infrared (FTIR) spectra were obtained on a PHILIPS PU9800 spectrometer using KBr pills (5 mm \varnothing , 60 mg KBr, ~ 0.1 mm³ johninnesite; 13 mm \varnothing , 220 mg KBr, ~ 0.5 mm³ johninnesite). The spectra of johninnesite from the type locality and from Val Ferrera mainly differ by an absorption peak at 1437 cm⁻¹ (Val Ferrera), which becomes very weak on the spectrum obtained on the co-type material (Fig. 4). Note that the IR-spectra of johninnesite and of saneroite [Na₂Mn₁₀VSi₁₁O₃₄(OH)₄] from the Gambatesa mine (Northern Italy) are very similar.

Raman spectra were collected on a RENISHAW spectrometer using the green line of an argon laser ($\lambda = 514.5$ nm). Both spectra are very similar (Fig. 5).

Discussion

Johninnesite is one of those minerals that occur in relatively large quantities but only in a very limited number of deposits world-wide. So far it has been described only from two carbonate-hosted Fe-Mn-deposits of syngenetic exhalative origin, which underwent regional metamorphism (Val Ferrera) or extensive hydrothermal alteration (Kombat mine).

We suggest that the geochemistry of the protolith is the most important limiting parameter responsible for the rarity of this mineral. A large positive As anomaly is characteristic for hydrothermal exhalative Mn-deposits (MARCHIG et al., 1982). Most of the deposits of this type are, however, related to hydrothermal activity at oceanic ridges (e.g., BONATTI, 1975; PETERS et al., 1980), and are embedded in deep sea sediments such as radiolarites. In contrast to the carbonate-hosted deposits in which johninnesite occurs,

oceanic deposits display higher Al contents (related to a higher detrital component); this fact may explain why the Al-mineral ardenite (Tab. 4), which has not been identified in the carbonate-hosted deposits of Val Ferrera and Kombat, is one of the most common silico-arsenates in metamorphic Mn-deposits. It has been recognized in many radiolarite-hosted Mn-deposits in the Alps, e.g., from Graubünden (Falotta: NIEVERGELT, personal communication [GEIGER and CABALZAR, 1989]; Parsettens: GEIGER and CABALZAR, 1989; Fur-

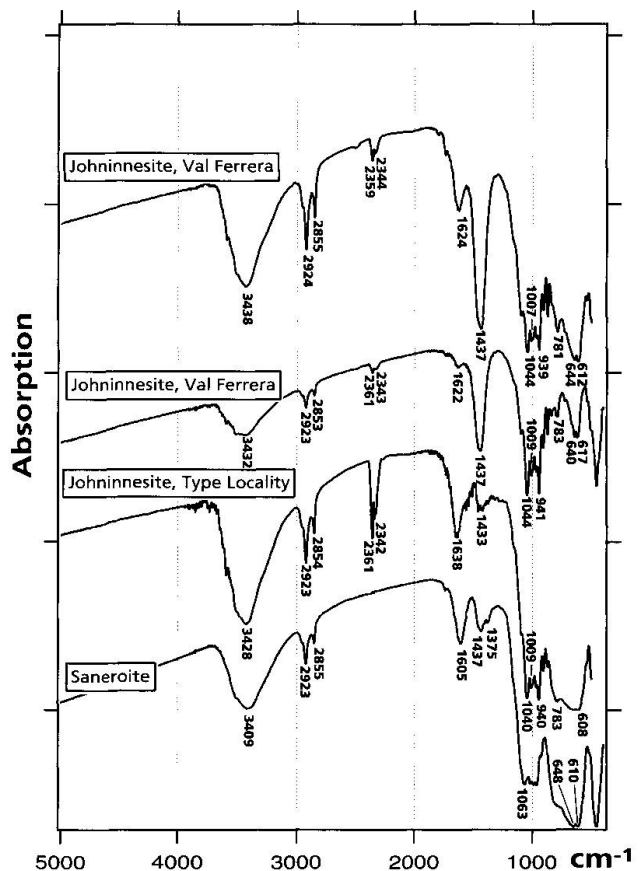


Fig. 4 IR-spectra of johninnesite from the type locality (Kombat mine), and from Schmorrasgrat, as well as of saneroite from the type locality (Val Graveglia, Italy).

