glacial period 1.4° to 2.1°C warmer than today (*9*), which is in good agreement with the results from core 7 and with an estimate of a 1.9°C higher temperature for the mid-postglacial period from the White Mountains of eastern California (*10*). Although core 4 does not show a marked mid-postglacial warm period, this result may reflect the more generalized record it represents.

The temperature curve for core 7 also agrees with an uncalibrated temperature curve based on growth annuli of fish scales from the same core (*11*), which showed that tule perch scales from middle Holocene deposits have wider growth rings than scales from early or late Holocene deposits. This difference was interpreted as resulting from higher water temperatures during the mid-Holocene.

Equation 1 estimates a considerably greater temperature range than that obtained from deep-sea cores and coastal pollen records. Summer sea-surface temperatures were 1° to 2°C cooler and winter (February) temperatures were up to 4°C cooler along the California coast 18,000 years ago (*12*); maximum coolings of 4° to 5°C are estimated for the Tanner Basin off southern California (*13*) and for Kalaloch on the Washington coast (*3*). A 2° to 3°C change is estimated from pollen data north of Monterey Bay (*14*).

We attribute the greater temperature range calculated at Clear Lake to the much higher continentality of the site, which is separated from the Pacific by two ranges of mountains, and to the effects of coastal upwelling in minimizing temperature changes in the immediate vicinity of the coast (*14*). Work on plant debris from fossil pack rat middens from southern Nevada has yielded estimates that summer temperatures during full glacial times were 7° to 8°C cooler than at present (*15*), in agreement with our estimate.

The precipitation curves (Fig. 2) are based on the biologic responses of oak and pine to the modern climate of the northern Coast Ranges. Several theoretical considerations, including differences in the area-elevation characteristics of the various sites used for calibration and changes in atmospheric water vapor content resulting from lower sea-surface temperatures during glacial intervals, could modify these curves. Because sea-surface temperatures were lower during glacial intervals (*12*), the moisture capacity of the air masses must also have been lower, so that the winters must have been much stormier or longer than at present. However, the absence of significant amounts of spruce (*Picea*) pollen from the Clear Lake samples (*8*) implies that summer droughts persisted in the northern Coast Ranges throughout the last glacial cycle (*16*).

The reconstructed precipitation for the Clear Lake record shows a remarkably wide range, with as much as 2 m of additional precipitation during full glacial times. Our precipitation reconstruction is probably much less reliable than the temperature reconstruction and should be used with caution; we present it here because it is the best reconstruction presently available for California.

Although the transfer functions used here are not independent of each other, we believe that the available climatic data do not justify the use of more complicated techniques. Our results are crude, but they provide a better measure of past temperature and precipitation changes in the northern Coast Ranges of California than has been heretofore available.

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Neutron-Induced Fission of Uranium: A Dating Method for Lunar Surface Material

Abstract. *Volcanic glasses collected on the rim of Shorty Crater in the Apollo 17 area were formed 3.63 × 10⁹ years ago. The amounts of xenon-136 produced by neutron-induced fission of uranium-235 indicate that the glasses resided on the lunar surface for about 38 million years before they were deeply buried. The glass spherules were reexcavated by the impact that formed Shorty Crater 17 million years ago, and remained undisturbed until they were collected.*

The most unusual material discovered by the Apollo 17 astronauts was an "orange soil," which constituted a 25-cm layer on the rim of Shorty Crater (110 m in diameter and 10 m deep). This was one of the few colorful spots observed on the moon. The orange color of this soil is due to a relatively high abundance of trivalent titanium. This soil is also unusual for another reason: it contains an excess of fission xenon isotopes attributable to neutron-induced fission of ^{235}U. Although neutron-induced fission components have been considered before, this sample represents, to our knowledge, the first case where the radionuclide ^{235}U can provide information on the timing of cosmic-ray irradiation.

A tube, driven 68 cm into the regolith on the rim of Shorty Crater to obtain a core, sampled a layer of homogeneous orange and, at greater depth, black glass droplets (*1*). The upper part of the core is NASA sample 74002 and the lower part is sample 74001. Most investigators of core 74001/2 agree that these glasses represent a pyroclastic deposit, probably formed by lava fountaining along the rim of Mare Serenitatis (*2*). Noble gases were extracted from 1 g of the bottom part of the core at a sampling depth of 144 g/cm^2 and were analyzed mass spectrometrically (*3*).

