Menezesite, the first natural heteropolyniobate, from Cajati, São Paulo, Brazil: Description and crystal structure

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ABSTRACT

Menezesite, ideally $\text{Ba}_2\text{MgZr}_4(\text{BaNb}_{12}\text{O}_{42})\cdot12\text{H}_2\text{O}$, occurs as a vug mineral in the contact zone between dolomite carbonatite and "jacupirangite" (=a pyroxenite) at the Jacupiranga mine, in Cajati county, São Paulo state, Brazil, associated with dolomite, calcite, magnetite, clinohumite, phlogopite, ancylite-(Ce), strontianite, pyrite, and tochilinite. This is also the type locality for quintinite-2H. The mineral forms rhombohedral up to 1 mm, isolated or in aggregates. Menezesite is transparent and displays a vitreous luster; it is reddish brown with a white streak. It is non-fluorescent. Mohs hardness is about 4. Calculated density derived from the empirical formula is 4.181 g/cm³. It is isotropic, $n_{\text{meas}} > 1.93(1)$ (white light); $n_{\text{alc}} = 2.034$. Menezesite exhibits weak anomalous birefringence. The empirical formula is $(\text{Ba}_{1.47}\text{K}_{0.53}\text{Ca}_{0.31}\text{Ce}_{0.17}\text{Nd}_{0.10}\text{Na}_{0.06})\Sigma_{n=1}^{1.00}(\text{Nb}9.23\text{Ti}2.29\text{Ta}0.36\text{Si}0.12)\Sigma_{n=1}^{1.43}(\text{Zr}2.75\text{Ti}0.96\text{Th}0.29)\Sigma_{n=1}^{12.00}(\text{OH})_{1.93(1)}(\text{OH})_{2.66}(\text{Mg}0.94\text{Mn}0.23\text{Fe}0.23\text{Al}0.03)\Sigma_{n=1}^{2.66}(\text{Mg}0.96\text{Mn}0.04\text{Fe}0.23\text{Al}0.03)\Sigma_{n=1}^{1.43}(\text{Zr}2.75\text{Ti}0.96\text{Th}0.29)\Sigma_{n=1}^{24.00}(\text{Ba}_{0.72}\text{Th}_{0.26}\text{U}_{0.02})\Sigma_{n=1}^{22.08}(\text{Nb}_{0.23}\text{Ti}_{0.29}\text{Ta}_{0.08}\text{Sn}_{0.12}\text{Si}_{0.12}\text{O}_{42})\Sigma_{n=1}^{12}\Sigma_{n=1}^{2}\Sigma_{n=1}^{1}(\text{Ba}_{1.47}\text{K}_{0.53}\text{Ca}_{0.31}\text{Ce}_{0.17}\text{Nd}_{0.10}\text{Na}_{0.06})\Sigma_{n=1}^{1.00}(\text{Nb}9.23\text{Ti}2.29\text{Ta}0.36\text{Si}0.12)\Sigma_{n=1}^{1.43}(\text{Zr}2.75\text{Ti}0.96\text{Th}0.29)\Sigma_{n=1}^{12.00}(\text{OH})_{1.93(1)}(\text{OH})_{2.66}(\text{Mg}0.94\text{Mn}0.23\text{Fe}0.23\text{Al}0.03)\Sigma_{n=1}^{2.66}(\text{Mg}0.96\text{Mn}0.04\text{Fe}0.23\text{Al}0.03)\Sigma_{n=1}^{1.43}(\text{Zr}2.75\text{Ti}0.96\text{Th}0.29)\Sigma_{n=1}^{24.00}(\text{Ba}_{0.72}\text{Th}_{0.26}\text{U}_{0.02})\Sigma_{n=1}^{22.08}(\text{Nb}_{0.23}\text{Ti}_{0.29}\text{Ta}_{0.08}\text{Sn}_{0.12}\text{Si}_{0.12}\text{O}_{42})\Sigma_{n=1}^{12}\Sigma_{n=1}^{2}\Sigma_{n=1}^{1}$. Menezesite is isostructural with the synthetic compound $\text{Mg}_2[\text{MgW}_{12}\text{O}_{42}](\text{OH})_2\Sigma_{n=1}^{1.93}\Sigma_{n=1}^{2.66}\Sigma_{n=1}^{1.43}\Sigma_{n=1}^{24.00}$.

