

## Poppiite, the V<sup>3+</sup> end-member of the pumpellyite group: Description and crystal structure

MARIA FRANCA BRIGATTI,<sup>1,\*</sup> ENRICO CAPRILLI,<sup>1</sup> AND MARCO MARCHESINI<sup>2</sup>

<sup>1</sup>Dipartimento di Scienze della Terra, Università di Modena e Reggio Emilia, Largo S. Eufemia 19, I-41100 Modena, Italy

<sup>2</sup>ENI-AGIP Towers, I-20097 San Donato Milanese, Italy

### ABSTRACT

Poppiite, a new mineral from Gambatesa mine (Val Graveglia, Genova, Northern Italy), is the V<sup>3+</sup> end-member of the pumpellyite group [I<sup>VI</sup>](Ca<sub>7.68</sub>Na<sub>0.27</sub>K<sub>0.03</sub>Rb<sub>0.02</sub>)<sub>Σ8.00</sub> I<sup>VI</sup>(V<sub>1.26</sub>Fe<sub>3.02</sub>Mg<sub>0.78</sub>Mn<sub>0.59</sub>Al<sub>0.31</sub>Cu<sub>0.04</sub>)<sub>Σ4.00</sub> I<sup>VI</sup>(V<sub>6.89</sub>Al<sub>1.07</sub>Ti<sub>0.04</sub>)<sub>Σ8.00</sub> I<sup>VI</sup>(Si<sub>11.69</sub>Al<sub>0.31</sub>)<sub>Σ12.00</sub> O<sub>42</sub>(OH)<sub>14</sub>; *C*2/*m*, *a* = 19.2889(6), *b* = 6.0444(2), *c* = 8.8783(3) Å, β = 97.328(2)°, *V* = 1026.66(6) Å<sup>3</sup>, *D*<sub>meas</sub> = 3.36(2) g/cm<sup>3</sup>, and *D*<sub>calc</sub> = 3.44 g/cm<sup>3</sup>. Poppiite crystals, with size varying from 0.1 to 0.6 mm, are minute, greenish-brown, and prismatic, and are associated with roscoelite, ganophyllite, manganaxinite, goldmanite, and calcite.

The strongest lines in the X-ray powder diffraction pattern [*d*<sub>obs</sub> (Å), *I*<sub>rel.</sub>, (*hkl*)] are: 2.930, 100, (511); 3.817, 70, (202); 2.548, 65, ( $\bar{3}$ 13); 2.551, 62, (420); 1.612, 57, ( $\bar{7}$ 31,424); and 2.367, 51, (222, 403). Poppiite is optically negative, with 2*V*<sub>calc</sub> = 44°, *n*<sub>α</sub> = 1.768(9), *n*<sub>β</sub> = 1.804(8), *n*<sub>γ</sub> = 1.810(9). The pleochroic scheme is α = light yellowish brown, β = deep greenish brown, and γ = brown to reddish brown. The crystal structure was refined using 1918 unique reflections to *R* = 0.0307. Like the other pumpellyite-group minerals the crystal structure of poppiite consists of chains of edge-sharing octahedra linked by SiO<sub>4</sub>, Si<sub>2</sub>O<sub>7</sub>, and CaO<sub>7</sub> polyhedra.

**Keywords:** New mineral, analysis chemical (mineral), crystal structure, optical properties, XRD data

### INTRODUCTION

The general formula of pumpellyite-group minerals, characterized by a flexible crystal structure that can accommodate various cations, is W<sub>8</sub>X<sub>4</sub>Y<sub>8</sub>T<sub>12</sub>O<sub>56-n</sub>(OH)<sub>n</sub>. Natural end-members were described with Al, Fe<sup>2+</sup>, Fe<sup>3+</sup>, Mg, and Mn<sup>2+</sup> as dominating cations in the octahedral X sites, and with Al, Fe<sup>3+</sup>, Mn<sup>3+</sup>, and Cr<sup>3+</sup> as dominating cations in the octahedral Y sites. Alkali and alkaline earths metals, mostly Ca, occupy the seven-coordinated W sites and Si, together with a usually small Al amount, occupies tetrahedral T positions.

Pumpellyite group minerals are classified based on the dominating cation in Y position. In pumpellyite (Palache and Vassar 1925; Galli and Alberti 1969; Allmann and Donnay 1971; Yoshiasa and Matsumoto 1985) Al is the dominating cation. Julgoldite (Moore 1971; Allmann and Donnay 1973; Artioli et al. 2003), shuiskite (Ivanov et al. 1981), and okotskite (Togari and Akasaka 1987; Artioli et al. 1996; Akasaka et al. 1997) are isomorphous of pumpellyite with Fe<sup>3+</sup>, Cr<sup>3+</sup>, and Mn<sup>3+</sup> partly or completely replacing Al<sup>3+</sup>. Different species are then identified based on the dominating cation in X position. A suffix indicating the dominating cation in X site should thus be added to the subgroup name (Passaglia and Gottardi 1973).

Some structural data on pumpellyite and its isomorphs were derived from a limited number of single-crystal X-ray refinements available in the literature, despite the usual poor quality of naturally occurring crystals. The structural model of pumpellyite (space group *A*2/*m*), first proposed by Gottardi (1965), was subsequently investigated by Galli and Alberti (1969), Yoshiasa and Matsumoto (1985), and Artioli and Geiger (1994). The

structure of julgoldite was described by Allmann and Donnay (1973), and later revised by Artioli et al. (2003), who suggested that Fe on X and Y sites only occurs in the ferric state, based on synchrotron X-ray powder diffraction and Mössbauer spectroscopy evidence.

