Article

Isselite, Cu$_6$(SO$_4$)(OH)$_{10}$(H$_2$O)$_4$·H$_2$O, a new mineral species from Eastern Liguria, Italy

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Abstract

The new mineral isselite, Cu$_6$(SO$_4$)(OH)$_{10}$(H$_2$O)$_4$·H$_2$O, has been discovered in the Lagoscuro mine, Monte Ramazzo mining complex, Genoa, Eastern Liguria, Italy. It occurs as sprays of blue acicular crystals, up to 0.1 mm long, associated with brochantite and posnjakite. Streak is light blue and the lustre is vitreous. Isselite is brittle, with irregular fracture and good cleavage on {001} and {100}. Measured density is 3.00(2) g/cm$^3$. Isselite is optically biaxial (−), with $\alpha = 1.599(2)$, $\beta = 1.633(2)$ and $\gamma = 1.647(2)$ (determined in white light). The measured 2V is 63.6(5)°. Dispersion is moderate, with $r > v$. The optical orientation is $X = b$, $Y = c$ and $Z = a$. Isselite is pleochroic, with $X =$ light blue, $Y =$ blue, $Z =$ blue; $X < Z < Y$. Electron microprobe analyses give (wt.%): SO$_3$ 11.45(21), MgO 0.31(7), CoO 1.07(14), NiO 9.41(90), CuO 51.29(126), ZnO 1.10(20), H$_2$O$_{total}$ 24.21, total 98.84. The empirical formula of isselite, based on $\Sigma$(Mg,Co,Ni,Cu,Zn) = 6 atoms per formula unit, is Cu$_{8.80}$Ni$_{0.94}$Co$_{0.11}$Zn$_{1.03}$Mg$_{0.06}$Se$_{0.06}$Si$_{0.00}$O$_{4.19}$(OH)$_{10}$.5H$_2$O. Isselite is orthorhombic, space group Pnnm, with unit-cell parameters $a = 6.8070(14)$, $b = 5.8970(12)$, $c = 20.653(4)$ Å, $V = 829.0(3)$ Å$^3$ and $Z = 2$. The crystal structure of isselite was refined from single-crystal X-ray diffraction data to $R_1 = 0.067$ on the basis of 2964 reflections with $F_0 > 4\sigma(F_0)$. It shows a layered structure formed by zig-zag [001] layers of Cu-centred polyhedra. Sulfate groups occur in the interlayer along with one H$_2$O group. Isselite is chemically related to redgillite and montetrisaite.

Keywords: isselite, new mineral species, sulfate, copper, crystal structure, Monte Ramazzo mining complex, Eastern Liguria, Italy

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Introduction

The ore deposits of Eastern Liguria, Northern Apennines, Italy, are well-known among mineralogists for the occurrence of several rare species from the Mn ore deposits hosted in middle Jurassic metacherts of the Graveglia Valley, Genoa Province (Cabella et al., 1998; Bindi et al., 2013; Biagioni et al., 2019a) and the Cerchiara Mine, La Spezia Province (Kampf et al., 2013; Kolitsch et al., 2018). In addition, Cu–Fe–Ni–Co sulfide ore deposits are also hosted in ophiolithic rocks of the Northern Apennines and the Sestri–Voltaggio Zone, where several types of Volcanic Massive Sulfide (VMS) deposits occur in mafic–ultramafic rocks at different stratigraphic positions within the ophiolitic sequences (Ferrario and Garuti, 1980; Zaccarini and Garuti, 2008; Schwarzenbach et al., 2012). Among them, stockwork-vein and seafloor stratiform orebodies are associated with serpentinitised mantle peridotites and serpentinite breccias (e.g. Ferrario and Garuti, 1980), like in the Monte Ramazzo–Lagoscuro area, where a pyrrhotite-dominated mineralisation had been actively exploited since the beginning of the 19th Century (Rolandi, 1974; Pipino, 1977). The primary mineralisation underwent subsequent fluid–rock interaction, hydrothermal mobilisation, and multi-stage alteration processes which led, on the one hand, to sulfide reconcentration and recrystallisation in tectonic structures, on the other hand to metal reworking and the formation of secondary phases, such as (Ni,Co)-bearing oxy-hydroxides (asbolane and heterogenite), carbonates (kolwezite, Co-rich malachite and spherochalcostite) and silicates (pecorite). This peculiar mineral assemblage occurring in the Monte Ramazzo–Lagoscuro ore deposit is quite different from other hydrothermal sulfide mineralisation described so far in ophiolites from the Eastern Liguria, where (Ni,Co)-enrichment occurs mostly in pyrite and/or accessory minerals like millerite, siegenite and pentlandite (e.g. Cortesogno et al., 1977; Schwarzenbach et al., 2012; Moroni et al., 2019).

During the examination of secondary minerals from the Monte Ramazzo mining complex, blue acicular crystals from the Lagoscuro mine were encountered. Crystallographic studies and chemical analyses showed this phase to be a new mineral species, which we describe herein and name isselite. The mineral and its name have been approved by the International Mineralogical Society of Great Britain and Ireland 2020. This is an Open Access article, distributed under the terms of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/4.0/), which permits unrestricted re-use, distribution, and reproduction in any medium, provided the original work is properly cited.

