Comparison of cation exchange in ganophyllite and [Na + Al]-substituted tobermorite: crystal-chemical implications

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Abstract

Ganophyllite and [$Na^+ + Al^{3+}$]-substituted tobermorite exhibited similar cation exchange properties and, in particular, selective cesium exchange. [$Na^+ + Al^{3+}$]-substituted tobermorite and ganophyllite showed a selective Cs exchange of 10.77 and 8.71 meq/100 g from 0.02N NaCl and of 11.08 and 9.04 meq/100 g from 0.02N $CaCl_2$, respectively. The [$Na^+ + Al^{3+}$]-substituted tobermorite is structurally similar to ganophyllite: both are roughly analogous to 2:1 layer silicates, both have cross-linking tetrahedra across the interlayer region, and both have exchangeable cations located in zeolite-like sites in the interlayer region. The similarities in cation exchange properties imply that the residual charge configuration of the analogue 2:1 layer must be approximately equivalent also.

KEYWORDS: ganophyllite, tobermorite, cation exchange.

Introduction

GANOPHYLLITE, approximately $(K,Na,Ca)_6(Mn,Fe,Mg)_{24}(Si,Al)_{40}O_{96}(OH)_{16}.21H_2O$ and tobermorite, $Ca_5Si_6O_{16}(OH)_2.4H_2O$, are not phyllosilicates in the traditional sense. They have infinite, two-dimensional planes of cations (Mn in the case of ganophyllite and Ca in tobermorite), which may be considered analogous to the octahedral cation plane of Mg ions in talc. The variation in size between either Mn or Ca and Mg makes this comparison interesting. The larger Mn or Ca cations prevent perfect congruency between the component tetrahedral and octahedral sheets, unlike the situation in Mg talc, so that the simple hexagonal-based pattern of six-fold rings of the tetrahedral sheet is modified in ganophyllite and tobermorite.

In ganophyllite, a continuous octahedral sheet of edge-sharing Mn octahedra is coordinated by opposing triple chains of tetrahedra, parallel to the X direction (Kato, 1980). The tetrahedral chains are also linked together by tetrahedra (Eggleton and Guggenheim, 1986) which not only link adjacent triple chains but also adjacent 2:1 layers, thereby forming 'interlayer' tunnels along X and zeolite-like sites associated with tunnel sides. The K, Na, Ca atoms in these sites have been shown to be exchangeable (Guggenheim and Eggleton, 1986). Thus the ganophyllite structure is different from that of a talc-like structure with no interlayer cations and tetrahedral connectors, or other 2:1 layer phyllosilicates, such as the micas which have interlayer alkali elements but no interlayer tetrahedral connectors. Guggenheim and Eggleton (1987) have classified ganophyllite as a 'modulated 2:1 layer silicate' because of the periodic perturbation involving the tetrahedral sheet and they have compared the ganophyllite structure to other structures containing small (Al,Fe^{3+}) and medium-size (Mg,Mn,Fe^{3+}, etc.) octahedral cations.

The crystal structure of tobermorite has been described previously as 'layer-like' by Taylor and

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Howison (1956) and Taylor (1963). Megaw and Kelsey (1956) and Hamid (1981) showed that calcium represented a central plane between *dreierketten* of Si tetrahedra oriented parallel to Y. The calcium atoms are coordinated to seven oxygens or OH groups (Hamid, 1981) rather than six as in an ideal octahedral sheet. Two statistically occupied octahedral Ca sites are located in the 'interlayer' region along with H_2O molecules.

Solid-state magic angle spinning NMR spectroscopic studies (Wieker *et al.*, 1982; Komarneni *et al.*, 1985) confirm an earlier suggestion by Mitsuda and Taylor (1978) that tetrahedra may link across the 'interlayer' regions. The number of interlayer tetrahedral linkages affects both the cation exchange characteristics and the response to heating. 'Normal' tobermorite with few interlayer tetrahedral linkages loses water at about 300 °C with a reduction in apparent layer thickness to about 9.5Å from 11.3Å (along Z). In contrast, 'anomalous' tobermorite, which has numerous interlayer linkages, does not collapse significantly (El-Hemaly *et al.*, 1977; Mitsuda and Taylor, 1978; Komarneni and Roy, 1983) after heating.

