Reports

Uranium Distribution in Separated Clinopyroxenes from Four Eclogites

Abstract. *Uranium concentrations and distributions in separated clinopyroxenes of eclogites from four different sites have been studied by the fission track method. Types of uranium occurrences included (i) inhomogeneously distributed clusters, (ii) line concentrations at cracks, and (iii) uniform distributions in the body of the mineral. Different grains from the same sample generally vary by factors of 2 to 4 in uniformly distributed uranium concentration. Samples from different locations vary in their average uniformly distributed uranium concentration by a factor of approximately 1000 (that is, from 0.01 to 20 parts per billion of uranium). The degree of homogeneity also varies markedly from one site to the next. The clinopyroxenes from the only oceanic locality studied (Salt Lake Crater) contained both the largest concentration of uranium (15 to 20 parts per billion) and the most uniform uranium distribution. This study suggests that, if total uranium concentrations in eclogitic clinopyroxenes are less than a few parts per billion, much if not most of the uranium may occur as contaminants along cracks or in microinclusions of unknown origin.*

The uranium abundances and distributions in clinopyroxenes from four eclogites from three different geologic environments were investigated. The basic method consisted of observing tracks of fission fragments produced by the thermal neutron-induced fission of uranium (*1*). The results show that there is a considerable variation in both the concentration and distribution of uranium in samples from different environments.

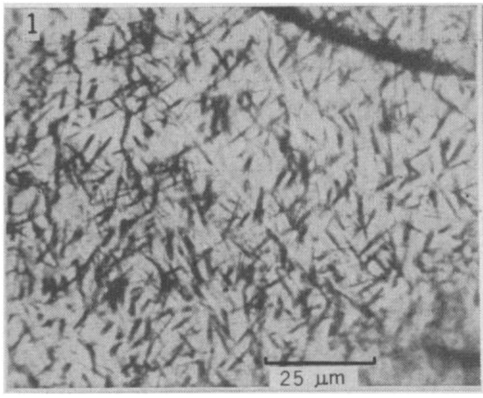
There are two general methods for the determination of uranium concentration by the fission track method. In the first method an auxiliary detector, such as Lexan polycarbonate or mica, is placed next to a sample and the detector-sample sandwich is irradiated with thermal neutrons. The detector is then removed and separately etched to reveal induced fission fragments that have recoiled from the sample into the detector. The uranium concentration in the auxiliary detector must be much smaller than that in the sample. This is the preferred method when uranium concentrations are fairly high but it becomes increasingly less attractive at low concentrations because of potential contamination problems. The choice of a suitable auxiliary detector also becomes increasingly difficult.

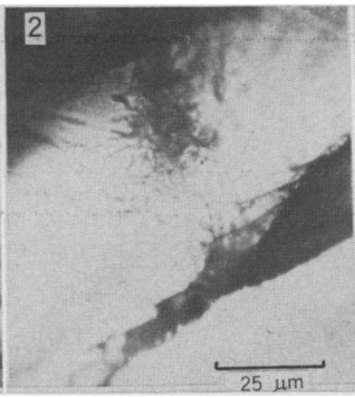
The second method, which was used here, completely avoids contamination problems and makes possible the measurement of uranium concentrations below 10^{-3} parts per billion in small grains. It necessitates only a measurement of the induced fission track densities in the samples themselves. Sufficient material is removed from the sample after irradiation to ensure that tracks from surface contaminants do not contribute to the measured densities. This method is more complicated than the first method, at least initially, and has several potential pitfalls that must be avoided. The major complication is the necessity to develop suitable track-etching techniques for the minerals studied. Although there is a considerable amount of published information on track-etching conditions in various minerals (*2*), these data must be treated with some caution for two reasons. First, the precise etching conditions depend on the detailed chemical composition of the mineral and can vary from one grain to the next. Second, and perhaps more important, the etching conditions for track revelation may depend strongly on crystal orientation. For any given mineral the number of tracks and their appearance may change from one surface orientation to the next. This behavior has been documented for olivine (*3*). In minerals that have well-defined cleavage surfaces, there is generally no problem. If, however, as in this case, the faces studied are polished surfaces inclined at random orientations, possible differences in the type of etchant and in the etching conditions from one sample to the next must be taken into account. Another complication in the internal track method is the possible contribution of preexisting, "fossil" fission tracks (*4*). Either these tracks can be measured before irradiation and their number subtracted from the total after irradiation, or they can be removed by thermal annealing. In the latter event care must be taken to verify that no uranium is either removed or added by the high-temperature treatment.

