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RECTORITE AND THE RECTORITE-LIKE LAYER STRUCTURES*

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Abstract—Recurrent reports of analyses of X-ray diffraction data from regularly alternating and nearly regularly alternating structures like rectorite provide opportunity for a descriptive discussion of their nature. MacEwan-transform-based analyses have uniformly shown higher incidence of unlike adjacent layers than would be expected from random distribution.

The continuous Fourier transforms for pairs of 2 : 1 layer silicate structures evaluated normal to the layers, provide a family of similar curves that are differently stretched out in reciprocal space for different assumed intervals between the two members of a pair.

For each exactly alternating example the relative amplitudes of the ordered reciprocal nodes distinguish the instances for which fixed interlayer populations are Na^+ from those for which they are K^+.

For sequences not exactly alternating scattering maxima are displaced from exact incremental positions in conformity with the Hendricks and Teller mixing functions, but relative intensities of adjacent observations still distinguish the alkali identities.

THE ORIGINAL description of rectorite (Brackett and Williams, 1891) antedated X-ray diffraction analyses. The schematic interpretations for alternation of complex layers for rectorite and related examples, as first presented, have since been amenable to distinct improvement as the quality of data from X-ray diffractometry has improved on that available from photographic observations. It seems to be especially true that some latitudes both of composition and of regularity of alternation exist.

Rather comprehensive collections of rectorite (or allevardite) from extensive occurrences in some Paleozoic shales in north-western Utah, (Ehlmann, 1958; Henderson, 1968) have provided a ground for extended study.

Details of exact distribution of the framework cations in the silicate skeleton and consequent allocations of layer charges are dependent on the purity of chemically analyzed specimens and on arbitrary reductions of the chemical analyses to structural formulae. They establish with certainty no more than the di-octahedral character. The distribution of fixed or exchangeable interlayer cations has been more reliable. A first diffraction analysis (Bradley, 1950) did not disclose evidence for the alkali cations, and they were presumed to be associated with vermiculite-like layers. Brindley (1956) established that in allevardite, their presence between the fixed mica-like layers was more important than association in swellable interlayer spaces. This disposition is confirmed by Brown and Weir (1963) and by Kodama (1966). These determined relative abundances of fixed and of exchangeable base ions establish that these fixed-layer pairs have the character of paragonite. Brown and Weir (1963) conclude that rectorite and allevardite are synonomous, and Kodama's observed abundance of fixed sodium ions indicates a related nature. Tomita and Sudo (1968) have more recently utilized a procedure of heating to dehydroxylation followed by boiling in 6NHCl to prepare a nearly regular alternating sequence from muscovite, in which the fixed alkali ions are potassium.

The characters of either natural or synthesized materials has essentially limited the several X-ray diffraction analyses to interpretations from one dimensional data, often available only for quite limited ranges of reciprocal dimensions, but several reliable interpretations have been achieved. Admitting the limitations imposed by limited data, it seems justified to give consideration to the

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possibilities of inspections less sophisticated than the current rigorous programs.

The existence of a definite transform for any given complex of coordination polyhedra is the basis of all structure analysis by diffraction methods. For any one chosen complex it is a continuous function and it becomes single-valued only when equal units are "infinitely" repetitive. For the layer silicates the evaluation of the transform along the single direction normal to the layers has been exploited in three senses:

(1) the analysis of intensities of single-valued nodes for meticulously repeating sequences for structures of the several mineral species;

(2) the analysis of the mixing function applicable to piles of two or more kinds of complexes with similar continuous transforms (Hendricks and Teller, 1942);

(3) the analysis by Fourier inversion of the observed important features selected from continuous scattering intensity records along the reciprocal axis normal to composites of layers (MacEwan, 1956).

The third method is adapted from radial distribution analysis, and has universal applicability. In practice it has encountered some difficulties. The summation of observations at incremental positions on a continuous curve is cumbersome, and the selection of some smaller number of the more important observations requires both accurate measure of diffraction angle chosen and accurate knowledge of the value of the transform at that spot. At small values of either significant errors may occur.

