Meteoritic Zircon

Abstract. *Zircon ($ZrSiO_4$) has been identified as an accessory mineral in the Vaca Muerta mesosiderite and in the troilite nodules of the Toluca iron meteorite. The occurrence in Vaca Muerta is a new discovery confirmed by electron-probe microanalysis of a grain in a polished section of the meteorite. Our identification of zircon in Toluca substantiates an occurrence in this meteorite reported in 1895 by Laspeyres and Kaiser.*

The name Vaca Muerta has been assigned to a large number of meteorite specimens found in the Atacama Desert of northern Chile, at about 25°45′S, 70°30′W, between 1861 and 1890. Most of these specimens are mesosiderites; some are achondrites. To date we have found zircon in two mesosiderite specimens.

Measurements of Al^{26} in the mesosiderite specimens were made by E. L. Fireman. The results indicate that the specimens came from small, lightly shielded fragments, probably less than 1 m in diameter, that have been in space for over a million years. Similar values of Al^{26} have been recorded for many stony meteorites (*1*). The date of fall of Vaca Muerta is unknown, but the meteorite has been preserved in fresh condition because of the dry climate of the Atacama Desert.

The zircon-bearing specimens are typical mesosiderites with about half the volume consisting of metallic nickel-iron showing Widmanstätten patterns in the individual grains and half a breccia of broken, irregular silicate fragments ranging in size from submicron powders up to 0.5 cm in cross section. The minerals present, and their relative abundance by volume, are as follows: kamacite-taenite (55 percent); orthopyroxenes (30 percent); anorthite (10 percent); accessory minerals (5 percent), including troilite, schreibersite, chromite, forsterite, tridymite, graphite, cliftonite, whitlockite, chlorapatite, clinopyroxene, rutile, and zircon. Electron-probe microanalyses show that the orthopyroxenes occur as three different phases: hypersthene (En_7Fs_3), and two bronzites ($En_{7.5}Fs_{2.5}$ and $En_{8.1}Fs_{1.9}$). The plagioclase feldspar is anorthite (An_{100}). Both the brecciated texture and the variation in composition of the pyroxenes indicate that the stony portion of Vaca Muerta is in a state of disequilibrium.

The zircon in Vaca Muerta occurs in irregular fragments, with conchoidal fracture, ranging in size from a few microns up to 1 mm in cross section. It was first discovered in the insoluble residues of uncrushed bulk specimens that had been leached in dilute acetic acid and separated in heavy liquids. The zircon concentrated in a fraction that sank in Clerici solution (specific gravity, 4.10). A total of about 2 mg (0.0015 percent) of zircon was obtained from 125 g of the mesosiderite.

Some of the zircon grains are transparent and colorless and have adamantine luster. Most of them, however, are yellowish or brown and semiopaque with a waxy luster. The opacity of these grains is due to very many inclusions a micron or less in size, which give the zircon a cloudy appearance in transmitted light (Fig. 1). The indices of refraction of the cloudy grains appear to be substantially lower than those of the clear ones. This effect is probably caused by interference from the inclusions with indices of refraction lower than the matrix zircon. The following optical properties were measured in sodium light on the two types of grains: (i) Clear zircon: indices of refraction, $\epsilon = 1.962 \pm 0.005$; $\omega = 1.920 \pm 0.005$; birefringence 0.042 ± 0.010, uniaxial (+). (ii) Zircon with inclusions: $\epsilon = 1.858 \pm 0.005$; $\omega = 1.841 \pm 0.005$; birefringence 0.017 ± 0.010, uniaxial (+).

The optical properties of the colorless zircon lie in the range of normal terrestrial zircon (*2*). Although the cloudy zircon grains have indices of refraction similar to those of metamict zircon, these indices, as already stated, are probably anomalously low because of the abundant inclusions.

