Reports

Fossil Particle Tracks and Uranium Distributions in Minerals of the Vaca Muerta Meteorite

Abstract. *Fossil tracks of charged particles have been observed in minerals separated from the Vaca Muerta mesosiderite. Irradiation of samples of the meteorite with thermal neutrons in a nuclear reactor, together with measurements of track-length distribution, indicate that some of the tracks result from the spontaneous fission of uranium impurities; others, however, are of different origin. Uranium concentrations, which ranged from about 4000 parts per million in a zircon grain to less than 10^{-3} parts per million in hypersthene and anorthite, were also measured by irradiating samples with thermal neutrons.*

It is now well established that minerals and natural glasses contain fossil records of their radiation history in the form of tracks caused by radiation damage, and that the tracks can be developed to visible sizes by selective chemical etching (*1–6*). Experiments with heavy-ion accelerators show that tracks which can be etched are formed only by massive charged particles whose rates of energy loss exceed a certain critical value that is a characteristic of the material (*7*). In samples that have not been exposed to cosmic rays, the only particles normally capable of forming tracks are fragments from the spontaneous fission of uranium impurities (*2*). From the known spontaneous fission rate of uranium and the observed track density, it is possible to compute a geological age which represents the time since the sample last cooled to a temperature at which tracks are stable (*2–6, 8*).

Bodies such as meteorites, which have been exposed to the primary cosmic radiation for long periods, should contain, in addition to tracks caused by spontaneous fission, tracks of cosmic-ray origin which can be used to obtain information both about the cosmic radiation and the history of the meteorite. Calculations show that there are several ways in which cosmic rays may give rise to particles with rates of energy loss sufficiently high to form tracks: (i) cosmic-ray-induced fission of heavy elements in the mineral; (ii) cosmic-ray-induced spallation recoils of medium and heavy elements in the mineral (*9*); (iii) heavy cosmic-ray primaries; and (iv) magnetic monopoles (*10*)—hypothetical particles for whose existence there is as yet no experimental evidence. Recently, Maurette *et al.* (*6*) observed particle tracks in meteoritic olivine crystals; they attributed the tracks to either spallation recoils induced by cosmic rays or to heavy primary cosmic radiation.

During our studies of fossil particle tracks in meteorites, we have devised experimental techniques for revealing tracks in several meteoritic minerals. Here we report the first observation of fossil tracks in samples of these minerals obtained from the Vaca Muerta meteorite. We also report measurements of uranium distributions among the various minerals in this meteorite.

Vaca Muerta, a brecciated mesosiderite, contains fragments of hypersthene, anorthite, and olivine exceeding 1 mm in diameter and smaller grains of a large number of accessory minerals, including zircon (*11*) with dimensions up to about 0.5 mm. The minerals used in these experiments were recovered from bulk specimens of the meteorite by dissolving the metallic Ni-Fe in acetic acid and separating the insoluble phases in heavy liquids. Each mineral was identified by optical and x-ray methods. Etching techniques for revealing particle tracks in the various minerals are listed in column 2 of Table 1. Densities of fossil tracks (column 3) ranged from unresolvably high (more than $10^8/cm^2$) in whitlockite crystals down to about $2 \times 10^3/cm^2$ in anorthite crystals. Two zircon grains were examined. Zircon A, which contained many dark inclusions less than a micron in size, had too high a track density to resolve. Zircon B, a clear, transparent crystal, contained about 10^7 to 10^8 tracks per square centimeter, which was too high a density for quantitative measurements to be made. No etchant has yet been developed for chromite and rutile, but they were included in the table because we have measured their uranium contents. Tridymite contained a high density of dislocations which etched in about the same way as tracks (*4*) and made analysis of the tracks difficult.

Because of its comparatively large size and convenient track density, it was easiest to make a detailed study of fossil tracks in the hypersthene. Figure 1 show a photomicrograph of etched tracks in a field of view measuring about 500 μ on each side. A total of 86 tracks were measured in scanning 1.6×10^{-2} cm^2 of freshly cleaved surface, giving a track density of $5.5 \times 10^3/cm^2$. The maximum length of these tracks is approximately equal to the range of fission fragments, and a certain fraction were undoubtedly produced by the spontaneous fission of uranium impurities. As we will now show, however, not all the tracks can be explained in this way and some must be attributed to other sources.