Pan and Fleet (1992) described some V<sup>3+</sup>-rich pumpellyite crystals, with V<sup>3+</sup> ranging from 0.43 to 7.39 apfu, occurring in green mica schist from Hemlo gold Deposit (Ontario). According to Pan and Fleet (1992), this occurrence represents a possible new mineral, with V as dominant cation in both Y and X sites. However, the limited amount of material available prevented a more detailed characterization.

This work provides a mineralogical and structural description of the V<sup>3+</sup>-pumpellyite group end-member, where V<sup>3+</sup> was demonstrated to be the dominating cation in both octahedral X and Y sites. The mineral occurs in the Mn-mine area of Gambatesa, near the village of Reppia (Val Graveglia, Northern Apennines, Italy) and was named *poppiite* in memory of Luciano Poppi, Professor of Mineralogy at Modena and Reggio Emilia University, and all his generous and fruitful efforts devoted to mineral science. The new mineral and its name were approved by the Commission on New Minerals and Mineral Names of IMA (vote 2005-018). The holotype material is deposited at the “Museo Mineralogico e Geologico Estense, GEMMA1786” at Modena and Reggio Emilia University, Italy (sample ST 005898).

### OCCURRENCE, PARAGENESIS, PHYSICAL, AND OPTICAL PROPERTIES

Poppiite was collected in the Mn-mine area of Gambatesa, near the village of Reppia (Val Graveglia, Northern Apennines, Italy). Mn-ores were deposited, as sedimentary layers (one centimeter to several meters thick), during the Middle Callovian

\* E-mail: brigatti@unimore.it

stage (Abbate et al. 1986) at the base of the cherts (M. Alpe Formation). During Alpine recrystallization, sedimentary-diagenetic phases were replaced by massive braunite + quartz + hematite aggregates under prehnite-pumpellyite facies conditions (Cortesogno et al. 1979). During this metamorphic event, a main tectonic phase induced mobilization of Mn and Si and thickening of the mineralized layers (up to some tens of meters), mainly at the fold hinges. Mn-silicate and carbonate assemblages thus developed extensively in the thickened lenses, mainly as bands, replacing the massive braunite, or as fracture-filling veins. A later extensional stage induced brittle deformation. These mineral assemblages were thus altered and progressively replaced. Caryopilite, inesite, parsettenite, neotocite, ranciéite, manganite, rhodochrosite, and manganoan calcite are the main replacing phases whereas pyrolusite, barian phillipsite, K-feldspar, calcite, aragonite, calcian kutnohorite, barite, chalcocite, pyrite, octahedrite, volborthite, and native copper are the most common fracture filling phases (Cortesogno et al. 1979).

Poppiite, identified during an extensive investigation of silicates from Gambatesa mine area (Caprilli 2004), is restricted to a few crystals associated with roscoelite (Brigatti et al. 2003), ganophyllite, manganaxinite, goldmanite, and calcite. The mineral forms radiating aggregates (about 2 mm in diameter) of minute, acicular prismatic platy crystals, up to 0.6 mm long, elongated, and frequently striated parallel to [010] (Fig. 1). The physical and optical properties of poppiite are summarized in Table 1.

### CHEMICAL COMPOSITION

The chemical composition of poppiite (Table 2) was determined using a wavelength-dispersive ARL-SEM electron microprobe (operating conditions: 15 kV accelerating voltage, 15 nA sample current, and beam diameter approximately 5  $\mu\text{m}$ ). Analyses and data reductions were performed using the Probe software package of Donovan (1995). The following standards were used: microcline (K, Al), albite (Na), spessartine (Mn), ilmenite (Fe, Ti), clinopyroxene (Si, Ca), olivine (Mg), chromite (Cr), pollucite (Cs), metallic vanadium (V), fluorite (F),  $\text{Cu}_{94}\text{Sn}_6$  (Cu), synthetic Rb glass (Rb). Minor elements (0.01 to 0.2 wt% oxide) are Ti, Cu, K, Rb, and F. No additional element with atomic number  $\geq 9$  was detected. The point analyses from a same fragment are homogeneous and only limited chemical variations

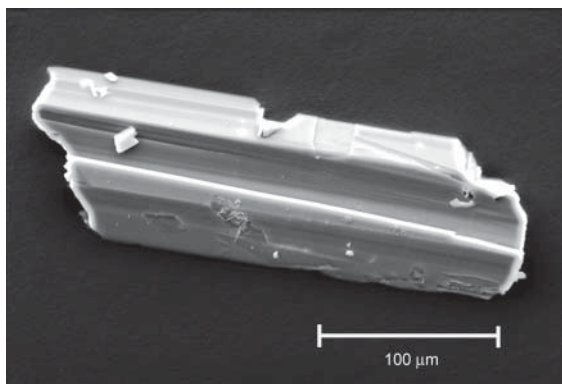
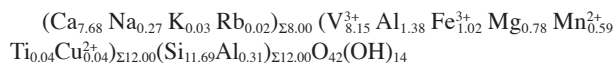


FIGURE 1. SEM micrograph of a poppiite crystal.

can be observed among different fragments.