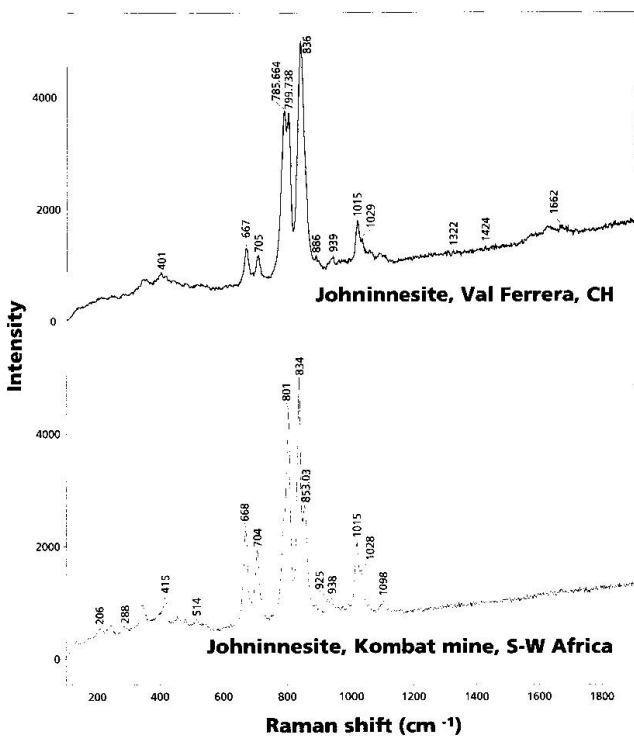


Fig. 5 Raman spectra of johnninesite from the type locality (Kombat mine), and from Schmorrasgrat.

tschellas: DE CAPITANI, 1983; Piz Cam: NIEVERGELT, personal communication [GEIGER and CABALZAR, 1989]; Northern Italy (Praborna, Val d'Aoste: MARTIN-VERNIZZI, 1984; Vedretta di Scerscen inferiore, Val Malenco: BEDOGNÉ et al., 1993), France (Haute Maurienne: CHOPIN, 1978), and in Greece (Southern Evia: REINECKE, 1986). The carbonate-hosted Mn-deposits are sometimes rich in vanadium. At Fianel, in another Fe–Mn deposit in the Val Ferrera (BRUGGER and BERLEPSCH, 1996), medaite is a very common mineral, and it seems that there the V/As ratio largely prevented the appearance of silico-arsenates. Johnninesite is also the only silico-arsenate which contains Na as a main constituent. This can be related to the geochemistry of the protolith, but also to the nature of the fluids from which johnninesite crystallized.

This study also draws attention to the difficulties in analyzing these rare minerals, which also have not received extensive crystal-chemical study. In particular, the discrepancy between the EMP analyses from this study and those of DUNN et al. (1986) is quite appreciable (Tab. 3). The non-stoichiometric analyses we obtained may be an artifact induced by the choice of the EMP standards. However, this is unlikely because the same calibration furnished good results for several other arseno-silicates. If the non-stoichiometry is real, it could be related to the presence of polysomatic

Tab. 4 The known manganese arseno-silicates and some manganese vanado-silicates.

Mineral	Chemical formula
Ardennite	$(\text{Mn}^{2+}, \text{Ca})_4(\text{Al}, \text{Mn}^{3+})_5\text{Mg}(\text{As}, \text{V})\text{Si}_4\text{O}_{18}(\text{OH}, \text{O})_{10}$
Johnninesite	$\text{Na}_2(\text{Mn}^{2+})_9(\text{Mg}, \text{Mn})_7(\text{AsO}_4)_2(\text{Si}_6\text{O}_{17})_2(\text{OH})_8$
Nellerite	$(\text{Mn}, \text{Fe})_{16}\text{As}_3\text{Si}_{12}\text{O}_{36}(\text{OH})_{17}$
Schallerite	$(\text{Mn}, \text{Fe})_{16}\text{As}_3\text{Si}_{12}\text{O}_{36}(\text{OH})_{17}$
Tiragalloite	$\text{Mn}_4\text{AsSi}_3\text{O}_{12}(\text{OH})$

disorder. To test this, a preliminary transmission electron microscope (TEM) investigation has been performed by Allan Pring (personal communication). Although interpretation of these data is complicated by the triclinic geometry and the fine twinning of the mineral, they do suggest that samples from Val Ferrera are subject to some kind of polysomatic or polytypic disorder. This aspect of the work is still in progress.

Acknowledgement

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