The density of tracks caused by the spontaneous fission of uranium, ρ_U, that has accumulated in a crystal of age T can be determined by means of an experiment in which new fission tracks are induced by thermal neutrons; ρ_i then represents the density of new tracks. When a fraction, F, of the uranium atoms have fissioned, ρ_U is given by

$$\rho_U = \rho_i[\exp(\lambda_D T) - 1]\,\lambda_F/\lambda_D F \quad (1)$$

where $\lambda_F = 6.85 \times 10^{-17}$/year and $\lambda_D = 1.54 \times 10^{-10}$/year are the spontaneous fission and total decay constants for uranium. The contribution to ρ_U is almost entirely from the isotope U^{238}, whereas only U^{235} contributes to ρ_i. Equation 1 is thus valid only when the U^{238}/U^{235} ratio is the same as in normal terrestrial uranium. Although this ratio has not been measured in Vaca Muerta, Hamaguchi *et al.* (*12*) have shown that it is equal to the terrestrial value within 10 percent in several different chondrites and in one achondrite. Measurements by Schmitt *et al.* (*13*) further indicate that exposure to thermal neutrons is not so radical as to upset the normal ratios of isotopes.

Now substituting into Eq. 1 the measured quantities $\rho_i = 9 \times 10^3/cm^2$, $F = 2.5 \times 10^{-6}$, and the gener-

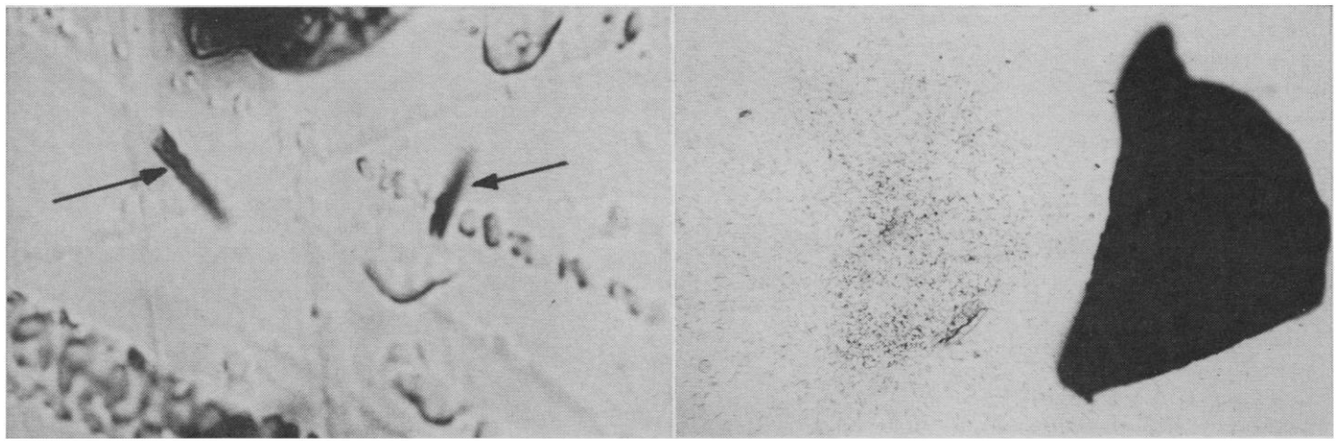

Fig. 1 (left). Fossil tracks (indicated by arrows) in a grain of hypersthene that has been cleaved open and etched for 30 minutes in KOH solution at 210°C (× 1800). Fig. 2 (right). Photomicrograph illustrating a method for measuring the uranium concentration in meteoritic material. The dark grain is a tiny crystal of zircon that was sandwiched between two sheets of mica and irradiated with thermal neutrons. After etching for 12 minutes in hydrofluoric acid, the mica contains a pattern of tracks resulting from uranium fissions in the portion of the zircon that was next to the mica. The zircon was moved to one side of the track pattern when the picture was taken (× 90).

ally accepted solidification age of meteorites (*14*), $T = 4.5 \times 10^9$ years, we calculate that $\rho_U = 1.6 \times 10^3/cm^2$. Thus, only about one-third of the observed fossil tracks come from spontaneous fission of uranium.

