Montmorillonite: Electron Diffraction from Two-Dimensional Single Crystals

Abstract. *Some selected area electron diffraction patterns of isolated monocrystalline particles of both Wyoming and Camp Berteaux sodium-montmorillonites fail to show the mirror plane symmetry required for the accepted structure. A triclinic model deserves consideration.*

Because of their extremely fine particle size any accurate determination of the structure of clay mineral montmorillonites must depend on electron diffraction. Selected area electron diffraction (SAD) studies of montmorillonite have been greatly hampered because of the very weak patterns and the difficulty of isolating single crystallites for study. Electron microscope studies (*1*) have shown that very fine fractions (less than 0.05 μm equivalent spherical diameter) of several Na-montmorillonites appear to be predominantly composed of individual crystallites of unit cell thickness. Having no three-dimensional order, a monocrystalline particle of montmorillonite is only one unit cell thick (approximately 10 Å) in the *c*-dimension, and thus the particles from these very fine fractions were judged ideal materials for a study by means of SAD techniques. Because good visual images of the highly dispersed isolated particles in the electron microscope are difficult to obtain under conditions suitable for good quality electron diffraction patterns the following technique was applied. Very dilute clay-water suspensions of the very fine fractions were allowed to air dry onto ionized, Parlodion-covered, carbon-coated, copper electron microscope grids. The electron microscope (Philips EM-200) was first adjusted for optimum selected area electron diffraction with a microfocus electron gun at 80 kv and double condenser illumination of small angular aperture. After the image of the specimen field was focused in the plane of the aperture formed by the adjustable diffraction blades, operator dark-adaptation was achieved and a diffraction image obtained. Thus, instead of first attempting to visually select a particle for diffraction, we scanned the field until we observed a set of spots which appeared to be the result of diffraction from a single crystallite. The patterns are extremely weak, and many of the photographs taken by using this technique required exposure times of 1 minute and longer. Although many showed spots representing diffraction from more than one crystallite, we were able to obtain several SAD patterns (Figs. 1 and 2) showing principal diffraction effects from only one crystallite (*2*).

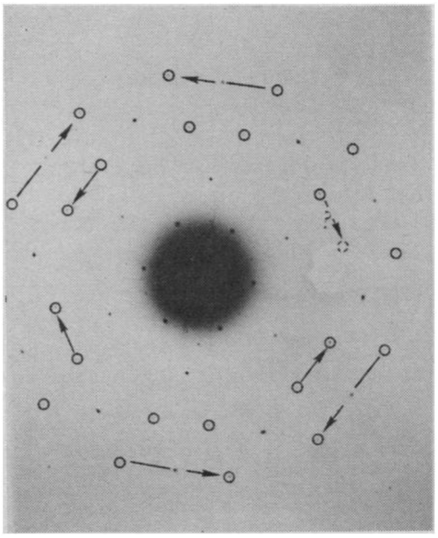

Fig. 1. Electron diffraction pattern from Wyoming montmorillonite. The arrows indicate the weak-to-strong intensity relationships of the important *hk* spots (encircled). The tip of the partially inserted beam stop marks the position of the 04, 22 *hk* ring.

In the selected area electron diffraction of thin particles of dioctahedral montmorillonites (*3, 4*), at least two types of patterns with monocrystalline appearance have been obtained. One type is that in which the entire diagram exhibits hexagonal symmetry. Cowley and Goswami (*4*) have shown such diagrams from Wyoming montmorillonite and pointed out that this is inconsistent with the twofold symmetry of the accepted structure. Mering and Oberlin (*3*) have also obtained such a diagram from the Camp Berteaux (Morocco) montmorillonite. In order to explain their SAD pattern of the Camp Berteaux material in terms of a structure having twofold symmetry, Mering and Oberlin suggested that the particles as they appear in the electron micrographs are not truly monocrystalline, but are edge-to-edge associations of smaller particles that are precisely joined to each other at angles of 60° and multiples of 60° and thus capable of simulating a monocrystalline pattern of hexagonal symmetry.

Cowley and Goswami (*4*) attempted to interpret their hexagonally symmetrical patterns in a similar fashion but were unable to obtain reasonable agreement between the observed intensities and those calculated on the basis of the assumption that disorder existed in either different parts of one crystal flake or separate parallel crystals with 60° or 120° orientations in the *ab* plane. Cowley and Goswami thus suggested an interpretation consistent with diffraction from bent crystals also structurally distorted from the ideal twofold symmetry model. This latter interpretation is helpful in explaining the hexagonally symmetrical patterns to be expected from coarser fractions but is not illuminating with respect to the diagrams obtainable from the flatter crystals of the very fine fractions of montmorillonites.