X-ray powder films (camera diameter 114.59 mm) were made of the clear zircon and of the brown semiopaque material. The two samples yielded identical diffraction patterns. The films were measured, and the diffraction lines were indexed by comparison with the zircon pattern already published (*3*). Eighteen unambiguously indexed lines of 2θ above 30° (Cu radiation), from the diffraction pattern of the cloudy grain, were used in the least-squares refinement program developed by Burnham (*4*). The following unit cell parameters were obtained: $a_0 = 6.615 \pm 0.001$ Å; $c_0 = 5.994 \pm 0.003$ Å. These unit cell dimensions are similar to those of normal, nonmetamict, terrestrial zircon (*2*).

An electron-probe x-ray analyzer (Applied Research Laboratories) has been used to determine the composition of the zircon and the coexisting silicates.

Table 1. Composition of zircon found in the Vaca Muerta mesosiderite from Chile.

Distribution of oxides	Found (%) Clear	Found (%) With inclusions	Theoretical (%)
ZrO_2	66.8	66.2	67.2
SiO_2	32.2	28.9	32.8
MnO	0	0.8	0
CaO	0	0.7	0
Total	99.0	96.6	100.0

The zircon analyses were performed on three grains (Table 1), one approximately 50 μ and two about 200 μ in diameter, which were obtained from the insoluble residue. The grains were polished and coated with a layer of carbon a few hundred angstroms thick. At least ten measurements were made on each grain. The specimen current for these measurements was 0.4 μa; the accelerating voltage, 20 kv; and the probe diameter, 2 μ. The Zr$L\alpha$ and Si$K\alpha$ intensities were compared with the intensities of these elements in two different analyzed terrestrial zircons. In these determinations only background corrections were made. The Mn$K\alpha$ intensity in the zircon was compared with the Mn$K\alpha$ intensity of pure MnO_2. The Ca$K\alpha$ intensity was compared with the Ca$K\alpha$ intensity in synthetic andradite ($Ca_3Fe_2Si_3O_{12}$). In both cases absorption corrections were applied according to the method of Philibert (*5*). Mass absorption coefficients were taken from Birks (*6*). The final analysis reported below for the cloudy zircon does not add up to 100 percent because of the very numerous inclusions, of micron and submicron size, which consist of an iron-rich phase and probably a carbon phase. The composition of the clear grain is the same as that of pure terrestrial zircon.

One additional zircon grain was analyzed semiquantitatively. This grain, which is clear, was located *in situ* in a polished section of the Vaca Muerta meteorite. Its largest dimension is 10 μ. Like the clear grains from the insoluble residue, it emitted a bright pinkish-blue fluorescence under the electron beam (Fig. 2). The ratio of Zr to Si was similar to that of the other analyzed grains. A quantitative analysis was impossible because of interference by neighboring phases. The presence of this grain in a polished section dispelled all doubt that the

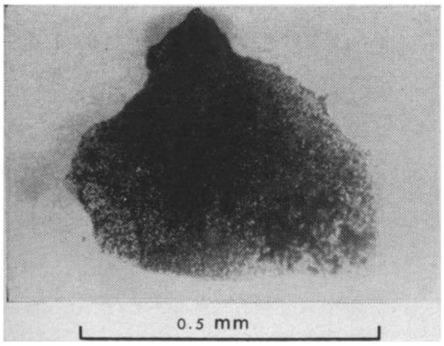

Fig. 1. A cloudy grain of Vaca Muerta zircon photographed under the petrographic microscope, showing minute brown and black inclusions. The clear areas are colorless.

fragments in the insoluble residue might be contaminants and established zircon as a valid meteoritic mineral.

Zircon was described by Laspeyres and Kaiser (*7*) as occurring in insoluble residues of the iron meteorite from Toluca, Mexico (19°34'N, 99°3'W). Doubt about the authenticity of this zircon was expressed by Cohen (*8*), who pointed out that all of the Toluca specimens dissolved by Laspeyres and Kaiser included parts of the weathered exterior of the meteorite and were therefore likely to carry mineral contaminants. Cohen cited a number of other doubtful reports of zircon in meteorites and suggested that careful reexamination of Toluca and others would be required before zircon could be accepted as a valid meteoritic mineral. Up to the present time the occurrence in Toluca had not been substantiated.