Of the possible ways in which cosmic rays may cause track formation, the most probable are heavy cosmic ray primaries, spallation recoils of medium and heavy elements (*15*), and the fission of heavy elements caused by neutrons generated in spallation reactions. Another possibility is spontaneous fission of Pu^{244}, which was a source of tracks from the time the mineral was formed and cooled until all of the Pu^{244} decayed (half-life, 7.6×10^7 years). The relative contributions from cosmic rays and from Pu^{244}, and the relevance of Pu^{244} fission tracks to the early history of meteoritic crystals, are discussed elsewhere (*16*).

Since we have not been able to measure the response of the hypersthene crystal to high energy protons, and since the time during which Vaca Muerta was exposed to cosmic rays is not known, we cannot decide between these alternatives.

The production of new tracks by irradiation in a nuclear reactor gives a simple method of measuring the uranium concentration in the different mineral phases (*17*). If ρ_i is the density of such induced tracks then the uranium concentration C_U at any given location in a crystal is given by (*5*)

$$C_U \text{ (wt, ppm)} \approx 8 \times 10^6 \rho_i / F N_v R \quad (2)$$

where N_v is the atomic density of the mineral and R is the average depth at which a fission event can result in an etched-out track intersecting the surface.

Results for seven different minerals from Vaca Muerta are given in columns 4, 5, and 6 of Table 1. The spread of values listed for each entry of column 5 indicates the rather large variation in uranium concentration in

Table 1. Fossil tracks in Vaca Muerta minerals.

Minerals	Etching conditions	Fossil track density	Fraction of uranium atoms fissioned in reactor	Induced track density	Uranium conc. (ppm)	Comments
Zircon A $ZrSiO_4$	H_3PO_4 at 480°C, 1 min	Too dense to resolve	4×10^{-10}	$\sim 7 \times 10^6/cm^2$	800–4000 in different fragments	Diffuse x-ray spots indicative of radiation damage
Zircon B	H_3PO_4 at 480°C, 1 min	10^7–$10^8/cm^2$	4×10^{-9}	$(0.2–2) \times 10^5$	1–10	Sharp x-ray spots
Whitlockite $Ca_3(PO_4)_2$	70% HNO_3, 10 sec	Too dense to resolve ($\sim 2 \times 10^8/cm^2$)	4×10^{-10}	$\sim 1.8 \times 10^5$	≤ 90	
Chromite $FeCr_2O_4$	?	?	2.5×10^{-6}	$(3–6) \times 10^6$	0.5–1	No etchant found
Rutile TiO_2	?	?	2.3×10^{-6}	$\sim 4 \times 10^5$	3×10^{-2}	No etchant found
Tridymite SiO_2	10% HF, 60 min	$(0.2–5) \times 10^5/cm^2$	2.5×10^{-6}	$(0.3–5) \times 10^5$	$(3–50) \times 10^{-3}$	Dislocations also etch
Hypersthene $(Mg,Fe)SiO_3$	KOH at 210°C, 30 min	$\sim 6 \times 10^3/cm^2$	2.5×10^{-6}	$(0.7–3) \times 10^4$	$(0.7–3.0) \times 10^{-3}$	See Fig. 1
Anorthite $CaAl_2Si_2O_8$	KOH at 210°C, 30 min	$\sim 2 \times 10^3/cm^2$	2.5×10^{-6}	$(3–9) \times 10^3$	$(3–9) \times 10^{-4}$	

different regions of a single grain of a mineral.

The results for the tridymite, hypersthene, and anorthite crystals are most accurate. These crystals were large enough so that they could be annealed to erase fossil tracks, then irradiated, cleaved, and etched and the densities of new tracks determined on the fresh surfaces. This procedure eliminated any possibility of contamination by stray uranium. Zircon B and the whitlockite crystals were too small to cleave but were cleaned in various reagents and sandwiched between freshly cleaved muscovite mica sheets that were chosen for their low uranium content (less than 10^{-4} parts per million). Zircon A and the chromite and rutile crystals were cleaved into several fragments before being inserted between the mica sheets. After irradiation with thermal neutrons, the mica sheets were etched and track densities in the regions of the mica adjacent to the mineral grains were used to calculate the uranium concentrations in the grains. The procedure is illustrated in Fig. 2. In calculating uranium concentrations from Eq. 2, R was taken to be 8 μ for the crystals that were cleaved open after irradiation and 4 μ for crystals with one surface placed next to mica (*5*).