INTRODUCTION

Menezesite is the first natural heteropolyaniobate. Polyoxometalates are a large and rapidly growing class of compounds. Heteropolyoxoanions are negatively charged clusters of corner-sharing early transition-metal octahedra ($M$ usually Mo, W, V, Nb, or Ta) and heteroatom located in the interior of the cluster. Over half of the elements in the periodic table are known to function as heteroatoms in heteropoly compounds. The “heteropolyanions” obtained by Dale and Pope (1967), Dale et al. (1969), and Flynn and Stucky (1969a, 1969b) are not heteropolyoxoniobates sensu stricto, because the ligands do not form a cage about the heteroatom. The first heteropolyoxometalate, $(\text{NH}_4)_3[\text{PMo}_{12}\text{O}_{40}]$, was obtained by Berzelius (1826) as a yellow crystalline precipitate. The formation of this precipitate is still used for the classic qualitative detection and quantitative analysis of phosphorus. The crystal structure of a similar compound, with formula $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$, was determined using X-ray diffraction by Keggin (1933, 1934). The names “Keggin anion” and “Keggin structure” were introduced for this polyoxotungstate and, for extension, for the whole series $[\text{XM}_{12}\text{O}_{40}]^n–$. There are several other structural types of polyoxoanions (Jeannin 1998). The first synthetic heteropolyanions were obtained by Nyman et al. (2002, 2004).

The geometry, composition, and charge of these clusters are varied through synthesis parameters, and cluster properties are highly tuneable as a function of these characteristics. Recent studies of the Lindqvist ion $[\text{H}_{n}\text{Nb}_{n}\text{O}_{3n}]^{n–}$ as a model compound were useful to understand aqueous reactions of geochemical interest (Black et al. 2006). Casey (2006) studied large aqueous aluminum hydroxide molecules as experimental models to determine reaction rates and pathways at a fundamental level because they expose functional groups that resemble those found on the minerals. Heteropolyanions have been employed in a range of applications that include virus-binding inorganic drugs (including the AIDs virus), homogeneous and heterogeneous catalysts, electro-optic and electrochromic materials, metal and protein binding, and as building blocks for nanostructuring of materials.

Keywords: Menezesite, new mineral, polyoxometalates, heteropolyaniobate, heteropolyanions, crystal structure, chemical composition, Jacupiranga mine, Cajati, Brazil

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found numerous applications, are formed simply by acidification of solutions of their oxoanions. Under similar conditions, these oxoanion precursors are not available for Nb, and Nb-oxo chemistry is dominated by formation of the Lindqvist ion only. However, heteropolyboration formation is favoured in hydrothermal reactions of aqueous, alkaline precursor mixtures. The conditions of synthesis agree with the geological environment in which the new mineral was discovered. Unlike other heteropolyanions, heteropolyborates are basic rather than acidic, which means they can survive longer and possibly even thrive in the generally basic or neutral environments of radioactive wastes and blood, respectively. Once such compounds bind with a virus, it is no longer capable of entering a cell to damage it. Heteropolyanions may also bind with radionuclides (actinides), which remove them from the mixture by phase separation for easier and safer storage (http://www.sandia.gov/news-center/news-releases/2002/mat-chem/mayday.html).

Some naturally occurring polyvanadates (as sherwoodite and pascoite) are known (Schindler et al. 2000) and an unnamed heteropolyborate was recently described by Kolitsch and Witzke (2005).

Menezesite has been found in the last years of the decade of 1970 by Luiz Alberto Dias Menezes Filho, but its study has begun only in May 2003. The mineral was named in honor of Menezes (born 1950), mining engineer, mineral collector, and merchant. He studied the minerals from the Jacupiranga mine (Menezes and Martins 1984) and collected the samples that were used for the first official description of several new Brazilian minerals (for instance: lanthanite-(Nd), quintinite-(2H), fluorotramicrolite, lindbergite, rufraicone, guimarãesite, and also menezesite).