In this work we used clinopyroxene separated from eclogites from the following localities: (i) Salt Lake Crater in Hawaii (inclusion in alkali basalt); (ii) Bavaria (from a regional metamorphic terrane); (iii) Roberts-Victor mine, South Africa (kimberlite inclusion); and (iv) Bultfontein, South Africa (kimberlite inclusion). Petrographic descriptions and the abundances of K, Rb, Sr, and Ba in these samples have been reported by Griffin and Murthy (*5, 6*).

Approximately five clinopyroxene crystals from each of these eclogites were chosen at random and mounted on glass slides with epoxy resin. They were then polished in succession with emery paper, 5-μm Al_2O_3 powder, and 0.3-μm Al_2O_3 powder. The samples were then exposed to a standard irradiation with fission fragments from a Cf^{252} spontaneous-fission source. The best etching conditions for each grain were determined by immersing the samples for varying periods of time in an etching solution consisting of a mixture of 2 parts 48 percent HF, 1 part 96 percent H_2SO_4, and 4 parts H_2O. Optimum etching times ranged from 10 to 20 minutes at room temperature. After etching, some samples were lightly repolished to remove surface deposits produced by the attack.

The tracks were studied by means of a Leitz Ortholux microscope equipped with metallographic objectives. Tracks were counted and the area of the irregular grains was measured by means of a standard ground-glass accessory screen. After the image was transferred to tracing paper, its area was measured with a planimeter.





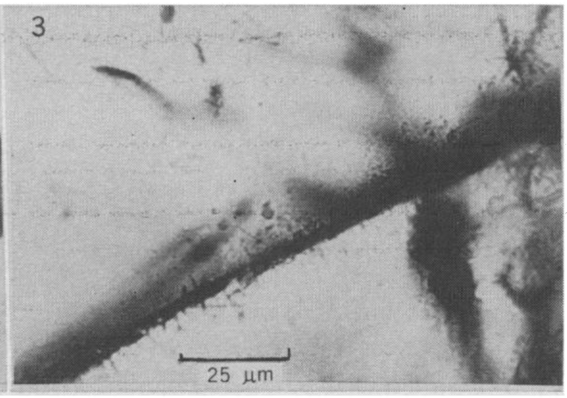


Fig. 1. Homogeneous distribution of fission tracks in a clinopyroxene grain from the Salt Lake Crater eclogite. Fig. 2. Inhomogeneous distribution of fission tracks in a clinopyroxene grain from the Bultfontein eclogite. Tracks radiate from what appears to be a microinclusion in the upper center part of photograph. A few questionable tracks can also be seen emanating from the large crack crossing the lower right side of the photograph. Fig. 3. Inhomogeneous distribution of fission tracks in a clinopyroxene grain from the Bultfontein eclogite. Many tracks emanate from the large crack crossing the grain, and a small track point-source (microinclusion) is visible in the extreme upper right corner of the photograph. A few homogeneously distributed tracks occur in the upper center part of the photograph.

The efficiency of track registration was determined for each grain by comparing the experimental track density with the total number of incident particles. The latter quantity was measured by counting the induced track density in mica which is known to register fission fragments with close to 100 percent efficiency (*7*). Within the precision of the measurements (± 20 percent), all the efficiencies were consistent with a 100 percent track revelation with the exception of the Bultfontein eclogite which had an average efficiency of 60 ± 20 percent. The tracks generally have a typical cylindrical shape, although they occasionally show up as flat etch pits or thin lamellae as in olivine (*3*).

After we had experimentally verified that fission tracks could be seen on each of the grains, the grains were repolished and reetched to make possible a search for fossil fission tracks. The failure to observe a measurable density of such fossil fission tracks is consistent with the estimated ages of the specimens and the very low concentrations of uranium that were subsequently measured.