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Occurrence and physical properties

Isselite occurs as a secondary phase in the Fe–Ni–Co sulfide mineralisation formerly exploited at the Lagoscuro mine (44°28′35″N, 8°51′35″E), Ceranesi, Genoa Province, Liguria, Italy. This mine, which belongs to the Monte Ramazzo mining complex, operated from 1815 to 1825, mainly for magnesium sulfate (Pippino, 1977). The Co-rich pyrrhotite + pentlandite + sphalerite sulfide ore, hosted within serpentine and serpentinite breccia in contact with basaltic rocks belonging to the Figogna Unit in the Ligurian Alps (Galli, 1954 and 1963; Capponi and Crispini, 2008), underwent multi-stage alteration processes and hydrothermal mobilisation, which developed a mineral assemblage formed by violarite + valleriite + andradite ± magnetite, along with other Ni–Co secondary minerals (e.g. pectarite, heterogenite and asbolane) and hydrated Mg–Cu(–Ni) carbonates and sulfates such as malachite, brochantite, langite, posnjakite and hydromagnesite. The transformation of pentlandite to violarite in the sulfide ore seems to constrain the first stage of hydrothermal alteration to $T < 210°C$ under strongly acidic to neutral (i.e. $1 < pH < 6$) and reducing (i.e. log$_{10}$($\delta^{13}$C) $< -35$) conditions (Tenaillleau et al., 2006; Xia et al., 2009).

Isselite was identified in only a few specimens as sprays of blue acicular crystals, striated parallel to [100] and tabular on [001], up to 0.1 mm long (Fig. 1). Observed forms are {001}, {010}, {103} and {105}. The streak is light blue. Isselite is vitreous and transparent. The mineral is brittle, with an irregular fracture and good cleavage on {001} and {100}. Hardness was not measured, owing to the small crystal size. The density measured by sink-float in methylene iodine $= 3.00(2)$ g/cm$^3$, compared with a density of 2.946 g/cm$^3$, calculated on the basis of the empirical formula and the measured density. The density of H$_2$O by direct measurement; consequently, the H$_2$O content was inferred from the crystal structure analysis. Its presence is confirmed by Raman spectroscopy (see below).

**Table 1.** Electron microprobe analysis of isselite (average of six spot analyses – in wt.%).

| Oxide | Mean | Range | S.D. |
|-------|------|-------|------|
| SO$_4$ | 11.45 | 11.30–11.73 | 0.21 |
| MgO  | 0.31  | 0.20–0.40   | 0.07 |
| CoO  | 1.07  | 0.89–1.22   | 0.14 |
| NiO  | 9.41  | 8.63–11.01  | 0.90 |
| CuO  | 51.29 | 49.03–52.55 | 1.26 |
| ZnO  | 1.10  | 0.86–1.42   | 0.20 |
| H$_2$O$_{calc}$ | 24.21 |
| Total | 98.84 | | |

S.D. – standard deviation

**Chemical and spectroscopic analyses**

Preliminary energy-dispersive spectroscopy (EDS) chemical analyses showed that isselite contains Cu, Ni, Co and S as the only elements with $Z > 8$. Quantitative chemical analyses were performed using a CAMECA SX50 electron microprobe (Istituto di Geologia Ambientale e Geoingegneria, CNR, Rome) operating in wave-length dispersive mode. Operating conditions were: accelerating voltage 15 kV, beam current 15 nA, and beam diameter 5 μm. Standards (element, emission line) were: periclase (MgKα), baryte (SKα), synthetic Co (CoKα), synthetic Ni (NiKα), synthetic Cu (CuKα) and synthetic Zn (ZnKα). Iron and Pb were sought but found to be below detection limits. The small amount of available material precluded the determination of H$_2$O by direct measurement; consequently, the H$_2$O content was inferred from the crystal structure analysis. Its presence is confirmed by Raman spectroscopy (see below).
The electron microprobe analysis results are given in Table 1. The empirical formula of isselite, based on $\Sigma (Mg, Co, Ni, Cu, Zn) = 6$ atoms per formula unit, is $(Cu_{4.80}Ni_{0.94}Co_{0.11}Zn_{0.10}Mg_{0.06})\Sigma 6.00 (S_{1.06}O_{4.19})(OH)_{10} \cdot 5H_2O$. The ideal formula of isselite is $Cu_6(SO_4)\,(OH)_{10} \cdot 5H_2O$, which requires $SO_3 10.86$, $CuO 64.71$, $H_2O 24.43$, total 100.00.

Micro-Raman spectra were obtained on an unpolished sample of isselite in nearly back-scattered geometry with a Jobin-Yvon Horiba XploRA Plus apparatus, equipped with a motorised $x$–$y$ stage and an Olympus BX41 microscope with a 10× objective (Dipartimento di Scienze della Terra, Università di Pisa). The 532 nm line of a solid-state laser was used. The minimum lateral and depth resolution was set to a few $\mu m$. The system was calibrated using the 520.6 cm$^{-1}$ Raman band of silicon before each experimental session. Spectra were collected through multiple acquisitions with single counting times of 60 s. Back-scattered radiation was analysed with a 1200 gr/mm grating monochromator. The Raman spectrum of isselite is shown in Fig. 2.

The strongest band occurs at 984 cm$^{-1}$ and can be related to the symmetrical stretching $\nu_1$ of the SO$_4$ group. The bands at 386, 440 and 495 cm$^{-1}$ can be interpreted as due to the symmetrical bending $\nu_2$ of the SO$_4$ group, whereas the weak band at 630 cm$^{-1}$ could be related to the antisymmetrical bending $\nu_4$. Finally, the band at 250 cm$^{-1}$ may be attributed to lattice modes. The broad band at 3484 cm$^{-1}$ can be attributed to the O–H stretching modes. No evident bending of H–O–H bonds, in the typical range between 1595–1700 cm$^{-1}$ (e.g. Kolesov).

