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*In memory of Filippo Olmi (1959-2005)*

# History of ardennite and the new mineral ardennite-(V)

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**Abstract:** Ardennite-(V), ideally $Mn_4[Al_4(AlMg)][Si_5V]O_{22}(OH)_6$, is the analogue of ardennite, ideally $Mn_4[Al_4(AlMg)][Si_5As]O_{22}(OH)_6$, with V dominant at the T4 site. The history of the discovery of ardennite is outlined, with special accent on its chemical composition; revision of the old literature evidenced that even if vanadium-containing specimens were considered since the first description, the analytical data contained in the first papers are very questionable, and ardennite has been so far considered an arsenate-silicate. A new occurrence of ardennite-(V) is described from Sparone, Locana Valley (TO), Piedmont, Italy. Here ardennite-(V) occurs within a piemontite-bearing micaschist. Crystals are elongated along [010] and very thin (up to 1 mm in length and a few microns in diameter), are yellow with a white streak, transparent with a vitreous lustre, and brittle. No cleavage or parting were observed. The calculated density is 3.55 g/cm$^3$. Optically, ardennite-(V) is biaxial, with $\alpha > 1.765(5)$, $\beta < 1.775(5)$, and $\gamma = 1.775(5)$, and is weakly pleochroic, with X, Y = pale yellow; Z = yellowish. Electron microprobe analyses ($P_2O_5$ 0.38 wt.%, $As_2O_5$ 0.37, $V_2O_5$ 4.60, $SiO_2$ 31.21, $TiO_2$ 0.21, $Al_2O_3$ 22.60, $Fe_2O_3$ 1.64, $Cr_2O_3$ 0.34, MgO 4.44, $MnO_{tot}$ 23.28, CaO 4.24, $Na_2O$ 0.02, F 0.17, $H_2O_{calc}$ 5.70), gave the following empirical formula: $[Mn^{2+}_{3.221}Ca_{0.774}Na_{0.006}]_{\Sigma=4.001}$ $[Al_{4.456}Mg_{1.127}Fe^{3+}_{0.210}Mn^{3+}_{0.137}Cr_{0.046}Ti_{0.027}]_{\Sigma=6.003}$ $[Si_{5.000}]$ $[V_{0.518}Si_{0.315}Al_{0.080}P_{0.055}As_{0.033}]_{\Sigma=1.001}$ $O_{21.433}$ $(OH)_{6.475}$ $F_{0.092}$. The five strongest peaks in the X-ray powder diffraction pattern [*d*(Å)(*I*)(*hkl*)] are: 2.948(90)(115), 2.609(100)(310/116), 2.033(55)(225), 1.585(75)(425), 1.477(45)(2.2.10). Ardennite-(V) is orthorhombic, space group *Pnmm*, with *a* 8.760(3), *b* 5.838(2), *c* 18.56(2) Å. Both the new mineral and its name were approved by the IMA CNMNC. Chemical analyses which point to the occurrence of ardennite-(V) were recorded also at Varenche mine, S. Barthelemy, Aosta Valley, Italy, but the crystal showed a marked zoning.

**Key-words:** ardennite-(V), new mineral species, Sparone, Piedmont, Italy, ardennite.

## Introduction

The general formula of ardennite may be written as $A_4M_6T_6O_{22}(OH)_6$, in which A are large, seven-fold coordinated sites which can host $Mn^{2+}$ and in smaller amount $Ca^{2+}$ and $Mg^{2+}$, M are octahedral sites which can host $Al^{3+}$, $Fe^{3+}$, $Mn^{3+}$, $Mg^{2+}$ and other minor six-fold coordinated cations, T are tetrahedral sites which can host $Si^{4+}$, $As^{5+}$, $V^{5+}$, and $P^{5+}$.

The crystal structure of ardennite (Donnay & Allmann, 1968) has orthorhombic symmetry, with space group *Pnmm*, and $a \approx 8.8$, $b \approx 5.8$, $c \approx 18.6$ Å. It consists of chains of edge-sharing $[MO_6]$ octahedra running along [010], linked together through $[TO_4]$ and $[T_3O_{10}]$ ortho- and trisilicate groups, with A cations finding place within the larger structural voids (Fig. 1). In the asymmetric unit there are four independent T sites – T1 to T4 – arranged into one $[(T2\text{-}T3\text{-}T2)O_{10}]$ group, two $[T1O_4]$ tetrahedra, and one $[T4O_4]$ tetrahedron. Typically, whereas T1, T2, and T3 sites are occupied by silicon, a pentavalent cation dominates at the T4 site. Since the A sites are invariably occupied by divalent cations, the charge balance is ruled by the coupled substitution $T^{4+} + M^{3+} \Leftrightarrow T^{5+} + M^{2+}$. Accordingly, the general formula of ardennite can be better written as $A^{2+}_4(M^{3+}_5M^{2+})(T^{4+}_5T^{5+})O_{22}(OH)_6$. And this is somewhat problematic, since in the structure of ardennite the T4 site is in the Wyckoff position 2(*b*), and the M3 site (the one which hosts divalent cations) is in the Wyckoff position 4(*e*). Therefore, both divalent and trivalent cations share the same M3 position, with the ideal occupancy at that site being $M^{3+}_{0.5}M^{2+}_{0.5}$ for stoichiometric balance. The implications of the octahedral site occupancies (especially at the M3 site) on the ardennite nomenclature have yet to be clarified. As a matter of fact, in all known ardennite samples the dominating $M^{2+}$ cation [the "charge-compensating cation", according to Chopin (2006)] is $Mg^{2+}$. Therefore, distinction among different species should be made on the basis of the dominant cation at the T4 site.