By drawing upon careful analyses which have become available in recent individual publications it is possible to establish that arbitrary inspection methods can provide comparably useful appraisals of the nature of mixed systems from data which would not otherwise have been adequate. This approach is applied to the Utah shale collections examined by Henderson (1968). It is based on the recognition that the incidence of unlike pairs as neighbors have been proven to exceed the probability from random mixing in each of the recent references cited (Cole, 1966; Hamilton, 1967; Morelli, Favretto and Bystrom,-Asklund, 1967; and Tomita and Sudo, 1968). In each of these instances the alternating sequences were found to be less perfect than that of rectorite, but the mica components were potassium populated.

Figure 1 is constructed to illustrate the correspondences between pertinent continuous transforms along normals to pairs of layers with selected normalized observed data. The curves A, B and D are calculated for assumed distances between octahedral aluminum levels in two pyrophyllite skeletons separated by 9·2, 9·6 and 10·0 A, respectively. They have a common shape but differ in lateral (and in vertical) scale. The dimensions are chosen to provide interlayer space for no-, for Na^+-, or K^+-ions. Enveloped in the several curves are relative amplitudes for representative data collections, each erected on base lines which reflect the displacement from the "pyrophyllite" zero level due to addition of contribution of Na or K ions in interlayer space. The relative lengths of these various sets of bars are normalized separately from each present observation or literature citation, and are entered at about one-half of the scale of the transform amplitude, and oriented with due regard to the apparent sign of the amplitude.

Enveloped in the transform B are Brindley's observations for allevardite with two layers of hydration water and our observations for rectorite with two layers of ethylene glycol. Both have known Na interlayer content and are essentially exactly alternating with fixed interval between successive single value 00l reciprocal nodes. Below this envelope are data for air dry and for glycol swollen Utah rectorite examples for which the interlayer ions are also Na, but the regularity of alternation less exact. For example, the interval between the 13th and 14th nodes for the swollen example is less than the average interval.

Enveloped in the transform D are the data from Tomita and Sudo (1968) for the specimen prepared from potassium mica. Both his hydrate and his glycol-solvated records reveal only one layer of solvation molecules between the mica interlayers which were made swellable. This is in consequence of the high layer charge of muscovite and is comparable to the single-layer glycol configuration assumed by high-layer-charge mica-derived vermiculites. Below the D transform envelope are swollen and unswollen examples from Hamilton (1967) and from Cole (1966) for which interlayer fixed ions are potassium. Both authors cite data for glycerol swollen states with two layers of glycerol in the swollen interlayers, and their observations are too nearly duplicate to be entered in one figure. The same is true for data cited by Morelli, Favretto and Bystrom Asklund (1967). Each case is less than perfect for exact alternation but relative intensities of nodes are essentially consistent with the transform shape, even when successive nodes are spaced differently from exact regular increments.

The observed amplitudes reduced from the data of Kodama (1966) are enveloped in curve A because he concluded that unswollen layers measures 9·2 Å. His chemical analyses and deduced structural formula clearly identify Na ions as the predominant fixed interlayer species, but

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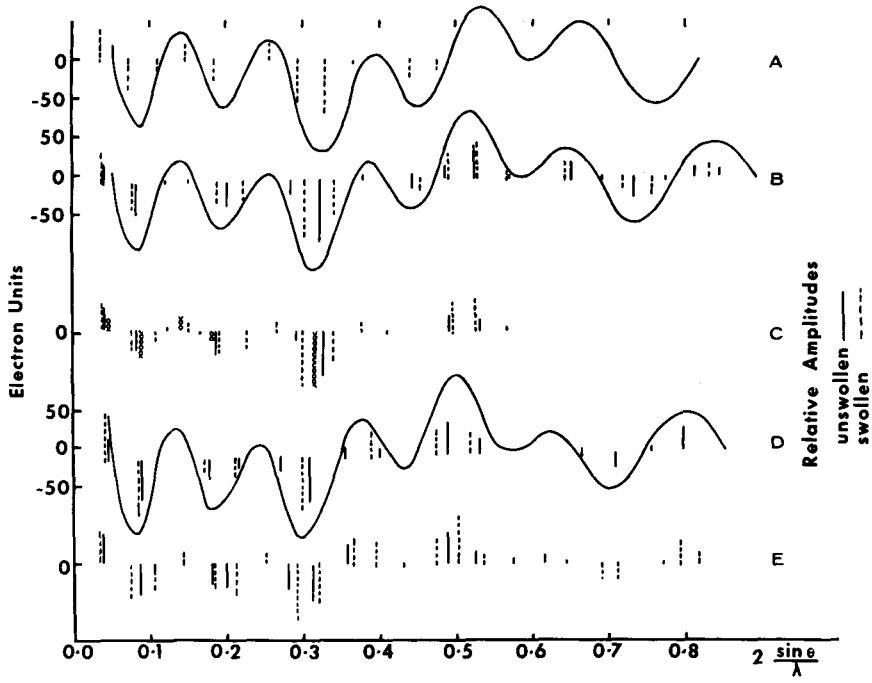


