Clays and Clay Minerals, 1973, Vol. 21, pp. 131–136. Pergamon Press. Printed in Great Britain

EXCHANGEABLE CATION DISTRIBUTION IN NICKEL– AND MAGNESIUM–VERMICULITES

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(*Received* 1 *December* 1972)

Abstract—Abnormal scatterings of X-rays take place between Bragg spots. Their study in hydrated Mg– and Ni–vermiculites shows that they appear in reciprocal space in the form of modulated lines, elongated along the Z^* axis. These scatterings demonstrate a two-dimensional organization of the compensating cations and of the water molecules in the interlamellar layer. In such ordered domains, the cations are situated at the nodes of a biperiodic centered lattice with parameters $3a,b$.

The distribution of compensating cations must conform with the charge distribution which they neutralize; it can therefore be concluded that the distribution of effective negative charges (tetrahedral negative charges less positive octahedral charges) is also at least partially ordered.

INTRODUCTION

SINCE the works of Gruner (1934), and Hendricks and Jefferson (1938), the structure of vermiculite has been more precisely determined by Mathieson and Walker (1954); Mathieson (1958); Bradley and Serratosa (1960) and Shirozu and Bailey (1966). In regard to the organization of the interlamellar layer, there are several models to represent the distribution of the compensating cations and their associated hydration shells.

Mathieson and Walker (1954) and Mathieson (1958) gave the interlamellar layer a structure analogous to the brucite sheet of chlorites but where the Mg would occupy only $\frac{1}{3}$ of the available sites and the water $\frac{2}{3}$ of these. The proposed model for an ordered distribution of cations and water molecules in each layer, with formation of a superstructure with parameters $3a,b$ is based entirely on consideration of dimension and mutual repulsion. Bradley and Serratosa (1960) have considered in particular the organization of the water molecules in the interlamellar layer. They proposed periodic models for two extreme values of the exchange capacity: for the higher level a periodic structure compatible with the cell of vermiculite, for the lower level a structure extending over a centered triple cell with parameters $3a,b$. These ordered structures would extend only over limited domains inside the crystal.

Shirozu and Bailey (1966) have determined precisely the location of the interlamellar Mg cation in a vermiculite of Llano (Texas). The cation is present in only one of the possible sites in this layer (M_{IV}) and occupies this position with a probability of only 41 per cent. This localization between the T_I tetrahedra is particularly affected by the aluminum-silicon substitutions and ensures the local compensation of charges.

The structures determined from X-ray diffraction data can only give an average distribution of the compensating cations on the crystallographic sites attributed to them, for the number of these cations is less than the number of equivalent positions defined by the space group. Our object has been to determine whether this distribution is truly statistical, i.e. whether the cations are randomly distributed in the expected positions, or whether there exists a short range order in the disposition of the compensating ions.

To decide between these two possibilities, the study of discrete diffraction spots (Bragg spots) is no longer sufficient; it is also necessary to consider the scattering which occur between them.

If this scattering is continuous and diffuse (Laue scattering) then the random distribution of the exchangeable ions will be confirmed, but if on the other hand this scattering is condensed into discrete shapes, then it will be possible from the study of such shapes to determine ordered relationships in the disposition of the compensating cations.

EXPERIMENTAL

The scattering phenomena which give the required information are of low intensity. For observation, we placed a fixed single crystal ($4 \times 4 \times 0{\cdot}3$ mm) before a monochromatic X-ray beam (Mo Kα) (Fig. 1). The monochromatization was achieved by a doubly-curved crystal of LiF, which ensured roughly a point focusing of the monochromatic beam. The tube voltage was maintained at 30 kV to avoid exciting the second har-

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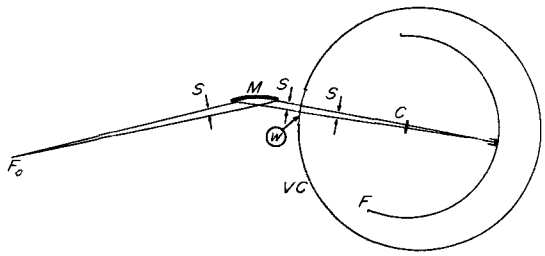


Fig. 1. Schematic experimental arrangement, F_o: X-ray focus, M: doubly bent monochromator, S: slit, C: Crystal, F: film, VC: vacuum chamber, W: Be-window.

monic of the beam in the continuous spectrum. Each exposure was for approximately 24 hr.