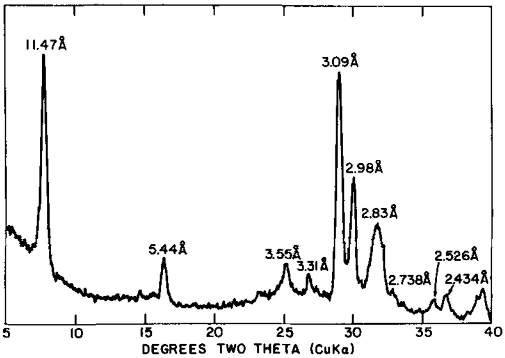

FIG. 1. X-ray powder diffractogram of the synthesized $[Na^+ + Al^{3+}]$-substituted tobermorite from a Picker-Seimens X-ray diffractometer using graphite monochromated Cu-$K\alpha$ radiation.

El-Hemaly *et al.* (1977) found that anomalous tobermorite may be more readily synthesized in the presence of alkali and Al^{3+} cations. These substituted forms, especially involving $Na^+ + Al^{3+}$ substitutions, exhibit more pronounced cation exchange characteristics and greater selectivity of Cs over Na or Ca from various dilute salt solutions (Komarneni and Roy, 1983, 1985). Cation exchange characteristics vary depending on the extent of $Na^+ + Al^{3+}$ substitutions in tobermorite.

Because ganophyllite and tobermorite have roughly analogous structures and both show cation exchange capabilities, the cation exchange properties of these two minerals may be similar. The crystal structure of ganophyllite has been refined (Eggleton and Guggenheim, 1986) and, therefore, it may be possible to relate structural and chemical characteristics to an $[Na^+ + Al^{3+}]$-substituted tobermorite. Such tobermorites are anomalous, and crystals of suitable size and quality for a structural refinement are unknown.

Experimental

Starting material. A tobermorite with an expected chemical composition of $(Ca_5Na_{0.9})_{\Sigma=5.9}[(Si_{5.1}Al_{0.9})_{\Sigma=6.0}O_{16}(OH)_2]\cdot 4H_2O$ was synthesized hydrothermally by heating an aluminosilicate gel (Si/Al ≈ 5.6/1), NaOH, CaO and H_2O in a Parr bomb for two weeks at 175 °C. Energy-dispersive spectroscopy (EDS) confirmed the presence of Na, Al, Ca and Si in the product. Figs. 1 and 2 show X-ray powder diffraction and differential thermal analytical (DTA) data, respectively, for this tobermorite. Transmission electron micrographs and corresponding electron diffraction patterns (not shown) of representative grains showed both platy and lath-like single crystals approximately 0.6 to 0.9 μm in length. X-ray powder patterns taken after heat treatment at 300 °C for 20 hrs indicated no change in the *c*-axis spacing.

A naturally-occurring ganophyllite from Franklin, N.J. (Harvard Museum No. 82837) was used for the cation exchange experiments. This sample was

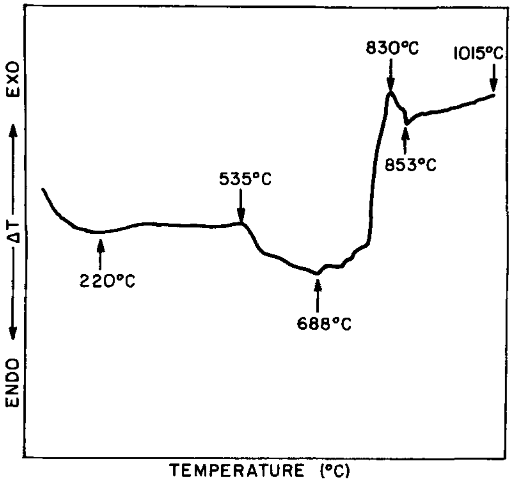

FIG. 2. Differential thermal analysis (DTA) curve for $[Na^+ + Al^{3+}]$-substituted tobermorite. A DuPont [model No. 900] thermal analyser was used and the data were collected in air.

characterized earlier by single-crystal X-ray diffraction, X-ray powder diffraction, electron microscopy by both low-resolution and high-resolution techniques, and by X-ray energy spectra (Guggenheim and Eggleton, 1986). The ganophyllite sample was previously ground (Guggenheim and Eggleton, 1986) to a powder with a grain size of approximately 0.03 mm and this powder was used here without any further grinding to preserve the current state of the sample.

Cation exchange. Total cation exchange capacity (CEC) of the tobermorite sample and selective Cs exchange properties of the two samples were determined. The total CEC for $[Al^{3+}+Na^{+}]$-substituted tobermorite was determined by the repeated saturation of the sample with NaCl solution, followed by washing with 0.01N NaCl solution to remove excess NaCl (a correction for the 0.01N solution was made by weighing), and then by displacing the Na^+ from the tobermorite with KCl (Jackson, 1974). The Na^+ concentration in solution was then measured by atomic emission spectroscopy using a SpectraMetrics SpectrsSpan III instrument to calculate the total CEC. The total CEC of ganophyllite was not determined here because the available quantity of sample was insufficient. Exchange experiments by Guggenheim and Eggleton (1986) showed that the CEC of this sample is 90 meq/100 g. However, if it is assumed that all the CaO, K_2O and Na_2O present in ganophyllite (Guggenheim and Eggleton, 1986) is exchangeable, the theoretical total CEC is approximately 159 meq/100 g based on the chemical analysis given.