After these preliminary experiments ten good crystals, ranging in size from 300 to 500 µm, were selected from each of the four eclogites for neutron irradiation. The grains were placed in holes in a fused-quartz sample holder. This was then covered with a second, flat quartz plate to form an irradiation package. The assembly was then wrapped in aluminum foil and irradiated with thermal neutrons to a dose of 10^{19} neutron/cm^2 in the Brookhaven high-flux reactor. The quoted neutron dose was verified with an accuracy of ± 10 percent with calibrated uranium glass standards (*8*). After irradiation the samples were mounted on glass slides and were polished and etched as described above. At least 20 µm of crystal surface was removed to eliminate tracks from surface contaminants.

Three types of track (and hence uranium) distributions were observed in the clinopyroxenes studied (Table 1): (i) an apparently homogeneous distribution throughout the crystal matrix (Fig. 1), (ii) an inhomogeneous distribution consisting of point and line clusters apparently occurring in the crystal matrix (Fig. 2), and (iii) an inhomogeneous distribution consisting of track clusters emanating from cracks and other gross flaws (Fig. 3).

Table 1. Uranium concentrations in separated clinopyroxenes from eclogites. Numbers in parentheses give actual tracks counted; the precision of this determination is limited by the precision of measurements of grain area to $\leqslant$ 10 percent or the statistical uncertainty of track count, whichever is larger.

Grain No.	Uranium concentration (ppb)		
	Uniformly distributed	Inclusions*	Cracks*
	Eclogite from Salt Lake Crater		
1	18.6(643)		
2	16.9(585)		
3	19.3(670)		
4	18.3(627)		
5	17.3(598)		
6	15.6(531)		
7	15.9(552)		
8	14.5(502)		
	Bavarian eclogite		
1	0.08(5)	0.1(6)	0.1(8)
2	.08(5)		.10(6)
3	.08(7)		.02(2)
4	.18(5)		
5	.31(12)		.2(6)
6	.18(18)		$\leqslant$ .03(3)
7	.08(8)	.20(20)	
8	.33(21)		.05(3)
	Roberts-Victor eclogite		
1	1.7(70)		0.04(13)
2	2.0(73)	$>$ 0.10(36)	$\geqslant$ .10(37)
3	1.2(42)		.01(5)
	Bultfontein eclogite		
1	0.004(1)	$\geqslant$ 0.27(65)	
2		$>$ .04(17)	$>$ 0.11(46)
3		$\geqslant$ .15(51)	
4	.007(3)	$\geqslant$ .05(26)	.01(6)

* These values are subject to considerable uncertainty and are not as reliable as those for uniformly distributed concentrations.

All the grains from the Salt Lake Crater eclogite and most of the grains from the Bavarian eclogite show an apparently homogeneous distribution of uranium. For such a uniform distribution, the concentration of uranium C_u (in parts per billion) can be calculated from the measured track density ρ_t by the following expression

$$C_u = 11\rho_t/N_0 n\sigma IR$$

where N_0 is the number of atoms per cubic centimeter, n is the neutron dose, σ is the cross section for thermal neutron-induced fission of U^{235}, I is the isotopic fraction of U^{235}, and R is a geometrical factor that is approximately equal to the range of fission fragments in the material. Application of this formula to the observed track densities in the Salt Lake Crater and Bavarian eclogites indicates uranium concentrations, respectively, of 15 to 19 ppb and 0.1 to 0.3 ppb (Table 1). Collectively, $\leqslant$ 0.1 ppb of uranium occurs in cracks and in inclusions in Bavarian clinopyroxenes.

The Roberts-Victor and Bultfontein eclogites exhibit heterogeneous distributions with the Bultfontein samples being the most extreme case. Most of the uranium in the Bultfontein samples, however, appears to be concentrated in inclusions, or, less commonly, in cracks. Griffin and Murthy (*6*) reported inclusions of both rutile and garnet in these samples, with rutile by far the predominant. This suggests that most of the uranium in the Bultfontein clinopyroxenes may be associated with acicular inclusions of rutile. Two grains from the Bultfontein locality had a few individual tracks in the matrix, which gives an estimated matrix conconcentration of $\lesssim 0.01$ ppb. The Roberts-Victor samples were somewhat more homogeneous with the three grains studied showing apparently randomly distributed tracks; estimated matrix concentrations in these samples are 1 to 2 ppb. A large number of the tracks in one of the grains, however, were concentrated along cracks resulting in a crack concentration of uranium, very much greater than 0.1 ppb.