The image obtained on film then corresponded to a section of the reciprocal space by the Ewald sphere. From successive exposures, in which the incidence angles of the X-rays on the crystal were varied, it was possible, with adjoining sections, to reconstitute part of the reciprocal space and to show the continuity of the scattering phenomena. The diffuse spots on the photographs so obtained correspond to line scatterings and the diffuse lines to planar scatterings. The appearance of Bragg spots on these photographs is due to the angular aperture of the focused beam and makes it possible to locate the scatterings with respect to the nodes of the reciprocal lattice. The study has been made on a vermiculite from Kenya, with the structural formula:

$$(Mg_{2,47}Fe^{2+}_{0,08}Fe^{3+}_{0,40}Ti_{0,05})(Si_{2,76}Al_{1,24})O_{10}(OH)_2$$

$$(Mg_{0,35}\,Ca_{0,02})\,n\,H_2O$$

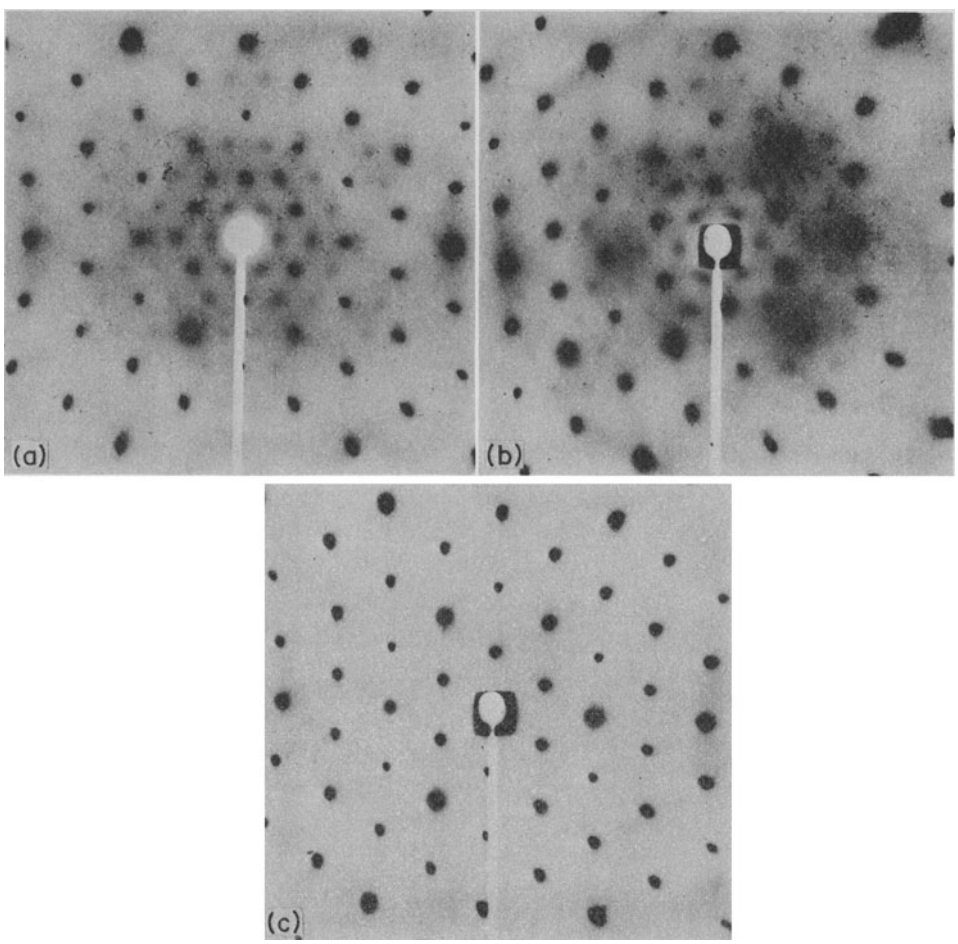


Fig. 2. Mg–Vermiculite, X-ray diffraction photographs. (a) Hydrated specimen with the crystal perpendicular to the X-ray beam. (b) Hydrated specimen with the crystal at 20° to the X-ray beam (c) Dehydrated specimen.

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Hydrated Mg- and Ni-vermiculites

Under normal conditions of temperature and humidity (air dry), a single crystal of Mg-vermiculite was exposed perpendicularly to a beam of X-rays (Z^* axis parallel to the beam). On the photographs (Fig. 2a) there appeared diffuse spots between Bragg spots. Successive exposures with increasing incidence angles have shown the continuity of these scatterings along Z^* axis and have also revealed a modulation of their intensity in this direction (Fig. 2b). When one projects these line scatterings, thus reconstituted on the X^*Y^* plane, it is found that they are placed at the nodes of a lattice defined by the parameters $A/3$ and B, and that they occupy the positions where $n + m = 2p$ (n, m, p:integers) in the expression $nA/3 + mB$; (Fig. 4).