Previous radiochemical measurements of uranium concentrations in large samples of meteorites have given results which vary somewhat from sample to sample and from one experimenter to another (*18*). This variability is hardly surprising in view of the present results, which show a remarkable variation in the uranium concentrations of different small grains of a given meteorite. For example, the amount of uranium in zircon A, a 250-μg sample, is roughly equal to the average uranium content of a 50-g sample of a typical chondrite and to the uranium content of a 250-g sample of troilite from an iron meteorite. Thus the presence or absence of a barely visible grain can completely change the measure of the average uranium concentration.

Recently, Lovering and Morgan (*18*) measured uranium (and thorium) concentrations in large samples from Orgueil and other meteorites. They found a high uranium concentration in Orgueil, close to a predicted primordial abundance, and have taken this as evidence for the primitive nature of Orgueil. They also found a steady progression of uranium concentration from one type of meteorite to the next. However, their value for Orgueil was considerably higher than that measured by Reed *et al.* (*19*) who actually found a lower value than is characteristic of average chondrite material. It would thus be interesting to measure Orgueil (and other meteorites where variable results have been found) by the methods reported here.

Table 2. X-ray and optical data for zircons.

Sample and reference	a_0(Å)	c_0(Å)	Quality of spots or lines	Indices of refraction	Calc. radiation dose (α-particles/mg)
Zircon A (with inclusions)	6.616 ± 0.005	5.989 ± 0.005	Diffuse		$\sim 1 \times 10^{17}$
Zircon A (*11*) (with inclusions)	6.615 ± 0.001	5.994 ± 0.003	Fairly sharp	$\varepsilon = 1.858 \pm 0.005$ $\omega = 1.841 \pm 0.005$	$\sim 1 \times 10^{17}$
Zircon B (*11*) (clear)	6.615 ± 0.001	5.994 ± 0.003	Fairly sharp	$\varepsilon = 1.962 \pm 0.005$ $\omega = 1.920 \pm 0.005$	2.5 to 25×10^{13}
Nonmetamict Ceylon zircon (*15*)	6.603	5.980	Very sharp	$\varepsilon = 1.972$ $\omega = 1.920$	0
Nearly metamict Ceylon zircon (*15*)	6.710	6.090	Very diffuse	$\varepsilon = 1.87$ $\omega = 1.86$	$\sim 1 \times 10^{16}$

We wish to emphasize that the technique of measuring uranium concentrations on a microscopic scale by placing cleaved mica next to the sample to be studied is applicable to all types of meteorites since it does not depend on the ability to etch tracks in the meteoritic material itself. Thus our method gives a way of measuring the variations in uranium concentrations from one phase to the next in a given meteorite and the changing fractionation from one class of meteorite to the next.

We have also measured the lattice parameters of zircon A (C_U, 800 to 4000 ppm) to determine whether there is a correlation between age and increase in the unit cell dimensions resulting from radiation damage as shown by Holland and Gottfried (*20*) in terrestrial zircons. Although the x-ray spots of zircon A are diffuse, suggesting extensive damage, the values of a_0 and c_0 are not much larger than those of a nonmetamict Ceylon zircon of low uranium content measured by Holland and Gottfried (see Table 2). Our unit cell determinations for zircon A are in agreement with those of Marvin and Klein (*11*) who obtained identical parameters for zircon A (C_U, 800 to 4000 ppm) and zircon B (C_U, 1 to 10 ppm) from Vaca Muerta.

The presence of these two types of zircon with strikingly different uranium contents within the same meteorite is difficult to explain except on the basis that Vaca Muerta is a breccia of crushed fragments of minerals, out of equilibrium with one another, probably derived from at least two separate sources. The silicates of Vaca Muerta include four different pyroxenes as well as two types of zircon (*11*).

