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Article

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A contribution to the mineralogy of Sicily, Italy – Kintoreite from the Tripi mine, Peloritani Mountains: occurrence and crystal structure

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Abstract

A new occurrence of kintoreite, ideally PbFe3(PO4)(PO3OH)(OH)6, is described from the Tripi mine, Ali, Peloritani Mountains, northeastern Sicily, Italy. Kintoreite occurs as yellow equant crystals, up to 0.05 mm in size, on quartz, associated with another alunite-supergroup mineral currently under study. The studied grains of kintoreite are chemically zoned, showing the occurrence of two distinct domains. Electron microprobe analyses gave (in wt.%): SO3 5.47(27), P2O5 17.55(14), Al2O3 7.81(35), Fe2O3 23.81(44), PbO 35.11(41), H2Ocalc 9.93, total 99.68 (darker domains) and SO3 6.03(5), P2O5 16.66(23), Al2O3 4.22(2), Fe2O3 27.31(6), PbO 33.78(22), H2Ocalc 10.25, total 98.25 (brighter domains). On the basis of the 14 O atoms per formula unit (apfu) and (P+S)=2 apfu, the darker and brighter domains have chemical formula Pb1.00(Fe3+0.53)Σ2.74[Fe3.64Al0.97Σ4.61O2.74(OH)0.51]Σ6.00[(OH)5.18(H2O)0.82]Σ9.93, respectively. Single-crystal X-ray diffraction was performed on a grain extracted from the same sample. Unit-cell parameters are a = 7.2191(10), c = 16.834(3) Å, V = 759.8(3) Å3 and Z = 3; space group R3m. The crystal structure was refined on the basis of 226 unique reflections with Feo > 4σ(Feo) and 31 least-square parameters to R1 = 0.0415. Kintoreite is isotypic with other alunite-supergroup minerals. Micro-Raman spectroscopy suggests the possible occurrence of H2O groups, supporting the possible protonation of (OH) groups as a charge-balance mechanism in this mineral. Kintoreite may play an environmental role in the Ali area, where previous authors detected high concentrations of potentially toxic elements in soils.

Keywords: kintoreite, phosphate, alunite supergroup, crystal structure, hydrogen bonds, Peloritani Mountains, Sicily, Italy

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Introduction

Several polymetallic ore deposits were exploited in the Peloritani Mountains, northeastern Sicily, Italy, where small Pb–Zn–Fe–As–Sb–Cu–Ag–W–(Au) ore bodies are hosted within tectonic slices affected by both Variscan and Alpine tectono-metamorphic events. Previous authors focused their attention mainly on primary ore minerals (e.g. Saccà et al., 2015, and references therein), whereas little is known about secondary phases occurring in these mineralisations. Some oxides (cervantite, goethite and stibiconite), carbonates (azurite, hydrozincite, malachite and pyrite), hydroxides (annabergite, erythrite, scorodite and symplesite) and arsenates (annerbergite, erythrite, scorodite and symplesite) have been reported (Seguenza, 1856; La Valle, 1898, 1899; De Vivo et al., 1993) pointed out the presence of anomalies of As, Hg, Sb, Zn and Pb in stream sediments from the Peloritani Mountains. Cosenza et al. (2015) investigated the soil geochemistry in this area, reporting high contents of PTE such as As, Zn, Sb and Pb. One of the two anomalous areas found in this region is located between Fiumedinisi, Budali and Ali, and Pb isotopes indicate a geogenic contribution to this contamination, related to the weathering of ore deposits and mine wastes in the area studied.

In the framework of a survey of the mineralogy of the Peloritani Mountains, a sample of galena-bearing quartz vein was sampled from the adit of one of the tunnels belonging to the abandoned Tripi mine, Ali, Messina Province. The observation of this sample in this area, reporting high contents of PTE such as As, Zn, Sb and Pb. One of the two anomalous areas found in this region is located between Fiumedinisi, Budali and Ali, and Pb isotopes indicate a geogenic contribution to this contamination, related to the weathering of ore deposits and mine wastes in the area studied.

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This paper is part of a thematic set that honours the contributions of Peter Williams

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uncommon phase first described by Pring et al. (1995) from Broken Hill, New South Wales, Australia.