Noble gases have been useful for unraveling the history of extraterrestrial matter: the ^{39}Ar-^{40}Ar gas retention age for glasses such as those investigated here usually indicates the time of formation. Amounts and isotopic ratios of the cosmic-ray–produced noble gases give the residence time and burial depth of the samples within the top few meters of the lunar surface, where cosmic-ray particles can react with lunar material. The amounts of cosmic-ray–produced isotopes give the total irradiation time but do not tell when the irradiation occurred. Xenon isotopes from neutron-induced fission of ^{232}Th, ^{238}U, and especially ^{235}U can give this information but must be carefully disentangled from other xenon components, in particular from xenon produced by spontaneous fission of heavy elements. In contrast to these components, which are produced in situ, other components originate externally and are called trapped noble gases (*4*). They give information on the composition of the solar wind and the lunar atmosphere. Thus the combination of all these types of information yields the detailed history of this regolith material.

The amounts of xenon isotopes produced by neutron-induced fission of ^{235}U (which subsequently stands for ^{235}U, ^{232}Th, and ^{238}U) are usually extremely small and not detectable, whereas all the other components mentioned above have been readily observed in lunar and meteoritic samples. In this report we focus on the excess of ^{134}Xe and ^{136}Xe observed in a sample of core 74001 and show that this excess can be attributed to fission of ^{235}U induced by neutrons which originated from the interactions of cosmic-ray particles with lunar material.

Sample 74001,1095 consists of material from a depth of 66 cm (144 g/cm^2) below the lunar surface. The amounts of ^{136}Xe and ^{134}Xe we obtained for this sample, after subtraction of trapped xenon and of a small cosmic-ray–produced spallation component, are 55×10^{-14} and 71×10^{-14} cm^3 STP (standard temperature and pressure) per gram, respectively. The ratio of fission-produced ^{134}Xe to ^{136}Xe is 1.29 ± 0.18. This value indicates that fission xenon in the 74001 soils mainly originated from neutron-induced fission of ^{235}U, for which the expected ^{134}Xe/^{136}Xe ratio is 1.25. The amount of fission xenon due to spontaneous fission of ^{238}U can be calculated if we know the gas retention age and the uranium concentration, and it will then be possible to calculate the fraction of fission xenon attributable to neutron-induced fission of ^{235}U.

The gas retention age of a sample from 1 cm below 74001,1095 was determined by the ^{39}Ar-^{40}Ar method (*5*). The ^{39}Ar-^{40}Ar release pattern shown in Fig. 1 corresponds to an age of $3.63 \pm 0.04 \times 10^9$ years. It seems certain that the glass droplets formed at this time after the flooding of Mare Serenitatis 3.7×10^9 years ago (*6*). The uranium concentration of sample 74001,1095 was determined by neutron activation and found to be 0.12 ppm (*7*). On the basis of this concentration, we calculate that the amount of ^{136}Xe produced by spontaneous fission of ^{238}U during the past 3.63×10^9 years is 24×10^{-14} cm^3 STP/g. The remaining fission ^{136}Xe, 31×10^{-14} cm^3 STP/g, must therefore be due to neutron-induced fission of ^{235}U. A corresponding amount is calculated for ^{134}Xe from neutron-induced fission.

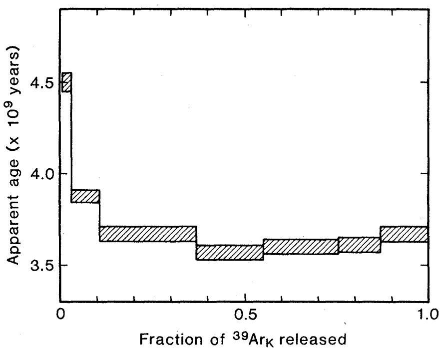

Fig. 1. Apparent ^{39}Ar-^{40}Ar age versus fractional ^{39}Ar release for the grain size fraction 150 to 530 μm from sample 74001,15; the sample is from a depth of 67 cm in core 74001/2. The plateau obtained corresponds to a gas retention age and thus presumably to the formation age of the black glass droplets, 3.63×10^9 years (*5*).

We now consider whether the measured amount of ^{136}Xe from neutron fission (^{136}Xe$_{nf}$) is consistent with the neutron fluence to which the soil was exposed. The amount of ^{136}Xe$_{nf}$ is calculated from