## Historical background

The discovery of ardennite [shortly outlined in Lacroix (1893) and later on summarised by Buttgenbach (1947),

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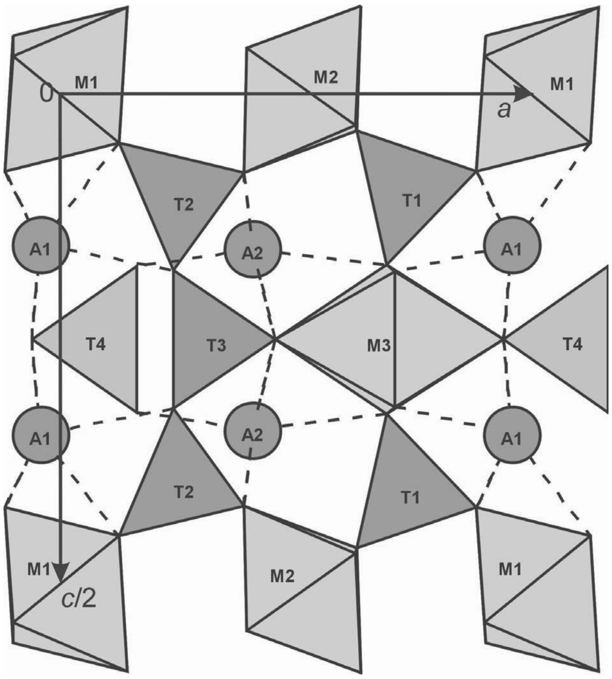

Fig. 1. Polyhedral labelling in the crystal structure of ardennite (half unit cell view along [010]). For ardennite-(V) it is: A1, A2 = $Mn^{2+}$; M1, M2 = Al; M3 = $Al_{0.5}Mg_{0.5}$; T1, T2, T3 = Si; T4 = $V^{5+}$.

who also provided more detail about the original occurrence] dates back to the second half of the 19th Century, and was the subject of a lively dispute between A. von Lasaulx and F. Pisani. Both of them ever claimed the paternity of the mineral. Von Lasaulx (1872a) first described the mineral as "mangandisthène", namely a $Mn^{3+}$-substituted kyanite. Soon thereafter, a chemical analysis by Bettendorff (von Lasaulx, 1872b, 1872c) led to its recognition as a new mineral, which was called ardennite, from the region of occurrence (the locality was given generically as "near the village of Ottré", in the Stavelot Massif, Luxembourg Province, Belgian Ardennes); in this analysis a relatively high content of vanadium oxide was evidenced (about 6 wt.%), but the data reported were largely incorrect: the manganese was considered as trivalent, spurious elements from the crucible were included and the mineral was still considered similar to kyanite. The same mineral was independently described – a week later – by Pisani (1872) and was called dewalquite after the Belgian geologist G. Dewalque. Pisani (1872), who reported precisely the provenance from the village of Salm-Château, at that time did not succeed in the determination of arsenic, found a lower content of vanadium than Bettendorff, but recognized the occurrence of manganese as $Mn^{2+}$, suggesting a monoclinic symmetry for the crystals.

Early in 1873, von Lasaulx and Bettendorff presented new analyses of V-bearing ardennite, and its orthorhombic symmetry was assessed by von Rath (von Lasaulx & Bettendorff, 1873; von Lasaulx, 1873). In these papers ardennite was described as a vanadate-silicoaluminate mineral, and the first chemical formula proposed for ardennite corresponded to a term of pure vanadium: $5(R_2O_3SiO_2.RO.SiO_2)+3RO.VO_5+5aq$. In fact, in the original chemical study arsenic was not recognized, whereas an even higher content of vanadium was detected in the new analysis, actually corresponding to a value a bit greater than 1 atom p.f.u.; to correctly read the above formula, it must be remembered that at that time vanadium (and similarly arsenic) was considered as pentavalent with respect to oxygen, with a double atomic weight in comparison to the actual one, and thus $VO_5$ corresponds to $V_2O_5$ in modern notation. Unfortunately the original formula proposed was affected by a mistake in the stoichiometric calculation concerning Mg, that was underestimated by one order of magnitude: this can be easily ascertained simply looking at the original calculations reported by von Lasaulx & Bettendorff (1873).

Pisani (1873) first recognized the presence of arsenic in ardennite, and this was the first description of an arsenic-bearing silicate mineral: for that reason, and for the correct assignment of the valence state of manganese, he claimed his priority rights in the definition of the new species. Von Lasaulx (1874) challenged Pisani's right, and showed that those analyses corresponded to two varieties of the same mineral, where As can substitute for V. The first quotation of ardennite in a textbook of mineralogy was made by Pisani (1875), who reported – of course under the name dewalquite – a chemical analysis with As > V. Later on von Lasaulx (1876) and Bettendorff (1877) carried out a crystallographic and chemical reinvestigation of the mineral ardennite, publishing two new complete analyses on two different crystals, the former light yellow and opaque, the latter brown and transparent, which turned out to correspond to As-rich and V-rich varieties, respectively. This time arsenic was found in all the samples, even if in different amounts; some partial analyses of other specimens were also reported, in which the content in arsenic oxide was 1.83, 2.31, 2.53, 2.98, and 6.64 wt.%, thus showing that a large variation in the As/V ratio was possible. Also Doelter (1921) states that two varieties of ardennite exist.