After positive identification of zircon in Vaca Muerta, we investigated a specimen of the Toluca iron, cutting away the weathered portions of the meteorite and working with nodules from the interior. Several nodules were dissolved in dilute HCl before one of them yielded two minute crystals of zircon which are euhedral, colorless, and clear except for a few inclusions. A qualitative electron-probe analysis of one crystal which is 0.08 mm long proved the presence of Zr and Si. The optical properties are $\epsilon = 1.970 \pm 0.005$; $\omega = 1.924 \pm 0.005$; birefringence, 0.046 ± 0.010, uniaxial (+).

No x-ray diffraction data were obtained for this crystal, but the optical properties indicate that it is normal, unmetamict zircon.

As the two crystals that we studied are similar to those described by Laspeyres and Kaiser, we conclude that they discovered authentic meteoritic zircon.

Zircon has always been a mineral of choice for radiogenic age determinations on terrestrial rocks. Since it concentrates uranium and thorium, it can be used for age determinations by the "lead-alpha" method (*9*) and by measurements of isotopic ratios in the U-Th-Pb-He system (*10*). Zircon also acts as a host mineral for rare earths and for hafnium, an element invariably associated with zirconium.

To date most age determinations and all measurements of uranium, thorium, zirconium, hafnium and rare-earth abundances in meteorites have been made on bulk samples. Little or no information is available on what mineral or minerals carry these elements. If any of them besides Zr are present in the Vaca Muerta zircon, they occur in amounts that are below the limit of detection by the electron-probe microanalyzer, which for these heavy elements is approximately 0.3 percent by weight. We have evidence, however, that the Vaca Muerta zircon is radioactive. Individual grains of it produce blackening of x-ray film within an exposure time of 1 week. Trace-element analyses of these grains are being postponed until the completion of various nondestructive studies on the zircon.

Zirconium abundances, measured on bulk samples, show that the maximum possible content of zircon in meteorites is very low. In ordinary chondrites and carbonaceous chondrites the average abundance of Zr is about 10 parts per million (*11*). If the Zr is all in zircon, this mineral makes up about 0.002 percent by weight (20 mg/kg) of these types of chondritic material. We have no information on the Zr content of Vaca Muerta or other mesosiderites, but our sample produced 16 mg per kilogram of the total meteorite, or 40 mg per kilogram of the stony portion.

The meteorites richest in Zr are the Ca-rich achondrites, which contain an average of 60 parts per million (*11*). This amount of Zr could produce about 120 mg of zircon per kilogram of achondrite (0.01 percent by weight). The Ca-rich achondrites contain more Zr, by a factor of about 4, than ordinary chondrites and would therefore seem a promising source of meteoritic zircon. Meteorites of this class are, however, rare, and the amount of bulk sample that can be obtained for the recovery of zircon is small.

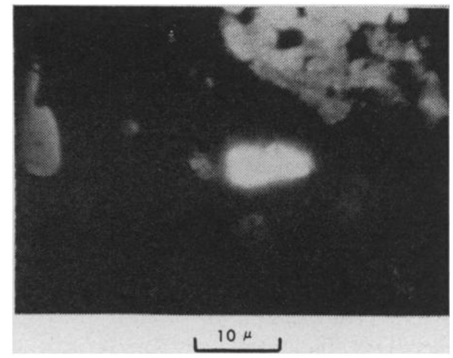

Fig. 2. A grain of zircon (white) *in situ* in a polished section of Vaca Muerta showing fluorescence under the electron beam. Light gray areas consist of fluorescing anorthite and tridymite. Black areas are kamacite and chromite.

In spite of its low abundance, if techniques can be devised for working with microgram rather than milligram quantities, zircon may well prove one of the most valuable minerals in meteorites for determinations of age data, rare-earth distribution, and ratios of zirconium to hafnium.

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