There are several reasons for characterising this new occurrence of kintoreite. From an environmental perspective, this phase, whose origin is related to the weathering of primary ores, could be a potential host for the Pb anomaly observed in soils in the Ali area (Cosenza et al., 2015), in agreement with previous studies showing the presence of nanoparticles of kintoreite in soils (e.g. Schindler and Hochella, 2017). Moreover, the finding of kintoreite from the Peloritani Mountains is the third Italian occurrence of this mineral, following the identification reported by Albertini (2014) from the Monte Falò mine, Piedmont, and by Guastoni et al. (2018) from the nearby locality of Chiotta Strivera, Piedmont. Only few data are reported for these occurrences and no crystal-chemical characterisation was performed. Finally, kintoreite from the Tripi mine is enriched in Al and S and consequently its full description can provide interesting insights on the crystal chemistry of alunite-supergroup minerals.

Geological background

The Peloritani Mountains represent the southernmost portion of the Calabria–Peloritani Arc, an arc-like structure that connects the Apennines with the Maghrebian Chain. It is delimited by the Pollino line, in the north, and the Taormina line, in the south (Messina et al., 2004, and references therein). This mountain belt is formed by the stacking of several tectonic units. Ore bodies are hosted mainly in the Mandanici Unit, a tectonic slice formed by low- to medium-grade metamorphic rocks affected by the Variscan orogeny; the Alpine event gave rise to cataclastic-to-mylonitic processes (Ferla and Meli, 2007; Carbone et al., 2007, and references therein). The actual genesis and evolution of the ore deposits of the Peloritani Mountains have been debated by several authors (e.g. Ferla, 1982/1983; Ferla and Omenetto, 2000; Saccà et al., 2003).

Among the most important mining sites, the Tripi mine (38°00′50″N; 15°24′27″E) is located some hundred metres SSW of the small hamlet of Ali, Messina Province, Sicily. It exploited a stratabound fine-banded ore, composed mainly of sphalerite and Ag-bearing galena, with rare pyrite and trace amounts of chalcopyrite, arsenopyrite, pyrrhotite and covellite; quartz and fluorite are gangue minerals (Saccà et al., 2007). Secondary products are smithsonite, gypsum, hydrozincite, ‘limonite’ and malachite (Saccà et al., 2007).

Experimental

Specimen studied

Kintoreite occurs as yellow equant crystals, up to 0.05 mm in size, on quartz, associated with another alunite-supergroup mineral currently under study (Fig. 1a). The sample studied is deposited in the mineralogical collection of the Museo di Storia Naturale of the Università di Pisa, under the catalogue number 19928.

Chemical analysis

Quantitative chemical analyses were performed at the ‘Eugen F. Stumpfl’ laboratory, University of Leoben (Austria) using a Superprobe JEOL JXA 8200 electron microprobe (WDS mode, accelerating voltage = 20 kV, beam current = 10 nA and beam size = 1 μm). The following standards (element, emission line) were used: crocoite (PbKα), magnetite (FeKα), apatite (PKα), corundum (AlKα) and anhydrite (SKα). Other elements (K, Sr, Ba and As) were sought but were below the detection limit. The ZAF routine was applied for the correction of the recorded raw data. Counting times were 15 s for peak and 5 s for backgrounds. Table 1 gives chemical data.

Micro-Raman spectroscopy

Micro-Raman spectra were collected using a Horiba Jobin-Yvon XploRA Plus apparatus, equipped with a motorised x-y stage and an Olympus BX41 microscope with a 50× objective (Dipartimento di Scienze della Terra, Università di Pisa). Raman spectra were excited using the 532 nm line of a solid-state laser, attenuated to 25% (i.e. 6.25 mW) in order to avoid any potential sample damage. The minimum lateral and depth resolution was set to a few μm. The system was calibrated using the 520.6 cm$^{-1}$ Raman band of silicon before each experimental session. Spectra were collected through multiple acquisitions (3) with variable counting times, ranging from 30 to 60 s. Back-scattered radiation was analysed with a 1200 gr/mm grating monochromator. Raman spectra were processed using Fityk.
(Wojdyr, 2010), subtracting the background and fitting the spectra to theoretical peak shapes using Voigt functions. Experimental precision can be estimated at ± 2 cm⁻¹.