The empirical formula, computed from chemical data, was based on 98 anion charges, namely  $\text{O}_{42}(\text{OH})_{14}$ , thus following the example of most of the authors who characterized pumpellyite-group minerals and the recommendations of Passaglia and Gottardi (1973). The resulting chemical formula is:



The simplified formula, based on  $(\text{O}, \text{OH})_{14}$  is:

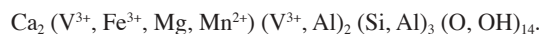


TABLE 1. Physical and optical properties of poppiite

|                           |  |
|---------------------------|--|
| Density <sub>meas</sub> * | 3.36(2) g/cm <sup>3</sup>  |
| Density <sub>calc</sub> † | 3.44 g/cm <sup>3</sup>   |
| Color                     | brown to greenish brown  |
| Streak                    | greenish white   |
| Luster                    | vitreous, transparent, non-fluorescent (UV)  |
| Tenacity                  | Brittle  |
| Fracture                  | sub-conchoidal   |
| Cleavage                  | {100} and {001}  |
| Twinning                  | Sometime polysynthetic   |
| Optical class             | biaxial (-)  |
| Pleochroism               | $\alpha$ = light yellowish brown<br>$\beta$ = deep greenish brown<br>$\gamma$ = brown to reddish brown |
| $2V_{\text{calc}}$        | 44°  |
| $n_{\alpha\ddagger}$      | 1.768(9)   |
| $n_{\beta\ddagger}$       | 1.804(8)   |
| $n_{\gamma\ddagger}$      | 1.810(9)   |
| Orientation               | OAP $\perp$ [010] and $\beta = \gamma$   |

\* Measured by torsion microbalance VDF "United" (Bermann 1939).

† Calculated from electron microprobe chemical analysis, with a cell volume of 1026.66(6)  $\text{\AA}^3$ .

‡ Immersion method (Cargille immersion liquids).

TABLE 2. Chemical data of poppiite from Gambatesa mine (Northern Italy) compared to vanadium pumpellyite from Golden Giant mine (Hemlo Gold deposit, Ontario) (Pan and Fleet 1994, analysis No. 1, Table 2)

|                         | wt%       |               | Atoms pfu‡ |                                 |       |       |
|-------------------------|-----------|---------------|------------|---------------------------------|-------|-------|
|                         | Gambatesa | Golden Giant  | Gambatesa  | Golden Giant                    |       |       |
| $\text{SiO}_2$          | 33.19     | (32.63–33.33) | 33.23      | Si                              | 11.69 | 11.94 |
| $\text{TiO}_2$          | 0.14      | (0.09–0.18)   | 1.13       | Al                              | 0.31  | 0.06  |
| $\text{Al}_2\text{O}_3$ | 4.08      | (4.00–4.17)   | 4.55       | T sites                         | 12.0  | 12.0  |
| $\text{V}_2\text{O}_5$  | 28.86     | (28.40–28.92) | 25.67      | Ti                              | 0.04  | 0.30  |
| $\text{Cr}_2\text{O}_3$ | b.d.t.    |               | 0.56       | Al                              | 1.38  | 1.87  |
| MgO                     | 1.49      | (1.24–1.66)   | 2.10       | Cr                              | –     | 0.16  |
| $\text{Fe}_2\text{O}_3$ | 3.85      | (3.49–4.20)   | 3.34       | V                               | 8.15  | 7.39  |
| MnO                     | 1.99      | (1.84–2.20)   | 0.50       | $\text{Fe}^{3+}$                | 1.02  | 1.00  |
| CuO                     | 0.14      | 0.10–0.15     |            | Mn                              | 0.59  | 0.15  |
| CaO                     | 20.35     | (20.00–20.50) | 20.56      | Mg                              | 0.78  | 1.13  |
| $\text{Na}_2\text{O}$   | 0.39      | (0.22–0.47)   | 0.14       | Cu                              | 0.04  | –     |
| $\text{K}_2\text{O}$    | 0.08      | (0.03–0.10)   | 0.09       | $\Sigma(\text{X}+\text{Y})$     | 12.00 | 12.00 |
|                         |           |               |            | sites                           |       |       |
| $\text{Rb}_2\text{O}$   | 0.08      | (0.00–0.10)   |            | Ca                              | 7.68  | 7.93  |
| BaO                     | b.d.t.    |               | 0.09       | Ba                              | –     | 0.01  |
| F                       | 0.01      | (0.00–0.04)   | 0.00       | Na                              | 0.27  | 0.10  |
| $\text{H}_2\text{O}^*$  | 5.35      |               |            | K                               | 0.03  | 0.04  |
| Sum                     | 100.00    |               | 91.96      | Rb                              | 0.02  | –     |
|                         |           |               |            | $\Sigma(\text{W}_1+\text{W}_2)$ | 8.00  | 8.08  |
|                         |           |               |            | sites                           |       |       |

Notes: In parenthesis is reported the range of variation obtained on different crystal fragments.

\* By difference.

† Iron was assumed to be trivalent (see text).

‡ The empirical formula was calculated from crystal-structure refinement data on the basis of 98 negative charges,  $\text{O}_{42}(\text{OH})_{14}$ .

All iron was considered to be trivalent, based on the evidence from Artioli et al. (2003) in their study of julgoldite-Fe<sup>3+</sup> and on a slightly better agreement with refined distances, whereas Mn was assumed to be divalent following the association to other Mn<sup>2+</sup> minerals occurring in this area (e.g., reppiaite). Unfortunately the limited iron and manganese content characterizing poppiite and the limited material available prevented a final conclusion on Fe and Mn oxidation state.