$$^{136}\mathrm{Xe}_{nf} = n(d)\ T_e\ ^{136}y\ [^{235}\mathrm{U}]$$

where $n(d)$ is the fission rate of ^{235}U as a function of depth below the surface, T_e the cosmic-ray exposure age (that is, the duration of the irradiation by secondary neutrons), ^{136}y the ^{136}Xe fission yield for ^{235}U, and [^{235}U] the measured ^{235}U concentration. Using $n = 3.4$ sec^{-1} g^{-1} from the Apollo 17 lunar neutron probe experiment (*8*) for a shielding depth of 144 g/cm^2, $^{136}y = 0.0646$ (*9*), [^{235}U] $= 0.87 \times 10^{-9}$ g/g (*7*), and a cosmic-ray exposure age of 55 million years (*3*), we calculate 0.9×10^{-14} cm^3 STP/g for ^{136}Xe$_{nf}$. The expected amount of ^{136}Xe$_{nf}$ from neutron-induced fission of ^{232}Th and ^{238}U (*10*) is 0.5×10^{-14} cm^3 STP/g. The total amount of ^{136}Xe$_{nf}$ for a recent exposure, 1.4×10^{-14} cm^3 STP/g, is far less than the observed amount, 31×10^{-14} cm^3 STP/g. Since the cosmic-ray exposure age of 55 million years for the 74001 soil is greater than the age of Shorty Crater, 17 million years (*11*), we conclude that the soil from the crater rim was exposed to cosmic rays before the crater-forming impact. The large amount of ^{136}Xe$_{nf}$ indicates that this preexposure of duration T_e' (that is, the earlier period of cosmic-ray irradiation) must have been at a time, T, when the abundance of ^{235}U was enhanced by the factor $e^{\lambda T}$ relative to the present measured abundance, λ being the decay constant of ^{235}U. The amount of ^{136}Xe$_{nf}$ produced during the preexposure period is calculated from

$$^{136}\mathrm{Xe}_{nf} = n(d')\ T_e'\ ^{136}y\ [^{235}\mathrm{U}]\ e^{\lambda T}$$

where d' is the average calculated depth at which the glass spherules resided during the period of early irradiation. The shielding depth d' during the preexposure period was determined from the depth-sensitive ratio ^{131}Xe/^{126}Xe and found to be 143 g/cm^2 (*3*).

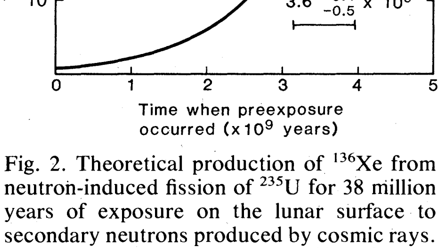

Fig. 2. Theoretical production of ^{136}Xe from neutron-induced fission of ^{235}U for 38 million years of exposure on the lunar surface to secondary neutrons produced by cosmic rays. The concentration of 31×10^{-14} cm^3 STP/g, observed for sample 74001,1095 from a depth of 66 cm in core 74001/2, indicates that the exposure occurred 3.6×10^9 years ago.

In Fig. 2 we show that $(30 \pm 12) \times 10^{-14}$ cm^3 STP/g of ^{136}Xe$_{nf}$ must have been produced by a neutron irradiation that occurred $3.6^{+0.4}_{-0.5} \times 10^9$ years ago, allowing 10^{-14} cm^3 STP/g of ^{136}Xe$_{nf}$ to have been produced during a recent exposure after excavation by the Shorty impact. It is remarkable that the time when the preexposure for the glass droplets occurred is identical to their ^{39}Ar-^{39}Ar age of 3.63×10^9 years.

The history of this peculiar lunar surface material, as reconstructed by the study of various nuclear effects on noble gas isotopes, can be summarized as follows. The glass droplets from the bottom of core 74001/2 were produced, probably by lava fountaining, 3.63×10^9 years ago, a few tens of million years after the end of the lava flooding of Mare Serenitatis. Immediately or soon afterward, they were exposed to cosmic rays for about 38 million years. After this preexposure, the glass layer was completely shielded from cosmic rays by a layer several meters thick and was reexcavated by the impact that created Shorty Crater 17 million years ago. Since that time, the orange and black glasses remained undisturbed until collection.

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4. The trapped noble gases may have been incorporated into the sample by one or more of the following processes: implantation by solar wind irradiation, implantation of lunar atmospheric ions accelerated by the electric and magnetic fields generated by the solar wind, and adsorption of lunar atmospheric species with subsequent diffusion of gases into lunar material. In order to separate the components produced in situ from the trapped components five grain size fractions were prepared (approximate grain sizes $\geqq 26$, 17, 9, 3, and 1 μm) and for the fraction $\geqq 26$ μm noble gas extraction was performed in two temperature steps ($\leqq 900°$C and 900° to 1700°C). By these methods the concentrations and composition of the trapped component were determined [O. Eugster, N. Grögler, P. Eberhardt, J. Geiss, *Geochim. Cosmochim. Acta Suppl. 14* (1980), p. 1565]. Thus we were able to ensure that the fission xenon discussed in this report was produced from local uranium within the sample.
5. In the ^{39}Ar-^{40}Ar dating method a measured fraction of ^{39}K in the sample is converted to ^{39}Ar by neutron activation; the sample is then heated in stages to release this ^{39}Ar, together with radiogenic ^{40}Ar, by thermal diffusion. The argon is subsequently analyzed in a mass spectrometer. An ^{39}Ar-^{40}Ar age of 3.7×10^9 years for soil sample 74001,15 was given by P. Eberhardt, O. Eugster, J. Geiss, N. Grögler, M. Jungck, P. Maurer, M. Mörgeli, and A. Stettler [*Meteoritics* **10**, 93 (1975) (abstract)]. The age is recalculated in this report with constants given by R. H. Steiger and E. Jäger [*Earth Planet. Sci. Lett.* **36**, 359 (1977)].
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Crystalline Todorokite Associated with Biogenic Debris in Manganese Nodules