**X-ray crystallography**

Single-crystal X-ray diffraction data were collected at the Dipartimento di Scienze della Terra, Università di Pisa, Italy, using a Bruker Apex II diffractometer operating at 50 kV and 30 mA and equipped with an air-cooled Photon II CCD detector. Graphite-monochromatised MoKα radiation was used. The detector-to-crystal working distance was set to 50 mm. Intensity data were integrated and corrected for Lorentz, polarisation, background effects and absorption using the APEX3 software package (Bruker AXS Inc., 2016). Crystal structure refinement was performed using Shelx-2018 (Sheldrick, 2015) starting from the atomic coordinates given by Kharisun et al. (1997) for kintoreite. Neutral scattering curves were taken from the International Tables for Crystallography (Wilson, 1992). The following scattering curves were used: Pb at the Pb site, Fe at the Fe site, P at the P site, and O at the O(1)–O(3) sites. After several cycles of isotropic refinement, the R₁ factor converged to 0.0674, thus confirming the correctness of the structural model. Taking into account chemical data, the site occupancy at the Fe site was calculated using the scattering curves of Fe vs. Al, improving the quality of refinement to R₁ = 0.0447. Owing to the similar scattering factors for P (Z = 15) and S (Z = 16), only the scattering curve of the former was used. Introducing the anisotropic displacement parameters for all atoms decreased the R₁ to 0.0376. However, Pb was negatively defined and consequently the final model was refined using anisotropic displacement parameters for all atoms but Pb. A maximum residual, interpreted as an H atom bonded to O(3), was located in the difference-Fourier map and a restraint on the O(3)–H bond distance was added. The refinement converged to R₁ = 0.0415 for 226 unique reflections with Fo > 4σ(Fo) and 31 least-square parameters. Details of data collection and structure refinement are in Table 2, whereas atomic coordinates and displacement parameters are shown in Table 3. Bond distances and bond-valence sums, calculated according to the bond parameters of Gagné and Hawthorne (2015), are given in Table 3. Bond and structure refinement are in Table 2, whereas atomic coordinates and displacement parameters are shown in Table 3. Bond distances and bond-valence sums, calculated according to the bond parameters of Gagné and Hawthorne (2015), are given in Tables 4 and 5, respectively. The crystallographic information file has been deposited with the Principal Editor of Mineralogical Magazine and is available as Supplementary material (see below).

**Results and discussion**

**Chemical data**

The back-scattered electron image of the grain studied revealed a compositional inhomogeneity (Fig. 1b), with dark and bright domains, related to different Fe/Al atomic ratios. Electron micro-probe data were recalculated on the basis of 14 O atoms per formula unit (apfu), calculating the amount of H₂O in order to constrain the sum of (P + S) to 2 apfu. The darker domains have the chemical formula Pb₁₀₀(Fe₁·₈₉Al₀·₁₁)₁₂·₅₁ [P₁·₇₂O₄·₄₅(OH)₀·₅₇][(OH)₅·₅₈(H₂O)₀·₄₂][Al₁·₄₅O₄·₄₁(OH)₀·₅₈(H₂O)₀·₄₅], whereas the brighter ones correspond to Pb₀·₀₉(Fe₂·₀₀Al₀·₃₅)₁₂·₂₇₄ [P₁·₇₂O₄·₄₅(OH)₀·₅₇][(OH)₅·₅₈(H₂O)₀·₄₂][Al₁·₄₅O₄·₄₁(OH)₀·₄₅].

To the best of our knowledge, the sample from the Tripi mine has the highest S content among kintoreite occurrences reported in literature. Kharisun et al. (1997) described a kintoreite with a significant As and S substitution for P, i.e. 0.40 As apfu and 0.30 S apfu. On the contrary, several findings from Slovakia and the Czech Republic have negligible S contents (Pauliš et al., 2012; Števko et al., 2016; Vrtiška et al., 2019, 2021). The substitution of Fe⁶⁺ by Al³⁺ in the octahedral site agrees with the wide substitution observed between kintoreite and plumbogummite, ideally PbAl₆(OPO₃)(PO₃OH)(OH)₆, by other authors (e.g. Vrtiška et al., 2016).

