

**A ZONED LUNAR ZIRCON IN A QUARTZ-MONZODIORITE BRECCIA FROM APOLLO 14: U, TH, OTHER TRACE ELEMENTS, AND RAMAN SPECTRAL PARAMETERS.**  
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A single 200 micrometer zircon grain from sample 14161,7069, a quartz-monzodioritic breccia, is zoned in its concentrations of U, Th, and other high-field-strength elements as determined by secondary-ion mass spectrometry (SIMS). Raman spectral signatures correlate well with the U concentrations and indicate the degree of structural damage due to alpha-particle decay. In the parent sample, incompatible trace elements (ITE), including Zr, Hf, REE, U, Th, and Ba, are present in KREEP-like proportions, but at even higher concentrations than in high-K KREEP [1]. Thus, we infer that the zoned zircon grain formed by crystallization in an interval during which concentrations of ITEs (other than Zr and Hf) increased in the residual melt by factors of 3 to 4. The leveling-off of the REE concentrations in the zircon grain indicate that this interval overlapped in its late stage with the crystallization of whitlockite. The trace elements are zoned across the whole zircon fragment indicating that there was no overgrowth of zircon subsequent to initial crystallization (as part of brecciation/recrystallization). Thus, the compositional variations are primary and might allow a U-Th-Pb age determination that is unaffected by the impact-brecciation and recrystallization event. Good correlations between trace-element contents and Raman spectroscopic parameters make the laser Raman microprobe a useful tool to rapidly and nondestructively determine whether individual zircon grains, either in geologic thin section or as separate grains, are suitable for isotopic age dating.

Sample 14161,7069 is a partially recrystallized impact breccia of quartz-monzodiorite (QMD) bulk composition and mineralogy, including K-feldspar-bearing granophyre [1]. Its unusually high incompatible-element contents (ITE  $\sim 2 \times$  average high-K KREEP [2]), low siderophile-element concentrations, and uniform mineral compositions indicate that it is monomict [1,3]. Lunar quartz monzodiorites and associated granites are rare among the Apollo samples. The ages of lunar granites and QMD range from 3.9 to 4.4 Ga [reviewed by 4,5]; however, the susceptibility of some dating methods to resetting by impact events involving reheating and recrystallization makes age determinations ambiguous in rocks so affected. The stability of zircon and its resistance to impact modification make it a valuable target for geochronologic study of impact-altered lunar rocks. This is especially important for rare rock types such as QMD of which there are few pristine samples with unmodified igneous textures. Determination of the primary crystallization ages of these samples is essential to understanding how they fit in the history of lunar magmatism, e.g., are they related to residual liquid from primordial lunar differentiation (urKREEP), or are they products of later, separate magmatic events related to Mg-suite plutonic rocks, as appears to be the case for lunar granites, of which numerous samples have been dated [e.g., 4-7].

The large zircon grain in sample 14161,7069, a fragment of an originally larger crystal, retains chemical zoning that we attribute to its original magmatic crystallization. The grain is optically zoned from a "relict core" (Fig. 1, point A) to a "relict rim" (Fig. 1, points D,E) in terms of its interference colors, with a decrease of about 50% in birefringence. From point A to E (Fig. 1), the concentrations of U and Th increase from 21 to 55 ppm and 6 to 31 ppm, respectively (Table 1). Concentrations of P, REE (including Y), Ti, Nb, and Ba correlate well with concentrations of U and Th. In the compositionally "evolved" zones (spots D & E), concentrations of the REE level off (Fig. 2, Table 1) relative to, for example, Nb and Ba, probably due to the onset of whitlockite crystallization in the residual melt.