After exchange during several weeks in a normal solution of $NiCl_2$ at 60°C, the crystal gave analogous diffraction photographs. We find in Fig. 3a and 3b a similar system of diffused spots, whose continuity along the Z^* axis shows the presence of line scatterings, the only difference from the patterns in Fig. 2 being the shape of modulation along the Z^* axis. This difference is due to the increase of the contribution of the cation to the "structure factor" of the group formed by the cation and its six surrounding water molecules. The projection of these diffusions on the X^*Y^* plane gives us a diagram similar to that produced by Mg-vermiculite.

Dehydrated Mg- and Ni-vermiculites

After desiccation at 500°C and exposure in a vacuum, and under the experimental conditions specified above, the observed scatterings no longer

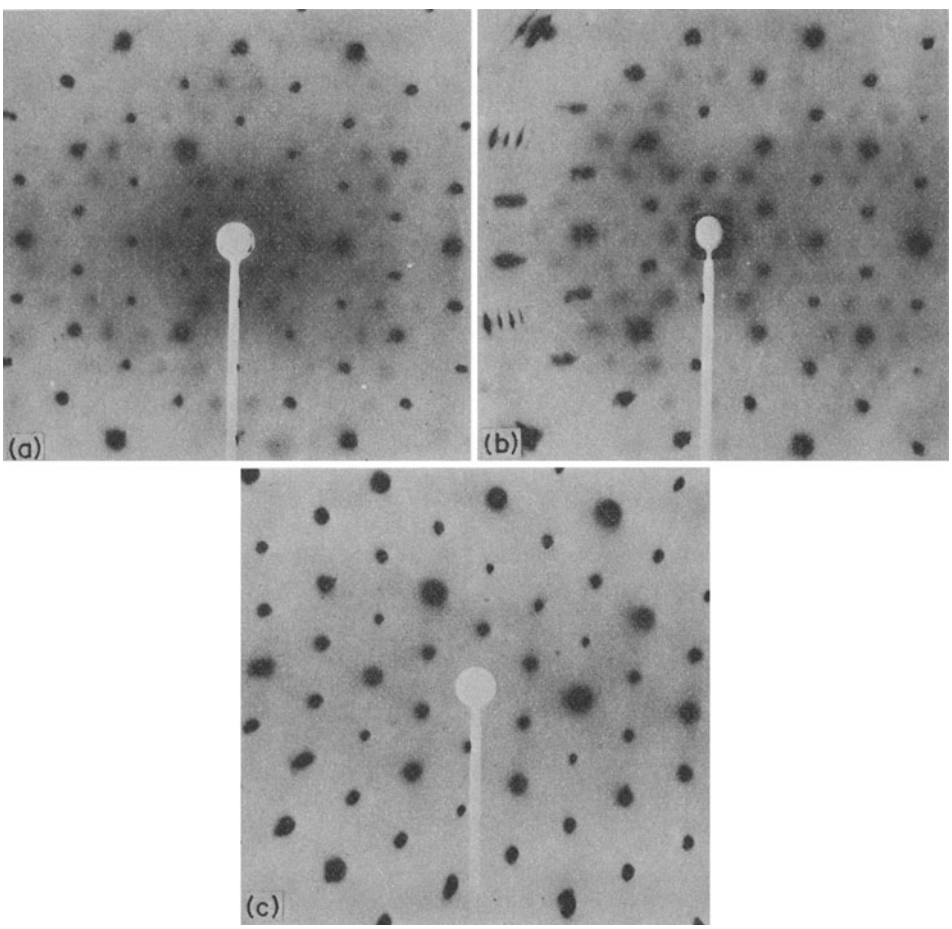


Fig. 3. Ni-vermiculite, X-ray diffraction photographs. (a) Hydrated specimen with the crystal perpendicular to the X-ray beam (b) Hydrated specimen with the crystal at 20° to the X-ray beam (c) Dehydrated specimen.

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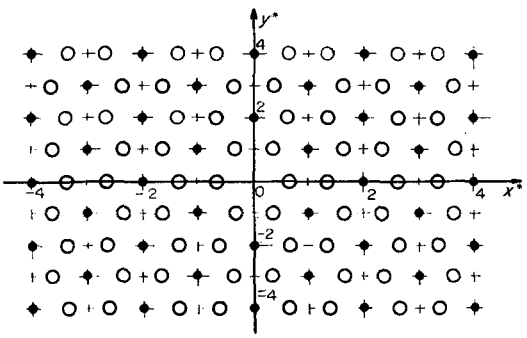


Fig. 4. Projection of the reciprocal space on the X^*Y^* plan. Black circles are the projections of Bragg spots, white circles are the projections of linear diffusions.

exist for the Mg–vermiculite or for the Ni–vermiculite (Figs. 2c and 3c).