**Micro-Raman spectroscopy**

The Raman spectral features of kintoreite from the Tripi mine are shown in Fig. 2. Between 100 and 1200 cm⁻¹ (Fig. 2a), two regions can be distinguished. The first one, between 900 and 1200 cm⁻¹, is characterised by stretching modes of P–O bonds and, probably, of S–O bonds. In the second region, between 100 and 650 cm⁻¹, bending modes of O–P–O and O–S–O bonds, as well as M–O (M = Pb, Fe and Al) and lattice vibrations occur. Observed

**Table 1.** Electron microprobe data for kintoreite from the Tripi mine.

| Oxide          | wt.%     | range | σ    | wt.%     | range | σ    |
|----------------|----------|-------|------|----------|-------|------|
| SO₃            | 5.47     | 5.18–5.71 | 0.27 | 6.03     | 5.99–6.06 | 0.05 |
| P₂O₅           | 17.55    | 17.40–17.68 | 0.14 | 16.66    | 16.50–16.82 | 0.23 |
| Al₂O₃          | 7.81     | 7.57–8.21  | 0.35 | 4.22     | 4.21–4.23  | 0.02 |
| Fe₂O₃          | 23.81    | 23.31–24.14 | 0.44 | 27.31    | 27.27–27.36 | 0.06 |
| PbO            | 35.11    | 34.82–35.58 | 0.41 | 33.78    | 33.62–33.94 | 0.22 |
| H₂Ocalc         | 9.93     |          |      | 10.25    |        |      |
| Total          | 99.68    |          |      | 98.25    |        |      |

n = number of spot analyses. *Calculated in agreement with structural data. σ = estimated standard deviation.

**Table 2.** Summary of crystal data and parameters describing data collection and refinement for kintoreite from the Tripi mine.

| Crystal data                  | Pb[Fe₁·₈₉Al₀·₁₁](PO₃.₅(OH)₀·₅)(OH)₆ | Pb[Fe₁·₈₉Al₀·₁₁](PO₃.₅(OH)₀·₅)(OH)₆ |
|-------------------------------|--------------------------------------|--------------------------------------|
| X-ray formula                 | Pb[Fe₁·₈₉Al₀·₁₁](PO₃.₅(OH)₀·₅)(OH)₆ | Pb[Fe₁·₈₉Al₀·₁₁](PO₃.₅(OH)₀·₅)(OH)₆ |
| Crystal size (mm)             | 0.080 × 0.080 × 0.050                 | 0.080 × 0.080 × 0.050                 |
| Cell setting, space group     | Trigonal, R3m                         | Trigonal, R3m                         |
| α (Å)                        | 7.2191(10)                            | 7.2191(10)                            |
| c (Å)                        | 16.834(3)                             | 16.834(3)                             |
| V (Å³)                       | 790.8(3)                              | 790.8(3)                              |
| Z                            | 3                                     | 3                                     |

**Data collection and refinement**

| Radiation, wavelength (Å)      | MoKα, λ = 0.71073                     | MoKα, λ = 0.71073                     |
|-------------------------------|--------------------------------------|--------------------------------------|
| Temperature (K)               | 293(2)                               | 293(2)                               |
| 2θmax (°)                    | 54.91                                | 54.91                                |
| Measured reflections         | 1160                                  | 1160                                  |
| Unique reflections            | 242                                   | 242                                   |
| Reflections with Fobs > 4σ(Fo)| 226                                  | 226                                  |
| Rint                         | 0.0300                               | 0.0300                               |
| Rσ                           | 0.0258                               | 0.0258                               |
| Range of h, k, l             | −9 ≤ h ≤ 9, −9 ≤ k ≤ 8, −11 ≤ l ≤ 21 | −9 ≤ h ≤ 9, −9 ≤ k ≤ 8, −11 ≤ l ≤ 21 |
| R (all data)                 | 0.0415                               | 0.0415                               |
| wR (on F2)                   | 0.0985                               | 0.0985                               |
| Goof                         | 1.226                                | 1.226                                |
| Number of least-squares parameters | 30                                  | 30                                  |
| Max. and min. residual peak (Å⁻¹) | 1.21 [at 0.66 Å from Pb]             | 1.21 [at 0.66 Å from Pb]             |

w = 1/[σ²(Få²)]/[0.0252σ² + 41.9069P²], where P = (Få² + Fp²)/3.
The kintoreite studied.

