

STRUCTURE, CHEMISTRY, AND OPTICAL CHARACTERISTICS OF ZIRCON

Zircon occurs as a widespread accessory mineral in almost all types of terrestrial rocks, but it also occurs in meteorites and lunar rocks. It is one of the earliest accessory minerals to crystallize in a magma and continues to precipitate over long periods of time and ranges of temperature. Individual crystals can develop extensive chemical zonation, which reflects the changing chemical composition of residual magma (Hinton and Upton 1991).

As summarized by Speer (1982), the chemical composition of zircon is complex, and besides Hf, which is always present (concentrations up to 7 wt%), more than 50 other elements have been found in zircon. The most important ions substituting for $^{181}\text{Zr}^{4+}$ are Hf^{4+} , U^{4+} , Th^{4+} , Y^{3+} , and the REE^{3+} . Only P^{5+} and sometimes Nb^{5+} and Al^{3+} can replace Si^{4+} in its tetrahedral site. A close correlation between the concentrations of atoms of P and REE (including Y) in many zircon crystals suggests that most of the REEs are present in the form of phosphate molecules (i.e., REEPO_4) as in xenotime (YPO_4).

The incorporation of various elements substituting for Zr^{4+} changes the physical characteristics of the mineral and results in optical zonation, metamictization, and fluorescence. Transmission electron microscopy on zoned single crystals of zircon reveals that some of the zones are perfectly crystalline, whereas other zones show some structural damage or are even amorphous (Murakami et al. 1991). Metamictization in zircon results from α -decay events in the natural radioactive decay of ^{238}U , ^{235}U , and ^{232}Th and their daughter products. Specifically, the high-energy α particle produces hundreds of atomic displacements with a range of $\sim 10\ \mu\text{m}$, and the energetic recoil nucleus, with a range of $\sim 20\ \text{nm}$, produces localized damage with about 1000 atomic displacements (Weber et al. 1994). Zircon may contain substantial concentrations of U and Th and may therefore be exposed to doses as high as 10^{15} – 10^{16} α -decay events per milligram of zircon over its geologic life time. The physical changes in zircon that result from radiation damage include an increase in unit-cell dimensions and decreases in density and hardness (Holland and Gottfried 1955; Speer 1982). The different interference colors frequently observed in thin sections of zircon are known to be due to differing levels of α -decay damage. Increasing radiation damage decreases birefringence until the fully metamict crystal is optically isotropic (Sahama 1981). The totally metamict state is a structure that appears to be amorphous when analyzed by X-ray and electron diffraction techniques (e.g., Yada et al. 1981).

SAMPLE

We report here the analytical results obtained on a single zoned zircon grain in a thin section of a 23 mg lithic fragment, lunar sample 14161,7069, from an Apollo 14 soil. This sample is a partially recrystallized impact breccia

of quartz-monzodioritic (QMD) bulk composition and mineralogy, including regions of potassium feldspar-bearing granophyre (Jolliff et al. 1991; Jolliff 1991). The unusually high incompatible trace element concentrations ($\text{ITE} \approx 2 \times$ average high-K KREEP; Warren 1989), low siderophile-element concentrations, and uniform major mineral compositions indicate that this breccia is monomict (Jolliff 1991; Warren 1993). The original 23 mg sample comprised ~ 30 vol% pyroxene (average $\text{En}_{24}\text{Fs}_{68}\text{Wo}_8$ and $\text{En}_{20}\text{Fs}_{52}\text{Wo}_{28}$), $\sim 30\%$ plagioclase (An_{78-61}), 23% quartz plus silica-potassium feldspar granophyre, 11% barian potassium feldspar, 3.7% phosphates (whitlockite, apatite), 2.4% ilmenite, approximately 0.6% zircon, and a trace of fayalite (Jolliff 1991). Baddeleyite (ZrO_2), zirconolite $[(\text{Fe,Ca,REE})(\text{Zr,Ti,REE})_3\text{O}_7]$; Wark et al. 1973], and yttrobetafite $[(\text{Ca,Fe,Y,REE,U,Th})_2(\text{Ti,Nb})_2\text{O}_7]$; Meyer and Yang 1988], which have been found in other evolved lunar rocks (e.g., Smith and Steele 1976), were not found in the thin section of 14161,7069; however, the high bulk Th concentration of the sample (44 ppm; Jolliff 1991) suggests the presence in the rock sample of a Th-rich phase. Sample 14161,7069 was derived from a rock that was brecciated by a meteorite impact at ~ 4 Ga. We suspect the zircon to be older, perhaps as old as 4.1–4.35 Ga, by analogy to other samples of lunar granite and quartz monzodiorite (Compston et al. 1984; Shih et al. 1985, 1993; Meyer et al. 1989b, 1991).

The zircon grain we selected is a clast (about $200 \times 80\ \mu\text{m}$), a fragment of an originally larger crystal, and was analyzed in a polished thin section of ~ 10 – $15\ \mu\text{m}$ thickness. The mounting medium was Araldite, which does not show any laser-induced fluorescence and thus does not interfere with a successful interpretation of the Raman spectra obtained from the sample. The zircon grain is fractured, but it is free of mineral inclusions (Figs. 1a and 1b). Fractures extend into the surrounding matrix but appear to be related to the sample's impact history, not to radiation damage in the zircon. In cross-polarized light, zoning appears as a change in interference colors across the zircon grain, and in the backscattered electron image (Fig. 1b), the bright area on the right side of the grain indicates a high concentration of elements heavier than Zr, such as U, Th, and REE. From the optical appearance in cross-polarized light, and from the backscattered electron image, we inferred this grain to be zoned in chemical composition.

ANALYTICAL CHARACTERIZATION

The chemical composition and some vibrational spectroscopic characteristics were determined with an ion microprobe, an electron microprobe, and a Raman microprobe. All three microprobe techniques were applied to the same five points labeled A, B, C, D, and E (Fig. 1c) to characterize chemical and structural variations normal to the optical zoning of the grain. The individual measurement points can be seen easily in the backscattered electron image (Fig. 1b) that was obtained after the sam-