![Raman spectrum of isselite in the range 200–1200 cm$^{-1}$ (a) and 2700–4000 cm$^{-1}$ (b).](image)

### Table 2. X-ray powder diffraction ($d$ in Å) data for isselite.*

| $I_{obs}$ | $d_{obs}$ | $I_{calc}$ | $d_{calc}$ | $h$ | $k$ | $l$ |
|-----------|-----------|-----------|-----------|-----|-----|-----|
| s         | 10.3      | 92        | 10.3      | 0   | 0   | 2   |
| m         | 6.4       | 29        | 6.46      | 1   | 0   | 1   |
| mw        | 5.67      | 25        | 5.67      | 0   | 1   | 1   |
| w         | 5.14      | 11        | 5.12      | 0   | 1   | 2   |
| vs        | 4.84      | 100       | 4.84      | 1   | 0   | 3   |
| vw        | 4.47      | 9         | 4.48      | 0   | 1   | 3   |
| vv        | 4.32      | 4         | 4.36      | 1   | 1   | 1   |
| w         | 4.14      | 1         | 4.09      | 1   | 1   | 2   |
| w         | 3.742     | 7         | 3.741     | 1   | 1   | 3   |
| vw        | 3.462     | 4         | 3.442     | 0   | 0   | 6   |
| mw        | 3.400     | 8, 11     | 3.404, 3.383 | 2 | 0 | 0 | 0 | 1 | 5 |
| vw        | 3.237     | 4         | 3.232     | 2   | 0   | 2   |
| vv        | 3.035     | 4         | 3.029     | 1   | 1   | 5   |
| w         | 2.919     | 7         | 2.918     | 2   | 1   | 1   |
| w         | 2.838     | 10        | 2.842     | 2   | 0   | 4   |
| s         | 2.708     | 4, 16, 22, 14, 12 | 2.710, 2.710, 2.708, 2.706, 2.683 | 0 | 2 | 3 | 2 | 1 | 3 | 1 | 0 | 7 | 1 | 2 | 0 | 1 | 2 | 1 |
| vw        | 2.628     | 3         | 2.638     | 0   | 1   | 7   |
| w         | 2.589     | 10        | 2.582     | 0   | 0   | 8   |
| vw        | 2.516     | 3         | 2.518     | 1   | 2   | 3   |
| w         | 2.406     | 6         | 2.420     | 2   | 0   | 6   |
| m         | 2.225     | 5, 13     | 2.229, 2.216 | 2 | 2 | 0 | 2 | 2 | 1 |
| mw        | 2.179     | 11        | 2.178     | 2   | 2   | 2   |
| mw        | 2.129     | 7         | 2.120     | 2   | 2   | 3   |
| mw        | 2.065     | 10        | 2.065     | 0   | 0   | 10  |
| w         | 2.044     | 2, 1      | 2.046, 2.040 | 2 | 2 | 4 | 1 | 1 | 9 |
| w         | 1.943     | 2         | 1.931     | 0   | 3   | 2   |
| vv        | 1.866     | 2, 1      | 1.871, 1.868 | 2 | 2 | 6 | 1 | 2 | 8 |
| mw        | 1.796     | 2, 2, 5, 6, 6 | 1.810, 1.799, 1.798, 1.791, 1.778 | 1 | 0 | 11 | 3 | 0 | 7 | 3 | 2 | 0 | 3 | 2 | 1 | 2 | 2 | 7 |
| mw        | 1.701     | 6         | 1.698     | 4   | 0   | 0   |
|            | 3         | 1.698     | 3   | 2   | 4   |
|            | 6         | 1.687     | 2   | 2   | 8   |

*Notes: the $d_{calc}$ values were calculated on the basis of the unit cell refined by using single-crystal data. Intensities were calculated on the basis of the structural model reported in Table 4. Observed intensities were visually estimated: vs = very strong; s = strong; m = medium; mw = medium–weak; w = weak; vw = very weak. Only reflections with $I_{calc} > 5$ are listed, if not observed. The strongest reflections are shown in bold.
Number of least-squares parameters 140

Gof 1.013

= 830.4(2) Å³ and

V

and Redfern, 1997), are

2006), was observed. The interpretation of the spectral bands is in agreement with Frost et al. (2004).

Crystallography

The powder X-ray diffraction pattern of isselite was obtained using a 114.6 mm diameter Gandolfi camera, with Ni-filtered CuKα radiation. The observed powder X-ray diffraction pattern is compared with the calculated one (obtained using the software PowderCell; Kraus and Nolze, 1996) in Table 2. Unit-cell parameters, refined from the powder data on the basis of 22 unequivocally indexed reflections through the software UnitCell (Holland and Redfern, 1997), are a = 6.789(1), b = 5.923(1), c = 20.651(3) Å, V = 830.4(2) Å³ and Z = 2.

The single-crystal X-ray diffraction study was carried out at the XRD1 beamline, ELETTRA synchrotron facility (Lausi et al., 2015). A monochromatic wavelength of 0.59040 Å was used on a 50 μm × 50 μm beam size, using a Dectris Pilatus 2M hybrid pixel area detector at a distance of 85 mm. A total of 500 frames was collected using φ scan mode in Δφ = 0.5° slices, with an exposure time of 1 s per frame. The diffraction data, collected at room temperature, were indexed, integrated, scaled, and corrected for the Lorentz-polarisation factor using the software XDS (Kabsch, 2010). The refined unit-cell parameters are a = 6.8070(14), b = 5.8970(12), c = 20.653(4) Å and V = 829.0(3) Å³. The a:b:c ratio calculated from unit-cell parameters is 1.1543:1:3.5023.

