

## Cation exchange in ganophyllite

STEPHEN GUGGENHEIM

Department of Geological Sciences, University of Illinois, Chicago, Illinois 60680, USA

AND

RICHARD A. EGGLETON

Geology Department, Australian National University, Canberra, ACT, Australia

**ABSTRACT.** Ganophyllite has been shown to have alkali cation exchange capability. Partial cesium exchange for K+Na in large (> 0.3 mm) grains shows that the exchangeable cations migrate parallel to *X*, the crystallographic direction for the 'interlayer' tunnels. Such exchange capability supports the suggestion that the alkali elements are located in zeolite-like sites attached to the sides of the tunnels. Exchange experiments show that complete sodium substitution for potassium is possible also. Eggletonite, the Na analogue of ganophyllite, is shown to have an identical superlattice to ganophyllite, indicating that eggletonite differs from ganophyllite only by the exchangeable cation.

**KEY WORDS:** ganophyllite, eggletonite, cation exchange.

THE Mn layer silicate ganophyllite, approximately  $(K,Na,Ca)_6Mn_{24}(Si_2Al)_{40}(O,OH)_{112} \cdot 21H_2O$ , has a structure in which a continuous octahedral sheet of Mn(O,OH) is coordinated by opposing triple chains of tetrahedra extending parallel to the *X* direction (Kato, 1980). Based on X-ray subcell data, Kato concluded that the tetrahedral chains are connected laterally by K, Na, and Ca. A re-examination of ganophyllite by Eggleton and Guggenheim (1986) indicates that the tetrahedral chains are linked across the 'interlayer' by additional tetrahedra and not by alkali cations. Such a model provides only zeolite-type sites for the

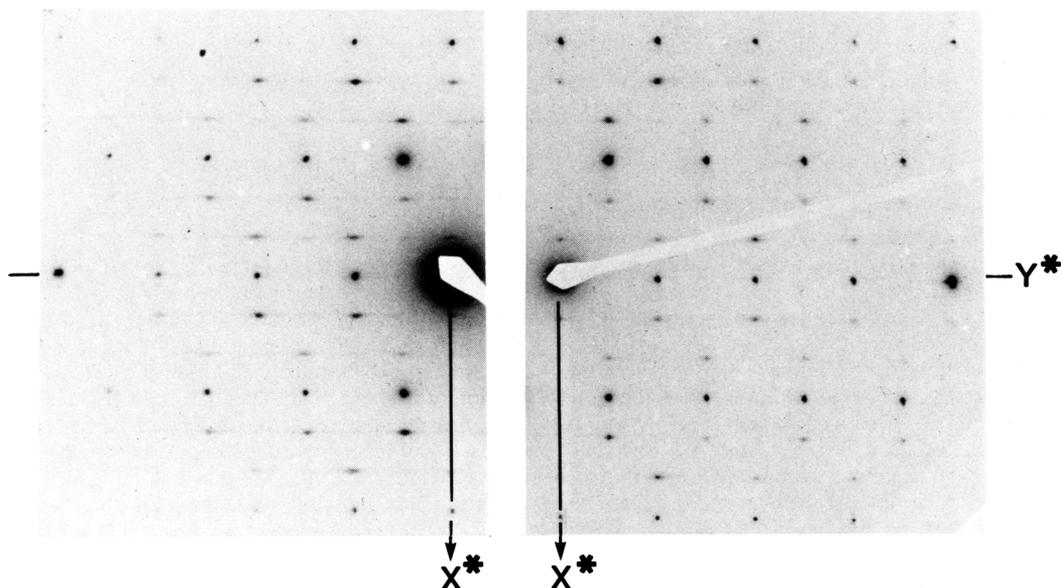


FIG. 1. *hk0* electron diffraction patterns from eggletonite (left) and Franklin Furnace ganophyllite (right).

alkali atoms, sites in which the alkalis are very weakly bonded.

The new mineral eggletonite was described by Peacor *et al.* (1984) as the Na analogue of ganophyllite, on the basis of chemistry and X-ray powder data. Although noting the close similarity between the observed powder patterns for eggletonite and the strong subcell reflections of ganophyllite, Peacor *et al.* were unable to detect superlattice reflections in eggletonite. Such reflections are known to occur in ganophyllite (Smith and Frondel, 1968; Jefferson, 1978) and produce a supercell with dimensions of  $a = 3a_0$ ,  $b = 2b_0$  and  $c = 2c_0$ . Kato (1980) suggested that the superlattice along  $X$  develops primarily from alkali cation ordering, whereas Eggleton and Guggenheim (1986) postulate that it is a consequence of the tetrahedral linkage across the interlayer.

Electron diffraction is an ideal technique to detect weak superlattice reflections from small crystals. Such a technique might be useful also to distinguish the cause of the superlattice. If the origin of the superlattice is related to tetrahedral linkage, then there should be little difference between the diffraction patterns of ganophyllite and eggletonite. In contrast, if the superlattice is developed by alkali order/disorder, then significant differences in the superlattices of ganophyllite and eggletonite would be expected.