Selective Cs exchange by both tobermorite and ganophyllite was measured as follows: 10 mg sample was equilibrated with 5 ml of a solution containing 2×10^{-4}N CsCl in 0.02N NaCl or 0.02N $CaCl_2$ for 1 and 7 days without any shaking. After equilibration, the solid and supernatant were separated by centrifuging, and the supernatant was analysed. Caesium in the solution phase was determined by atomic absorption spectrophotometry with an electrodeless discharge lamp using a Perkin Elmer PE703 instrument. The selective caesium exchange was expressed as a distribution coefficient, K_d. At least two replicates were used in all the cation exchange experiments.

Results and discussion

X-ray diffraction (Fig. 1) shows the tobermorite sample to be highly crystalline and apparently pure. Additional X-ray patterns taken after heat treatment at 300 °C for 20 hours indicated that the tobermorite is anomalous. The DTA results (Fig. 2) indicate tobermorite decomposition at 830 °C.

Based on the chemical composition of $(Ca_5Na_{0.9})[(Si_{5.1}Al_{0.9})O_{16}(OH)_2].4H_2O$, the ideal total exchange capacity is 120 meq/100 g (Table 1) for all exchangeable sodium ions. The total measured exchange capacity, however, is 59 meq/100 g. This incomplete exchange indicates that charge balance probably occurred with both Na^+ and Ca^{2+} and the Ca^{2+} would not be expected to readily exchange with the lower-charged and less hydrated Na^+ during the CEC measurement (Komarneni *et al.*, 1987). Similarly, Guggenheim and Eggleton (1986) showed that Na^+ and K^+ from the zeolite-like sites in ganophyllite are exchangeable, although Ca^{2+} was not. They attributed the non-exchangeable nature of Ca^{2+} to its cation charge, size and hydration state. The difference between the theoretical and experimental CECs (Table 1) is analogous to that of tobermorite.

The selective Cs exchange studies (Table 1) show that Cs^+ is preferentially sorbed from the $CaCl_2$ solution than from the NaCl solution based on total CEC and the equivalent concentrations in the solutions. For example, the ratios of Na^+ to Cs^+ and Ca^{2+} to Cs^+ are 100:1 in solution. Presumably, Na^+ can easily enter the exchangeable site, thereby blocking Cs exchange, whereas the relatively highly hydrated Ca^{2+} cannot readily enter the structure.

The selective Cs exchange K_d in ganophyllite is lower than that of the tobermorite (Table 1), although ganophyllite has a greater exchange capacity. However, exchange equilibrium was not achieved in ganophyllite even after one day because of its large crystallite size, whereas the tobermorite crystallites were small and equilibrium was achieved. Nevertheless, both $[Na^{+}+Al^{3+}]$-substituted tobermorite and ganophyllite exhibit selective exchange for Cs.

This suggests strong similarities in the cation exchange properties of $[Na^{+}+Al^{3+}]$-substituted tobermorite and ganophyllite. Because the zeolite-like sites are involved in cation exchange and these sites are located in the interlayer region in both minerals, it follows that the interlayer environment for $[Na^{+}+Al^{3+}]$-substituted tobermorite and ganophyllite should be approximately equivalent. Both minerals, because they are 2:1 layer silicate analogues with tetrahedral connectors across the interlayer region, must have strong similarities in the general topology of the interlayer region. However, structural topology alone does not determine exchange properties of a substance. It is suggested, therefore, that the residual charge configuration of the analogue 2:1 layer must be approximately equivalent in both minerals also.

In the X-ray refinement of the ganophyllite structure, Eggleton and Guggenheim (1986) found

TABLE 1. Cation exchange properties of $[Na^{+}+Al^{3+}]$-substituted synthetic tobermorite and ganophyllite.

	Total cation exchange capacity, meq/100g		Selective cesium exchange# in			
			0.02N NaCl		0.02N $CaCl_2$	
Sample	Theoretical	Experimental	meq/100g	K_d*(ml/g)	meq/100g	K_d*(ml/g)
$[Na^{+}+Al^{3+}]$-substituted tobermorite	120**	59	10.77	7200	11.08	12,900
Ganophyllite	159**	90+	8.71 (9.39)	3400 (7700)	9.04 (9.47)	4700 (8800)

\# Numbers are for 1 day equilibration while the numbers in parentheses are for 7 day equilibration.