The menezesite IMA number is 2005-023. Type material is deposited under the number DR458 in the Museu de Geociências, Instituto de Geociências, Universidade de São Paulo, Rua do Lago, 562, 05508-080—São Paulo, SP, Brazil.

There is no apparent relation to other mineral species.

**Occurrence**

The mineral occurs in the contact zone between dolomite carbonatite and “jacupirangite” (=a pyroxenite) at the Jacupiranga mine, in Cajati county, São Paulo state, Brazil (Menezes and Martins 1984). This is also the type locality for quintinite-2H (Chao and Gault 1997). The associated minerals are dolomite, calcite, magnetite, clinohumite, phlogopite, ancyline-(Ce), strontianite, pyrite, and tochilinite. Menezesite was formed as a vug mineral.

**Habit and Physical Properties**

Menezesite occurs as rhombododecahedra up to 1 mm (Figs. 1 and 2) isolated or in aggregates. Cleavage and twinning were not observed. The mineral is transparent and displays a vitreous luster; it is reddish brown and the streak is white. It is non-fluorescent under both short (254 nm) and long wavelength (366 nm) ultraviolet radiation. The Mohs hardness is about 4. Fracture was not determined. Density was not measured due to the paucity of material but the calculated density is 4.181 g/cm³ (based on empirical formula). Optical the mineral is isotropic, with n_meas > 1.93(1) (white light); n_ab is 2.034 using the Gladstone-Dale relationship. Menezesite exhibits weak anomalous birefringence.

**Mineral Chemistry**

Menezesite crystals were embedded in epoxy resin and polished. The chemical analyses (10 point analysis on different spots) were done at the Instituto de Geociências of the Universidade de São Paulo by means of a JEOL JXA-8600 electron microprobe (WDS mode, 15 kV, 20 nA, 5 µm beam diameter) and a Noran system for automation and data reduction. H₂O was inferred from the crystal-structure determination. Analytical results are represented in Table 1. No elements with Z > 8 other than those reported herein were indicated by EDS. The empirical formula is:

\[
\text{Ba}_{1.47}\text{K}_{0.53}\text{Ca}_{0.31}\text{Ce}_{0.17}\text{Nd}_{0.10}\text{Na}_{0.06}\text{La}_{0.02}\text{Mg}_{0.94}\text{Mn}_{0.23}\text{Fe}_{0.23}\text{Al}_{0.03}\Zr_{2.75}\text{Ti}_{0.96}\text{Th}_{0.29}\text{Nb}_{9.23}\text{Ta}_{0.36}\text{Si}_{0.12}\text{O}_{42}\cdot12\text{H}_{2}\text{O}
\]

The ideal formula Ba₂MgZr₄(Ba⁺Nb₁₂O₄₂)·12H₂O yields the following wt% oxide values: BaO = 16.40, MgO = 1.44, ZrO₂ = 17.58, Nb₂O₅ = 56.87, H₂O = 7.71, total 100.00.

**Crystallographic Data**

Powder X-ray diffraction data (XRD) were obtained with a Siemens D5000 diffractometer equipped with a Göbel mirror.
and a position-sensitive detector using CuKα radiation and 40 kV and 40 μA at Instituto de Geociências of the Universidade de São Paulo (Table 2).

A single crystal was selected for intensity measurements on an Enraf-Nonius Kappa-CCD diffractometer using graphite-monochromatized MoKα radiation, at the Instituto de Física de São Carlos, Universidade de São Paulo. The diffraction intensities were measured by the ω-2θ scan technique. Data collection (φ scans and ω scans with κ offsets) was made using the program COLLECT (Enraf Nonius, Delft, The Netherlands, 1997). Final cell parameters based on all reflections, integration, and scaling of the reflections intensities were performed with the HKL DENZO SCALEPACK system of programs (Otwinowski and Minor 1997). The structure was solved using direct methods and refined by full matrix least squares procedure on SHELXL-97 (Sheldrick 1997). The crystal-structure data and characteristics of the XRD study are given in Table 3. The unit cell is cubic, and the space group is Im3 (204), with a = 13.017(1) Å, V = 2206(1) Å³, Z = 2.