Actually most of these analyses are doubtful; the first ones are affected by errors that were partly evidenced already in the successive papers, but also the last analyses by Bettendorff (1877) seem questionable, if the data are critically evaluated in the light of the ardennite crystal-chemistry: in fact, the range of some cations, specifically Mg and Mn, is largely outside the acceptable value. But the most uncertain data are those relative to the arsenic and, even more, the vanadium contents; this is not strange considering the difficulty of the wet analysis of these elements in silicates, well discussed in some descriptions of the analytical work on ardennite, that showed how the final wt.% of arsenic and vanadium oxide was strongly influenced by the procedure followed (von Lasaulx & Bettendorff, 1873; Bettendorff, 1877; Zambonini, 1922). Actually, if we consider the elements which enter the T sites, it appears that the total, and particularly the sum of As+V, is in defect in the analyses of As-rich samples, and in large excess in the V-rich samples, thus confirming the suspect of a significant underestimation of arsenic, and overestimation of vanadium, in all earlier analyses.

Table 1. Chemical analyses and atomic proportions (recalculated on the basis of 28 oxygen atoms) taken from old literature for ardennite (all samples from Salm-Château, Belgium).

| **Constituent** | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| $As_2O_5$ | 9.33 | 2.76 | 9.91 | 4.30 |
| $V_2O_5$ | 0.53 | 9.2 | 0.81 | 4.90 |
| $SiO_2$ | 27.5 | 27.84 | 27.77 | 28.76 |
| $Al_2O_3$ | 22.76 | } 24.22 | 25.25 | 24.65 |
| $Fe_2O_3$ | 1.15 | | 0.53 | 0.08 |
| MgO | 1.38 | 3.01 | 5.20 | 2.08 |
| MnO | 30.61 | 26.7 | 22.70 | 26.41 |
| CaO | 1.83 | 2.17 | 1.44 | 2.56 |
| FeO | - | - | 0.65 | 0.96 |
| CuO | 0.17 | - | - | - |
| $H_2O$ | 5.13 | 5.01 | 5.24 | 5.08 |
| **Total** | **100.39** | **100.91** | **99.50** | **99.78** |
| | | | | |
| $Si^{4+}$ | 4.91 | 4.77 | 4.81 | 5.01 |
| $As^{5+}$ | 0.87 | 0.25 | 0.90 | 0.39 |
| $V^{5+}$ | 0.06 | 1.04 | 0.09 | 0.56 |
| $Al^{3+}$ | 4.79 | } 4.89 | 5.16 | 5.06 |
| $Fe^{3+}$ | 0.16 | | 0.07 | 0.01 |
| $Mg^{2+}$ | 0.37 | 0.77 | 1.34 | 0.54 |
| $Cu^{2+}$ | 0.02 | - | - | - |
| $Fe^{2+}$ | - | - | 0.09 | 0.14 |
| $Ca^{2+}$ | 0.35 | 0.40 | 0.27 | 0.48 |
| $Mn^{2+}$ | 4.63 | 3.87 | 3.33 | 3.89 |
| **Σ (A+M+T)** | **16.16** | **15.99** | **16.06** | **16.08** |
| $(OH)^-$ | 6.11 | 5.73 | 6.06 | 5.90 |
| $O^{2-}$ | 21.89 | 22.27 | 21.94 | 22.10 |

1, 2. Von Lasaulx (1876) and Bettendorff (1877): sample 1, light yellow and opaque crystal (As-rich); sample 2, brown and trasparent crystal (V-rich). Arsenic and vanadium given as $AsO_5$ and $VO_5$, respectively, in the chemical analysis; in analysis 2, $Al_2O_3$ and $Fe_2O_3$ are weighted together.

3. Prandtl (1905).

4. Gossner & Strunz (1932); average of 2 analyses.

A couple of new analyses on the same Belgian ardennite were published in the following years by Prandtl (1905) and Gossner & Strunz (1932): they showed a maximum vanadium content much lower with respect to the early analyses and on this basis, especially considering the fact that the analysis of Prandtl (1905) corresponded to a very As-rich term, Gossner & Strunz (1932) proposed for the species the following formula: $[SiO_4]_5[AsO_4]Al_3Mn[AlOH]_2Mn_4.2H_2O$. A selection of old chemical analyses of ardennite from Salm-Château, together with the recalculated chemical formulae, is reported in Table 1.

In the meantime a second occurrence of ardennite had been discovered near Ceres, Piedmont (Italy), that showed an extremely low vanadium content (Zambonini, 1922).