Raman spectroscopic parameters determined with a laser microprobe correlate well with trace-element contents of the zircon grain. Increasing concentrations of the heavy trace elements from points A to E correlate with a continuous shift of the SiO stretching mode from 1008 to 1000  $\Delta\text{cm}^{-1}$  (Figs. 3 & 4). We attribute this shift to the substitution of heavy trace elements for Zr and Hf. Increasing U concentrations correlate with decreasing Raman band intensities and increasing Raman peak widths, which we attribute to a gradual disruption (incipient metamictization and expansion [8]) of the zircon structure by alpha particles from  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$  over the lifetime of the zircon grain. From radioactive decay of these isotopes, we estimate a minimum dose of alpha decays per mg of zircon (assuming age of 4 Ga) of  $4.6 \times 10^{14}$  in the core (43 ppm U and 7 ppm Th, initially) to  $1.2 \times 10^{15}$  in the rim (110 ppm U and 31 ppm Th, initially), slightly less than the  $2 \times 10^{15}$  to  $10^{16}$  events per mg estimated by [9] for complete metamictization of zircon. The good correlation shown in Fig. 4 indicates that the laser Raman microprobe is useful for non-destructive analysis of loose grains or geologic thin sections of lunar samples. It can identify zircons with potential for age-dating of rare rock types by sensitive, high mass-resolution ion microprobe analysis [e.g., 7,10]. If Pb loss in zircons is related to expansion of the structure due to metamictization, calibration of the Raman parameters resulting from metamictization may enable an assessment of potential Pb loss, which is a problem in U-Pb dating techniques.

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*References:* [1] Jolliff B.L. (1991) *PLPS* 21, 101–118. [2] Warren P.H. (1989) in *Workshop on Moon in Transition: Apollo 14, KREEP, and evolved Lunar Rocks*, 153. [3] Warren P.H. (1993) *Am. Min.* 78, 360–376. [4] Shih C.-Y., Nyquist L.E., Bogard D.D., Wooden J.L., Bansal B.M., and Wiesmann H. (1985) *Geochim. Cosmochim. Acta* 49, 411–426. [5] Shih C.-Y., Nyquist L.E., and Wiesmann H. (1993) *Geochim. Cosmochim. Acta* 57, 4827–4841. [6] Meyer C. Jr., Williams I. S., and Compston W. (1988) in *Workshop on Moon in Transition: Apollo 14, KREEP, and evolved Lunar Rocks*, 39–42. [7] Meyer C. Jr., Williams I. S., and Compston W. (1989) *LPS XX*, 691–692. [8] Sahama T.G. (1981) *Bull. Mineral.* 104, 89–94. [9] Chakoumakos et al. (1987) *Science* 236, 1556–1559. [10] Compston W., Williams I.S., and Meyer C. (1984) *PLPSC 14th*, in *JGR* 89, B525–B534.

## TRACE-ELEMENT ZONING IN ZIRCON: Jolliff, Wopenka, Zinner, &amp; Kremser

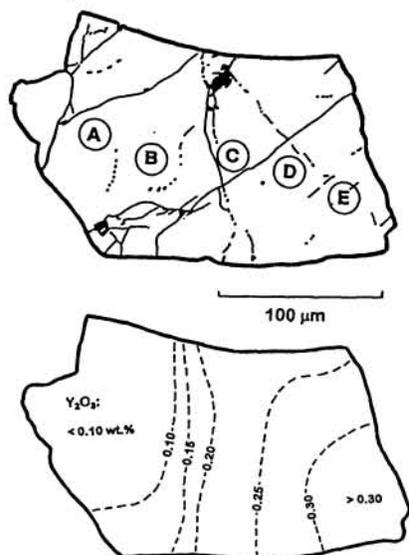


Figure 1. (a) Sketch of zircon grain in sample 14161,7069. Circled letters mark locations of spots of ion microprobe and Raman microprobe analyses. (b) Sketch showing contours of  $Y_2O_3$  concentrations, based on gridded electron-microprobe wavelength-dispersive analyses and backscattered-electron imaging.

Table 1. Composition of zircon from sample 14161,7069 for analysis spots A through E. Major-element composition determined with a JEOL 733 electron microprobe, trace-element concentrations determined with a modified Cameca IMS-3f ion microprobe.