The purpose of this paper is to further characterize eggletonite and to help establish the origin of the superlattice in ganophyllite. We describe electron diffraction data of both minerals and give results of cation exchange experiments on ganophyllite.

**Experimental.** Precession photographs of crystals of ganophyllite from Franklin, NJ (Harvard Museum No. 82837), confirmed its identity, its monoclinic subcell and its supercell dimension along  $X$ . Twinning prevented a more complete characterization. Eggletonite (Smithsonian No. 137143) from the type locality and Franklin ganophyllite were each prepared for viewing in a Jeol 100CX and a Jeol 200CX electron microscope by dispersing crushed grains on holey carbon grids.

Electron diffraction data were collected for the three axial zones and a number of other directions. The ganophyllite results compare well to the monoclinic data presented by Jefferson (1978). Although eggletonite was acicular to prismatic before crushing, grains were similar to ganophyllite in morphology when viewed in the electron microscope. There was no detectable difference between the electron diffraction patterns of the two minerals (see fig. 1).

X-ray powder diffraction data were obtained using a 114.6 mm Debye-Scherrer camera, Fe- $K\alpha$  radiation, and the line positions referred to a Si internal standard. Intensities were measured by

photometer, and the pattern indexed by comparison with the subcell single-crystal ganophyllite intensities collected by Kato and kindly made available to us. Seventeen reflections in the range of  $1.62 < d < 4.2 \text{ \AA}$  could be unambiguously indexed, and these were used to determine cell parameters by least-squares (Table I). Based on these values, the eggletonite superlattice has cell parameters  $a = 16.647(3)$ ,  $b = 27.012(4)$ ,  $c = 50.06(2) \text{ \AA}$ ,  $\beta = 94.02(3)^\circ$ , and the space group is  $Aa$  or  $A2/a$ .

Table I : X-ray powder diffraction data for the eggletonite I-centred subcell. Fe  $K\alpha$  radiation.

hkl	$I_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$
002	>100	12	12.5
020	10	6.8	6.8
004	10	6	6.24
110	25	5.11	5.12
112	15	4.59	4.63
031	15	4.42	4.43
006	40	4.17	4.16
033	40	3.96	3.96
123	15	3.722	3.726
017	35	3.449	3.449
008	50*	-	3.122
141	45	2.850	2.852
037	15	2.794	2.796
118, 202	30	2.741	-
143,	100	2.694	2.694
204	55	2.598	2.599
145	55	2.458	2.458
206	30	2.385	2.383
147	15	2.284	2.283
206	20	2.234	2.234
147	30	2.203	2.203
149	15	2.036	2.036
14.11, 13.12	15	1.754	-
080	20	1.689	1.688
082	20	1.673	1.673
341	45	1.622	1.622
341, 343	30	1.608	-

$I_{\text{obs}}$  by photometer trace from 114.6mm Debye-Scherrer film.

\* obscured by Si(111) internal standard; I calculated from single crystal data

$a = 5.549 (1)$

$b = 13.506 (2)$

$c = 25.03 (1)$

$\beta = 94.02 (3)$

The Franklin ganophyllite was prepared for the cation exchange experiments by crushing to fragments of about 0.3 mm. Although such large fragments would be expected to exchange slowly and incompletely, the crystallographic direction of cation movement might be determined by X-ray or microprobe analysis. In the first set of experiments, grains were placed in a 0.1 N solution of CsCl and sampled after 1 day, 17 days, and 50 days. The solution was agitated constantly for the first 17 days. Retrieved grains were washed repeatedly with distilled water and acetone and then mounted and sectioned for chemical analysis. Fig. 2 shows a back-scattered electron map and two X-ray energy spectra, one from the grain centre and one from near the edge.

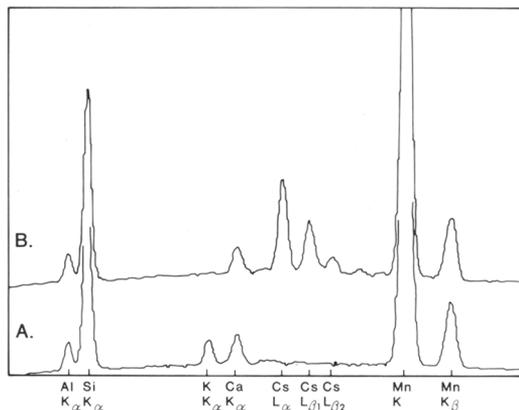
In a second set of exchange experiments, Franklin ganophyllite was placed in a 1N solution of NaCl after preparing material in a manner similar to that described above. Grains were retrieved at one week intervals and the solution was agitated constantly. Electron microprobe analyses are given in Table II.

Table II : Partial chemical analysis by electron microprobe of ganophyllite, Franklin, N. J. before and after sodium cation exchange.