Theor. 2.00 3.00 5.22

Table 3. Sites, Wyckoff positions, site occupancy factors (s.o.f.), fractional atomic coordinates and isotropic (*) or equivalent isotropic displacement parameters (Å²) for kintoreite from the Tripi mine.

| Site | Wyckoff position | s.o.f. | x/a | y/b | z/c | U_iso/Å² |
|------|------------------|--------|-----|-----|-----|---------|
| Pb   | 18h              | Pb1.00 | -0.0256(14) | 0.0256(14) | 0.0000(7) | 0.0187(6)* |
| Fe   | 9d               | Fe1.00 | 0         | 0   | 0.50 | 0.0029(8) |
| P    | 6c               | P1.00  | 0         | 0   | 0.50 | 0.3098(3)  |
| O(1) | 6c               | O1.00  | 0         | 0   | 0.6005(7) | 0.013(3) |
| O(2) | 18h              | O1.00  | 0.2186(6) | -0.2186(6) | 0.1334(4) | 0.0142(13) |
| O(3) | 18h              | O1.00  | 0.1272(6) | -0.1272(6) | 0.110(10) | 0.08(6)* |
| H    | 18h              | H1.00  | 0.198(7)  | -0.198(7)  | 0.110(10) | 0.08(6)* |

Table 4. Selected bond distances (Å) for kintoreite from the Tripi mine.

| Pb–O(3) | 2.579(12) | Fe–O(3) | 1.968(3) |
|---------|----------|--------|---------|
| Pb–O(2) | 2.587(8) | Fe–O(2) | 1.96(7)  |
| Pb–O(3) | 2.677(12) | <Fe–O>  | 1.972   |
| Pb–O(2) | 2.751(8) | ×2     |         |
| Pb–O(3) | 2.860(11) | ×2     | 1.510(12) |
| Pb–O(3) | 2.949(12) | ×2     | 1.522(7) |
| Pb–O(2) | 3.054(8) | ×2     | 1.526   |
| Pb–O(2) | 3.194(8) | ×2     |         |
| <Pb–O> | 2.833   |        |         |

Table 5. Weighted bond-valence sums (in valence unit) for kintoreite from the Tripi mine.

| Site | Pb | Fe | P | Σanions | Σanions ² | Theor. |
|------|----|----|---|---------|-----------|-------|
| O(1) | 1.34 | 1.34 | 1.97² | 1.25² | 2.00 |
| O(2) | 0.28 | 0.47³ | 0.47³ | 1.27² | 1.81–2.02 | 1.81–2.02² | 1.90–2.11² | 2.00 |
| O(3) | 0.07 | 0.28 | 0.49 | 0.49⁴ | 1.10–1.26 | 0.92–1.08⁴ | 1.01–1.17⁴ | 1.00 |

Cation sites

Lead is hosted in a distorted icosahedron and is displaced from the origin, being distributed in a ring-like structure in the (0001) plane at the 18th position. In hindsdalite, PbAl₃(PO₄)(SO₄)(OH)₆, Pb occurs at the 18f position (Kolitsch et al., 1999), in the refinement of kintoreite reported by Grey et al. (2009). On the contrary, Kharisun et al. (1997) proposed a model where Pb is located on a 36i site. Moreover, this element is located at the origin in corkite, PbFe₃(PO₄)(SO₄)(OH)₆, and osarizawaite, Pb(Al₂Cu²⁺)(SO₄)₂(OH)₆ but with anomalously large displacement parameters (Giuseppetti and Tadini, 1980, 1987). The distorted twelve-fold coordination shown by Pb in kintoreite from the Tripi mine is characterised by six short bonds (Pb–O distance shorter than 2.80 Å) and six longer ones. This distortion is probably due to the activity of the 6² lone-pair of Pb⁺². The average <Pb–O> distance is 2.833 Å, to be compared with 2.842 Å and 2.846 Å for kintoreite studied by Kharisun et al. (1997) and Grey et al. (2009), respectively. These values can be compared with those observed in other Pb-bearing alunite-supergroup minerals, e.g. 2.79 Å in hindsdalite and plumbogummite, Pb occurs at the 18f position (Kolitsch et al., 1999), as in the refinement of kintoreite reported by Grey et al. (2009).