The statistical tests on the distribution of |E| values (|E² − 1| = 0,703) suggest the acentric nature of isselite. The examination of the systematic absences indicated the possible space groups P2₁mm and Pmm2₁. Only the choice of this latter space group allowed the solution of the crystal structure through direct methods using Shelxs-97 (Sheldrick, 1997). After having located the heavier elements, the structure was completed through successive difference-Fourier maps; owing to the quality of available material, H atoms were not located. After several cycles of anisotropic refinement, performed using Shelx-2018 (Sheldrick, 2015) and using neutral scattering curves taken from the International Tables for Crystallography (Wilson, 1992), the refinement converged to R₁ = 0.0669 for 2964 unique reflections with F > 4σ(Fo) and 140 refined parameters. The occurrence of high electron density residuals (up to 6.19 e/Å³) is related to the less-than-ideal quality of the available crystals of isselite. An attenuation of the residuals can be obtained by truncating the intensity data to low angular values. For instance, the truncation of the dataset to 30° in 2θ results in a highest residual |E| of 2.3 e/Å³. However, the ratio between observed reflections and |E| ≤ 1 e/Å³ is related to the less-than-ideal quality of the available crystals of isselite. An attenuation of the residuals can be obtained by truncating the intensity data to low angular values. For instance, the truncation of the dataset to 30° in 2θ results in a highest residual |E| of 2.3 e/Å³. However, the ratio between observed reflections and |E| ≤ 1 e/Å³ is related to the less-than-ideal quality of the available crystals of isselite.

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displacement parameters are reported in Table 4, whereas Table 5 gives selected bond distances. Bond-valence calculations, shown in Table 6, were performed using the bond parameters of Brese and O’Keeffe (1991). The crystallographic information file has been deposited with the Principal Editor of Mineralogical Magazine and is available as Supplementary material (see below).

**Crystal structure description**

**General organisation**

The crystal structure of isselite (Fig. 3) includes five independent Cu sites, one S site, and fourteen O positions. It can be described as formed by \{001\} zig-zag layers of CuΦ\textsubscript{4+6} polyhedra, where Φ = (OH or H\textsubscript{2}O). Sulfate groups occur in the interlayer, together with one H\textsubscript{2}O group. No H positions were located from the structure determination; the assignments of OH and H\textsubscript{2}O groups were based on the bond-valence analysis (see Table 6).

**Cation coordination and site occupancies**

In isselite, the Cu sites display different kinds of coordination (Fig. 4). The Cu(2) and Cu(3) sites show the typically distorted (4 + 2) octahedral coordination of Cu\textsuperscript{2+}, related to the Jahn-Teller effect (e.g. Burns and Hawthorne, 1996). The average value of the four shorter distances is 2.013 Å for both sites, somewhat longer than the equatorial bond length of 1.97 Å reported by Eby and Hawthorne (1993). The two apical Cu–O distances have average values of 2.237 and 2.197 Å at the Cu(2) and Cu(3) sites, respectively, shorter than the average value of 2.44 Å reported by Eby and Hawthorne (1993). The smaller than typical octahedral distortions observed for the Cu(2) and Cu(3) sites suggest that minor Ni and Co detected in isselite are located at these two sites. Taking into account the nature of the ligands, Cu(2) and Cu(3) octahedra can be defined both as Cu(OH)\textsubscript{4}(H\textsubscript{2}O)\textsubscript{2} polyhedra. The Cu(1) and Cu(5) sites have a square pyramidal coordination, with four equatorial bonds ranging between 1.941 and 1.965 Å (average value of 1.954 Å); the fifth bond is at a longer distance, i.e. 2.571 Å [Cu(5)–Ow(13)] and 2.623 Å [Cu(1)–Ow(12)]. Taking into account the ligand nature, the cations at the Cu(1) and Cu(5) sites can be related to the Cu(OH)\textsubscript{4}(H\textsubscript{2}O) polyhedra.

A square-planar coordination is shown by the Cu(4) site, having four ligands at an average distance of 1.944 Å, in agreement with the ideal mean value of 1.94 Å for square-planar Cu\textsuperscript{2+} (Eby and Hawthorne, 1993). Taking into account the two very long distances Cu(4)–Ow(12) and Cu(4)–Ow(13), ≈2.9 Å, a very distorted octahedron Cu(OH)\textsubscript{2}H\textsubscript{2}O can be identified, instead of a square-planar group Cu(OH)\textsubscript{2}.

Bond-valence sums (BVS) at the Cu sites range between 1.98 and 2.13 valence units (vu), in agreement with the occurrence of Cu in the divalent state. The higher values occur at the Cu(2) and Cu(3) sites and can be related to the admixture of minor Ni\textsuperscript{2+} and very small amounts of Co\textsuperscript{2+}, Zn\textsuperscript{2+} and Mg\textsuperscript{2+}.

The SO\textsubscript{4} group is hosted in the interlayer and is bonded to the \{001\} Cu layers through hydrogen bonds, as revealed by the occurrence of several underbonded O in the bond-valence calculation (Table 6) and the occurrence of short O⋯O distances (Table 7). The BVS at the S site is 6.48 vu, considerably greater than expected for S\textsuperscript{6+}. In this regard, it should be noted that the position of O(11) seems to be affected by disorder, as indicated by a U\textsubscript{eq} value larger than those of other O atoms belonging to the SO\textsubscript{4} group.

**Hydrogen bonds**

The short O⋯O distances are given in Table 7, confirming the importance of H bonds in the crystal structure of isselite, in agreement with the undersaturation of all O atoms. Taking into account the results of BVS given in Table 6, three distinct groups of O atoms can be found: (1) O atoms having BVS close to ~1.6 vu; (2) O atoms with BVS of ~1.2–1.3 vu; and (3) O atoms showing BVS of ~0.2 vu. These three different O groups correspond to O\textsuperscript{2−}, (OH)\textsuperscript{−} and H\textsubscript{2}O groups, respectively.