The sample under investigation approaches closely the chemical composition of V<sup>3+</sup>-pumpellyite described by Pan and Fleet (1992) (analysis 1; Table 2). More precisely the sample from Gambatesa mine is even closer to the V end-member of pumpellyite, given the lower amount in Al and Ti that substitutes for V in octahedral Y site (Table 2).

### X-ray powder diffraction

The X-ray powder pattern (Table 3) was collected with a Rigaku RINT RAPID micro-diffractometer (CuK $\alpha$  radiation, operating at 40 kV and 30 mA, diameter of collimator 50  $\mu$ m, and image plate detector). The refinement of powder diffraction data gives a monoclinic cell [ $a = 19.273(9)$ ,  $b = 6.020(2)$ ,  $c = 8.872(3)$   $\text{\AA}$ ,  $\beta = 97.31(3)^\circ$ ,  $V = 1021.0(7)$   $\text{\AA}^3$ ] in close agreement with single-crystal data.

### Crystal structure

Some pumpellyite crystals, optically homogeneous and inclusion-free, were hand-picked from the bulk sample for single-crystal X-ray study. A small crystal fragment  $0.12 \times 0.08 \times 0.06$  mm<sup>3</sup> was analyzed using a Bruker X8 APEX four circle diffractometer combined with APEX 4K CCD detector, flat graphite monochromator and MoK $\alpha$ -radiation from a fine focus sealed tube. Refined cell-parameters and other crystal data are listed in Table 4. The SMART package was used to determine unit-cell and for X-ray data collection. Redundant data were collected for an approximate sphere of reciprocal space and were

TABLE 3. Powder diffraction data for poppiite

| $I_{rel}$ | $2\theta(^\circ)$ | $d_{obs}(\text{\AA})$ | $d_{calc}(\text{\AA})$ | $hkl$ | $I_{rel}$ | $2\theta(^\circ)$ | $d_{obs}(\text{\AA})$ | $d_{calc}(\text{\AA})$ | $hkl$  |
|-----------|-------------------|-----------------------|------------------------|-------|-----------|-------------------|-----------------------|------------------------|--------|
| 19        | 18.57             | 4.778                 | 4.779                  | 4 0 0 | 14        | 36.67             | 2.451                 | 2.448                  | 2 2 2  |
| 34        | 18.72             | 4.739                 | 4.727                  | 1 1 1 | 51        | 38.02             | 2.367                 | 2.369                  | 2 2 2  |
| 16        | 20.16             | 4.405                 | 4.400                  | 0 0 2 |           |                   |                       | 2.363                  | 4 0 3  |
| 1         | 21.73             | 4.089                 | 4.062                  | 3 1 1 | 17        | 38.38             | 2.345                 | 2.344                  | 3 1 3  |
| 13        | 22.15             | 4.014                 | 3.992                  | 4 0 1 | 4         | 39.02             | 2.308                 | 2.309                  | 6 0 3  |
| 70        | 23.31             | 3.817                 | 3.817                  | 2 0 2 | 25        | 41.22             | 2.190                 | 2.188                  | 6 2 0  |
| 4         | 24.93             | 3.572                 | 3.559                  | 1 1 2 | 29        | 42.16             | 2.143                 | 2.142                  | 4 2 2  |
| 8         | 25.74             | 3.461                 | 3.464                  | 4 0 2 | 7         | 48.01             | 1.895                 | 1.894                  | 6 2 2  |
| 21        | 29.25             | 3.053                 | 3.049                  | 4 0 2 | 29        | 48.64             | 1.872                 | 1.872                  | 8 2 0  |
| 4         | 30.42             | 2.939                 | 2.933                  | 0 0 3 | 13        | 51.30             | 1.781                 | 1.780                  | 3 3 2  |
| 100       | 30.51             | 2.930                 | 2.930                  | 5 1 1 | 8         | 51.39             | 1.778                 | 1.777                  | 5 3 0  |
| 3         | 30.69             | 2.914                 | 2.910                  | 2 0 3 | 3         | 51.88             | 1.762                 | 1.762                  | 5 5 1  |
| 5         | 31.12             | 2.874                 | 2.871                  | 2 2 0 | 6         | 53.05             | 1.726                 | 1.725                  | 4 0 5  |
| 22        | 31.41             | 2.848                 | 2.848                  | 0 2 1 | 6         | 53.10             | 1.725                 | 1.724                  | 4 2 4  |
| 7         | 32.40             | 2.763                 | 2.761                  | 2 2 1 | 6         | 54.09             | 1.695                 | 1.693                  | 2 0 5  |
| 34        | 32.49             | 2.756                 | 2.752                  | 6 0 2 | 19        | 55.24             | 1.661                 | 1.664                  | 8 2 2  |
| 7         | 33.08             | 2.708                 | 2.709                  | 2 0 3 |           |                   |                       | 1.660                  | 1 3 3  |
| 6         | 33.12             | 2.705                 | 2.699                  | 2 2 1 | 57        | 57.15             | 1.612                 | 1.612                  | 7 3 1  |
| 16        | 33.75             | 2.656                 | 2.655                  | 4 0 3 |           |                   |                       | 1.612                  | 4 2 4  |
| 28        | 33.79             | 2.653                 | 2.654                  | 1 1 3 | 19        | 58.75             | 1.572                 | 1.571                  | 10 2 2 |
| 62        | 35.18             | 2.551                 | 2.547                  | 4 2 0 | 7         | 60.68             | 1.526                 |                        | 2 2 5  |
| 65        | 35.23             | 2.548                 | 2.541                  | 3 1 3 |           |                   |                       |                        | 8 0 4  |
| 1         | 36.00             | 2.495                 | 2.492                  | 4 2 1 | 13        | 61.78             | 1.502                 | 1.501                  | 8 2 4  |
| 24        | 36.13             | 2.486                 | 2.484                  | 0 2 2 | 5         | 71.32             | 1.322                 | 1.321                  | 3 3 5  |
| 12        | 36.32             | 2.474                 | 2.479                  | 5 1 2 | 5         | 72.06             | 1.311                 | 1.311                  | 1 3 5  |
|           |                   |                       | 2.469                  | 7 1 1 |           |                   |                       | 1.310                  | 4 2 6  |