Crystal-chemistry of kintoreite from the Tripi mine

Kintoreite is isotypic with other alunite-supergroup minerals, a series of phases having the general formula DG₃(TO₄)₂(OH, H₂O)₆ (Stoffregen et al., 2000); in the sample studied, D = Pb²⁺, G = (Fe,Al)²⁺ and T = (P⁵⁺ and S⁶⁰⁻). The crystal structure is characterised by sheets of corner-sharing (Fe,Al)₆O₁₂ [O = O²⁻ and (OH)⁻] octahedra parallel to (0001) and decorated on both sides by (P,S)₆O₁₄ tetrahedra. Lead atoms are hosted within cavities occurring between the octahedral sheets (Fig. 3).
Iron, replaced partially by Al and a minor vacancy, is the main G constituent and is hosted in a quite regular octahedron, formed by four equatorial O(3) sites and two apical O(2) sites. Average \( <G–\phi> \) distance is 1.972 Å, shorter than those reported by Kharisun et al. (1997) and Grey et al. (2009), i.e. 2.011 Å in both structural models, owing to the extensive Al-to-Fe\(^{3+}\) replacement. Using the ionic radii proposed by Shannon (1976), the observed average bond distance would correspond to the Fe site occupancy (Fe\(_{0.70}\)Al\(_{0.30}\)). This would correspond to the site population (Fe\(_{2.10}\)Al\(_{0.90}\)), to be compared with (Fe\(_{1.89}\)Al\(_{0.97}\)\(\square_{0.14}\)) and (Fe\(_{2.21}\)Al\(_{0.53}\)\(\square_{0.26}\)) for the dark and bright domains, respectively.

The discrepancy between electron microprobe data and calculated site population is probably due to the unaccounted occurrence of a vacancy. Refined site scattering at the Fe site is 63.2 electrons per formula unit (epfu), to be compared with 61.8 epfu calculated for the dark domain and 64.4 epfu for the brighter ones. The observed value is intermediate between these two values. The bond-valence sum at the Fe site was calculated on the basis of the site occupancy (Fe\(_{0.68}\)Al\(_{0.32}\)) refined from single-crystal X-ray diffraction data and it corresponds to 2.90 \( \nu\).

Phosphorus and minor S are tetrahedrally coordinated, with an average \( <T–\phi> \) distance of 1.526 Å. This distance is shorter than that reported by Kharisun et al. (1997), i.e. 1.563 Å, related to the partial substitution of P\(^{5+}\) by the larger As\(^{5+}\) cation. In ‘pure’ kintoreite studied by Grey et al. (2009), the corresponding distance is 1.537 Å, in agreement with the grand \( <P–\phi> \) distance given by Huminicki and Hawthorne (2002). In the sample from the Tripi mine, P is replaced partially by S. On the basis of the observed average distance, using the ideal distances reported by Huminicki and Hawthorne (2002) and Hawthorne et al.

![Fig. 2. Raman spectrum of kintoreite from the Tripi mine in the region (a) between 100 and 1300 cm\(^{-1}\); (b) 1500–1700 cm\(^{-1}\); and (c) 2800–3400 cm\(^{-1}\).](image)
for $<P-\phi>$ and $<S-\phi>$, respectively, the site occupancy $(P_{0.83}S_{0.17})$ for the $P$ site can be proposed. In comparison those observed in the dark and bright domains are $(P_{0.785}S_{0.215})$ and $(P_{0.755}S_{0.245})$, respectively. The bond-valence sum, calculated assuming the site occupancy $(P_{0.78}S_{0.22})$, is 5.15 vu, in accord with the partial replacement of $P^{5+}$ by $S^{6+}$.

In kintoreite, $P$ and $S$ are disordered, as observed in other mixed $(P,S)$ phases belonging to the alunite supergroup, e.g. woodhouseite, $CaAl_3(PO_4)(SO_4)(OH)_6$ (Kato, 1977), svanbergite, $SrAl_3(PO_4)(SO_4)(OH)_6$ (Kato and Miura, 1977) and hinsdalite (Kolitsch et al., 1999). The ordering of $P$ and $S$ in corkite reported by Giuseppetti and Tadini (1987) is considered questionable (e.g. Bayliss et al., 2010).