	A	B	C	D	E
<i>Oxides (weight percent)</i>					
SiO <sub>2</sub>	32.5	32.8	32.8	32.6	32.7
ZrO <sub>2</sub>	66.2	65.1	66.5	65.8	66.3
HfO <sub>2</sub>	1.28	1.37	1.22	1.28	1.24
Al <sub>2</sub> O <sub>3</sub>	0.02	0.01	0.01	0.02	0.03
Y <sub>2</sub> O <sub>3</sub>	0.10	0.16	0.27	0.32	0.35
FeO	0.10	0.02	0.02	0.05	0.06
P <sub>2</sub> O <sub>5</sub>	0.05	0.09	0.13	0.16	0.18
RE <sub>2</sub> O <sub>3</sub>	0.05	0.08	0.13	0.16	0.16
<i>Trace Elements (parts per million)</i>					
P	227	380	566	715	766
Ca	38	24	63	125	70
Sc	49	58	59	69	72
Ti	59	66	80	79	161
Sr	3.0	2.7	2.8	3.4	3.5
Y	776	1250	2136	2519	2660
Nb	66	86	119	179	378
Ba	1.8	1.1	1.8	2.7	7.5
La	0.2	0.1	0.4	2.4	0.4
Ce	0.7	0.5	1.7	6.7	2.3
Pr	0.1	0.1	0.3	1.1	0.6
Nd	0.9	1.5	4.9	7.6	7.3
Sm	2.0	3.3	8.3	11	10
Eu	0.05	0.03	0.12	0.03	0.03
Gd	14	23	49	72	68
Tb	3.3	5.9	11	17	14
Dy	58	90	167	222	213
Ho	22	35	60	77	78
Er	113	171	291	344	358
Tm	23	36	55	68	71
Yb	197	286	438	499	540
Lu	30	8	14	76	15
Th	6	11	21	29	31
U	21	31	44	51	55

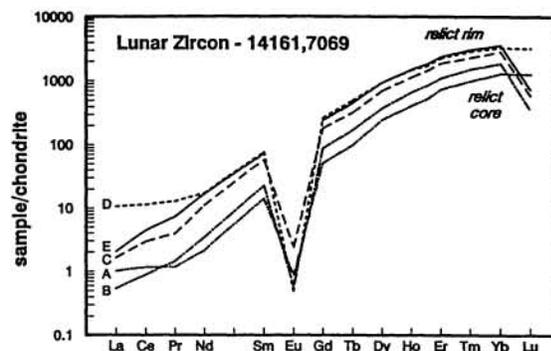


Figure 2. Chondrite-normalized rare-earth element concentrations for ion-microprobe spots A through E.

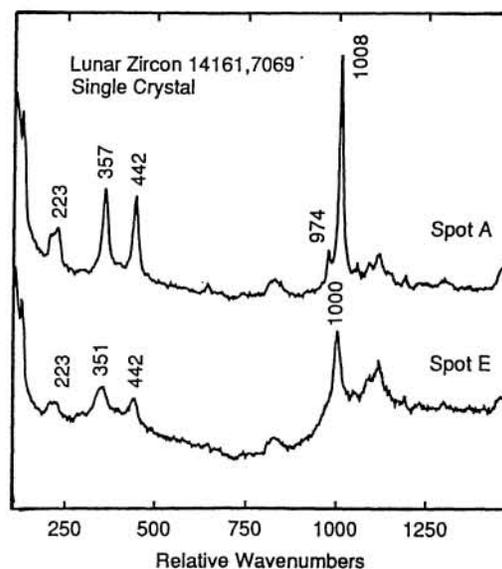


Figure 3. Raman spectra of sampling points A and E. Elevated "background" above about 1100 relative wavenumbers is fluorescence due to one or several of the heavy, trivalent rare-earth element ions, probably Dy<sup>3+</sup>. Raman spectra were obtained with an ISA S-3000 laser Raman microprobe.

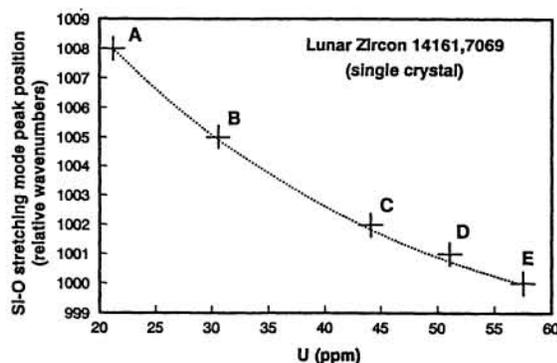


Figure 4. Concentration of U measured by SIMS vs. Si-O stretching mode peak position measured by Raman microprobe spectroscopy.