Hypothetical phyllophosphate structure for taranakite

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Abstract

Rather then 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_3). The Al of the octahedral layer also may be replaced by protons (H_3) to a significant extent, and the interlayer K ranges from 8 to 18 atoms for the four compositions considered. The unit cell (volume 6300 Å³) 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). To this latter material Haseman *et al.* assigned the empirical formula $H_{1.3}K_{1.1}Al_{1.8}Fe_{0.4}(PO_4)_3 \cdot 5.4 H_2O$. Later, however, Smith and Brown (1959) ascribed to it the alternative formula $H_6K_3Al_5(PO_4)_8 \cdot 18H_2O$

plus a hexagonal unit cell ($a = 8.71$, $c = 96.1$Å, $Z = 6$). Sakae and Sudo's (1975) formula for taranakite— $H_{7.09}K_{1.97}(Al,Fe)_{4.90}(PO_4)_8 \cdot 19.7H_2O$—entails an equal number of PO_4 groups but differs with respect to potassium (2 instead of 3), hydrogen (7.1 instead of 6), and H_2O (19.7 instead of 18). They cite a unit cell with $a = 8.718$ and $c = 95.18$Å.

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 $[Al_xP_{(4-x-z)}(H_3)_zO_{10}]$ sheets analogous to the $[Al_xSi_{4-x}O_{10}]$ 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 $a = 8.62$–8.71Å and $c = 95.2$–96.1Å. 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**.
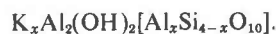
The formula for this modified model may thus be written

$$K_x[Al_{2-y}(H_3)_y] (OH)_2 [Al_xP_{4-x-z}(H_3)_zO_{10}]$$
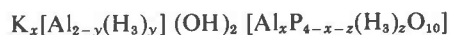
in analogy to that of illite

$$K_xAl_2(OH)_2[Al_xSi_{4-x}O_{10}].$$

TABLE 1. Chemical analyses of taranakite and
synthetic products

Oxides	1	2	3	4
K_2O	7.09	4.64	9.87	10.8
Na_2O	tr.	0.14	n.d.	—
CaO	tr.	0.10	—	—
MgO	tr.	tr.	—	—
Al_2O_3	19.03	18.2	18.65	18.3
Fe_2O_3	0.42	0.81	n.d.	6.3
P_2O_5	42.32	46.4	42.39	43.7
$H_2O(+)^*$	31.10	30.4	29.51	22.3
Sum	99.96	100.7	100.42	102.2

1. *Taranakite from Onino-Iwaya limestone cave, Hiroshima Prefecture, Japan. T. Sakae, analyst.*
2. *Taranakite from Mimegarra, W. Australia (Payne, 1972).*
3. *Synthetic product. T. Sakae, analyst.*
4. *Synthetized from illite, showing lowest residual SiO_2 (0.8%). Haseman et al. (1950).*

*Although reported as $H_2O(-)$ 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_2O may account for the high summation.
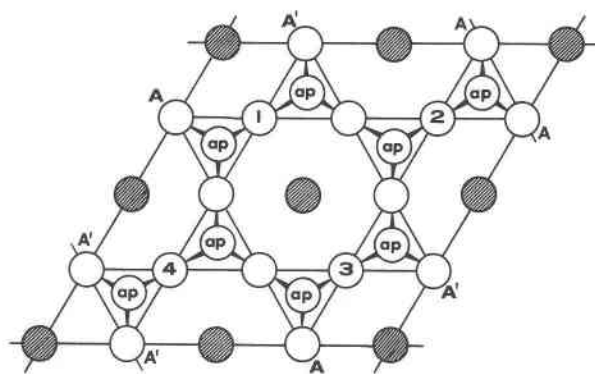

FIG. 1. Idealized arrangement of oxygens and hydroxyls (shaded) of the lower half of a double sheet. There is the probability that the hexagonal rings become ditrigonal, or that there is tilting of the tetrahedra, or both. For example, if basal oxygens (1) to (4) are assigned $z = 0.02$ (instead of $z = 0$), then the apical oxygens (*ap*) shift toward lines AA or A'A', and there is a consequent reduction of the unit cell dimension *a*.

For the unit cell (volume: 6300Å³) these formula need 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 Å³ 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_3) 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	Vashegyite	Pyrophyllite	Illite	Taranakite
331 × 16	375 × 16	874 × 6	933 × 6	1050 × 6
5296	6000	5244	5598	6300 Å³

Thus, the volume of vashegyite is 13 percent greater

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

Analysis No. (Table 1)	Formula	Imbalance (Charges)
Type	$K_{10}[Al_{48}](OH)_{48}[Al_{10}Si_{86}]O_{240}$	0
1	$K_{10}[Al_{18}(H_3)_{30}](OH)_{48}[Al_{10}P_{45}(H_3)_{41}]O_{240}$	4
2	$(K,Na,Ca)_8[Al_{19}(H_3)_{29}](OH)_{48}[Al_8P_{48}(H_3)_{40}]O_{240}$	8
3	$K_{16}[Al_{12}(H_3)_{36}](OH)_{48}[Al_{16}P_{45}(H_3)_{35}]O_{240}$	10
4	$K_{18}[Al_{11}(H_3)_{37}](OH)_{48}[Al_{18}Fe_6P_{50}Si(H_3)_{21}]O_{240}$	23

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

References

GRUNER, J. W. (1934) Crystal structure of talc and pyrophyllite. *Z. Kristallogr.* **88**, 412–419.

HASEMAN, J. F., E. H. BROWN, AND C. D. WHITT (1950) Some reactions of phosphate with clays and hydrous oxides of iron and aluminum. *Soil Sci.* **70**, 257–271.

KOCH, S., AND I. SARUDI (1963) The hydrous basic aluminum phosphates of Železnik (Vashegy), Slovakia (ČSSR). *Acta Univ. Szeged.* **16**, 3–10.

McCONNELL, D. (1967) Crystal chemical calculations. *Geochim. Cosmochim. Acta,* **31**, 1479–1487.

—— (1974) Are vashegyite and kingite hydrous aluminum phyllophosphates with kaolinite-type structures? *Mineral. Mag.* **39**, 802–806.

PAYNE, G. H. (1972) [No title] *Rep. Gov. Chem. Labs. West. Aust. for 1971,* 24–32. [See *Mineral. Abstr.* 74–476.]

SAKAE, T., AND T. SUDO (1975) Taranakite from the Onino-Iwaya limestone cave at Hiroshima Prefecture, Japan: a new occurrence. *Am. Mineral.* **60**, 331–334.

SMITH, J. P., AND W. E. BROWN (1959) X-ray studies of aluminum and iron phosphates containing potassium or ammonium. *Am. Mineral.* **44**, 138–142.