The estimates of total uranium concentrations, however, may be very inaccurate in cases where heterogeneous distributions occur. These should be treated as order-of-magnitude estimates only. Apart from the obvious sampling problem, the track densities in clusters are frequently so high as to be unresolvable. In the case of cracks that propagate into the interior, an unknown amount of surface area is etched and the estimates are especially unreliable. In addition, cracks may contain contaminants introduced by the polishing. Finally, cracks are also sources of dislocation etch lines that can be confused with fission tracks.

Limited sampling of separated clinopyroxenes from four different eclogites indicates that the uranium in these minerals may occur as random atoms uniformly distributed throughout the crystal, as clusters of atoms occurring at points or lines within the crystals, or as contaminants along cracks and flaws in the grains. The concentration of uniformly distributed uranium varies by a factor of approximately 1000 among the clinopyroxenes from the four eclogites studied. The total uranium present in whatever form appears to vary by a factor of about 100. The latter conclusion is less certain because of difficulty in estimating total uranium by this technique when the concentration is not homogeneous. There is some suggestion in the data that the amount of uniformly distributed uranium increases in the clinopyroxenes as the total uranium concentration increases.

The ratios of K to U in these clinopyroxenes are noteworthy. Using the potassium values reported by Griffin and Murthy (*5*) we obtain K/U ratios of about 3×10^3 for the samples from Salt Lake Crater and ratios of about 10^6 to 10^7 for the Roberts-Victor and Bultfontein samples. Even if the heterogeneously distributed uranium were included, the latter two samples would still show high K/U ratios of about 10^6. This suggests that, although there is a broad coherence between potassium and uranium in many surface terrestrial materials as indicated by the relatively constant K/U ratio of 10^4 for such materials (*9*), it may be possible to fractionate potassium and uranium in some minerals important in the upper mantle.

In terms of the concentrations of uranium in the oceanic upper mantle, it may be significant that the clinopyroxenes from the only oceanic locality studied (Salt Lake Crater) contained both the largest concentration of uranium and the most uniform uranium distribution. This investigation indicates, however, that the total uranium concentration in clinopyroxene (and, presumably, in other minerals) may be misleading to one who is estimating the amount of uranium in their source regions. If the total uranium concentrations are less than a few parts per billion, much if not most of the uranium may occur as contaminants along cracks, in microinclusions, or as grain boundary films. The reported lability of potassium in these minerals (*5*) suggests that the same is true for this element. We suggest that the abundance of potassium and uranium and the K/U ratio of a substantial fraction of the earth's inventory of these elements remains poorly known. Models of heat flow for the earth based on reported concentrations of these heat-producing elements in either separated minerals or whole-rock samples from eclogites, ultramafic rocks, or chondritic meteorites must be considered tenuous until the amount and source of contaminant uranium and potassium have been determined in these rocks and meteorites.

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Pecoraite, $Ni_6Si_4O_{10}(OH)_8$, Nickel Analog of Clinochrysotile, Formed in the Wolf Creek Meteorite

Abstract. *Pecoraite is a new phase in the natural system* H_2O*-NiO-MgO-*SiO_2*, the nickel analog of clinochrysotile. It occurs in cracks in the Wolf Creek meteorite in Australia where it was formed under hydrothermal conditions. Particles of pecoraite are very small curved plates which have begun to coil; some have achieved spiral form.*

A green mineral of the serpentine group, rich in nickel, was described (*1*) from the Wolf Creek meteorite in the desert of Western Australia. This mineral is the nickel analog of the well-known magnesium silicate, clinochrysotile.

The new mineral is named pecoraite after Dr. William T. Pecora, Director of the U.S. Geological Survey, in recognition of his contributions (*2*) to the mineralogy and geology of nickel silicate deposits in North America and South America (*3*).

Pecoraite occurs as green grains, 0.1 to 5 mm in diameter, that fill cracks in the Wolf Creek meteorite. The color is the "Oriental Green" of Ridgway (*4*). The phase is weakly doubly refracting and has indices of refraction varying from 1.565 to 1.603 depending on the quantity of adsorbed water. A sample of pecoraite dried over magnesium perchlorate to remove the excess water has a mean index of refraction close to 1.650. The specific gravity of the pecoraite containing adsorbed water is 3.08_4.

A carefully purified sample (0.1 g) contained in weight percentages: SiO_2, 31.0; NiO, 51.5; FeO, 0.7; MgO,