As a matter of fact, for a very long time after the early descriptions, all the recent known chemical data for ardennite from Salm-Château (Semet & Moreau, 1965; Reinecke & Hatzipanagiotou, 1987) and from other localities [Kajlidongri, India (Nayak, 1967); Bonneval-sur-Arc, French Western Alps (Chopin, 1978; Reinecke & Hatzipanagiotou, 1987; Pasero & Reinecke, 1991); Asemi-gawa river, Japan (Enami, 1986); Tinos and Andros islands, Greece (Reinecke & Hatzipanagiotou, 1987; Pasero *et al.*, 1994); Val Sora and Alpe Airale, Valmalenco, Italy (Bedogné *et al.*, 1993); Varenche mine, Italy (Pasero *et al.*, 1994)] corresponded to the As-rich member. Also a chemical analysis on the sample from Salm-Château used for the structure solution and refinement (Donnay & Allmann, 1968) indicated a V-poor, As-rich ardennite. And, despite the fact that the very first description was for a V-rich sample, today ardennite is considered *de facto* a silicate-arsenate mineral (*cf.* Anthony *et al.*, 1995; Gaines *et al.*, 1997; Strunz & Nickel, 2001). More recently, other occurrences of V-dominant ardennite were reported, even if only as microprobe spot analyses: Sanba-gawa, Japan (Matsubara & Kato, 1987); Bierleux and Bihain, Ardennes, Belgium; Mili, Evvia Island, Greece (Pasero *et al.*, 1994). According to the accepted definition of mineral, As-dominant and V-dominant ardennite are different species, and deserve two distinct names. Since ardennite is the worldwide accepted name for the As-dominant species, we submitted to the IMA CNMNC a proposal for the definition of the species ardennite-(V) (# 2005-037), based on a new occurrence from Italy[1]. Both the mineral and its name were approved. The name is for the obvious relationship with ardennite. The present paper represents the official certificate of birth of ardennite-(V) and fills a gap in the systematics of mixed-anion silicates. Type material is stored in the mineralogical collections of the Centro Interdipartimentale Museo di Storia Naturale e del Territorio, Università di Pisa, via Roma 103, 56011 Calci (PI), Italy (catalogue No. 15525), and in the mineralogical collections of Museo Regionale di Scienze Naturali, via Giolitti 36, 10123 Torino, Italy (catalogue M/U 15544).

## Occurrence

Ardennite-(V) has been identified on a single specimen of piemontite-bearing micaschist now in the collection of Museo Regionale di Scienze Naturali, Torino. The historic provenance of the specimen, with the ardennite-containing area measuring only a few centimetres, is from the regional collection of the former Mineralogical Museum of the University of Torino (drawer 509.3); according to the label ["micascisto a piemontite e ardennite, Sparone (Orco)"], it has been found within an outcrop in the locality of Sparone, Locana Valley (TO), Piedmont, Italy. The collection date is not reported; since that specimen was not yet known to Gennaro (1925), it was reasonably collected in the following years, when prof. Repossi, who succeeded to Zambonini as director of the Mineralogical Institute of

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[1] It was brought to our attention by one of the referees (IP) that after the approval of the new mineral name ardennite-(V) – with a Levinson modifier – all already existing related minerals should be renamed in a similar way, as it was done, *e.g.*, for pumpellyite, jahnsite, and monazite. Therefore the mineral ardennite should be renamed ardennite-(As), leaving the name ardennite – without modifier – as a series name. As talked about with E.A.J. Burke, Chairman of the IMA CNMNC, those changes in nomenclature must be agreed within the Commission and will be formalized in due time.

the Royal University of Torino, solicited the continuation of Zambonini's work on ardennite- and piemontite-bearing micaschists. In fact, several ardennite-bearing micaschist samples from other localities in the Torino province entered the collection in those years.

The new mineral is of metamorphic origin. It occurs as acicular crystals, typically very thin, tabular and elongated along [010], which can reach 1 mm in length and a few microns in diameter (Fig. 2). Aggregates of crystals parallel to the elongation are also common. Associated minerals are quartz, piemontite, and hematite; muscovite is abundant in the specimen, but not in direct contact with ardennite-(V). Ardennite-(V) occurs only in one thin quartzitic layer in the studied specimens, with minor piemontite and very rare and small hematite crystals; other layers are very rich in piemontite or, alternatively, in golden-yellow muscovite and hematite, without any ardennite-(V).

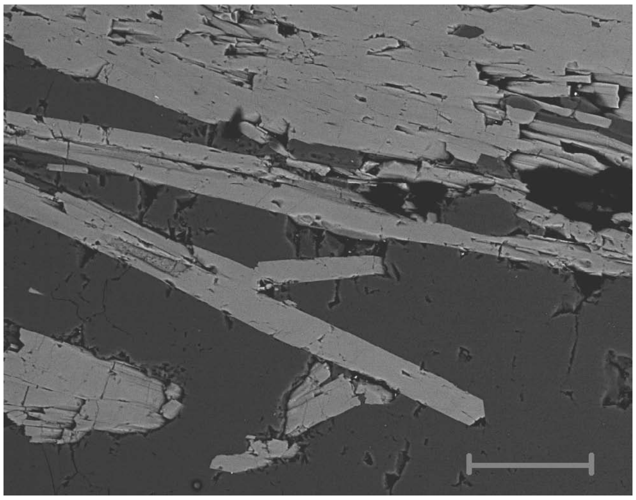

Fig. 2. Backscattered electron image of ardennite-(V) from Sparone (light grey), associated with quartz (dark grey). Scale bar: 50 $\mu$m.