integrated and corrected for background and Lorentz-polarization factors using the Bruker program SAINT+ (Bruker 1999a). The Bruker SADABS (Bruker 1999b) package was used to make the semi-empirical absorption correction. The crystal structure was refined in space group  $C2/m$  with neutral atomic scattering factors and starting parameters from Yoshiasa and Matsumoto (1985) [SHELX-97; Sheldrick 1997]. Atom positions and anisotropic displacement parameters for all atoms except H are reported in Table 5. Selected interatomic distances and parameters are listed in Table 6. The mean electron counts at W, X, and Y sites were determined based on the crystal structure refinement and electron microprobe analysis (Table 7). Table 8<sup>1</sup> reports observed and calculated structure factors.

The structure of poppiite, like pumpellyite and julgoldite, consists of chains of edge-sharing octahedra linked by SiO<sub>4</sub>, Si<sub>2</sub>O<sub>6</sub>(OH), and CaO<sub>7</sub> polyhedra. Both X- and Y-sites are parallel to [010] direction (Fig. 2). In particular, the structure is characterized by three symmetrically independent tetrahedra (i.e., T1 and T2 pair and T3). Similarly to other pumpellyite group minerals, one of the coordinating atoms of T2 is an OH group. The X octahedral site is larger than Y, thus suggesting a preferential ordering of larger cations in X. Poppiite is rich in V<sup>3+</sup> and shows intermediate octahedral distances ( $\langle X-O \rangle = 2.049$   $\text{\AA}$ ;

<sup>1</sup> Deposit item AM-06-018, Table 8. Deposit items are available two ways: For a paper copy contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. For an electronic copy visit the MSA web site at <http://www.minsocam.org>, go to the American Mineralogist Contents, find the table of contents for the specific volume/issue wanted, and then click on the deposit link there.

TABLE 4. Miscellaneous information pertaining to the structure refinement and unit-cell parameters for poppiite from Gambatesa mine (Northern Italy)

|  |  |
|--|--|
| Crystal system   | Monoclinic   |
| Space group  | $C2/m$   |
| Crystal size   | $0.12 \times 0.08 \times 0.06$ mm <sup>3</sup>   |
| Cell parameters  | $a = 19.2889(6)$ , $b = 6.0444(2)$ ,<br>$c = 8.8783(3)$ $\text{\AA}$ , $\beta = 97.328(2)^\circ$ |
| Volume   | 1026.66(6) $\text{\AA}^3$  |
| Radiation type   | MoK $\alpha$   |
| Data collection wavelength   | 0.71073 $\text{\AA}$   |
| Monochromator  | Graphite   |
| Measurement method   | $\phi$ and $\omega$ scan   |
| Absorption correction  | Bruker SADABS  |
| Reflections collected  | 8050   |
| Independent reflections  | 1942 ( $R_{int}^* = 0.041$ )   |
| Reflections $F_o > 2\sigma(F_o)$   | 1918   |
| Completeness to $\theta = 32.0^\circ$  | 99.7%  |
| $\theta_{min}$   | 2.31 $^\circ$  |
| $\theta_{max}$   | 32.0 $^\circ$  |
| Miller index limits  | $-28 \leq h \leq +28$<br>$-9 \leq k \leq +6$<br>$-13 \leq l \leq +13$                            |
| Number of frames   | 1370   |
| Refinement method  | Full-matrix least-squares on $F^2$   |
| Parameters refined   | 127  |
| R indices [ $F_o > 2\sigma(F_o)$ ]   | $R(F) \ddagger = 0.0307$ ; $wR(F^2)\S = 0.0720$  |
| R indices (all data)   | $R(F) \ddagger = 0.0445$ ; $wR(F^2) \S = 0.0773$   |
| Goof†  | 1.052  |
| * $R_{int} = \sum  F_o^2 - F_c^2(\text{mean})  / \sum F_o^2$ .   |  |
| † $\text{Goof} = S = \{ \sum [w(F_o^2 - F_c^2)^2] / (n - p) \}^{1/2}$ .  |  |
| ‡ $R(F) = \sum  F_o  -  F_c  / \sum  F_o $ .   |  |
| § $wR(F^2) = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}$ ; $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P$ is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$ . |  |

