

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 *p2*.

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.

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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 $(\text{Pu}/\text{U})_0$ (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 $\sim 4.0 \times 10^9$ 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 ($\rho_{\text{Pu}}/\rho_{\text{U}}$) should vary with age. The solid lines were calculated from the equation

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

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 $\rho_{\text{Pu}}/\rho_{\text{U}}$ 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,

Table 1. Fission track analysis of whitlockite in lunar rock 14321.

Track contributions	Track density ($\text{cm}^{-2} \times 10^{-7}$)
Total tracks in whitlockite	9.36 ± 0.72
Fe-group cosmic-ray tracks	0.18 ± 0.08
Reactor neutron-induced fission tracks	0.60 ± 0.08
Cosmic-ray, neutron-induced fission tracks	≈ 0.02
High-energy, cosmic ray-induced tracks*	≈ 0.03
Spontaneous fission tracks	8.54 ± 0.73
Tracks from ^{238}U fission in 3.95×10^9 years	5.66 ± 0.42
Tracks from ^{244}Pu fission in 3.95×10^9 years	2.88 ± 0.82
Observed $\rho_{\text{Pu}}/\rho_{\text{U}} = 0.51 \pm 0.15$	

* On the assumption, as discussed in the text, of the erasure of any tracks existing before breccia formation.

Fig. 1 shows that, in the absence of a special Pu enrichment, one must work with rocks whose track-retention ages exceed $\sim 3.85 \times 10^9$ years.

What makes the task of establishing the presence of ^{244}Pu fission tracks in lunar rocks a difficult one is the background of tracks resulting from bombardment by energetic solar particles and galactic cosmic rays. Long tracks, similar to fission tracks in appearance, result from energetic nuclei with atomic number $Z \approx 22$ (mainly Fe) stopping at various depths in rocks. Even at the deepest points inside the largest lunar rocks studied so far, we find that the cosmic-ray track density exceeds $10^6/\text{cm}^2$. Easier to discriminate against are the very short spallation recoil tracks resulting from nuclear reactions induced mainly by the abundant, penetrating, high-energy protons. These are a problem mainly if one is using a scanning electron microscope to view an etched rock surface, since very little information on track lengths is obtained in this way.

Our approach in this work has been to search for large crystals sufficiently rich in U that the density of fission tracks from U and Pu will be enormously greater than the density of cosmic-ray tracks. One can then take into account the small cosmic-ray background by examining tracks in neighboring uranium-poor crystals at the same depth in the rock.

Of the eight samples of Apollo 14 rocks that we were allocated for study, only one was igneous; the remainder were breccias. Individual crystals in breccias tend to be fractured as a consequence of shock processes and are best studied in situ so that one can observe tracks over as large an area of the same crystals as possible. Lexan plastic prints (12), giving accurate quantitative uranium distributions in the rock sections against which they were placed, were obtained by irradiating a

compact sandwich of sections and their plastic sheets with 1.90×10^{16} thermal neutrons per square centimeter at a maximum temperature of 46°C in the Livermore reactor. On the top and bottom of the sandwich were calibrated glass squares containing a known ^{235}U and ^{238}U concentration for dosimetry purposes (13). Each of them was covered with Lexan on one side and mica on the other side. The fact that the