Sparone was not considered so far an important mineralogical locality, and its mineralization was never described. The geology and the petrographic types of the Locana Valley were described by Novarese (1894) and Stella (1894), who carried out the geological survey of this area in preparation of the new geological map of Italy; Stella (1894), in particular, reported the occurrence of piemontite-bearing micaschists in the Sparone area, on the right side of the Orco river, evidencing their similarity with those already known in the Lanzo Valley (Val Grande di Lanzo). Gennaro (1925), studying the new occurrences of piemontite and ardennite-bearing micaschists near Ceres, at Colle Forcola, and near Viù, in the Lanzo Valleys, which cut the same zone with fine gneiss and micaschists as the Locana Valley, commenting the previous find of piemontite-micaschist by Stella (1894), agreed on the common origin of these rocks.

Table 2. Chemical data (average of 9 analyses) for ardennite-(V) from Sparone.

| **Constituent** | Wt.% | **Range** | Probe Standard |
|---|---|---|---|
| $P_2O_5$ | 0.38 | 0.11–0.62 | Apatite |
| $As_2O_5$ | 0.37 | 0.00–1.07 | Metallic As |
| $V_2O_5$ | 4.60 | 3.75–5.13 | Metallic V |
| $SiO_2$ | 31.21 | 30.42–32.82 | Diopside |
| $TiO_2$ | 0.21 | 0.13–0.32 | Ilmenite |
| $Al_2O_3$ | 22.60 | 22.09–23.06 | Plagioclase |
| $Fe_2O_3$ | 1.64 | 1.38–1.82 | Ilmenite |
| $Cr_2O_3$ | 0.34 | 0.00–0.85 | Chromite |
| MgO | 4.44 | 3.96–4.71 | Olivine |
| MnO (tot) * | 23.28 | 22.49–24.04 | Bustamite |
| CaO | 4.24 | 3.76–4.84 | Diopside |
| $Na_2O$ | 0.02 | 0.00–0.05 | Albite |
| F | 0.17 | 0.00–0.44 | Fluorite |
| $H_2O$ (calc) ** | 5.70 | | |
| O = F | - 0.07 | | |
| **Total** *** | **99.24** | | |

* Recalculated as MnO 22.33, $Mn_2O_3$ 1.06 as to fill the A sites with $Mn^{2+}$ and the M sites with $Mn^{3+}$. ** Calculated as to give 28 total anions per formula unit and an O/OH ratio as to achieve the charge balance. *** Including $H_2O$ (calc), and the recalculated MnO and $Mn_2O_3$ instead of MnO (tot).

## Physical and optical properties

Crystals of ardennite-(V) are yellow, transparent with a white streak, and brittle. The lustre is vitreous; fluorescence was not observed. The hardness has been estimated as 6−7 (Mohs). No cleavage or parting were observed. Density was not measured due to the very small dimensions of crystals; the calculated value is 3.55 g/cm$^3$, somewhat lower with respect to the typical values for As-rich ardennite (*e.g.*, 3.74 g/cm$^3$ for the sample studied by Donnay & Allmann, 1968).

Optically, ardennite-(V) is biaxial, with $\alpha > 1.765(5), \beta < 1.775(5)$, and $\gamma = 1.775(5)$. Dispersion was not observed. Optical orientation: Z = *b*. Pleochroism is very weak, with X, Y = pale yellow; Z = yellowish.

## Chemical data

The chemical composition of ardennite-(V) has been obtained with a ARL-SEMQ electron microprobe. Operating conditions were: WDS mode, 15 kV, 20 nA, beam diameter 1 $\mu$m.

The analytical data (wt.% – average of 9 points – and range of components, and probe standards) are given in Table 2.

The chemical data were processed as to give a chemical formula recalculated on the basis of 16 cations and 28 (O+F). The analytical value of $MnO_{(tot)}$ was splitted between MnO and $Mn_2O_3$ in such a way as to fill the A sites with $Mn^{2+}$ and the M sites with $Mn^{3+}$. The O/(OH) ratio was adjusted as to achieve the charge balance; correspondingly, the wt.% of $H_2O$ (calc) was included in the analytical data.

Table 3. X-ray powder diffraction pattern for ardennite-(V) from Sparone.