**TABLE 5.** Atomic coordinates, equivalent and anisotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) of poppiite

| Atom | x         | y         | z         | $U_{eq}$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|------|-----------|-----------|-----------|----------|----------|----------|----------|----------|----------|----------|
| T1   | 0.0932(1) | 0         | 0.0509(1) | 9(1)     | 8(1)     | 9(1)     | 9(1)     | 0        | 1(1)     | 0        |
| T2   | 0.2489(1) | 0         | 0.1637(1) | 10(1)    | 10(1)    | 8(1)     | 11(1)    | 0        | -1(1)    | 0        |
| T3   | 0.4020(1) | 0         | 0.4653(1) | 9(1)     | 8(1)     | 10(1)    | 9(1)     | 0        | 1(1)     | 0        |
| X    | 0.25      | 0.25      | 0.5       | 10(1)    | 11(1)    | 9(1)     | 12(1)    | 1(1)     | 2(1)     | 1(1)     |
| Y    | 0.4954(1) | 0.2476(1) | 0.2536(1) | 8(1)     | 8(1)     | 8(1)     | 9(1)     | 0(1)     | 1(1)     | 0(1)     |
| W1   | 0.3397(1) | 0.5       | 0.2525(1) | 12(1)    | 10(1)    | 13(1)    | 15(1)    | 0        | 3(1)     | 0        |
| W2   | 0.1556(1) | 0.5       | 0.1918(1) | 15(1)    | 11(1)    | 10(1)    | 23(1)    | 0        | -1(1)    | 0        |
| O1   | 0.0754(1) | 0.2218(2) | 0.1386(2) | 12(1)    | 13(1)    | 11(1)    | 14(1)    | -1(1)    | 4(1)     | 1(1)     |
| O2   | 0.2471(1) | 0.2280(2) | 0.2627(2) | 12(1)    | 13(1)    | 10(1)    | 14(1)    | -2(1)    | 1(1)     | 0(1)     |
| O3   | 0.4140(1) | 0.2193(2) | 0.3649(2) | 12(1)    | 12(1)    | 11(1)    | 13(1)    | 2(1)     | 2(1)     | 2(1)     |
| O4   | 0.4425(1) | 0.5       | 0.1274(2) | 10(1)    | 11(1)    | 11(1)    | 9(1)     | 0        | 0(1)     | 0        |
| O5   | 0.4580(1) | 0         | 0.1253(2) | 13(1)    | 14(1)    | 16(1)    | 9(1)     | 0        | 0(1)     | 0        |
| O6   | 0.0458(1) | 0.5       | 0.3736(2) | 11(1)    | 10(1)    | 11(1)    | 11(1)    | 0        | -1(1)    | 0        |
| O7   | 0.5329(1) | 0.5       | 0.3752(2) | 14(1)    | 20(1)    | 13(1)    | 9(1)     | 0        | 1(1)     | 0        |
| O8   | 0.1781(1) | 0         | 0.0346(2) | 12(1)    | 9(1)     | 15(1)    | 12(1)    | 0        | 0(1)     | 0        |
| O9   | 0.3244(1) | 0         | 0.5252(2) | 14(1)    | 8(1)     | 20(1)    | 14(1)    | 0        | 1(1)     | 0        |
| O10  | 0.3143(1) | 0         | 0.0638(2) | 16(1)    | 10(1)    | 22(1)    | 15(1)    | 0        | 3(1)     | 0        |
| O11  | 0.1846(1) | 0         | 0.4980(2) | 14(1)    | 11(1)    | 19(1)    | 12(1)    | 0        | 2(1)     | 0        |
| H5   | 0.468(4)  | 0         | 0.034(5)  | 25(2)    |          |          |          |          |          |          |
| H7   | 0.541(2)  | 0.5       | 0.483(6)  | 20(2)    |          |          |          |          |          |          |
| H10  | 0.365(4)  | 0         | 0.104(8)  | 21(1)    |          |          |          |          |          |          |
| H11  | 0.142(4)  | 0         | 0.438(8)  | 25(1)    |          |          |          |          |          |          |

Notes: Estimated standard deviations in parenthesis.  $U_{eq}$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor. The anisotropic displacement factor exponent takes the form:  $\exp \{-2\pi^2 [h^2(a^*)^2 U_{11} + \dots + 2hka^*b^* U_{12} + \dots]\}$ .