Atomic coordinates, equivalent isotropic displacement parameters, occupancy, apfu, and number of electrons in each site are represented in Table 4. The ADP harmonic and anharmonic parameters of menezesite are shown in Tables 5 and 6, respectively. Selected bond lengths and angles are given in Table 7. Calculated and observed structure factors are provided in Table 8.

Menezesite is isostructural with the synthetic compound Mg2[MgW12O42](OH)8H2O studied by Günter et al. (1990) where Mg cations occupy three different sites, named Mg1, Mg2, and Mg3. The main building unit of the structure is the [MgW12O42]10– heteropolyanion, formed by 12 face and corner sharing WO6-octahedra, enclosing a 12-fold coordinated cavity, which is occupied by Mg (Mg3). The heteropolyanions occupy the corners and the body centered position of the unit cell and are cross-linked in three dimensions by MgO6-octahedra to form a rigid three-dimensional lattice in two ways. In the first, Mg1 links the central polyanion to its eight neighbors in the corners

### Table 1. Chemical composition of menezesite from Jacupiranga mine (in wt%)

<table>
<thead>
<tr>
<th>Constituent</th>
<th>wt%</th>
<th>Range</th>
<th>Standard deviation</th>
<th>Probe standard</th>
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<tbody>
<tr>
<td>Na2O</td>
<td>0.06</td>
<td>b.d.–0.12</td>
<td>0.05</td>
<td>Amela albite</td>
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<tr>
<td>K2O</td>
<td>0.86</td>
<td>0.39–1.09</td>
<td>0.04</td>
<td>feldspar</td>
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<tr>
<td>CaO</td>
<td>0.60</td>
<td>0.47–0.77</td>
<td>0.04</td>
<td>wollastonite</td>
</tr>
<tr>
<td>BaO</td>
<td>11.50</td>
<td>10.53–13.14</td>
<td>0.6</td>
<td>celsian</td>
</tr>
<tr>
<td>La2O3</td>
<td>0.09</td>
<td>b.d.–0.19</td>
<td>0.09</td>
<td>REE3</td>
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<tr>
<td>Ce2O3</td>
<td>0.94</td>
<td>0.74–1.29</td>
<td>0.1</td>
<td>REE3</td>
</tr>
<tr>
<td>Nd2O3</td>
<td>0.57</td>
<td>0.31–0.90</td>
<td>0.2</td>
<td>REE2</td>
</tr>
<tr>
<td>MgO</td>
<td>1.29</td>
<td>1.21–1.38</td>
<td>0.02</td>
<td>diopside</td>
</tr>
<tr>
<td>FeO</td>
<td>0.57</td>
<td>0.38–0.84</td>
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<tr>
<td>MnO</td>
<td>0.55</td>
<td>0.27–0.83</td>
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<td>Al2O3</td>
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<td>Aresh amphibole</td>
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<td>ZrO2</td>
<td>11.58</td>
<td>10.86–12.53</td>
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<tr>
<td>ThO2</td>
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<td>4.10–5.87</td>
<td>0.3</td>
<td>ThO2</td>
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<tr>
<td>UO2</td>
<td>0.23</td>
<td>0.16–0.29</td>
<td>0.09</td>
<td>UO1</td>
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<tr>
<td>TiO2</td>
<td>8.90</td>
<td>7.86–10.38</td>
<td>0.4</td>
<td>TiO2</td>
</tr>
<tr>
<td>Nb2O5</td>
<td>41.97</td>
<td>39.30–44.81</td>
<td>0.7</td>
<td>Nb</td>
</tr>
<tr>
<td>Ta2O5</td>
<td>2.71</td>
<td>2.06–3.24</td>
<td>0.4</td>
<td>Ta</td>
</tr>
<tr>
<td>SiO2</td>
<td>0.25</td>
<td>0.17–0.44</td>
<td>0.03</td>
<td>wollastonite</td>
</tr>
<tr>
<td>H2O</td>
<td>7.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>95.06</td>
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</table>

Note: b.d. = below detection.