Fig. 1. A comparison of relative amplitudes reduced from diffraction data from various representative rectorite and rectorite-like clay minerals with pertinent one dimensional transforms for double layers.

A. A rectorite from the Fort Sandeman district, Baluchistan, Pakistan (Kodama, 1966) solvated with 2 layers of glycerol, and the transform for a pair of pyrophyllite layers.

B. Allevardite (Brindley, 1956) with two water layers and rectorite from Garland County, Arkansas solvated with 2 layers of ethylene glycol, and the transform for a pair of paragonite layers.

C. Typical records for the nearly regular rectorite-like mineral from north central Utah with one water layer, with two water layers, and with two layers of solvating ethylene glycol.

D. The one water layer and one ethylene glycol layer complexes for the interstratified material prepared from sericite (Tomita and Sudo, 1968) and the transform for a pair of muscovite layers.

E. Data from Cole (1966) for the two-water layer state, and from Hamilton (1967) for the two glycerol layer states for partially ordered potassium bearing clays from Tasmania and from New South Wales.

In each case the organic molecule solvated state is distinguished by the broken-line bars. All bars are normalized to approximately one-half of the scale for amplitude curves.

the bounded nature of the Patterson-function aspect of the inversion from a regular sequence of basal reflections, when modified by the weighting scheme based on a single layer transform precludes a separate measure of the thicknesses of individual component layers.* In Fig. 1 it is apparent that the observed amplitudes conform much better with the 1 B curve than with the 1 A.

The departures of the Utah rectorite and the illustrated potassium bearing examples are all three in the direction that less than one half of the total interlayer levels swell. Each record includes observations at positions near odd numbered nodes for sequences reciprocal to 19 or 20 Å which are also near nodes for the regularly alternating sequence. The inference to be drawn is that, from a potentially exact alternating sequence, some small number of interlayers that were in the proper order to be swellable, failed to do so. Those

*The one dimensional bounded Patterson utilizes the sum $\sum_{1}^{\lambda} I_{001}/\Xi \cos 2\pi l$ but the MacEwan inversion for an exactly regular sequence is $\sum_{1}^{l} \cos 2\pi l$, with $I_{001}/F_{001}^{2}\Xi = 1$ for all values of l.

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observed nodes which bracket the hypothetical positions for 10 Å mica nodes are displaced toward the mica node to degrees commensurate with the relative abundance of 10 Å mica layers, and these nodes near the odd order positions for 20 Å reciprocal spacings emphasize the importance of the double unit. The MacEwan transform method application made by Cole (1966) confirms this information. He observed maxima for 10 Å, 20 Å and 30 Å displacement of neighbors, but no maximum for 40 Å displacements. In terms of an ABAB... sequence the extension is of the nature:

ABABABAAABAB....

Inspection may also be extended to provide an approximate estimate of the relative abundances of the two kinds of layers. Within a pile of layers it must be true that some selected interval must have a thickness equal to the sums of the thicknesses of a unitary number of layers of each of the two species. Observed apparent d spacings are prominent when a hypothetical order node for one species falls near to coincidence with a hypothetical order node for the other species. An observed apparent d spacing then represents a weighted average of the form:

$$d_{obs} = \frac{\Sigma\, n_i t_i}{\Sigma\, l_i n_i}$$

when n_i and t_i are the number and thickness of the layers present and l_i are the ordinal Miller index numbers for the respective nodes which nearly coincide. The weighted average is on a volume basis. In observed sequences like the dashed entries in Fig. 1 E adjacent pairs in intervals in which the transform denotes large amplitudes show intervals of about eight tenths of the average interval. This is indicative of about 5:4 ratio of mica to swollen units by volume or about 6·4–3·6 by census count. The swollen Utah rectorite illustrated in Fig. 1 C indicates about 6:4 ratio of unswollen to swollen layers.