**Anion sites and H bonds in kintoreite**

Three anion sites occur in the crystal structure of kintoreite, i.e. $O(1)$, $O(2)$ and $O(3)$.

$O(1)$ is bonded to $(P,S)$ only, with a relatively short distance of 1.510 Å. Its bond-valence sum indicates a significant underbonding, 1.34 vu. $O(2)$ is corner-shared between one $(P,S)$-centred tetrahedron and an $(Fe,Al)$-centred octahedron. Moreover, it is

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**Fig. 3.** Crystal structure of kintoreite as seen down $b$. Iron-centred and $P$-centred polyhedra are shown in brown and green, respectively. Large dark grey circles are $Pb$ atoms, whereas $O$ sites are shown as red circles. The $(OH)$-bearing $O(3)$ site is shown as light blue circles. Hydrogen atoms are not shown. The unit-cell is shown as blue dotted lines.
bonded to disordered Pb atoms. Its bond-valence sum ranges between 1.81 and 2.02 \( \text{vu} \), in relation to the different Pb ordered positions. O(3) is shared between two (Fe,Al)-centred octahedra and one disordered Pb atom. Its bond-valence sum ranges between 1.10 and 1.26 \( \text{vu} \). The difference-Fourier map revealed an H atom at 0.97(5) Å from O(3) and forming an O(3)–H(1)⋯O(1) H bond with O(1)⋯O(3) distance of 2.814(9) Å and an angle of 179(17)°.

Using the relations proposed by Ferraris and Ivaksi (1988), a bond strength of 0.18 \( \text{vu} \) can be calculated for this H bond. In this way, the bond-valence sum at O(3), that acts as a donor, ranges between 0.92 and 1.08 \( \text{vu} \), whereas O(1), acceptor of three H bonds, increases its bond-valence sum up to 1.88 \( \text{vu} \). However, as stressed by Cooper and Hawthorne (2012), O(1) should have a mixed occupancy \([\text{O}_2\text{OH}]_{0.5}\) in alunite-supergroup minerals having the general formula \( \text{D}^{2+}\text{G}_3^{2+}\text{O}^{(8-\text{a})}\text{O}_2\text{O}^{(8-\text{a})}\text{OH}(\text{OH})_{\text{m}} \) as in kintoreite (e.g. Grey et al., 2009). In agreement with Cooper and Hawthorne (2012), when O(1) is occupied by O\text{2}–, then it is the acceptor of H bonds from three symmetry-related OH groups hosted at O(3) and one weak H bond from an OH group hosted at opposing O(1) apices of a \( \text{T}_6 \) group; on the contrary, when O(1) is an OH group, then it cannot be the acceptor of the three H bonds from O(3). In this case, following Cooper and Hawthorne (2012), it can be hypothesised that the H bonds are accepted by the O\text{2}– atoms hosted at the O(2) sites, located at the base of the \( \text{T}_6 \) groups. The H atom bonded to O(1) was not located. The O(1)⋯O(1) distance is ∼3.38 Å, corresponding to a very weak H bond, having a bond strength of 0.09 \( \text{vu} \). Also the O(3)⋯O(2) distance is long, i.e. ∼3.38 Å. The O(3)⋯H(1)⋯O(2) angle, ∼121°, is very small, close to the lower limit of observed O–H⋯O bonds and indicative of a very weak bond (Brown, 1976). These values can be compared with those given by Cooper and Hawthorne (2012) for philibornite-hidalgoite, i.e. O(3)⋯O(2) = 3.54 Å and O(3)⋯H(1)⋯O(2) = 116°. The proposed H-bonding is shown in Fig. 4.

Micro-Raman spectroscopy reveals the occurrence of possible H–O–H bonding modes in kintoreite, thus supporting the presence of H\text{2}O groups. Although H\text{2}O groups may be the result of the protonation of (OH)– groups, as suggested by Szymański (1985), a more reliable hypothesis is that the occurrence of H\text{2}O is related to the presence of octahedral vacancies. Their occurrence has been suggested by previous investigators (e.g. Jambor and Dutrizac, 1983; Szymański, 1985) and they seem to be coupled with the protonation of equatorial H\text{2}O groups of octahedral sites, as described by Nielsen et al. (2007).}

**Variation of unit-cell parameters**

Unit-cell parameters of alunite-supergroup minerals are sensitive to the complex homo- and heterovalent substitutions accepted by their crystal structure.