	Control (No exchange)	After 1 week core	After 3 weeks edge	After 3 weeks core	After 3 weeks edge
SiO <sub>2</sub>	39.96	40.92	40.83	41.01	40.55
Al <sub>2</sub> O <sub>3</sub>	7.66	7.53	7.62	7.76	7.72
FeO	b.d.	n.a.	n.a.	n.a.	n.a.
MnO	34.39	35.30	34.76	34.65	34.66
MgO	0.18	0.18	0.23	0.28	0.24
CaO	1.67	1.53	1.68	1.59	1.65
K <sub>2</sub> O	2.71	0.31	0.28	0.12	0.05
Na <sub>2</sub> O	1.29	2.30	2.16	2.62	2.78
Cl	0.05	b.d.	b.d.	0.05	0.06
TOTAL	87.91	88.08	87.55	88.07	87.71

*Discussion.* It is apparent from fig. 1 that the electron diffraction data for ganophyllite and eggletonite are very similar. Therefore, these data confirm that eggletonite is an Na-rich ganophyllite structure in accord with the suggestion of Peacor *et al.* (1984). On the other hand, if the alkali elements are important contributors to the origin of the superlattice, it would be expected that the difference in atomic number between Na and K should affect the relative intensities of the superlattice reflections between these two minerals. Therefore, these data suggest that the alkali elements are not imperative for the development of the superstructure and raise additional doubts about the validity of the Kato (1980) subcell model for ganophyllite.

One alternative to this model is that the alkali elements reside in the tunnels between the layers in zeolite-like sites (Eggleton and Guggenheim, 1986). If such weakly bonded sites exist, exchangeable cations would be expected to migrate parallel to *X*, the tunnel direction. The Cs distribution map of fig. 2, which shows a partially exchanged grain, is in good agreement with the predicted direction of cation migration. In contrast, cations should not be readily exchangeable in the model proposed by Kato (1980) because of the high residual negative



X-Ray Spectra

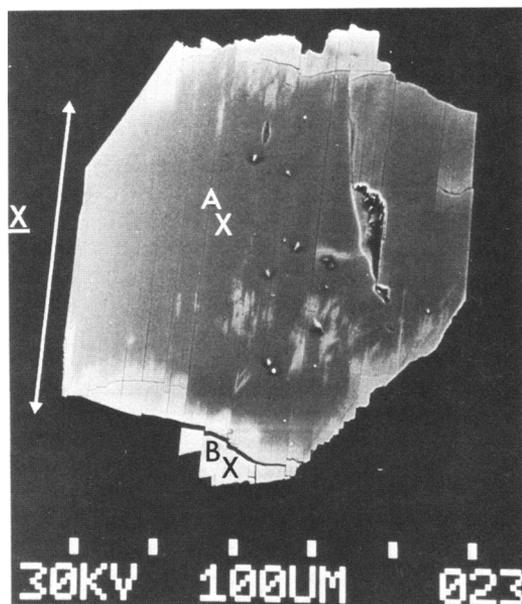


FIG. 2. Above: X-ray spectra from the centre (A) and rim (B) of a ganophyllite crystal after 17 days in 0.1N CsCl solution. Below: Backscattered electron image of the crystal. The direction of the *X*-axis is indicated. The Cs-rich (brighter) area reveal Cs migration parallel to *X*.

charge associated with the O(5) oxygen(s) coordinating to the alkali site.

The sodium exchange experiments (Table I) clearly indicate that sodium exchange is rapid and nearly complete, even for large grains. The amount of sodium exchanged for potassium is consistent with a one-for-one replacement. The calcium content does not appear to be affected by the exchange

reaction and this may be related to the differences in cation charge, size or hydration state. The charge associated with total alkali content may be related to aluminium content in ganophyllite, although this conclusion should be considered tentative without additional data.

*Acknowledgements.* We thank P. J. Dunn of the Smithsonian Institute, Washington DC, I. M. Threadgold, University of Sydney, Australia, and C. A. Francis, Harvard Museum, Cambridge, Massachusetts, for providing samples. In addition, we thank Professor B. Hyde of the Australian National University Research School of Chemistry, Canberra, Australia, for access to the microscopes and T. Kato, Yamaguchi University, Japan, for reviewing the manuscript. Portions of this work were

supported by the National Science Foundation under grant EAR80-18222.

#### REFERENCES

- Eggleton, R. A., and Guggenheim, S. (1986) *Mineral. Mag.* **50**, 307-15.  
Jefferson, D. A. (1978) *Acta Crystallogr.* **A34**, 491-7.  
Kato, T. (1980) *Mineral. J. (Japan)* **10**, 1-13.  
Peacor, D. R., Dunn, P. J., and Simmons, W. B. (1984) *Mineral. Mag.* **48**, 93-6.  
Smith, M. L., and Frondel, C. (1968) *Ibid.* **36**, 893-913.

[*Manuscript received 28 December 1984;*  
*revised 12 February 1985*]