The other type of SAD pattern is one in which the intensities of certain (*hk*) spots with $k \neq 3n$ do not show hexagonal symmetry. Mering and Oberlin (*3*) have obtained SAD patterns of this type with a Wyoming montmorillonite and they attributed the principal diffraction effects to diffraction from a monocrystalline particle of montmorillonite. They have interpreted the SAD pattern of this Wyoming montmorillonite so that it can be as-

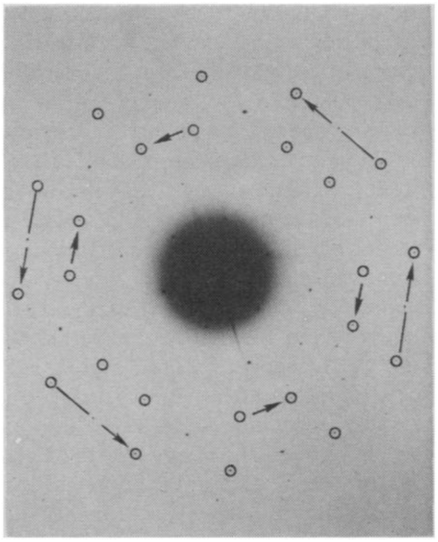

Fig. 2. Electron diffraction pattern from Camp Berteaux (Morocco) montmorillonite. The outer ring of encircled spots is of the type 42, 35, 17. The inner encircled ring is the 24, 15, 31 group.

signed to the *clml* plane symmetry group and thus be in agreement with the twofold symmetry of the accepted structure.

We have obtained high-resolution SAD patterns of a Wyoming montmorillonite (Na-Upton, very fine fraction), several of which are different in important respects from the pattern of Wyoming montmorillonite (thin particle) shown by Mering and Oberlin (*3*, plate 6). Attention is especially directed to the encircled *hk* spots of the inner 24, 15, 31 and outer 42, 35, 17 12-membered rings of Fig. 1, where a distinct pattern of a regular alternation of pairs of weak and strong intensity distributions (arrows) can be seen.

Because of the two-dimensionality of the montmorillonite single crystals no contribution of upper level nodes to the observed intensities is possible, and tilt of the flake can be ruled out because of the centrosymmetrical distributions of related unencircled spots. In this pattern the distribution of intensities shows that while twofold symmetry appears to be present, there is no mirror plane symmetry such as would be required by the *clml* plane symmetry group suggested by Mering and Oberlin (*3*). The only plane symmetry group consistent with these diffraction data is *p*2.

We have also obtained SAD patterns from very fine fractions of a Na-Camp Berteaux (Morocco) sample. Although slight tilt is indicated by the deviation of the unencircled spots from centrosymmetry, the principal sets of spots encircled in Fig. 2 have a distribution of intensities similar to those shown in Fig. 1. This indicates that not only can monocrystalline particles of Camp Berteaux montmorillonite be isolated independent of any edge-to-edge association, but their structure is apparently compatible with that of the Wyoming montmorillonite type. Neither type requires a mirror in the structure. To explain the observed intensities, W. F. Bradley (*5*) has pointed out that a triclinic model ought to be considered as an alternative to the currently accepted monoclinic structure.

H. E. ROBERSON
Department of Geology,
State University of New York,
Binghamton 13901

K. M. TOWE
Department of Paleobiology,
Smithsonian Institution,
Washington, D.C. 20560

References and Notes

1. H. E. Roberson, A. H. Weir, R. D. Woods, *Clays Clay Miner.* **16**, 239 (1968).
2. It was assumed that the very fine fractions used were essentially monomineralic. Internal calibration by means of evaporated gold or aluminum films was not undertaken because of the increased scattering involved and its consequent adverse effect on the very weak montmorillonite patterns. Photographs of the crystals giving rise to the SAD patterns were not made because of the inconvenient modifications required in the electron optics.
3. J. Mering and A. Oberlin, *Clays Clay Miner.* **15**, 3 (1967).
4. J. M. Cowley and A. Goswami, *Acta Crystallogr.* **14**, 1071 (1961).
5. W. F. Bradley, personal communication.
6. We thank W. F. Bradley (University of Texas) for his advice regarding interpretation of the diffraction data and for reading a draft of the manuscript and offering helpful comments; J. E. Arem, who also reviewed the manuscript; A. Weir, who supplied the Camp Berteaux sample; M. O'Hare of LogEtronics, Inc., who assisted in obtaining prints from the original negatives; and L. Isham, who helped with drafting.