### Table 2. X-ray powder-diffraction data for menezesite from Jacupiranga mine

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>dmeas (Å)</th>
<th>dcalc (Å)</th>
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<td>100</td>
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<td>0</td>
<td>9.183</td>
<td>9.2044</td>
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<tr>
<td>12</td>
<td>1</td>
<td>1</td>
<td>4.592</td>
<td>4.6022</td>
</tr>
<tr>
<td>11</td>
<td>2</td>
<td>0</td>
<td>4.136</td>
<td>4.1163</td>
</tr>
<tr>
<td>16</td>
<td>2</td>
<td>1</td>
<td>3.256</td>
<td>3.2543</td>
</tr>
<tr>
<td>13</td>
<td>3</td>
<td>0</td>
<td>3.070</td>
<td>3.0681</td>
</tr>
<tr>
<td>11</td>
<td>4</td>
<td>2</td>
<td>2.923</td>
<td>2.9107</td>
</tr>
<tr>
<td>13</td>
<td>5</td>
<td>2</td>
<td>2.655</td>
<td>2.6571</td>
</tr>
<tr>
<td>21</td>
<td>6</td>
<td>1</td>
<td>1.741</td>
<td>1.7395</td>
</tr>
<tr>
<td>9</td>
<td>7</td>
<td>0</td>
<td>1.650</td>
<td>1.6532</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>1</td>
<td>1.6271</td>
<td>1.6023</td>
</tr>
<tr>
<td>11</td>
<td>9</td>
<td>1</td>
<td>1.5131</td>
<td>1.5132</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2</td>
<td>1.4525</td>
<td>1.4553</td>
</tr>
</tbody>
</table>

Note: The eight most intense reflections are in bold. *dcalc from crystal structure.
of the unit cell, whereas, in the second, Mg₂ links the polyanions with their six neighbors across the unit-cell faces. These latter cations complete their octahedral coordination with equatorial OH anions and water molecules in relation 1:2 to reach the electroneutrality of the compound. Günter et al. (1990) also obtained the isostructural compounds where the Mg sites are filled with Fe, Co, Mn, and Ni (Table 9).

The site “W” of Günter et al. (1990) compound is equivalent to the A site in menezesite, Mg₁ to B, Mg₂ to C, Mg₃ to D. The sites O₁, O₂, and O₃ are the same in the two compounds. They represent O²⁻ ions. The split O₄a and O₄b sites of Günter et al. (1990) are the same in the two compounds. They are OH⁻-groups and H₂O-molecules in the first compound and only H₂O-molecules in menezesite. Hydroxyl groups and water molecules are distributed by electroneutrality considerations complete their octahedral coordination with equatorial groups and water molecules are distributed by electroneutrality arguments. During the procedures of structure determination two extra sites separated by ~0.5 Å were found. Trial refinements using SHELXL-97 (Sheldrick 1997) have been used with the split-atom approach for these extra sites. However, since the extra sites are very close to one another, partially empty, and occupied by different cations, poor convergence was observed during the initial refinements. It is usually observed that the closer the refined positions in a disordered structure, the higher the correlations and the more unstable the refinements when a classical split-atom approach is used in the structural model. To avoid these ambiguities, two refinements were tested: (1) a classical split-atom model considering two sites, and (2) a nonharmonic model (Kuhs 1992; Bürgi et al. 2000) based upon a development of the atomic displacement parameters (ADP) with just one site labeled as E. To perform these comparative fits the JANA2000 crystallographic computing system (Pet ricke et al. 2000) was used. From a statistical point of view, the model 2 is better than model 1 and also converges easier than model 1, which is probably due to lower correlations between the refined ADP and occupancy parameters. However, the main benefit of the non-harmonic model over the split-atom one for menezesite is the better match between the Ba content obtained from XRD

![Image of the text](https://example.com/image.png)