Oxygen atoms belonging to the isolated SO\textsubscript{4} groups, that is O(9), O(10) and O(11), are acceptors of H bonds. Oxygen atom

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**Table 6. Bond-valence sums (BVS – in valence units) for isselite*.**

|          | Cu(1) | Cu(2) | Cu(3) | Cu(4) | Cu(5) | S | Σcations | Theoretical |
|----------|-------|-------|-------|-------|-------|---|----------|-------------|
| OH(1)    | 0.23  |       |       | 2×0.50|       | 1.23|          | 2.00        |
| OH(2)    | 0.22  |       |       | 2×0.51|       | 1.24|          | 2.00        |
| OH(3)    | 0.39+2| 0.46  | 0.46+2|       | 0.92  | 1.31|          | 2.00        |
| OH(4)    | 0.43+2| 0.49+2|       |       |       | 0.92|          | 2.00        |
| OH(5)    | 0.47+2| 0.39+2| 0.48  |       | 1.34  | 1.34|          | 2.00        |
| OH(6)    | 0.48+2| 0.43+2| 0.91  |       | 1.64+2| 1.64|          | 2.00        |
| Ow(7)    | 0.26  |       |       |       | 0.26  | 1.73|          | 2.00        |
| Ow(8)    | 0.23  |       |       |       | 0.23  | 1.73|          | 2.00        |
| O(9)     |       |       |       |       | 1.59  | 1.59|          | 2.00        |
| O(10)    |       |       |       |       | 1.61  | 1.61|          | 2.00        |
| O(11)    |       |       |       |       | 1.64+2| 1.64|          | 2.00        |
| Ow(12)   | 0.08  |       | 2×0.04| 0.91  | 0.17  | 0.51|          | 1.34        |
| Ow(13)   |       |       | 2×0.04| 0.16  |       |       |          | 1.34        |
| Ow(14)   |       |       |       |       |       |     |          | 1.34        |

Σcations: 1.98 2.09 2.13 2.03 1.99 6.48
Theoretical: 2.00 2.00 2.00 2.00 2.00 6.00

*Left and right superscripts indicate the number of equivalent bonds involving anions and cations, respectively.
hosted at O(9) is an acceptor of two H bonds from two symmetry-related (OH)$^-$ groups hosted at OH(5); the oxygen atom at O(10) is an acceptor of H bonds from two symmetry related (OH)$^-$ groups hosted at OH(6) and from an H$_2$O group occurring at the Ow(14) site. Finally, O(11) is involved in a more complex H-bond system. Indeed, O(11) is an acceptor of H bonds from OH(4) and it is at H-bond distances with Ow(7), Ow(8), and Ow(14). In addition, Ow(14) is an acceptor of H bonds from two symmetry-related OH(3) groups, whereas a still more complex situation involves the H$_2$O groups hosted at Ow(7) and Ow(8). These two H$_2$O groups are bonded to the Cu atoms hosted at Cu(3) and Cu(2) sites, respectively. Both are at short O⋯O distances with O(11). In addition, the distance Ow(7)⋯Ow(8), 2.85 Å, suggests another H-bond contact. Owing to the lack of knowledge about the H positions and the occurrence of different possible configurations, the actual H-bond system involving these atoms has to be considered only speculative and it will not be detailed here. As a matter of fact, the possibility of different configurations involving the oxygen atom hosted at O(11) could be the reason for its relatively high $U_{eq}$ value. Its position could be an average position between different H-bond configurations. Moreover, this uncertainty could affect the BVS of S, as discussed briefly above.

Oxygen atoms hosted at OH(4) and OH(6) are both donor (in the H bonds described above) and acceptor from H$_2$O groups hosted at Ow(12) and Ow(13), respectively. It is worth noting that Ow(12) and Ow(13) act as donor to two symmetry-related OH(4) and OH(6), respectively, whereas they are acceptors of H bonds from OH(2) and OH(1), respectively.

**Discussion**

**Isselite and relations with other Cu sulfates**

Fifteen different mineral species are currently known in the system CuO–SO$_3$–H$_2$O (Table 8). From a chemical point of view, the most simple species are those having the chemical formula Cu(SO$_4$)$_n$·nH$_2$O (0 < n < 7): chalcocyanite (n = 0), poitevinite (n = 1), bonattite (n = 3), chalcanthite (n = 5) and boothite (n = 7). Their crystal structures are reviewed by Eby and Hawthorne (1993). Chalcocyanite typically occurs in fumarolic environments. Indeed, it was first described from Vesuvius, Italy, by Scacchi (1873), along with another anhydrous copper oxy-sulfate, dolerophanite, Cu$_2$O(SO$_4$). The other hydrated copper sulfates listed above are usually related to the weathering of Cu ores, although in some case they can be found also as sublimates in fumaroles (e.g. Balassone et al., 2013).

The remaining species, commonly associated with weathered Cu ores (e.g. Zittlau et al., 2013), are represented by the two basic copper sulfates antlerite and brochantite and seven hydrated basic copper sulfates. Isselite belongs to this latter group of copper sulfates, showing the presence of (OH)$^-$ and H$_2$O groups. In particular, it is chemically related to redgillite, Cu$_6$(SO$_4$)$_5$H$_2$O (Table 7).