15 December 1971; revised 7 April 1972

Plutonium-244 Fission Tracks: Evidence in a Lunar Rock 3.95 Billion Years Old

Abstract. *Tracks attributed to the spontaneous fission of plutonium-244 and of uranium-238 were detected in a large whitlockite crystal in the lunar breccia 14321 from the Fra Mauro formation. For a track-retention age of 3.95 × 10^9 years the number of plutonium tracks relative to the number of uranium tracks is 0.51 ± 0.15, provided that the rock was not heavily neutron-irradiated 3.95 ×* 10^9 *years ago.*

The half-life of ^{244}Pu is of a magnitude, 82×10^6 years, that makes it valuable for studying the sequence of events during the first several hundred million years of solar system history. Two kinds of evidence for the early existence of ^{244}Pu in meteorites have been found: (i) tracks in transparent crystals resulting from its spontaneous fission (*1–3*); and (ii) ^{131}Xe, ^{132}Xe, ^{134}Xe, and ^{136}Xe in the proportions determined by Alexander *et al.* (*4*) to be characteristic of the ^{244}Pu spontaneous fission spectrum (*5*). On the basis of whole-rock analyses of several meteorites, Podosek and Huneke (*6*) have established that the ratio of ^{244}Pu to ^{238}U was ~0.013 at the time T_0 when meteorites first began to retain Xe. This time can be assumed to be the same as their ^{40}Ar-^{39}Ar age, determined by Turner (*7*) to be $4.58 \pm 0.09 \times 10^9$ years. This value for the gas-retention age is indistinguishable from the solidification ages of meteorites determined by Rb-Sr chronology. In this report we assume a value for $(\mathrm{Pu/U})_0$ (the ratio of ^{244}Pu to ^{238}U in solar system bodies at time T_0) of 0.013 at $T_0 = 4.58 \times 10^9$ years to be the "normal" value for solar system objects but consider also the possibility of variations from this value in specific minerals (*3*).

No terrestrial or lunar rocks with an antiquity comparable to that of the meteorites have yet been found, and until now no evidence for decay products of ^{244}Pu in objects other than meteorites has been reported. Igneous rocks from Mare Tranquillitatis (Apollo 11 mission) solidified about 3.65×10^9 years ago (*8*), and virtually all igneous rocks from Oceanus Procellarum (Apollo 12 mission) solidified about 3.3 × 10^9 years ago (*9*). (The rare lunar rock 12013 has a Rb-Sr age of ~ 4.0 × 10^9 years (*10*) but has not been allocated for general studies.) Ages of 3.3 to 3.7 × 10^9 years are too young to offer any hope of detecting decay products of ^{244}Pu, except possibly in some special mineral in which Pu had been highly enriched relative to U.

Recently several rocks from the Fra Mauro formation (Apollo 14 mission) have been dated at ~ 3.8 to 3.95 × 10^9 years (*11*), which makes them all interesting candidates in which to search for ^{244}Pu fission tracks. Figure 1 shows the sensitive way in which the number of Pu tracks relative to the number of U tracks ($\rho_{\mathrm{Pu}}/\rho_{\mathrm{U}}$) should vary with age. The solid lines were calculated from the equation

$$\frac{\rho_{\mathrm{Pu}}}{\rho_{\mathrm{U}}} = f\,\frac{\lambda_{\mathrm{FPu}}\lambda_{\mathrm{DU}}}{\lambda_{\mathrm{DPu}}\lambda_{\mathrm{FU}}}\left(\frac{\mathrm{Pu}}{\mathrm{U}}\right)_0 \frac{[1-\exp(-\lambda_{\mathrm{DPu}}T)]}{[1-\exp(-\lambda_{\mathrm{DU}}T)]} \times \exp[-(\lambda_{\mathrm{DPu}}-\lambda_{\mathrm{DU}})\,(T_0-T)]$$

where λ_F and λ_D are the decay constants for spontaneous fission and total decay, respectively; f is a factor giving the relative enrichments of Pu and U in a particular mineral; and T is the track-retention age of the mineral. The three lines give $\rho_{\mathrm{Pu}}/\rho_{\mathrm{U}}$ for $f = 3$, 1, and 0.33. If it is possible to detect a Pu fission contribution at the level of 20 percent of the U fission contribution,