After rehydration the previously observed scatterings reappear. It follows that these scatterings are indeed connected with the organization of the interlamellar layer (cation and water molecules) and cannot be attributed either to the organization of the silicate layer, or to a photon-phonon interaction. Identical scatterings have been observed with a Spanish vermiculite from Benhavis, which suggests that the phenomenon is a general one, not previously observed.

STRUCTURAL INTERPRETATION

Hydrated Mg– and Ni–vermiculites

The connection between these line scatterings and the organizational state of the interlamellar layer of hydrated vermiculite having been established, the Fourier transform of their projection on the X^*Y^* plane gives us the analogue of a Patterson section on the central plane of the interlamellar space (extremities of vectors joining the center of the cation and water molecule groups). The extremities of these vectors are situated at the nodes of a centered lattice with parameters $3a,b$ (Fig. 5). Since to a first approximation, the projection of the scattering intensities on the plane X^*Y^*, has made us give an identical charge to each occupied node in the lattice, the extremities of the Patterson vectors also will carry an equal weight.

The existence of line scatterings shows us that the order of the exchangeable cations and their associated water molecules is only biperiodical. On the photographs, the diffuse character of the observed spots, which are the sections of the lines of scatterings, leads to the belief that the extent of the domains, thus ordered, is limited in the crystal.

Dehydrated Mg– and Ni–vermiculite

The disappearance of the scatterings from the photographs of anhydrous vermiculite can mean

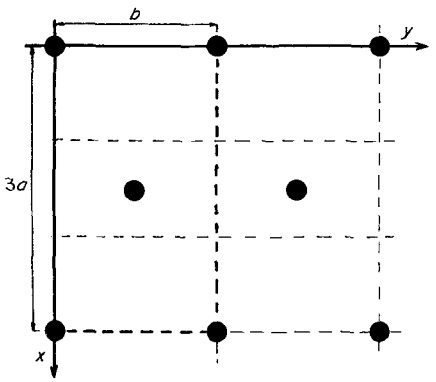


Fig. 5. Patterson section in the interlamellar space ob tained from Fourier transform of the preceding projection. The cations are distributed at the apex of $\vec{3a}$, $\vec{b}$ or $(\vec{3a}+\vec{b})/2$ vectors (black circles).

the existence of:

(a) Either a more ordered three-dimensional distribution of the cations (given the cation number determined by the chemical analysis, such a distribution would imply the existence of a three-dimensional superlattice and the appearance of more Bragg spots; this hypothesis seems therefore unlikely); or

(b) otherwise a disorderly distribution (the intensity of the observed diffusions is then distributed in a continuous manner in reciprocal space and cannot be distinguished from parasitic scatterings, fluorescence for example). It is then reasonable to think that with the closure of the sheets the compensating Mg– and Ni–ions become randomly distributed in the three nearest hexagonal cavities or even that in view of their small size some of these remain locked between the bases of the tetrhedra of two successive sheets. The two-dimensional order which existed in the hydrated state disappears and no scattering with discrete shapes can any longer be observed.

DISCUSSION

The Fourier transform of the line scattering projection described in the previous section gives us a two-dimensional Patterson section of the interlamellar space. This distribution can be completely understood only if the average structure of the studied sample is known, as it is usually defined according to the interpretation of Bragg spots.

However, since this average structure is already known, we shall be able to determine precisely the distribution of the exchangeable cations. That is, we shall be able to do better than the statistical type of distribution which we must accept when the number of atoms is less than the number of equivalent positions defined for the crystallographic sites.

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In the paper by Shirozu and Bailey (1966), the Mg exchangeable atoms are placed on the M_{IV} sites, between the tetrahedra, with a probability of 0·41. If, following Shirozu and Bailey, we place in the interlamellar space a Mg or Ni cation at the origin of the lattice, we can conclude, from the distribution found, that in a limited domain, all the other balancing cations and their associated water molecules will be found on the extremities of the $\vec{3a}$, $\vec{b}$; $(\vec{3a}+\vec{b})/2$ multiple vectors (Fig. 6, large circles).