Zircon B, which has a maximum of 10 ppm of uranium, has probably never been metamict. It is colorless, clear, and has substantially normal indices of refraction and unit cell parameters (Table 2). Zircon A, however, is dark in color, semi-opaque with submicron inclusions, and has indices of refraction that are difficult to measure but appear markedly low. The high uranium content of this zircon would lead one to predict extensive radiation damage to the structure. Its small lattice parameters, therefore, suggest restoration of the structure by annealing. The physical mixture of zircon A with other minerals, some of which display a large density of fission tracks, indicates that if annealing occurred it was either highly selective in its effects or it predated the present aggregation of mineral fragments in Vaca Muerta.

R. L. FLEISCHER, C. W. NAESER*
P. B. PRICE, R. M. WALKER
General Electric Research Laboratory, Schenectady, New York 12301
URSULA B. MARVIN
Smithsonian Astrophysical Observatory, Cambridge, Massachusetts

References and Notes

1. P. B. Price and R. M. Walker, *Nature* **196**, 4856 (1962).
2. ———, *J. Geophys. Res.* **68**, 4847 (1963).
3. R. L. Fleischer and P. B. Price, *ibid.* **69**, 331 (1964).
4. ———, *Geochim. Cosmochim. Acta* **28**, 1705 (1964).
5. R. L. Fleischer, P. B. Price, R. M. Walker, *J. Geophys. Res.* **69**, 4885 (1964).
6. M. Maurette, P. Pellas, R. M. Walker, *Nature* **204**, 821 (1964).
7. R. L. Fleischer, P. B. Price, R. M. Walker, E. L. Hubbard, *Phys. Rev.* **133**, A1443 (1964).
8. R. L. Fleischer, P. B. Price, E. M. Symes, D. S. Miller, *Science* **143**, 349 (1964); M. Maurette, P. Pellas, R. M. Walker, *Bull. Soc. Franc. Mineral. Crist.* **87**, 6 (1964); R. L. Fleischer and P. B. Price, *Geochim. Cosmochim. Acta* **28**, 755 (1964).
9. P. B. Price and R. M. Walker, *Phys. Rev. Letters* **8**, 217 (1962).
10. For a recent review, see K. W. Ford, *Sci. Am.* **209**, 122 (1963).
11. U. B. Marvin and C. Klein, *Science* **146**, 919 (1964).
12. H. Hamaguchi, G. W. Reed, A. Turkevich, *Geochim. Cosmochim. Acta* **12**, 337 (1957).
13. R. A. Schmitt, R. H. Smith, D. A. Olehy, *General Atomic Rept. GA-4221* (General Atomic Div. of General Dynamics Corp., San Diego, Calif., 1963).
14. For a review, see E. Anders, in *The Moon, Meteorites and Comets*, B. M. Middlehurst and G. P. Kuiper, Eds. (Univ. of Chicago Press, Chicago, 1963), p. 402.
15. M. Maurette and R. M. Walker, *J. Phys. Radium* **25**, 43 (1964).
16. R. L. Fleischer, P. B. Price, R. M. Walker, *J. Geophys. Res.*, in press.
17. P. B. Price and R. M. Walker, *Appl. Phys. Letters* **2**, 23 (1963).
18. For recent measurements and a summary of previous work, see J. F. Lovering and J. W. Morgan, *J. Geophys. Res.* **69**, 1979 (1964).
19. G. W. Reed, K. Kigoshi, A. Turkevich, *Geochim. Cosmochim. Acta* **20**, 122 (1960).
20. H. D. Holland and D. Gottfried, *Acta Cryst.* **8**, 291 (1955).

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* Present address: Southern Methodist University, Dallas, Texas.

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Enzymatic Synthesis of Tri- and Tetranucleotides of Defined Sequence

Abstract. *Conditions have been found under which polynucleotide phosphorylase adds only a few nucleotide residues to the 3′ end of a dinucleotide primer. Pure tri- and tetranucleotides can be isolated from reaction mixtures in high yield.*

Block oligonucleotides containing nearly any desired trinucleotide sequence at the point of union of the two blocks can be prepared in pure form (*1*). The polymerization of a nucleoside diphosphate (*2*) was primed with an appropriate oligonucleotide by means of polynucleotide phosphorylase from *Micrococcus lysodeikticus*. The successful synthesis of the desired product was due first to the enzyme having an essentially absolute primer requirement for initiation of polymerization (*3*), and second to our finding that high NaCl concentrations terminated chain growth at the desired length (*1*). Typical products were CpCpCpCpCpApApA and CpCpCpCpCpApUpUpU.