**Table 3.** Crystal data and experimental details

<table>
<thead>
<tr>
<th>TABLE 3. Crystal data and experimental details</th>
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<tbody>
<tr>
<td><strong>Temperature</strong></td>
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<tr>
<td><strong>Wavelength</strong></td>
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<tr>
<td><strong>Absorption coefficient</strong></td>
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<tr>
<td><strong>F(000)</strong></td>
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<tr>
<td><strong>Crystal size</strong></td>
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<tr>
<td><strong>Theta range for data collection</strong></td>
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<tr>
<td><strong>Index ranges</strong></td>
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<td><strong>Reflections collected</strong></td>
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<td><strong>Independent reflections</strong></td>
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<tr>
<td><strong>Completeness to theta = 24.91°</strong></td>
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<tr>
<td><strong>Reflections with I &gt; 2σ (I)</strong></td>
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<tr>
<td><strong>Goodness-of-fit on F²</strong></td>
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<tr>
<td><strong>Final R indices [l &gt; 2σ(l)]</strong></td>
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<tr>
<td><strong>R indices (all data)</strong></td>
</tr>
<tr>
<td><strong>Largest diff. peak and hole</strong></td>
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**Table 4.** Atomic coordinates, equivalent isotropic displacement parameters (Å² × 10⁶), occupancy, apfu, and number of electrons for menezesite

<table>
<thead>
<tr>
<th>TABLE 4. Atomic coordinates, equivalent isotropic displacement parameters (Å² × 10⁶), occupancy, apfu, and number of electrons for menezesite</th>
</tr>
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<tbody>
<tr>
<td><strong>Mult. Wyckoff</strong></td>
</tr>
<tr>
<td>A</td>
</tr>
<tr>
<td>B</td>
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<td>C</td>
</tr>
<tr>
<td>D</td>
</tr>
<tr>
<td>E</td>
</tr>
</tbody>
</table>

* U₁₁ is defined as one third of the trace of the orthogonalized Uᵢᵢ tensor.
† Constrained to be isotropic.
‡ For Z = 2.
Table 6. ADP anharmonic parameters of menezesite

<table>
<thead>
<tr>
<th>E</th>
<th>C111</th>
<th>C112</th>
<th>C113</th>
<th>C122</th>
<th>C132</th>
<th>C212</th>
<th>C222</th>
<th>C232</th>
<th>C322</th>
<th>C333</th>
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<tbody>
<tr>
<td></td>
<td>0.002(3)</td>
<td>-0.001(3)</td>
<td>0</td>
<td>0.036(8)</td>
<td>0</td>
<td>0.0017(15)</td>
<td>0.14(3)</td>
<td>0</td>
<td>0.000(3)</td>
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Table 7. Bond lengths (Å) and angles (°) for menezesite

<table>
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<tr>
<th>Bond Lengths</th>
<th>A-O1iv</th>
<th>A-O2vi</th>
<th>A-O3vi</th>
<th>B-O1xi</th>
<th>C-O2xvi–xix</th>
<th>C-O3i</th>
<th>C-O3ii–iii</th>
<th>C-O3</th>
<th>C-O41xviii</th>
<th>C-O41xxix</th>
<th>C-O42xviii</th>
<th>C-O42xxix</th>
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<tbody>
<tr>
<td></td>
<td>1.850(5)</td>
<td>2.004(7)</td>
<td>2.208(6)</td>
<td>all 2.053(5)</td>
<td>all 2.585(8)</td>
<td>72.7(3)</td>
<td>92.6(3)</td>
<td>90.1(2)</td>
<td>102.0(4)</td>
<td>98.3(2)</td>
<td>98.9(2)</td>
<td>82.8(4)</td>
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</tr>
</tbody>
</table>
| Table 9. Comparative data for menezesite and synthetic isostructural compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical formula</th>
<th>Unit cell parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>menezesite</td>
<td>Ba2Mg2(2BaNb2O6)(OH)4·8H2O</td>
<td>a = 13.07(1) Å</td>
</tr>
<tr>
<td>synthetic</td>
<td>Mg6Mg4(MgW12O42)(OH)4·8H2O</td>
<td>a = 12.862(2) Å</td>
</tr>
<tr>
<td>synthetic</td>
<td>Fe6Fe4(FeW12O42)(OH)4·8H2O</td>
<td>a = 12.75(4) Å</td>
</tr>
<tr>
<td>synthetic</td>
<td>Co6Co4(CoW12O42)(OH)4·8H2O</td>
<td>a = 12.878 Å</td>
</tr>
<tr>
<td>synthetic</td>
<td>Ni6Ni4(NiW12O42)(OH)4·8H2O</td>
<td>a = 12.824 Å</td>
</tr>
</tbody>
</table>

Note: Symmetry codes as in Figure 5.