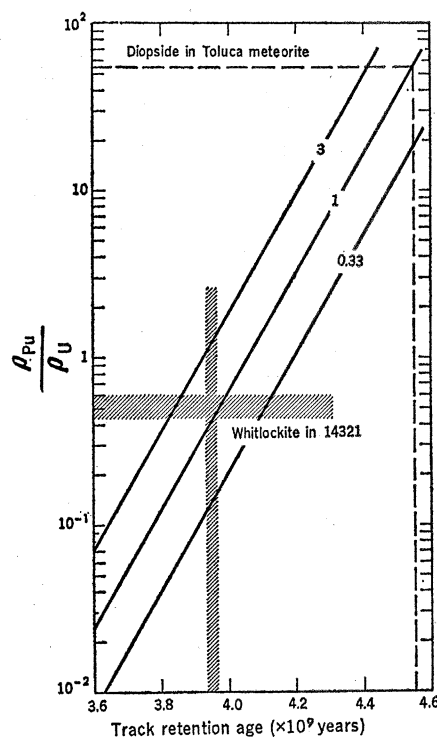


Fig. 1. The dependence of $\rho_{\text{Pu}}/\rho_{\text{U}}$ on track-retention age. The slanted lines were calculated on the basis of a relative enrichment factor f of 3, 1, and 0.33. The result for a whitlockite crystal from rock 14321 is indicated by the horizontal shaded band, on the assumption of a track-retention age equal to the Rb-Sr age of an igneous clast in rock 14321, indicated by the vertical shaded band (18). The dashed line at the top of the graph indicates the very much larger ^{244}Pu contribution previously found in diopside crystals from the Toluca meteorite (1).

track counts in mica and Lexan were the same established that no fading of tracks occurred in the Lexan, which is more susceptible to track annealing than mica.

After etching for 4 hours at 40°C in 6.25N NaOH solution, each Lexan sheet contained a faint image which facilitated its realignment with the corresponding rock section, and it also contained fission-track distributions that could be quantitatively related to the uranium distribution in the grains of the section. Numerous uranium-rich grains were spotted but rejected because of their small size ($< 50 \mu\text{m}$). Several larger crystals (up to $\sim 1 \text{ mm}$) of transparent minerals were found with ~ 0.2 to ~ 2 parts per million (ppm) of U, which would give rise to an expected fission track density of $\sim 10^6$ to $\sim 10^7/\text{cm}^2$. Although there is a way (14) to study fission tracks in such crystals by eliminating the cosmic-ray background, our aim in this work has been to build as strong a case as possible for the existence of ^{244}Pu tracks in at least one lunar rock. Fortunately, in one section of rock 14321 we found a crystal of whitlockite (500 by $300 \mu\text{m}$) with 19 ppm of U, which proved to have a fission track density ~ 50 times higher than the cosmic-ray track density.

In order to reveal the tracks in the whitlockite we etched the section for 30 seconds in 0.25 percent HNO_3 . In the optical microscope the track density was almost unresolvably high. To make an accurate count we examined a plastic replica in a scanning electron microscope, ignoring the very short etch pits characteristic of spallation recoils and counting only the true fission tracks. Table 1 summarizes our measurements and conclusions.

To obtain the density of the spontaneous fission tracks from $^{238}\text{U} + ^{244}\text{Pu}$, we subtract several minor contributions from the total track density. The density of heavy cosmic-ray tracks is taken to be $(1.8 \pm 0.8) \times 10^6/\text{cm}^2$ on the basis of observations in many neighboring feldspar crystals with very low U content in our section of rock 14321. From an earlier accelerator bombardment of apatite crystals with 3-GeV protons (15), we estimate the background track density due to cosmic ray-induced nuclear reactions in 25×10^6 years to be $\approx 3 \times 10^5/\text{cm}^2$, assuming the composition of whitlockite and apatite to be similar. Because the whitlockite was exposed in a reactor to

thermal neutrons before being etched, we must subtract the reactor-induced fission tracks, inferred from tracks in the adjacent Lexan sheet to be $(6.0 \pm 0.8) \times 10^6/\text{cm}^2$. From this density and the neutron dose we calculate (13, 16) a U concentration in the whitlockite of 19.4 ± 1.5 ppm.

The cosmic-ray neutron flux is a function of the exposure history of the whitlockite. The breccia 14321 as a whole has most probably been irradiated on or near the lunar surface for the past 25×10^6 years. Lugmair and Marti (17) find an upper limit on the integrated thermal neutron dose, 5.6×10^{14} neutron/cm², consistent with such an exposure history. If we assume that the whitlockite has been irradiated only in situ, the neutron-induced fission track density would be $< 3.5 \times 10^6/\text{cm}^2$ and the total spontaneous fission contribution (Table 1) is $(8.54 \pm 0.73) \times 10^7/\text{cm}^2$.