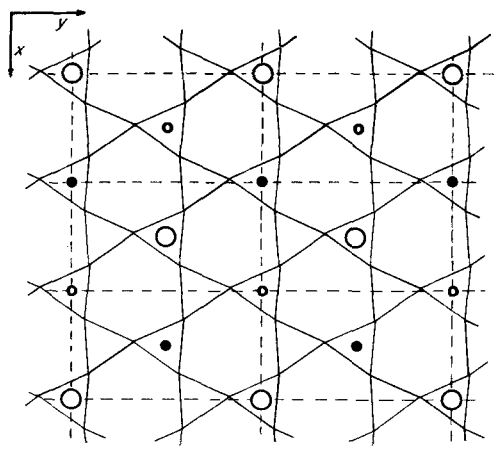


Fig. 6. Mg or Ni cation distribution in a domain. The cations are distributed on a centered lattice of 3a, b parameters (larges circles). In the neighboring domains, the cations may occupy one of the two other positions (black and white small circles).

The two-dimensional character of the observed order means that the cation distribution between two neighboring layers is not related to the cation distribution in the next interlayer spaces. That is to say, these distributions are not related by the space group and in neighboring interlayer spaces, the balancing cations will be able to occupy with the same distribution one of the two other possible M_{IV} positions (black or white small circles, Fig. 6). These "out of step" distributions might also take place in the same layer; they then define different domains.

This ordered placement, according to this biperiodic supersturcture, makes us place 0·33 divalent ions on each structural unity. The chemical analysis gives us 0·37 divalent cations and the small difference between these two values can easily be explained by the existence of a higher proportion of cations between the ordered domains of the same layer.

CONCLUSIONS

These results confirm experimentally the models presented before by Mathieson and Walker (1954), and by Bradley and Serratosa (1960).

It must be accepted that the distribution of the exchangeable cations is connected with the distribution of the charges which they neutralise (tetrahedral negative charges less octahedral positive charges). It can therefore be concluded that the distribution of effective negative charges must also be at least partially ordered.

Acknowledgements—The authors wish to thank Dr. Ideomi Kodama of the Soil Research Institute, Canada, who provided the sample of Kenya vermiculite and the chemical analysis. They also wish to thank Prof. Marianne Lambert for the help and advice she has given them in the construction of the monochromator which they have used.

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Résumé—Des diffusions anormales des rayons X existent entre les taches de Bragg. Leur étude, dans le cas des vermiculites Mg- et Ni-hydratées, montre qu'elles apparaissent dans l'espace réciproque, sous forme de lignes modulées, allongées le long de l'axe Z^*. Ces diffusions démontrent l'existence d'une organisation bidimendionnelle des cations compensateurs et des molécules d'eau dans l'espace interlamellaire. Dans de tels domaines ordonnés, les cations sont situés aux noeuds d'un réseau bipériodique centré, de paramètres **3** *a*, *b*.

La distribution des cations compensateurs doit se conformer à la distribution des charges qu'ils neutralisent; on peut ainsi en conclure que la distribution des charges négatives efficaces (charges négatives tétraédriques moins charges positives octaédriques) est ordonnée elle aussi au moins en partie.

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Kurzreferat – Unnormale Streuung von Röntgenstrahlen finden zwischen den Bragg'schen Punkten statt. Bei der Untersuchung an hydratisierten Mg- und Ni-Vermiculiten zeigen sie sich im reziproken Raum in Form modulierter Linien, die entlang der Z^*-Achse verlängert sind. Diese Streuung weist auf eine zweidimensionale Anordnung der zum Ladungsausgleich gebundenen Kationen und der Wassermoleküle in den Zwischenschichten hin. In solchen geordneten Bereichen befinden sich die Kationen an den Knoten eines biperiodisch zentrierten Gitters mit den Parametern 3a, b.

Die Verteilung der Kationen muß mit der Verteilung der Ladungen übereinstimmen, die sie kompensieren. Daher kann geschlossen werden, daß die Verteilung der wirksamen negativen Ladungen (negative Tetraederladung abzüglich positive Oktaederladung) gleichfalls mindestens teilweise geordnet vorliegt.

Резюме — Ненормальное рассеивание рентгеновских лучей происходит между брэгговскими пятнами. Их исследование в гидратированном Mg и Ni вермикулитах показало, что они появляются в сопряженном пространстве в форме модулированных линий, удлиненных по оси Z^*. Это рассеивание демонстрирует двухмерную организацию компенсирующих катионов и присутствие водяных молекул в интерламинарном слое. В таких хорошо организованных владениях катионы находятся на узловых точках двуякопериодически центрированной решетки с параметрами 3a, b.

Распределение компенсирующих катионов должно согласоваться с распределением заряда, который они нейтрализуют; поэтому можно заключить, что является необходимым распределение эффективного отрицательного заряда (тетраэдральные отрицательные заряды минус октаэдральные положительные заряды).

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