Table: fit with respect to that from electron microprobe.

Menezesite structure is rich and complex: five sites are occupied by cations (A, B, C, D, E), two of them (C and E) partially emptied. A great number of cations are present, some of them with very close scattering factors. Another difficulty is that the mean electron numbers for the sites A and B are almost the same (Table 4). Consequently, it is only possible to be conclusive with respect to the geometry of the sites and to the location of the different cations in the five possible metallic sites keeping the occupancy constrained to the total cation content calculated from EMPA. In summary, the trial models were accepted or rejected for (1) chemical reasons; (2) considering the mean electron numbers for the different metal sites; (3) paying attention to the maximum multiplicity and to the realistic values for occupancy and ADP; (4) ionic radii; (5) EMPA; (6) electronic neutrality; and (7) on the basis of the refinement results (statistical point of view). The best model was reached when all the cation populations were kept constant in agreement with the calculations by EMPA. However, when both occupation and displacement constraints were relaxed, the stoichiometric relationships remained the same for the main atoms, and similar discrepancy factors were observed. In this way, the refinement presented in Tables 3 and 4 seems to be the best model for cation distribution obtained in this X-ray diffraction experiment. The refined chemical formula and cation distribution is

\[
\begin{align*}
\text{Ba}_4 \cdot \text{Ba}_4 \cdot \text{K}_4 \cdot \text{K}_3 \cdot \text{Ca}_6 \cdot \text{Ca}_6 \cdot \text{Nd}_4 \cdot \text{Nd}_4 \cdot \text{La}_4 \cdot \text{La}_4 \cdot \text{La}_4 \cdot \text{La}_4 \\
\text{Mg}_2 \cdot \text{Mg}_2 \cdot \text{Mn}_2 \cdot \text{Mn}_2 \cdot \text{Fe}_2 \cdot \text{Fe}_2 \cdot \text{Al}_2 \cdot \text{Al}_2 \cdot \text{Al}_2 \cdot \text{Al}_2 \\
\text{Zr}_3 \cdot \text{Zr}_3 \cdot \text{Ti}_4 \cdot \text{Ti}_4 \\
\text{Ba}_2 \cdot \text{Ba}_2 \cdot \text{Ti}_4 \cdot \text{Ti}_4 \\
\text{Nb}_2 \cdot \text{Nb}_2 \cdot \text{Ti}_4 \cdot \text{Ti}_4 \\
\text{O}_1 \text{to} \text{O}_3 \\
\text{O}_41 \text{and} \text{O}_42 : \text{H}_2 \text{O}
\end{align*}
\]

Therefore, several models were tested during successive refinements. The microprobe analysis results were used as a first approximation for cation substitutions. In all refinements, different atoms on the same site were constrained to share the same displacement parameter. The Shannon ionic radii (Shannon 1976), taking into account the suitable oxidation number of the atoms, and the geometry and environment of the sites were used as a criterion to introduce constraints in the refinement models. For instance, Ba, K, and Ca cations, due to their large ionic radii, cannot be in A, B, and C (Figs. 3, 4, and 5) and are probable in D and E. The common occurrence of the cations calculated from EMPA in other similar minerals sharing a same site was also used as approximation for the cation substitution tests. However the main approach used to reach the final cation distribution presented here was the amount of electrons that each site is able to receive keeping its maximum multiplicity. For models containing atoms with very similar scattering factors occupying the same site, some refinements gave unrealistic negative values for some atoms when the occupancy was relaxed. Therefore, the best results were obtained trying to allocate the different cations in the five possible metallic sites keeping the occupancy constrained to the total cation content calculated from EMPA. In summary, the trial models were accepted or rejected for (1) chemical reasons; (2) considering the mean electron numbers for the different metal sites; (3) paying attention to the maximum multiplicity and to the realistic values for occupancy and ADP; (4) ionic radii; (5) EMPA; (6) electronic neutrality; and (7) on the basis of the refinement results (statistical point of view). The best model was reached when all the cation populations were kept constant in agreement with the calculations by EMPA. However, when both occupation and displacement constraints were relaxed, the stoichiometric relationships remained the same for the main atoms, and similar discrepancy factors were observed. In this way, the refinement presented in Tables 3 and 4 seems to be the best model for cation distribution obtained in this X-ray diffraction experiment. The refined chemical formula and cation distribution is