### Table 7. O⋯O distances (in Å) and corresponding bond strengths (in valence units, vu).

| O⋯O     | d (Å)   | vu*  |
|---------|---------|------|
| OH(1)⋯Ow(13) | 2.805(15) | 0.18 |
| OH(2)⋯Ow(12) | 2.813(15) | 0.18 |
| OH(3)⋯Ow(14) | 2.733(11) | 0.21 |
| OH(4)⋯O(11)  | 2.825(16) | 0.17 |
| Ow(12)⋯OH(4)  | 2.679(12) | 0.24 |
| OH(5)⋯O(9)    | 2.650(11) | 0.25 |
| OH(6)⋯O(10)  | 3.094(14) | 0.11 |
| Ow(13)⋯OH(6)  | 2.714(12) | 0.22 |
| Ow(7)⋯Ow(8)   | 2.85(2)   | 0.17 |
| Ow(7)⋯O(11)   | 3.04(2)   | 0.12 |
| Ow(8)⋯O(11)   | 2.62(2)   | 0.18 |
| Ow(14)⋯O(10)  | 2.75(2)   | 0.20 |
| Ow(14)⋯O(11)  | 3.07(2)   | 0.12 |

*Calculated using the relationships of Ferraris and Ivaldi (1988).
Table 8. Natural Cu sulfates in the system CuO–SO₃–H₂O.

| Mineral          | Chemical formula                      | a (Å) | b (Å) | c (Å) | α (°) | β (°) | γ (°) | Space group | Reference             |
|------------------|-------------------------------------|-------|-------|-------|-------|-------|-------|-------------|------------------------|
| Antlerite        | Cu₃(SO₄)(OH)₄                        | 8.24  | 6.04  | 11.99 | 90    | 90    | 90    | Pnma        | Hawthorne et al. (1989) |
| Bonattite        | Cu₂(SO₄)₃(H₂O)₃                      | 5.59  | 13.03 | 7.34  | 90    | 97.1  | 90    | Cc          | Zahrobsky and Baur (1966) |
| Boothite         | Cu₆(SO₄)(H₂O)₆·H₂O                   | 14.19 | 6.54  | 10.82 | 90    | 106.0 | 90    | P₂₁/c       | Leverett et al. (2004)  |
| Brochanite       | Cu₆(SO₄)(OH)₁₀                      | 13.14 | 9.86² | 6.02² | 90    | 103.2¹| 90    | P₂₁/a²      | Merlino et al. (2003)   |
|                  |                                     | 12.78 | 9.87² | 6.03² | 90.2³ | 90    | 90²   | P₂₁/n²      |                        |
| Chalcanthite     | Cu₆(SO₄)(H₂O)₄·H₂O                   | 6.14  | 10.74 | 5.99  | 82.3  | 104.7 | 102.7 | P1          | Bacon and Titterton (1975) |
| Chalcoyanite     | Cu₆(SO₄)                           | 8.41  | 6.71  | 4.83  | 90    | 90    | 90    | Pnma        | Wildner and Giester (1988) |
| Dolerophanite    | Cu₆O(SO₄)                          | 9.37  | 6.32  | 7.64  | 90    | 122.3 | 90    | C2/m        | Effenerberger (1985)     |
| Isselite         | Cu₆(SO₄)(OH)₁₂(H₂O)₄·H₂O            | 6.81  | 5.90  | 20.65 | 90    | 90    | 90    | Pmn2₁       | This work              |
| Kobyashevite     | Cu₆(SO₄)(OH)₁₂(H₂O)₄               | 6.07  | 11.06 | 5.51  | 102.9 | 92.3  | 92.6  | P1          | Pekov et al. (2013)      |
| Langite          | Cu₆(SO₄)(OH)₁₂(H₂O)₄·H₂O            | 7.14  | 6.03  | 11.22 | 90    | 90    | 90    | Pc          | Gentsch and Weber (1984) |
| Montetrisaite    | Cu₆(SO₄)(OH)₁₀₂H₂O                 | 2.99  | 16.97 | 14.81 | 90    | 90    | 90    | Cmc₂₁       | Orlandi and Bonaccorsi (2009) |
| Poitevinite      | Cu₅(SO₄)(H₂O)                    | 5.12  | 5.16  | 7.54  | 107.1 | 107.4 | 92.7  | P1          | Giester et al. (1994)    |
| Posnjakite       | Cu₅(SO₄)(OH)₆(H₂O)               | 10.58 | 6.34  | 7.86  | 90    | 118.0 | 90    | Pa          | Mellini and Merlino (1979) |
| Redgillite       | Cu₅(SO₄)(OH)₁₂(H₂O)               | 3.16  | 10.44 | 19.44 | 90    | 90.1  | 90    | P₂₁/c       | Pluth et al. (2005)      |
| Wroewolfeite     | Cu₅(SO₄)(OH)₁₂(H₂O)·2H₂O          | 6.04  | 5.65  | 14.34 | 90    | 93.4  | 90    | Pc          | Hawthorne and Groat (1985) |

¹MDO₁; ²MDO₂.

Fig. 5. Comparison between the crystal structure of isselite (a) and those of montetrisaite (b) and redgillite (c). The colour scheme is the same as in Fig. 3.

(OH)₁₀(H₂O) (Pluth et al., 2005) and montetrisaite, Cu₆(SO₄) (OH)₁₂(H₂O)₂ (Orlandi and Bonaccorsi, 2009). However, notwithstanding the chemical similarities, the crystal structure of isselite is different from those shown by redgillite and montetrisaite (Fig. 5). In addition, isselite could be the Cu analogue of guarinoite, Zn₆(SO₄)₁₂(OH)₁₀·5H₂O (Sarp, 1993). However, Mills et al. (2019) noted that guarinoite might have been misidentified in its original description and is more likely to be Na(Zn, Co)₆(SO₄)(OH)₂Cl·5-6H₂O and equivalent to Co-rich gordaite-2H.