| *I* | *d* (meas) | *d* (calc) | *hkl* |
|---|---|---|---|
| 4 | 4.65 | 4.64 | 004 |
| 8 | 4.27 | 4.26 | 201 |
| 4 | 3.96 | 3.96 | 202 |
| 10 | 3.82 | 3.82 | 113 |
| 6 | 3.57 | 3.57 | 202 |
| 18 | 3.186 | 3.185 | 204 |
| 3 | 3.043 | 3.049 | 213 |
| 90 | 2.948 | 2.950 | 115 |
| 4 | 2.826 | 2.832 | 205 |
| 3 | 2.785 | 2.785 | 302 |
|  |  | 2.784 | 022 |
| 100 | 2.609 | 2.612 | 310 |
|  |  | 2.609 | 116 |
| 18 | 2.530 | 2.528 | 123 |
|  |  | 2.527 | 206 |
| 25 | 2.469 | 2.471 | 304 |
|  |  |  | 024 |
| 2 | 2.428 | 2.429 | 220 |
| 1 | 2.413 | 2.414 | 017 |
| 38 | 2.329 | 2.327 | 117 |
| 37 | 2.271 | 2.268 | 207 |
| 4 | 2.218 | 2.220 | 125 |
| 14 | 2.174 | 2.175 | 401 |
| 35 | 2.124 | 2.123 | 306 |
|  |  | 2.123 | 026 |
| 13 | 2.059 | 2.063 | 126 |
| 55 | 2.033 | 2.033 | 225 |
| 2 | 1.997 | 1.995 | 316 |
| 1 | 1.966 | 1.963 | 307 |
| 3 | 1.917 | 1.915 | 127 |
| 3 | 1.885 | 1.886 | 405 |
|  |  | 1.886 | 324 |
| 1 | 1.863 | 1.866 | 209 |
| 30 | 1.819 | 1.816 | 308 |
|  |  | 1.816 | 028 |
|  |  | 1.816 | 133 |
| 12 | 1.794 | 1.795 | 415 |
| 3 | 1.734 | 1.734 | 1.1.10 |
| 3 | 1.718 | 1.717 | 326 |
| 3 | 1.688 | 1.688 | 407 |
| 1 | 1.672 | 1.671 | 511 |
| 12 | 1.639 | 1.639 | 505 |
|  |  | 1.639 | 424 |
| 7 | 1.622 | 1.622 | 417 |
| 75 | 1.585 | 1.584 | 425 |
| 17 | 1.550 | 1.547 | 0.0.12 |
| 39 | 1.525 | 1.524 | 426 |
| 45 | 1.477 | 1.475 | 2.2.10 |
| 23 | 1.463 | 1.462 | 427 |
| 10 | 1.418 | 1.416 | 610 |
| 3 | 1.394 | 1.393 | 604 |
| 5 | 1.354 | 1.355 | 614 |
|  |  | 1.354 | 435 |
| 12 | 1.333 | 1.335 | 429 |
|  |  | 1.331 | 3.1.12 |
| 8 | 1.304 | 1.305 | 2.2.12 |
|  |  | 1.303 | 4.1.11 |
| 15 | 1.277 | 1.278 | 623 |

The following chemical formula was obtained: $[\mathrm{Mn}^{2+}_{3.221}\mathrm{Ca}_{0.774}\mathrm{Na}_{0.006}]_{\Sigma=4.001}$ $[\mathrm{Al}_{4.456}\mathrm{Mg}_{1.127}$ $\mathrm{Fe}^{3+}_{0.210}$ $\mathrm{Mn}^{3+}_{0.137}\mathrm{Cr}_{0.046}$ $\mathrm{Ti}_{0.027}]_{\Sigma=6.003}$ $[\mathrm{Si}_{5.000}]$ $[\mathrm{V}_{0.518}\mathrm{Si}_{0.315}\mathrm{Al}_{0.080}$ $\mathrm{P}_{0.055}\mathrm{As}_{0.033}]_{\Sigma=1.001}$ $\mathrm{O}_{21.433}$ $(\mathrm{OH})_{6.475}$ $\mathrm{F}_{0.092}$.

The simplified formula is $\mathrm{Mn}^{2+}_{4}$ $[\mathrm{Al}_4(\mathrm{Mg,Al,Fe}^{3+},\mathrm{Mn}^{3+})_2]$ $[\mathrm{Si}_5(\mathrm{V,Si})]$ $\mathrm{O}_{22}$ $(\mathrm{OH})_6$.

The ideal formula has been given with $\mathrm{O}_{22}(\mathrm{OH})_6$ anions, although it should be better rounded to $\mathrm{O}_{21}(\mathrm{OH})_7$, as to have for ardennite-(V) a formula which parallels that of ardennite, $\mathrm{Mn}_4[\mathrm{Al}_4(\mathrm{AlMg})][\mathrm{Si}_5\mathrm{As}]\mathrm{O}_{22}(\mathrm{OH})_6$. The small difference in the O/OH ratio is the result of the combined excess of $\mathrm{Si}^{4+}$ in the place of $\mathrm{T}^{5+}$ cations (in T4) and $\mathrm{Mg}^{2+}$ in the place of $\mathrm{M}^{3+}$ cations (in M3) with respect to the ideal values of 0 and 1 a.p.f.u, respectively.

## X-ray crystallography

The X-ray powder diffraction pattern for ardennite-(V) was registered with a Gandolfi camera, $R = 57.3$ mm, Cu$K\alpha$, $\lambda = 1.5418$ Å (Table 3). The intensities were estimated with the help of a digitalized pattern. Some ambiguities in the indexing were solved with the help of a calculated pattern profile. Our XRPD data match well with those of ardennite (JCPDF 41-1391). The following unit-cell parameters for ardennite-(V) were refined using 35 unambiguously indexed lines: $a$ 8.760(3), $b$ 5.838(2), $c$ 18.56(2) Å.