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\begin{align*}
\text{Ba}_4 \cdot \text{Ba}_4 \cdot \text{K}_4 \cdot \text{K}_3 \cdot \text{Ca}_6 \cdot \text{Ca}_6 \cdot \text{Nd}_4 \cdot \text{Nd}_4 \cdot \text{La}_4 \cdot \text{La}_4 \cdot \text{La}_4 \cdot \text{La}_4 \\
\text{Mg}_2 \cdot \text{Mg}_2 \cdot \text{Mn}_2 \cdot \text{Mn}_2 \cdot \text{Fe}_2 \cdot \text{Fe}_2 \cdot \text{Al}_2 \cdot \text{Al}_2 \cdot \text{Al}_2 \cdot \text{Al}_2 \\
\text{Zr}_3 \cdot \text{Zr}_3 \cdot \text{Ti}_4 \cdot \text{Ti}_4 \\
\text{Ba}_2 \cdot \text{Ba}_2 \cdot \text{Ti}_4 \cdot \text{Ti}_4 \\
\text{Nb}_2 \cdot \text{Nb}_2 \cdot \text{Ti}_4 \cdot \text{Ti}_4 \\
\text{O}_1 \text{to} \text{O}_3 \\
\text{O}_41 \text{and} \text{O}_42 : \text{H}_2 \text{O}
\end{align*}
\]

This work.

Günter et al. (1990).
very similar electron density, the ionic radii were necessary to propose the cation distribution of the majority cations Nb and Zr between A and B.

The main geometric parameters for these minerals are given in Table 7. Considering the cation distribution obtained by the XRD experiment (Table 4) and the Shannon ionic radii (Shannon 1976), it is possible to calculate the expected cation-oxygen bond length for the octahedrons A, B, and C: $$X-O = \left[ \frac{(X_1Oc\times X_1\text{radii}) + ... + (X_iOc\times X_i\text{radii})}{\Sigma O\text{radii}} \right]$$, where X is the site label, X1, X2, ..., Xi refer to the different cations that can occupy an individual site, O radii is the oxygen ionic radii (1.25 Å), Σ is the total occupancy in each site, and the subscripts Oc and radii refer to the occupancy and ionic radii (6-coordinated, octahedral) of each atom, respectively. The calculated distances for A-O, B-O, and C-O separations are 2.02, 2.10, and 2.14 Å, respectively, which are comparable with the mean values shown in Table 7.

The site A (point symmetry m) has a distorted octahedral geometry with angles unevenly distributed from the ideal 90° [from 75.1(3)° to 102.0(4)°] and four independent distances, which are in the range from 1.850(5) to 2.208(6) Å. For the site B (point symmetry 3), which has an almost perfect octahedral geometry, the six A-O bond length are of course equivalent by symmetry [A-O = 2.053(5) Å] and angles are in the range from 89.9(1)° to 90.1(1)°. For octahedron C (point symmetry mmm), which is partially emptied (56% occupied), three non equivalent distances are observed. The third independent bond observed is due to the disordered sites O41 and O42 as observed by Günter et al. (1990) for Mg7[MgW12O42](OH)4·8H2O. In the D site, which is occupied by the heaviest atoms Ba and Th, the cations are coordinated to 12 oxygen ions, all of them at the same distance. The last metallic site (site E), which is partially empty (~19% occupied), is occupied by the largest cations Ba, K, and Ca. Besides its complex geometry, the ADP of the E site was treated using the non-harmonic approach as discussed above.
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Günter, J.R., Schmalle, H.-W., and Dubler, E. (1990) Crystal structure and properties of a new magnesium heteropoly-tungstate, Mg$_2$(MgW$_4$O$_{19}$)(OH)$_2$(H$_2$O)$_2$.

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