Abstract. *Platy intergrowths of crystalline todorokite are associated with biogenic debris in the cores of manganese nodules from a site in the Pacific Ocean. Analyses by electron diffraction and transmission electron microscopy demonstrate that this material is composed of tunnels of chains of linked MnO_6 octahedra. The chemical composition, morphology, and stability of the todorokite differ from those of nickel- and copper-rich manganese oxides in nodules that have been identified as todorokite or buserite in earlier investigations.*

The identities and structures of manganese oxyhydroxide phases in marine manganese nodules have been debated extensively for more than three decades (*1*). The phases are cryptocrystalline and intergrown on a microscopic scale with iron oxyhydroxides, biogenic debris, and aluminosilicate grains. The lack of suitable homogeneous samples has severely hampered mineralogical studies and structural interpretation. A question of particular interest is the identity of the host phase and the structural sites of copper and nickel in manganese nodules. X-ray diffraction patterns of this phase characteristically contain reflections at approximately 9.6, 4.8, 3.2, and 2.4 Å. This material, which we call a "10-Å phase," has been compared to both todorokite (*1*, *2*), a tektomanganate, and buserite, a phyllomanganate (*3*).

Recently, Chukhrov *et al.* (*4*) presented electron diffraction data and transmission electron micrographs of crystalline todorokite with $a_0 = 14.6$ Å from the core of a Pacific Basin nodule. Siegel (*5*, *6*) identified fibrous todorokite with $a_0 = 9.8$ Å in the cores of manganese nodules by scanning electron microscopy and electron diffraction. Recently, Turner *et al.* have shown by means of structural imaging with high-resolution transmission electron microscopy that the structure of this material is the same as that of samples of todorokite from terrestrial locales (*7*, *8*). The purpose of this report is to describe the chemistry, morphology, and geological occurrence of crystalline todorokite associated with biogenic debris in nodules from the north equatorial Pacific Ocean.

The samples were taken from free-fall grabs at station 19 of the Manganese Nodule Program BOMDROP cruise MN75-03. This station is centered at approximately 140°W, 11°N and includes Site S of the present Manganese Nodule Project (MANOP). The geology of this site has been described in (*6*, *9*). Nodules containing cores composed of crystalline todorokite are found almost exclusively in free-fall grabs located near the base of a series of fault scarps where indurated carbonate sediment is exposed. Nodules in which the crystalline todorokite was found are small (average diameter, 1.6 cm), are spheroidal or polyspheroidal in shape, and have smooth surface textures.

A polished cross section of a nodule from free-fall grab MN75-03-FFG001 is shown in Fig. 1a. The crystalline oxide core is more highly reflective and homogeneous than the mottled and laminated zones of the outer layers of the nodule. Partial chemical compositions obtained from quantitative microprobe analyses of the core and outer layers are shown in Table 1 (*10*). The presence of todorokite in the nodule cores was initially determined by x-ray powder diffraction studies. An orthorhombic unit cell with lattice constants of $a_0 = 9.82$ Å, $b_0 = 2.89$ Å, and $c_0 = 9.59$ Å was calculated with a least-squares refinement of the positions of 14 reflections (*11*).

Scanning electron micrographs (*5*, *6*) show that these cores are composed almost entirely of molds of biogenic debris (Fig. 1b). Well-preserved molds of discoasters and coccoliths are common, and impressions of Radiolaria also occur. Element mapping by energy-dispersive analysis of emitted x-rays (*5*, *6*) showed that the material is almost entirely manganese oxide; very little of the biogenic SiO_2 or $CaCO_3$ remains. Needles of manganese oxide and platy intergrowths with pseudohexagonal symmetry are shown in Fig. 1c. Transmission electron micrographs (*12*) show that the bulk of the material within these nodule cores is composed of plates with fine-scale hexagonal trillings (Fig. 1d). Selected-area electron diffraction patterns