Nickel partitioning in isselite

After the first identification of isselite on the type specimen from the Lagoscuoro mine, this mineral was identified, through powder X-ray diffraction, also on a sample from the Monte Ramazzo mine, as thin flattened acicular crystals associated with brochantite. Only EDS chemical data are available for this new occurrence; however, these data clearly indicated the occurrence of Ni, whereas Co and other elements are below the detection...
limit. The Ni/(Ni + Cu) atomic ratio is close to 0.19, similar to the value observed in the type material, where the Ni/(Mg + Co + Ni + Cu + Zn) atomic ratio is 0.16. In both cases, the ideal composition is close to NiCu6(SO4)(OH)10·5H2O.

The similar scattering factors of Ni (Z = 28) and Cu (Z = 29) precluded the reliable description of the distribution of Ni and Cu atoms among different cation sites. Nickel and Cu are ordered in some minerals. Gillarde and the related mineral paratacamite-(Ni), both ideally Cu2Ni(OH)2Cl2, are atacamite-group minerals where Ni is partitioned in the octahedrally coordinated sites not showing the Jahn–Teller effect, whereas Cu2+ is hosted at the distorted octahedrally coordinated sites (Clissold et al., 2007; Sciberras et al., 2013). Similarly, Ni2+ is preferentially partitioned in the less distorted octahedrally-coordinated Me2 site of the crystal structure of glaukosphaerite, (Cu,Ni)2(CO3)(OH)2, whereas the Me1 site shows the typical 4 + 2 distorted octahedral coordination of Cu2+ (Perchiazzi and Merlino, 2006). Another example is represented by hilukselite. This mineral, having the ideal formula NiCu4(AsO4)2(AsO3)OH2(H2O)9, is a member of the lindakerite supergroup and Ni is hosted at a mixed (Ni,Co) site not showing the typical distortion of Cu2+-centred polyhedra (Plasılı et al., 2014).

In isseelite, the Cu(2) and Cu(3) sites have octahedral coordinations, showing the typical (4 + 2) distortion due to the Jahn–Teller effect for Cu2+. As discussed above, these sites have slightly longer equatorial bonds and shorter apical distances with respect to those reported by Eby and Hawthorne (1993) for a typical Cu2+-centred octahedron. This could suggest the substitution of Cu2+ by Ni2+ at these two positions. However, as there is no certainty about the quantification of Cu–Ni site distribution, for classification purposes the Cu(2) and Cu(3) sites could be merged, as occurs in the nomenclature of other minerals (e.g. M1 + M2 + M3 in amphibole; Hawthorne et al., 2012). In accord with the IMA–CNMNC guidelines (Bosi et al., 2019), the end-member formula of isseelite can be considered Ni-free. However, the actual role of Ni in stabilising this phase deserves further study.

Conclusion

Isselite is a new secondary Cu mineral showing a novel crystal structure and a complex hydrogen-bond system. Its Ni content, observed at both of its occurrences, opens the question about the role of this element in favouring the crystallisation of this new mineral species. It is likely that isseelite could be more common than thought as an alteration product of Cu–Ni ores.

Along with ramazzite (Kampf et al., 2018), isseelite is the second new mineral discovered in the assemblages from the Monte Ramazzo mining complex, stressing the necessity for further investigation of this locality. In particular, a deep understanding of the geochemical relations between the Cu–Fe–Ni–Co primary mineralisation and their secondary alteration products would shed light on the possible role of hydrothermal fluids in Ni vs. Co selective mobilisation and enrichment as well as the degree of hydrothermal alteration of the Monte-Ramazzo–Lagoscuro ore deposit.

Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1180/mgm.2020.50.

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Hawthorne F.C. and Groat L.A. (1985) The crystal structure of roevoeileite, a mineral with $[\text{Cu}(\text{OH})(\text{SO}_4)(\text{H}_2\text{O})]$ sheets. *American Mineralogist*, **70**, 1050–1055.

Hawthorne F.C., Groat L.A., and Eby R.K. (1989) Antlerite, $\text{Cu}_3\text{SO}_4(\text{OH})_4$, a hetroepolyhedral wallpaper structure. *The Canadian Mineralogist*, **27**, 205–209.

Hawthorne F.C., Oberti R., Harlow G.E., Maresh W.V., Martin R.F., Schumacher J.C. and Welch M.D. (2012) Nomenclature of the amphibole supergroup. *American Mineralogist*, **97**, 2031–2048.

Holland T.J.B. and Redfern S.A.T. (1997) Unit cell refinement from powder diffraction data: the use of regression diagnostics. *Mineralogical Magazine*, **61**, 65–77.

Issel A. (1892) *Liguria Geologica e Preistorica*. Donath Editore, Genova, Italy.

Kabsch W. (2010) Integration, scaling, space-group assignment and post-refinement. *Acta Crystallographica*, **D66**, 125–132.

Kampf A.R., Roberts A.C., Venance K.E., Carbone C., Belmonte D., Dunning G.E. and Walstrom R.E. (2013) Cerchiaraite-(Fe) and cerchiaraite-(Al), two new barium cyclosilicate chlorides from Italy and California, USA. *Mineralogical Magazine*, **77**, 69–80.

Kampf A.R., Rossman G.R., Ma C., Belmonte D., Biagioni C., Castellano F. and Chiappino L. (2018) Ramazzozite, $[\text{Mg}(_2\text{Cu})_2(\text{PO}_4)(\text{CO}_3)_2(\text{OH})_2(\text{H}_2\text{O})_2]$, the first mineral with a polyoxometallate cation. *European Journal of Mineralogy*, **30**, 827–834.