**TABLE 6.** Selected interatomic distances ( $\text{\AA}$ ) for poppiite

|                        | Distance |                       | Distance |                      | Distance |
|------------------------|----------|-----------------------|----------|----------------------|----------|
| Tetrahedron T1         |          | Tetrahedron T2        |          | Tetrahedron T3       |          |
| T1-O1 ( $\times 2$ )   | 1.609(2) | T2-O2 ( $\times 2$ )  | 1.637(2) | T3-O3 ( $\times 2$ ) | 1.630(2) |
| T1-O4                  | 1.644(2) | T2-O8                 | 1.666(2) | T3-O6                | 1.641(2) |
| T1-O8                  | 1.662(2) | T2-O10                | 1.632(2) | T3-O9                | 1.652(2) |
| <T1-O>                 | 1.631    | <T2-O>                | 1.643    | <T3-O>               | 1.638    |
| O1-O1                  | 2.681(3) | O2-O2                 | 2.757(3) | O3-O3                | 2.651(3) |
| O1-O4 ( $\times 2$ )   | 2.699(2) | O2-O8 ( $\times 2$ )  | 2.661(2) | O3-O6 ( $\times 2$ ) | 2.700(2) |
| O1-O8 ( $\times 2$ )   | 2.654(2) | O2-O10 ( $\times 2$ ) | 2.698(2) | O3-O9 ( $\times 2$ ) | 2.721(2) |
| O4-O8                  | 2.575(3) | O8-O10                | 2.606(3) | O6-O9                | 2.550(3) |
| <O-O>                  | 2.660    | <O-O>                 | 2.680    | <O-O>                | 2.674    |
| Octahedron X           |          | Octahedron Y          |          | Polyhedron W1        |          |
| X-O2 ( $\times 2$ )    | 2.105(1) | Y-O1                  | 1.9641   | W1-O2 ( $\times 2$ ) | 2.437(2) |
| X-O9 ( $\times 2$ )    | 2.076(1) | Y-O3                  | 1.9661   | W1-O3 ( $\times 2$ ) | 2.359(1) |
| X-O11 ( $\times 2$ )   | 1.967(1) | Y-O4                  | 2.081(1) | W1-O4                | 2.394(2) |
| <X-O>                  | 2.049    | Y-O5                  | 1.962(1) | W1-O8                | 2.528(2) |
| O2-O9 ( $\times 2$ )   | 2.944(2) | Y-O6                  | 2.014(1) | W1-O11               | 2.322(2) |
| O2-O9' ( $\times 2$ )  | 2.969(2) | Y-O7                  | 1.954(1) | <W1-O>               | 2.405    |
| O2-O11 ( $\times 2$ )  | 2.872(2) | <Y-O>                 | 1.990    |                      |          |
| O2-O11' ( $\times 2$ ) | 2.892(2) | O1-O4                 | 2.882(2) |                      |          |
| O9-O11 ( $\times 2$ )  | 2.675(3) | O1-O5                 | 2.811(2) | Polyhedron W2        |          |
| O9-O11' ( $\times 2$ ) | 3.032(1) | O1-O6                 | 2.794(2) | W2-O1 ( $\times 2$ ) | 2.293(2) |
| <O-O>                  | 2.897    | O1-O7                 | 2.706(2) | W2-O2 ( $\times 2$ ) | 2.436(1) |
|                        |          | O3-O4                 | 2.815(2) | W2-O6                | 2.821(2) |
|                        |          | O3-O5                 | 2.731(2) | W2-O9                | 2.493(2) |
| O-H bond               |          | O3-O6                 | 2.859(2) | W2-O10               | 2.413(2) |
| O5-H5                  | 0.857(2) | O3-O7                 | 2.845(2) | <W2-O>               | 2.455    |
| O7-H7                  | 0.949(2) | O4-O5                 | 3.037(1) |                      |          |
| O10-H10                | 0.997(2) | O4-O7                 | 2.627(3) |                      |          |
| O11-H11                | 0.921(2) | O5-O6                 | 2.603(3) |                      |          |
|                        |          | O6-O7                 | 3.033(1) |                      |          |
|                        |          | <O-O>                 | 2.812    |                      |          |

( $\langle Y-O \rangle = 1.990 \text{ \AA}$ ) relative to those observed for Al-rich pumpellyite ( $\langle X-O \rangle = 2.008 \text{ \AA}$ ,  $\langle Y-O \rangle = 1.918 \text{ \AA}$ ; Yoshiasa and Matsumoto 1985) and juldite- $Fe^{3+}$  ( $\langle X-O \rangle = 2.08 \text{ \AA}$ ,  $\langle Y-O \rangle = 2.05 \text{ \AA}$ ; Artioli et al. 2003). Cation population in X and Y sites affects unit-cell parameters, mostly  $b$ , which is the direction parallel to the X- and Y-sites.

The distribution of cations between the two octahedral sites is based on refined distances (ionic radii from Shannon 1976) and on mean electron counts (Table 7). The best agreement was found as:

**TABLE 7.** Comparison between mean electron count (m.e.c) determined from structure refinement (Xref) and from chemical analysis (EPMA) of poppiite

| Site               | m.e.c. |
|--------------------|--------|
| X (Xref)           | 21.16  |
| Y (Xref)           | 21.62  |
| 4x (X + 2Y) (Xref) | 257.6  |
| 4x (X + 2Y) (EPMA) | 258.1  |
| W1 (Xref)          | 79.2   |
| W2 (Xref)          | 78.7   |
| (W1 + W2) (Xref)   | 157.9  |
| (W1 + W2) (EPMA)   | 157.9  |



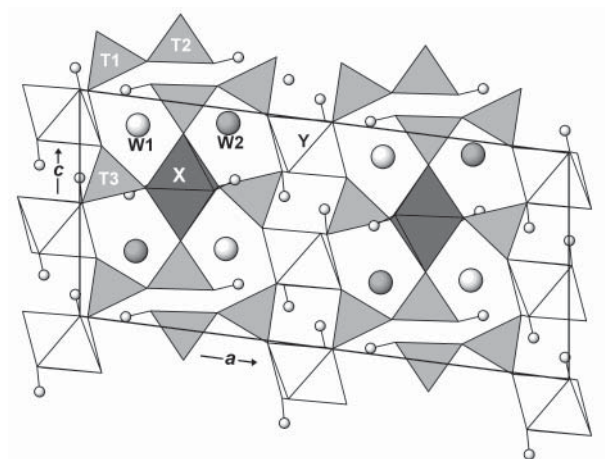


FIGURE 2. Poppiite structure projected along [010]. The small light-gray spheres denote H atoms.



for X site and



for Y site.

The dominating cation for both sites is  $V^{3+}$  and thus poppiite, following the Passaglia and Gottardi (1973) classification, has to be considered as a new pumpellyite-group end-member. The two seven-coordinated sites (i.e., W1 and W2) are mostly occupied by Ca, with limited Na, K, and Rb (mean bond lengths:  $\langle W1-O \rangle = 2.405$  and  $\langle W2-O \rangle = 2.455$  Å).