The single crystal X-ray diffraction study of ardennite-(V) has been prevented by the exceedingly small dimension of the crystals, which typically occur as thin fibers with a diameter of very few micrometers. Moreover fibers are always intergrown, therefore the manual separation of a single crystal is made difficult. After several trials, a very small needle-like crystal was selected, and a long-exposed (2+2 days) rotation photograph was taken with a Weissenberg camera. The photograph showed only a pair of very weak and diffuse spots, which were consistent with a parameter along the rotation axis of *ca.* 6 Å. A ($h0l$) Weissenberg photograph was collected (4-day exposure), but it resulted in a few almost vanishing spots.

The structural features of the ardennite family are well assessed (Donnay & Allmann, 1968). It is also known that the structure type of ardennite forms a polytypic series with sursassite and pumpellyite (Pasero & Reinecke, 1991).

## Discussion

Ardennite-(V) which is here described was studied in the frame of a detailed ongoing survey of ardennite samples from several Italian occurrences. Chemical analyses which point to the occurrence of ardennite-(V) were recorded also at another Italian locality (Varenche mine, St. Barthelemy, Aosta Valley). Ardennite from this latter locality is longtime known (Pelloux, 1946; Baldelli *et al.*, 1983), and chemical analyses available from literature have As $\gg$ V (Pasero *et al.*, 1994).

Several specimens, differing in some cases for the associated minerals, were field collected by one of the authors (AB) in the mine dump and analysed; in all cases ardennite occurred in quartz veins crosscutting the braunite ore, one of the occurrences originally described by Pelloux (1946). Our new chemical data showed a large variability in composition between specimens, and in some cases also a marked zoning of the crystals. In particular in one of the analysed specimens, the millimetric yellow prismatic crystals of ardennite included in a quartz vein at the contact with massive braunite, observed in backscattered electron emission, showed that the main mass was corresponding to ardennite-(V), but it was cross-cut by a series of fractures partially filled by As-rich ardennite, as a consequence of a secondary hydrothermal event. The chemical formula resulting from a single point analysis of the V-rich zone is the following: $[Mn^{2+}_{3.409}Ca_{0.338}Mg_{0.252}]_{\Sigma=3.999}$ $[Al_{5.013}Mg_{0.77}Fe^{3+}_{0.154}Cr_{0.043}Ti_{0.013}]_{\Sigma=5.999}$ $[Si_{5.000}]$ $[V_{0.719}As_{0.090}Si_{0.074}Al_{0.075}P_{0.042}]_{\Sigma=1.000}$ $O_{22.012}$ $(OH)_{5.988}$. Although the vanadium content is even higher here, we eventually preferred to consider Sparone, in the Locana Valley, as the type locality for ardennite-(V), due to the high homogeneity of those crystals.

For comparative purposes, during this work, also some crystals from Salm-Château (Belgium) were investigated; as in the previous case, the analysis showed a very large variability in the content of the tetrahedral sites, and the existence of micro-domains even in submillimetric crystals. It can be remembered that Cesàro (1910) already observed that the ardennite crystals from the type locality were strongly zoned, as the optical properties were changing abruptly moving from the centre to the periphery, and ascribed this phenomenon to a change in composition, and particularly to a variation in the As/V content. Overall, according to the new data on the analysed specimens, and in the light of both historical and recent literature data, it can be concluded that a complete solid solution exists between the vanadium and the arsenic terms.

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**Dedication**: This paper should have been coauthored also by Filippo Olmi, who died untimely on December 21, 2005. Filippo was the responsible of the electron microprobe laboratory at IGG-CNR, Firenze. He submitted together with us the proposal of the new mineral ardennite-(V), for which he carried out the chemical study with the utmost care, as always. He was informed of the approval of ardennite-(V) – which would have been his seventh new mineral – a few weeks before his death, and this paper today represents nothing but a posthumous dedication. The whole Italian mineralogical community will miss him very much.

## References

Anthony, J.W., Bideaux, R.A., Bladh, K.W., Nichols, M.C. (1995): Handbook of Mineralogy. Volume II: Silica, Silicates (part 1). Mineral Data Publishing, Tucson, 446 p.

Baldelli, C., Dal Piaz, G.V., Polino, R. (1983): Le quarziti a manganese e cromo di Varenche-St. Barthelemy, una sequenza di copertura oceanica della falda piemontese. *Ofioliti*, **8**, 207-221.

Bedogné, F., Montrasio, A., Sciesa, E. (1993): I minerali della provincia di Sondrio: Valmalenco. Bettini, Sondrio, 275 p.

Bettendorff, A. (1877): Ueber den Ardennit and über eine Method sur Scheidung der Vanadisäure von Thonerde und Eisenoxyd. *Ann. Phys. Chem.*, **160**, 126-131.

Buttgenbach, H. (1947): Les minéraux de Belgique et du Congo Belge. Dunod, Paris, 573 p.

Cesàro, G. (1910): Contribution à l'étude des minéraux. *Ann. Soc. Géol. Belgique*, **37**, B118-B131.

Chopin, C. (1978): Les paragenèses réduites ou oxidées de concentrations manganésifères des "schistes lustrés" de Haute-Maurienne (Alpes françaises). *Bull. Minéral.*, **101**, 514-531.

— (2006): Heterovalent substitutions in mineral nomenclature: the dominant-ion rule revisited. 19*th* General Meeting of the International Mineralogical Association, Kobe, Japan, July 23-28, 2006, abstr., 300.