According to an alternative explanation, the whitlockite may have been irradiated $\sim 3.95 \times 10^9$ years ago prior to its incorporation into the breccia. The neutron flux would be unknown, and any number of excess tracks could have been produced. However, our observations of crushed feldspar crystals from rock 14321 with a high-energy electron microscope (650 keV) have provided no evidence for the retention of etchable tracks from an irradiation prior to breccia formation. Dran *et al.* (18) have observed etched sections with a scanning electron microscope and likewise have concluded that existing tracks were erased during breccia formation. We therefore believe that it is extremely unlikely that the excess tracks resulted from neutron-induced fission, either recently or 3.95×10^9 years ago.

One further possibility is that, since rock 14321 is heterogeneous, the neutron exposure limits might apply only to those sections of the breccia that have been less irradiated than the whitlockite. This possibility, though unlikely, cannot be ruled out because it postulates a special history for one crystal, which is too small to permit its neutron exposure to be measured by the technique of Lugmair and Marti (17).

Because ^{244}Pu and ^{238}U fission tracks are indistinguishable in appearance, we cannot determine solely from fission tracks both the track-retention age T of the whitlockite and the enrichment factor f . The simplest and to us the

likeliest possibility is that the whitlockite is contemporaneous with other minerals in the breccia, and we therefore equate T with the age of an igneous clast in rock 14321, determined by the Rb-Sr method to be $3.95 \pm 0.04 \times 10^9$ years old (19). The spontaneous fission contribution of 19.4 ppm of U in 3.95×10^9 years is $(5.66 \pm 0.42) \times 10^7/\text{cm}^2$, and we ascribe the remaining tracks, $(2.88 \pm 0.82) \times 10^7/\text{cm}^2$, to ^{244}Pu . The ratio $\rho_{\text{Pu}}/\rho_{\text{U}}$ is then 0.51 ± 0.15 (horizontal shaded band in Fig. 1). From Fig. 1 we see that the enrichment factor would then be $f \approx 1.28 \pm 0.4$ if the age is $3.95 \pm 0.04 \times 10^9$ years. The relative contributions of ^{244}Pu and ^{238}U spontaneous fission are thus consistent with the value for $(\text{Pu}/\text{U})_0$ of 0.013 at $T_0 = 4.58 \times 10^9$ years, an age of 3.95×10^9 years for the component minerals within the breccia, and the geochemically similar behavior of Pu and U in the whitlockite.

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Valinomycin Crystal Structure Determination by Direct Methods

Abstract. *The conformation of an uncomplexed form of the antibiotic valinomycin ($\text{C}_{53}\text{N}_6\text{O}_{18}\text{H}_{90}$) has been determined by direct methods including a novel technique for strong enantiomorph discrimination via the calculation and systematic analysis of cosine invariants of a special type. The intramolecular hydrogen bonding scheme and the isopropyl group stereochemistry of uncomplexed valinomycin are compatible with interpretations of spectral measurements for the complexed and uncomplexed molecule in solution but are different from any previously proposed structure. The simple conformational change of a hydrogen bond shift, which could be induced by the process of potassium ion complexing, transforms the uncomplexed into the complexed structure.*

The antibiotic valinomycin has been shown to affect the energy-linked accumulation of alkali ions by mitochondria (1). The structure of uncomplexed valinomycin (Fig. 1a) was found to be more elongated than that of the doughnut-shaped K^+ complex (Fig. 1b) (2, 3). The conformational difference between the complexed and the uncomplexed forms of valinomycin involves a change in intramolecular hydrogen bonding. Two of the six intramolecular hydrogen bonds in the uncomplexed

molecule are of a type not previously suspected. The hydrogen bonding depicted in Fig. 2a is that observed in the K^+ complex. The compatibility of this hydrogen bond configuration with the interpretation of spectra of the complexed and uncomplexed forms of valinomycin in nonpolar solutions suggested to various authors (4, 5) that in nonpolar solvents the two forms have at least this hydrogen bonding structure in common. On the basis of their interpretation of spectral data, Ivanov