#### ACKNOWLEDGMENTS

We acknowledge E. Galli (Modena and Reggio Emilia University) and Luca Medici (CNR-IMAA, Tito Scalco, Potenza) for critical reading of the manuscript and for helping in the use of micro-diffractometer. We also acknowledge the constructive comments of Diego Gatta, associate editor, Luca Bindi, and an anonymous reviewer. This work was made possible by the financial support of Ministero dell'Università e della Ricerca Scientifica of Italy.

#### REFERENCE LIST

- Abbate, E., Bortolotti, V., Conti, M., Marcucci, M., Principi, G., Passerini, P., and Treves, B. (1986) Apennines and Alps ophiolites and the evolution of the Western Tethys. *Memorie Società Geologica Italiana*, 31, 23–44.
- Akasaka, M., Kimura, Y., Omori, Y., Sakakibara, M., Shinno, I., and Togari, K. (1997)  $^{57}Fe$  Mössbauer study of pumpellyite-okhotskite-julgoldite series

- minerals. *Mineralogy and Petrology*, 61, 181–198.
- Allmann, R. and Donnay, G. (1971) Structural relations between pumpellyite and ardeninite. *Acta Crystallographica*, B27, 1871–1875.
- (1973) Crystal structure of julgoldite. *Mineralogical Magazine*, 39, 271–281.
- Artioli, G. and Geiger, C.A. (1994) The crystal chemistry of pumpellyite: an X-ray Rietveld refinement and  $^{57}Fe$  Mössbauer study. *Physics and Chemistry of Minerals*, 20, 443–453.
- Artioli, G., Pavese, A., Bellotto, M., Collins, S.P., and Lucchetti G. (1996) Mn crystal chemistry in pumpellyite: A resonant scattering powder diffraction Rietveld study using synchrotron radiation. *American Mineralogist*, 81, 603–610.
- Artioli, G., Geiger, C.A., and Dapiaggi, M. (2003) The crystal chemistry of julgoldite- $Fe^{3+}$  from Bombay, India, studied using synchrotron X-ray powder diffraction and  $^{57}Fe$  Mössbauer spectroscopy. *American Mineralogist*, 88, 1084–1090.
- Berman, H. (1939) A torsion microbalance for the determination of specific gravities of minerals. *American Mineralogist*, 24, 434.
- Brigatti, M.F., Caprilli, E., Marchesini, M., and Poppi, L. (2003) The crystal structure of roscoelite-1M. *Clays and Clay Minerals*, 51, 301–308.
- Bruker, A.X.S. (1999a) SAINT+ (version 6.01). Bruker AXS Inc., Madison, Wisconsin.
- (1999b) SADABS (version 2.03). Bruker/Siemens area detector absorption and other corrections. Bruker AXS Inc., Madison, Wisconsin.
- Caprilli, E. (2004) *Miche e cloriti: implicazioni cristallografiche*, 205 p. PhD thesis, University of Modena and Reggio Emilia, Italy.
- Cortesogno, L., Lucchetti, G., and Penco, A.M. (1979) Le mineralizzazioni a manganese nei diaspri delle ofioliti liguri: mineralogia e genesi. *Rendiconti della Società Italiana di Mineralogia e Petrologia*, 35, 151–197 (in Italian).
- Donovan, J.J. (1995) PROBE: PC-based data acquisition and processing for electron microprobes. *Advanced Microbeam*, Vienna, Ohio.
- Galli, E. and Alberti, A. (1969) Crystal structure of pumpellyite. *Acta Crystallographica*, B25, 2276–2281.
- Gottardi, G. (1965) The crystal structure of pumpellyite. *Tschermaks Mineralogische und Petrographische Mitteilungen*, 10, 115–119.
- Ivanov, O.K., Arkhangel'skaya, V.A., Miroshnikova, L.D., and Shilova, T.A. (1981) Shuiskite—chromium analog of pumpellyite from the Biserkoe deposit, Ural. *Zapiski Vsesoyuznogo Mineralogicheskogo Obshchestva*, 110, 508–512 (abstract).
- Moore, P.B. (1971) Julgoldite, the  $Fe^{2+}$ - $Fe^{3+}$  dominant pumpellyite. *New mineral from Langban, Sweden*. *Lithos*, 4, 93–99.
- Palache, C. and Vassar, H. (1925) Some minerals of the Keweenaw copper deposits: pumpellyite, a new mineral, sericite, saponite. *American Mineralogist*, 10, 412–418.
- Pan, Y. and Fleet, M.E. (1992) Vanadium-rich minerals of the pumpellyite group from the Hemlo gold deposit, Ontario. *Canadian Mineralogist*, 30, 153–162.
- Passaglia, E. and Gottardi, G. (1973) Crystal chemistry and nomenclature of pumpellyites and julgoldites. *Canadian Mineralogist*, 12, 219–223.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, A32, 751–767.
- Sheldrick, G.M. (1997) SHELX-97, program for crystal structure determination. University of Göttingen, Germany.
- Togari, K. and Akasaka, M. (1987) Okhotskite, a new mineral, a manganese ion ( $^{3+}$ ), dominant member of the pumpellyite group, from the Kokuriki mine, Hokkaido, Japan. *Mineralogical Magazine*, 51, 611–614.
- Yoshiasa, A. and Matsumoto, T. (1985) Crystal structure refinement and crystal chemistry of pumpellyite. *American Mineralogist*, 70, 1011–1019.

MANUSCRIPT RECEIVED JULY 11, 2005

MANUSCRIPT ACCEPTED NOVEMBER 18, 2005

MANUSCRIPT HANDLED BY G. DIEGO GATTA