Hypothetical phyllophosphate structure for taranakite

DUNCAN McCONELL

Department of Geology and Mineralogy, The Ohio State University
Columbus, Ohio 43210

Abstract

Rather than being an orthophosphate, it seems probable that taranakite has a structure analogous to illite, from which it can be synthesized. The proposed hexagonal structure, with \(a = 8.7\) and \(c = 96\) Å, is composed of 6 double layers of \(4[(X_4O_{10})(OH)_2]\), where \(X = P, Al\) and/or \((H_2)\). The Al of the octahedral layer also may be replaced by protons \((H^+)\) to a significant extent, and the interlayer K ranges from 8 to 18 atoms for the four compositions considered. The unit cell (volume 6300 Å\(^3\)) presumably contains 288 oxygens.

Introduction

Recently the writer (McConnell, 1974) has suggested that vashegyite and kingite might be phyllophosphates with kaolinite-type structures. This hypothesis was based upon diffraction data, chemical analyses, and the usual calculations of densities based upon unit-cell dimensions. In addition, for vashegyite, the electron photomicrographs (produced by Koch and Sarudi, 1963) were reinterpreted, and the DTA plot was discussed.

More recently a paper has appeared by Sakae and Sudo (1975) on taranakite from Hiroshima Prefecture, Japan. In this work they describe the synthesis of taranakite—from treatment of ‘mica’ with phosphatic solutions—experiments originally carried out by Haseman et al. (1950) in order to ascertain mechanisms of fixation of phosphates in soils.

This present work indicates that taranakite probably is a hydrous aluminum phyllophosphate containing some potassium.

Chemical data

Table 1 summarizes analytical data for two natural taranakites, for the synthetic product obtained by Sakae and Sudo (1975) “from chemicals,” and for a product obtained by treating illite with a potassium phosphate solution at pH 3 (Haseman et al., 1950). In this work they describe the synthesis of taranakite—from treatment of ‘mica’ with phosphatic solutions—experiments originally carried out by Haseman et al. (1950) in order to ascertain mechanisms of fixation of phosphates in soils.

This present work indicates that taranakite probably is a hydrous aluminum phyllophosphate containing some potassium.

Crystal chemistry

Each of the foregoing calculated formulae assumed that taranakite was an orthophosphate—that is, contained PO\(_4\) groups. However, the possibility exists that taranakite may be a hydrated aluminum phyllosphate with \([\text{Al}_2\text{P}_{4-x-y}\text{Fe}_{x}\text{O}_{10}]\) sheets analogous to the \([\text{Al}_2\text{Si}_{4-x}\text{O}_{10}]\) sheets present in illite (hydromica).

A structure model like that in Figure 1 containing, parallel to \((0001)\), 6 double-sheet layers involving single sheets yields a pyrophyllite-like or mica-like arrangement, with \(a = 8.62\)–8.71 Å and \(c = 95.2\)–96.1 Å. This model is consonant with the intensities (boldface) that Sakae and Sudo (1975) observed for the following basal reflections: 0006, 100; 000.12, 21; 000.18, 0; 000.24, 0; 000.30, 7; 000.36, 9; and 000.42, 3.

The formula for this modified model may thus be written

\[
K_x[\text{Al}_{2-x-y}(H_2)_y](OH)_2[\text{Al}_2\text{P}_{4-x-y}(H_3)_y\text{O}_{10}]
\]

in analogy to that of illite

\[
K_x\text{Al}(OH)_2[\text{Al}_2\text{Si}_{4-x}\text{O}_{10}].
\]

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Table 1. Chemical analyses of taranakite and synthetic products

<table>
<thead>
<tr>
<th>Oxides</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>7.09</td>
<td>4.64</td>
<td>9.87</td>
<td>10.8</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>tr.</td>
<td>0.16</td>
<td>n.d.</td>
<td>—</td>
</tr>
<tr>
<td>CaO</td>
<td>tr.</td>
<td>0.10</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>MgO</td>
<td>tr.</td>
<td>tr.</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1.93</td>
<td>18.2</td>
<td>18.65</td>
<td>18.3</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>52.42</td>
<td>46.4</td>
<td>42.39</td>
<td>43.7</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O(+)</td>
<td>33.10</td>
<td>30.4</td>
<td>29.51</td>
<td>22.3</td>
</tr>
<tr>
<td>Sum</td>
<td>99.96</td>
<td>100.7</td>
<td>100.42</td>
<td>102.2</td>
</tr>
</tbody>
</table>

4. Synthesized from illite, showing lowest residual SiO<sub>2</sub> (0.8%). Haseman et al. (1960).

*Although reported as K<sub>2</sub>O(-) for analyses 1 and 3, the TG analyses indicate this to be an error; for analysis 4 ignition loss at 1,000°C is represented, rather than water, and volatilization of K<sub>2</sub>O may account for the high evaporation.