* K_d is a distribution coefficient and is defined as a ratio of the amont of Cs sorbed per g to the amount of unsorbed Cs per ml.

** Thoeretical cation exchange capacity based on chemical composition.

\+ Data from Guggenheim and Eggleton (1986).

that Al substitution for Si is structurally required for chains to be congruent with the (large) Mn octahedral sheet. This substitution produces undersaturated basal oxygens associated with the Al-containing tetrahedral site. Evidence from a Fourier map (Eggleton and Guggenheim, 1986) indicated that zeolite-like sites formed in association with these undersaturated basal oxygens within the interlayer region. We note, however, that the zeolite-like sites in ganophyllite are not all well-defined and many are present that are not directly related to these undersaturated basal oxygens.

Aluminium substitution for silicon in tobermorite would be expected also to produce undersaturated basal oxygens with approximately the same degree of undersaturated character as that found in ganophyllite. However, unlike the situation in ganophyllite, congruency between the large cation plane and the Si tetrahedral chains is independent of Al content. By analogy to true 2:1 layer silicates, congruency is accomplished in tobermorite by (*a*) the change in configuration around the calcium cations away from an octahedral coordination, (*b*) the perturbation of the tetrahedral sheet to a series of chain configurations, and (*c*) the change in the nature of the silicate chains to a *dreierketten*. If structural control for tetrahedral Al substitution exists in tobermorite, it may be related to site differences in the *dreierketten* or in the tetrahedral linkages across the interlayer. Such structural control may be related to the observation by El-Hemaly *et al.* (1977) that '... the presence of Al^{3+} and alkali is not necessary for the formation of anomalous tobermorite, though it may make it possible to obtain it as a stable phase'.

This study shows the structural affinities and the possible relationship in charge distribution between ganophyllite and $[Na^{+}+Al^{3+}]$-substituted tobermorite based on cation exchange experiments and previous structural studies. The preference for Cs as illustrated by the cation exchange experiments in $[Na^{+}+Al^{3+}]$-substituted tobermorite may be of potential use in radioactive waste disposal systems where radiogenic Cs is a common component. Tobermorite minerals are important in cement hydration and, therefore, $[Na^{+}+Al^{3+}]$-substituted tobermorite may be directly incorporated in containment cement. Both because $[Na^{+}+Al^{3+}]$-substituted tobermorite contains common constituent elements and because it may be readily synthesized, this phase can be economically produced in large quantities. In contrast, ganophyllite probably would not be economical for such use because Mn production is relatively expensive. Furthermore, ganophyllite phase relations are currently unknown.

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References

Eggleton, R. A., and Guggenheim, S. (1986) *Mineral. Mag.* **50**, 307-16.

El-Hemaly, S. A. S., Mitsuda, T., and Taylor, H. F. W. (1977) *Cement Concr. Res.* **7**, 429–38.

Guggenheim, S. and Eggleton, R. A. (1986) *Mineral. Mag.* **50**, 517–20.

————(1987) *Am. Mineral.* **72**, 724–38.

Hamid, S. A. (1981) *Z. Kristallogr.* **154**, 189–98.

Jackson, M. L. (1974) *Soil Chemical Analysis—Advanced Course.* Publ. by the author, Dept. of Soils, University of Wisconsin, Madison, WI 53706, pp. 895.

Kato, T. (1980) *Mineral. J.* (*Japan*) **10**, 1–13.

Komarneni, S. and Roy, D. M. (1983) *Science*, **221**, 647–8.

————(1985) *J. Mat. Sci.* **20**, 2930–6.

——Roy, R., Roy, D. M., Fyfe, C. A., Kennedy, G. J., Bothner-By, A. A., Dodok, J., and Chesnick, A. S. (1985) Ibid. **20**, 4209–14.

——Breval, E., Miyake, M., and Roy, R. (1987) *Clays Clay Minerals*, **35**, 385–90.

Megaw, H. D. and Kelsey, C. H. (1956) *Nature*, **177**, 390–1.

Mitsuda, T. and Taylor, H. F. W. (1978) *Mineral. Mag.* **42**, 229–35.

Taylor, H. F. W. (d.) (1964) *The Chemistry of Cements*, Academic Press, Vol. 1, 460 pp.

——and Howison, J. W. (1956) *Clay Mineral. Bull.* **31**, 98–111.

Wieker, W., Grimmer, A. R., Winkler, A., Magi, M., Tarmak, M., and Lippmaa, E. (1982) *Cement Concr. Res.* **12**, 333–9.

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