It is also true that for each swollen system the electron density for solvated intervals is less than that within the inorganic compositions. The low density intervals provide an average periodicity which serves to count the number of swollen intervals in some assumed thickness of composite pile. Observed apparent d spacings for the first diffuse maximum which exceed the sum of the thickness of the two component layers provide an independent, but imprecise estimate of the degree by which fixed layers predominate over swollen.

To conclude: by sacrifice of the hope for a level of quantitative precision which may not be attainable, a simple inspection can provide a fair estimate of what rigorous analysis would have disclosed.

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Résumé—Das rapports fréquents sur l'analyse des données de diffraction des rayons X à partir de structures régulièrement alternées et presque régulièrement alternées, comme le rectorite, donnent lieu à une discussion dans laquelle leur nature est décrite. Des analyses, basées sur la transformée de MacEwan, ont uniformément démontré une plus grande incidence des feuillets adjacentes différentes que celle prévue par une distribution au hasard.

Les transformations continues de Fourier pour des paires de structures de silicate à feuillet 2:1, estimées normales pour les feuillets, fournissent une famille de courbes similaires qui sont déployées différemment dans l'espace réciproque pour des intervalles supposés différents entre les deux membres d'une paire.

Pour chaque exemple alternant exactement, les amplitudes relatives des noeuds réciproques en

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ordre permettent de distinguer les cas pour lesquels des populations d'interfeuillets fixes sont Na^+ et ceux pour lesquels elles sont K^+.

Pour les séquences qui n'alternent pas exactement, des maximums de dispersion sont déplacés depuis des positions exactes graduelles conformément aux fonctions mixtes de Hendricks et Teller, mais des intensités relatives d'observations adjacentes permettent encore de distinguer les identités alcalis.

Kurzreferat– Eine Reihe von Berichten über Analysen von Röntgenbeugungswerten aus regelmässig abwechselnden und beinahe regelmässig abwechselnden Gefüngen, wie Rectorit bieten eine Gelegenheit für eine Erörterung ihres Charakters. Die auf der MacEwanschen Transformation basierten Analysen haben übereinstimmend auf ein höheres Vorkommen ungleicher Nachbarschichten hingewiesen, als bei zufälliger Verteilung zu erwarten wäre.

Die normal zu den Schichten bestimmten Fourierschen Transformierten für Paare von 2:1 Schichten Silikatgefüge. liefern eine Schar ähnlicher Kurven. die sich für verschieden angenommene Zwischenräume zwischen den zwei Mitgliedern eines Paares im reziproken Raum verschieden erstrecken.

Für jedes genau abwechselnde Beispiel lassen die relativen Amplituden der geordneten reziproken Knoten die Fälle in welchen die festen Zwischenschichtbevölkerungen Na_+ sind von denen unterscheiden in welchen sie K^+ sind.

Für nicht genau abwechselnde Folgen werden die Maxima gemäss der Hendricks und Tellerschen Mischfunktionen aus den genauen Zuwachsposition verschoben, aber die relativen Intensitäten benachbarter Beobachtungen unterscheiden immer noch die Idenitaten der Alkalien.

Резюме—Проведенные к настоящему времени анализы дифракционных картин от упорядоченно чередующихся или почти упорядоченно чередуюшихся структур типа ректорита создают благоприятную основу для детального обсуждения их природы. Анализы, основанные на преобразовании Мак-Юэна неизменно указывают на горазда более частые сочетания в этих структурах соседних слоев разной природы, чем это можно было ожидать при полностью неупорядоченном чередовании слоев.

Непрерывные фурье-преобразования для сочетания слоев типа 2 : 1 в структурах слоистых силикатов, рассмотренные в направлении перпендикулярно слоям, представляют собой семейства сходных кривых, вытянутых в обратном пространстве различным образом в зависимости от величины принимаемых интервалов между обоими членами пары.

Для каждого примера строгого чередования слоев по относительным амплитудам упорядоченно расположенных узлов обратной решетки можно различать те случаи, когда межслоевые положения заселены катионами Na или K.

Для последовательностей слоев с нестрогим чередованием слоев максимумы рассеяния смещены из строгих положений в соответствии со смешанной функцией Хендрикса и Теллера, однако по относительным интенсивностям все же можно судить о природе межслоевых катионов.

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