For the unit cell (volume: 6300 Å<sup>3</sup>) these formulas need to be multiplied by 24, whereupon 240 oxygens and 48 OH groups—or 288 oxygens in all—are seen to be present in the unit cell. Direct calculations from analyses and densities (McConnell, 1967) yield between 310 and 277 oxygens. For each of the (unit cell) formulas derived from the analyses (Table 2) the sum of the cationic charges exceeds 576 by at most 4 percent—and averages less than 2 percent. For analysis No. 2, as an example, this means that the empirical number of hydrogens reported (calculated to a base of 288 oxygens) was 247, whereas 255 was used in the formulation.

Discussion

Although the c dimension is about 96 Å, the assumption of 12 single sheets would permit a thickness of merely 8 Å, which might be reasonable for kaolinite-like layers. However, the a dimension (8.7 Å) is much less than that of a pyrophyllite sheet according to Gruner (1934). Therefore, in order to accommodate the 288 oxygens in a volume of 6300 Å<sup>3</sup> it becomes necessary to assume that there are 6 double-sheet layers which are 16 Å in thickness.

Although this thickness is greater than muscovite, it is to be remembered that the contraction of the a dimension and the substitution of (H<sub>3</sub>) for both Al and Si atoms both contribute to an increase in the thickness of the double-sheet layer. In this connection the following volumes are interesting (per 288 oxygens):

- **Kaolinite**
- **Vashgite**
- **Pyrophyllite**
- **Illite**
- **Taranakite**

<table>
<thead>
<tr>
<th></th>
<th>331 × 16</th>
<th>375 × 16</th>
<th>874 × 6</th>
<th>933 × 6</th>
<th>1050 × 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolinite</td>
<td>5296</td>
<td>6000</td>
<td>5244</td>
<td>5598</td>
<td>6300 Å&lt;sup&gt;3&lt;/sup&gt;</td>
</tr>
<tr>
<td>Vashgite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrophyllite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Illite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Taranakite</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Thus, the volume of vashgite is 13 percent greater

Table 2. Unit cell contents assigned to taranakite and synthetic products

<table>
<thead>
<tr>
<th>Analysis No. (Table 1)</th>
<th>Formula</th>
<th>Imbalance (Charges)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>K&lt;sub&gt;16&lt;/sub&gt;<a href="OH">Al&lt;sub&gt;16&lt;/sub&gt;Si&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;48&lt;/sub&gt;</a>&lt;sub&gt;4&lt;/sub&gt;Si&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;24&lt;/sub&gt;</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>(K,K,Na,Ca)&lt;sub&gt;16&lt;/sub&gt;<a href="OH">Al&lt;sub&gt;16&lt;/sub&gt;Si&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;48&lt;/sub&gt;</a>&lt;sub&gt;4&lt;/sub&gt;Si&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;24&lt;/sub&gt;</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>K&lt;sub&gt;16&lt;/sub&gt;<a href="OH">Al&lt;sub&gt;16&lt;/sub&gt;Si&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;48&lt;/sub&gt;</a>&lt;sub&gt;4&lt;/sub&gt;Si&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;24&lt;/sub&gt;</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>K&lt;sub&gt;16&lt;/sub&gt;<a href="OH">Al&lt;sub&gt;16&lt;/sub&gt;Si&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;48&lt;/sub&gt;</a>&lt;sub&gt;4&lt;/sub&gt;Si&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;24&lt;/sub&gt;</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>K&lt;sub&gt;16&lt;/sub&gt;<a href="OH">Al&lt;sub&gt;16&lt;/sub&gt;Si&lt;sub&gt;8&lt;/sub&gt;O&lt;sub&gt;48&lt;/sub&gt;</a>&lt;sub&gt;4&lt;/sub&gt;Si&lt;sub&gt;10&lt;/sub&gt;O&lt;sub&gt;24&lt;/sub&gt;</td>
<td>23</td>
</tr>
</tbody>
</table>
than kaolinite, and taranakite is 12.5 percent greater than illite and 20 percent greater than pyrophyllite.

Therefore, although it is not possible at this time to account for the 16 Å layers—that is, the nature of the stacking—this assumption seems reasonable from the volumetric relationships.

Finally, it should be indicated that substances closely resembling taranakite can be synthesized through the attack of illite by acid solutions (pH 3) of potassium phosphate at 95° C during about two weeks, and this suggests the structural analogy here proposed.

Acknowledgments

I wish to acknowledge helpful discussion of my manuscript by D. W. Foreman, Jr., R. T. Tettenhorst (Columbus), G. W. Brindley (University Park, Pennsylvania), and S. W. Bailey (Madison, Wisconsin). However, this statement is not intended to indicate their concurrence with the proposed structural hypothesis.

References


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