Krausk W. and Notze G. (1996) POWDER CELL – a program for the representation and manipulation of crystal structures and calculation of the resulting X-ray powder patterns. *Journal of Applied Crystallography*, **29**, 301–303.

Kolesov B.A. (2006) Raman spectra of single $\text{H}_2\text{O}$ molecules isolated in cavities of crystals. *Journal of Structural Chemistry*, **47**, 21–34.

Kolitsch U., Merlino S., Belmonte D., Carbone C., Cabella R., Lucchetti G. and Mellini M. and Merlino S. (1979) Posnjakite: a new devilline-group mineral from the Vishnevye Mountains, South Urals, Russia. *Mineralogy and Petrology*, **107**, 201–210.

Kobayashi N. and Merlino S. (2006) The malachite-rosasite group: crystal structures of glaukospherite and pokrovskite. *European Journal of Mineralogy*, **18**, 787–792.

Pigino G. (1977) L’antica miniera di Monte Ramazzo presso Genova e i suoi minerali. *Rivista Mineralogica Italiana*, **8**, 61–73.

Plassil J., Sjöka R., Skoda R., Novák M., Kasatkin A.V., Skácha P., Veselovský F., Fejfarová K. and Ondruš P. (2012) Hlušeškite, $(\text{Ni},\text{Co})\text{Cu}_4(\text{AsO}_4)(\text{AsO}_4\text{H}_2\text{O})_2$, a new member of the lindackerite supergroup from Jáchymov, Czech Republic. *Mineralogical Magazine*, **78**, 1341–1353.

Pluth J., Steele I.M., Kampf A.R. and Green D.I. (2005) Redgillette, $\text{Cu}_4(\text{OH})_6(\text{SO}_4)\cdot\text{H}_2\text{O}$, a new mineral from Caldbeck Fells, Cumbria, England: description and crystal structure. *Mineralogical Magazine*, **69**, 973–980.

Rolandi V. (1974) I giacimenti cuprifero di Molini, Monte Ramazzo e Sassello nel Gruppo di Voltri. MSc Thesis (unpublished), University of Milan, Italy, 111 pp.

Sarp H. (1993) Guarinoite $(\text{Zn,Co,Ni})_6(\text{SO}_4)(\text{OH},\text{Cl})_{10}\cdot\text{H}_2\text{O}$ et theresemagnanite $(\text{Co,Zn,Nil})(\text{SO}_4)(\text{OH},\text{Cl})_{10}\cdot\text{H}_2\text{O}$, deux nouveaux minéraux de la mine de Cap Garonne, Var, France. *Archives des Sciences, Genève*, **46**, 37–44.

Scacchi A. (1873) Nuove specie di solfati di rame. Idrociano. *Atti dell’Accademia delle Scienze Fisiche e Matematiche*, **5**, 26–29.

Schwarzenbach E.M., Früh-Green G.L., Bernasconi S.M., Alt I.C., Shanks III W.C., Gagetto L. and Crispinati L. (2012) Sulfur geochemistry of peridotite-hosted hydrothermal systems: comparing the Ligurian ophiolites with oceanic serpentinites. *Geochimica et Cosmochimica Acta*, **91**, 283–305.

Sciberras M.J., Leverett P., Williams P.A., Hibbs D.E., Downes P.J., Welch M.D. and Kampf A.R. (2013) Paratacamite-(Ni), $\text{Cu}_4(\text{Ni,Cu})_4\text{Cl}_2\cdot\text{H}_2\text{O}$, a new mineral from the Curr Boyd Rocks mine, Western Australia. *Australian Journal of Mineralogy*, **17**, 39–44.

Sheildrick G.M. (1997) SHEXL97 and SHEXL97. Program for Crystal Structure Solution and Refinement. University of Göttingen, Göttingen, Germany.

Sheildrick G.M. (2015) Crystal structure refinement with SHEXL. *Acta Crystallographica*, **C71**, 3–8.

Tennilleau C., Pring A., Etschmann B., Brugger J., Gurguric B. and Putnis A. (2006) Transformation of pentlandite to violarite under mild hydrothermal conditions. *American Mineralogist*, **91**, 706–709.

Wildnert M., Gschwend G. and Gierse K.H. (1988) Crystal structure refinements of synthetic chalcocyanite $(\text{Cu}_x\text{S})_2(\text{CuSO}_4)_{(1-x)}$ and zincosite $(\text{Zn}_x\text{S})_2(\text{ZnSO}_4)(1-x)$. *Journal of Mineralogy & Petrology*, **59**, 201–209.

Wilson A.J.C., Ed. (1992) *International Tables for Crystallography*, Volume C: Mathematical, physical and chemical tables. Kluwer Academic, Dordrecht, The Netherlands.

Xia F., Brugger J., Chen G., Ngothai Y., O’Neill B., Putnis A. and Pring A. (2009) Mechanism and kinetics of pseudomorphic mineral replacement reactions: A case study of the replacement of pentlandite by violarite. *Geochimica et Cosmochimica Acta*, **73**, 1945–1969.

Zaccarini F. and Garuti G. (2008) Mineralogy and chemical composition of VMS deposits of northern Apennine ophiolites, Italy: evidence for the influence of country rock type on ore composition. *Mineralogy and Petrology*, **39**, 61–83.

Zahrobsky R. and Baur W.H. (1966) The crystal structure of copper $(II)$ sulfate trihydrate. *American Mineralogist*, **51**, 276–276.

Zittlau A.H., Shi Q., Boerio-Gates J., Woodfield B.F. and Majzlan J. (2013) Thermodynamics of the basic copper sulfates antlerite, posnjakite, and brochantite. *Chemie der Erde*, **73**, 39–50.