Doelter, C. (1921): Handbuch der Mineralchemie. Band II, Dritter Teil. Steinkopff, Dresden, 472 p.

Donnay, G. & Allmann, R. (1968): $Si_3O_{10}$ groups in the crystal structure of ardennite. *Acta Crystallogr.*, **B24**, 845-855.

Enami, M. (1986): Ardennite in a quartz schist from the Asemigawa area in the Sanbagawa metamorphic terrain, central Shikoku, Japan. *Mineral. J.*, **13**, 151-160.

Gaines, R.V., Skinner, H.C.W., Foord, E.E., Mason, B., Rosenzweig, A. (1997): Dana's New Mineralogy. Wiley, New York, 1819 p.

Gennaro, V. (1925): Micascisti a piemontite nelle valli di Lanzo (Alpi Piemontesi). *Rend. R. Acc. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Ser. 6*, **2**, 508-510.

Gossner, B. & Strunz, H. (1932): Über strukturelle Beziehungen zwischen Phosphaten (Triphylin) und Silikaten (Olivin) und über die chemische Zusammensetzung von Ardennit. *Z. Kristallogr.*, **83**, 415-421.

Lacroix, A. (1893): Minéralogie de la France et de ses colonies. Tome premier. Baudry, Paris, 723 p.

Matsubara, S. & Kato, A. (1987): Ardennite from Sanbagawa in Sanbagawa metamorphic terrane, Kanto Mountains, Japan. *Bull. Nat. Sci. Museum, Tokyo, Ser. C*, **13**, 1-11.

Nayak, V.K. (1967): Ardennites from Kajilidongri, India: a new locality. *N. Jb. Mineral. Mh.*, **1967**, 295-304.

Novarese, V. (1894): Relazione sul rilevamento eseguito nelle Alpi Occidentali (valli dell'Orco e della Soana) nella campagna del 1893. *Boll. R. Com. Geol. It.*, **25**, 215-230.

Pasero, M. & Reinecke, T. (1991): Crystal chemistry, HRTEM analysis and polytypic behaviour of ardennite. *Eur. J. Mineral.*, **3**, 819-830.

Pasero, M., Reinecke, T., Fransolet, A.-M. (1994): Crystal structure refinements and compositional control of Mn-Mg-Ca ardennites from the Belgian Ardennes, Greece, and the Western Alps. *N. Jb. Mineral. Abh.*, **166**, 137-167.

Pelloux, A. (1946): Contributo alla mineralogia della valle d'Aosta (Ardennite della miniera di Varenche presso S. Barthelemy). *Rend. Soc. Mineral. It.*, **3**, 188-206.

Pisani, F. (1872): Sur un nouveau silico-aluminate de manganèse vanadinifère, trouvé à Salm Château, en Belgique. *C. R. Acad. Sci. Paris*, **75**, 1542-1544.

— (1873): Analyse de la dewalquite de Salm-Château en Belgique. *C. R. Acad. Sci. Paris* **77**, 329-333.

— (1875): Traité élémentaire de minéralogie. Masson, Paris, 407 p.

Prandtl, W. (1905): Über den Ardennit. *Z. Kristallogr. Mineral.*, **40**, 392-395.

Reinecke, T. & Hatzipanagiotou, K. (1987): Crystal chemistry and lattice parameters of ardennites from Andros Island, Greece, and Haute-Maurienne, Western Alps. *N. Jb. Mineral. Abh.*, **158**, 89-104.

Semet, M. & Moreau, J. (1965): L'ardennite: révision et données nouvelles. *Ann. Soc. Géol. Belgique*, **88**, 545-577.

Stella, A. (1894): Relazione sul rilevamento eseguito nell'anno 1893 nelle Alpi Occidentali (valli dell'Orco e della Soana). *Boll. R. Com. Geol. It.*, **25**, 343-371.

Strunz, H. & Nickel, E.H. (2001): Strunz Mineralogical Tables. Schweizerbart'sche Verlagsbuchhandlung, Stuttgart, 870 p.

von Lasaulx, A. (1872a): Vorläufige Mittheilung über ein neues Mineral. *Verh. Naturh. Ver. preuss. Rheinl. Westph.*, **29**, 174.

— (1872b): Über ein neues Mineral aus der Gegend von Ottrez. *Verh. Naturh. Ver. preuss. Rheinl. Westph.*, **29**, 189-192.

— (1872c): Ardennit, ein neues Mineral. *N. Jb. Mineral.*, **1872**, 930-934.

— (1873): Über den Ardennit. *N. Jb. Mineral.*, **1873**, 124-127.

— (1874): Über den Ardennit. *N. Jb. Mineral.*, **1874**, 276-278.

— (1876): Nachträge zur Kenntniss des Ardennites. *N. Jb. Mineral.*, **1876**, 363-368.

von Lasaulx, A. & Bettendorff, A. (1873): Ardennit, ein neues Mineral. *Ann. Phys. Chem.*, **149**, 241-251.

Zambonini, F. (1922): Ardennite di Ceres, in Val d'Ala (Piemonte). *Rend. R. Acc. Naz. Lincei, Ser. 5*, **31**, 147-151.

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