One remaining limitation of the preparative procedure arose from the failure of very short oligonucleotides such as the dimer, NpN, to prime polymerization at the high NaCl concentrations required: consequently, it was not possible to prepare trimers and tetramers of specified sequence. We now report how this may be done with the same system.

This new procedure has its origin in the observation that, in the absence of NaCl, reaction products were unutilized dinucleotide primer and long polynucleotide chains with primer at the 5′ end. Evidently these two species of polymer did not represent the product that should be obtained at thermodynamic equilibrium. Such a product should instead have a single peaked distribution of the type known as the "most probable" distribution with its mean value being determined by the mole ratio of NDP polymerized to primer. In principle, the continuation of the incubation for a sufficiently long time should bring about a redistribution of monomeric units to this state. We have now found conditions that make this redistribution possible in a practical time span and that result in a very low molecular weight product consisting of only a few species, such as ApUpA, ApUpApA and ApUpApApA, which can then readily be fractionated.

Polynucleotide phosphorylase from *M. lysodeikticus* was purified 90-fold (*3*). The purified enzyme was shown to be free of nuclease and phosphatase. It polymerized NDP at a very slow rate in the absence of added primer, but this endogenous activity was completely inhibited by the addition of 0.4*M* NaCl to the reaction mixture (*1*). In studies of reaction kinetics, the polymerization of NDP and the incorporation of radioactive primer into polymer was followed by removing samples from a reaction mixture at various time intervals and applying them to Whatman 3MM chromatography paper. Chromatograms were developed in a solvent in which primer and NDP migrated away from the origin, while oligonucleotides longer than the tetramer remained at the origin. Spots at the origin were eluted, and the amount of NDP polymerized was determined by absorbance measurement, whereas the amount of primer incorporated was determined by ra-

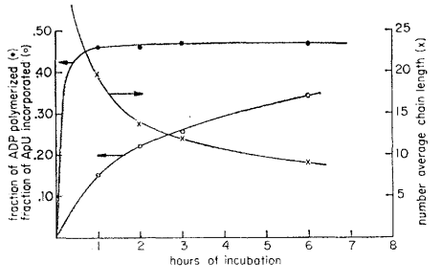

Fig. 1. Prolonged incubation of a polymerization reaction mixture. The ADP is polymerized in the presence of ApU-C^{14} primer. Samples of the reaction mixture (text), withdrawn at the indicated times, were applied to Whatman 3MM paper, and the chromatogram was developed in a solvent composed of 60 parts 95 percent ethanol to 40 parts 1*M* ammonium acetate. Origin spots were cut out and eluted with buffer (0.01*M* tris, *p*H 8.2, 1m*M* EDTA). The fraction of ADP polymerized (•) was determined by absorbance measurement at 260 mμ; the fraction of ApU-C^{14} incorporated into polymer (○) was determined by radioactivity measurement (*1*). The average chain length of polymer at the origin (×) is the mole ratio of polymer residues to incorporated primer residues.

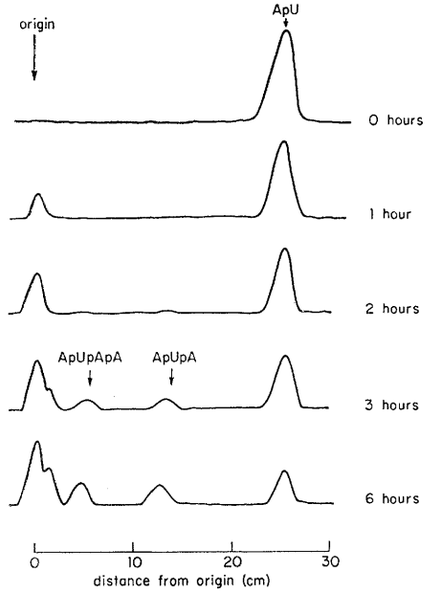

Fig. 2. Distribution of ApU-C^{14} primer as a function of time. The chromatogram from Fig. 1 was cut into strips (before elution of origin spots) and scanned for radioactivity in a Vanguard automatic chromatogram scanner. Radioactivity peaks corresponding to ApUpA and ApUpApA appear in the samples taken at 3 and 6 hours.