Pring et al. (1995) reported the following unit-cell parameters for type kintoreite: \( a = 7.325(1) \), \( c = 16.900(3) \) Å and \( V = 785.3(5) \) Å\text{3}. This type material showed significant As and S replacing P along with minor CO\text{3} groups. The compositionally similar sample studied by Kharissan et al. (1997) gave similar values: \( a = 7.3310 \) (7), \( c = 16.885(2) \) Å and \( V = 785.9(2) \) Å\text{3}. Pure kintoreite (i.e. with negligible substitution of P by S and no other octahedral cations than Fe\text{3}+) has unit-cell parameters \( a = 7.2963(5), c = 16.8491(5) \) Å and \( V = 776.8 \) Å\text{3} (Grey et al., 2009). Other unit-cell parameters for kintoreite available in literature are those reported by Pauliš et al. (2012) for a sample with minor Cu\text{2}+ as octahedral cation and As replacing P \( \{ a = 7.290(1), c = 16.865(4) \} \) Å and \( V = 776.2(2) \) Å\text{3}, and by Stevko et al. (2016), who reported the unit-cell parameters for a specimen showing a partial replacement of Fe\text{3}+ by Al (0.34 apfu), Cu\text{2}+ (0.14 apfu), and minor vacancy (0.04 apfu), with P replaced by Si (0.16 apfu), S (0.02 apfu) and As (0.01) \[ a = 7.286(8), c = 16.883(5) \) Å and \( V = 776(1) \) Å\text{3}. Haert et al. (2004) reported the unit-cell parameters for kintoreite from the Stavelot massif, Belgium, showing a very long \( c \) parameter, i.e. 17.08(2) Å. No quantitative chemical data are available.

The sample from the Tripi mine has an exceptionally small unit-cell volume, i.e. 759.8(3) Å\text{3}, with \( a = 7.219(10) \) and \( c = 16.834(3) \) Å. Assuming the unit-cell parameters of the specimen studied by Grey et al. (2009) as a reference for ideal kintoreite, the specimen from the Tripi mine has \( \Delta a = -1.1\% \), \( \Delta c = -0.1\% \) and \( \Delta V = -2.2\% \). As discussed by other authors (e.g. Stoffregen et al., 2000), the \( a \) unit-cell parameter is affected mainly by the Fe\text{3}+–Al substitution, whereas variations of the unit-cell parameter \( c \) are largely related to substitution at the twelve-fold coordinated site. Consequently, the contraction of the Tripi mine sample is probably due to the high Al content of the material studied, supporting the existence of a substitutional series with the Al-isotype plumbogummite.

**Conclusions**

Kintoreite from the Tripi mine represents the first well-characterised Italian occurrence of this uncommon member of the alunite supergroup. Using a multi-analytical approach (electron microprobe analysis, single-crystal X-ray diffraction, and micro-Raman spectroscopy), the crystal chemical features of this mineral species were determined, detailing the H-bond system and suggesting the occurrence of H\text{2}O groups, probably due to the presence of an octahedral vacancy. In this way, the plasticity of the alunite structure to accommodate several substitutions is further confirmed. This is particularly important as kintoreite is able to host PTE such as Pb. Indeed, in the Al\text{ii} area, high Pb content of geogenic origin in soils has been reported by Cosenza et al. (2015).

Notwithstanding the current lack of mineralogical studies aiming at constraining the mineralogy of secondary assemblages from...
the Peloritani Mountains, it is very likely that alunite-supergroup minerals may play a central role in determining the fate of PTE in this former mining district. The finding and characterisation of kintoreite could represent a first step in assessing the environmental role of these phases in this sector of northeastern Sicily.

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The Authors are delighted to contribute to the thematic issue honouring Prof. Peter A. Williams. We believe that the complex crystal chemistry of kintoreite and its environmental significance reflects well the main interest that Pete has had during his scientific activity.

Supplementary material. To view supplementary material for this article, please visit https://doi.org/10.1180/mgm.2021.85

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