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Th-U-Pb Dating of Lunar Granites by X-Ray Microanalysis

S.M. Seddio, B.L. Jolliff, R.L. Korotev, and P.K. Carpenter

Dept. of Earth and Planetary Sciences (EPS) and McDonnell Center for the Space Sciences, Washington University, One Brookings Dr., St. Louis, MO 63130 USA

Granitic rocks are rare among returned lunar samples [1], and the timing of the formation of lunar granite is still debated [1,2,3]. Conventional isotopic methods of geochronology typically require sample consumption—an undesirable requirement for uncommon lithologies. Geochronology using EPMA is a non-destructive alternative. Extended fractional crystallization, a process involved in lunar granite petrogenesis, concentrates incompatible elements (e.g., Th, U, Zr) in the liquid relative to the common crystallizing minerals. Lunar granites ultimately crystallize from the Th-, U-, and Zr-rich residual liquids. The major isotopes of Th and U are radioactive and all decay to Pb. In lunar granites, Th and U are typically concentrated in trace minerals such as monazite, yttrobetafite, zirconolite, apatite, and merrillite (ideally, $[La,Ce,Nd]PO_3$, $[Y,Ca,Th,U,Fe,REE]_5[Ti,Nb]_5O_{17}$, $[Ca,REE]ZrTi_2O_7$, $Ca_5(PO_4)_3$, and $Ca_3(PO_4)_2$), and rarely thorite ($[Th,U]SiO_4$) [1,4]. These minerals do not incorporate Pb. Our analyses of these phases show that they each include several wt% of Th, U, and Pb from which we calculate crystallization ages of two Apollo 12 granite samples.

Phases were identified using EDS (Fig. 1) and WDS using the Washington University EPS JEOL JXA-8200 Superprobe. We used WDS wavescans to confirm the elements present and identify background positions for use in all standards and samples. Phase compositions were determined by quantitative EPMA done at 15 kV accelerating voltage and 25 nA probe current. For Th, U, and Pb, we counted the Mα X-ray line on-peak for 30 s and off-peak for 15 s on a high-intensity PETH H-type spectrometer. Our measurements were made on a sealed Xe detector which does not exhibit the Ar absorption edge adjacent to the U Mβ peak—a major issue for measurement of U in materials. Probe for EPMA software (Probe Software, Inc.) was used for analysis and data correction including peak interference corrections (e.g., Th Mβ on U Mα). Due to electron transmission through micron-sized grains and secondary fluorescence, all thorite analyses contain some component of adjacent or underlying phases (frequently silica and/or feldspar; Table 1; Fig. 1). Analytical standards included synthetic and natural silicate, oxide, and REE glass standards of [5] and [6] for primary calibration, which were checked against secondary standards.

Following the method of [7], we calculated the crystallization ages of Apollo 12 granites 12023,147-10 and 12032,366-19 from our analyses of thorite, yttrobetafite, and monazite in 12023,147-10 and zirconolite in 12032,366-19 (Table 2). We assumed that all analyzed Pb is radiogenic which is valid since Pb should not be present in the analyzed minerals beyond trace concentrations. Given that assumption,

$$Pb=\frac{Th}{232}\left(e^{\lambda^{232}t}-1\right)208+0.9928\frac{U}{238.04}\left(e^{\lambda^{238}t}-1\right)206+0.0072\frac{U}{238.04}\left(e^{\lambda^{235}t}-1\right)207$$

where Pb, Th, and U are in ppm and λ^{232} (4.9475×10^{-11} yr^{-1}; [8]), λ^{235} (9.8485×10^{-10} yr^{-1}; [9]), and λ^{238} (1.55125×10^{-10} yr^{-1}; [9]) are the decay constants for Th^{232}, U^{235}, and U^{238}, respectively. Solving for *t* yields the age of the analyzed grain along with the fraction of Pb generated from each parent element.

From our analyses of thorite in sample 12023,147-10, we calculate a crystallization age of 3.87 ± 0.03 Ga (error is a 95% confidence interval). Analyses of yttrobetafite and monazite, which also occur in 12023,147-10, yield similar crystallization ages but with larger uncertainties. We calculate a crystallization age of 3.9 ± 0.3 Ga for sample 12032,366-19 from our analyses of zirconolite.

We conclude that geochronology using EPMA is an effect means to date extremely small (~1 μm) Th-, U-, and radiogenic Pb-bearing phases because of modern beam stability and analytical matrix and interference corrections. In terrestrial samples, the analysis of thorite has been deemed to produce unreliable crystallization ages owing to its inability to retain radiogenic Pb [10]. However, because similar ages were calculated from analyses of co-occurring thorite, yttrobetafite, and monazite ([10] recommend monazite for geochronology using EPMA), we think that the thorite in these lunar granite samples accurately records the crystallization age.

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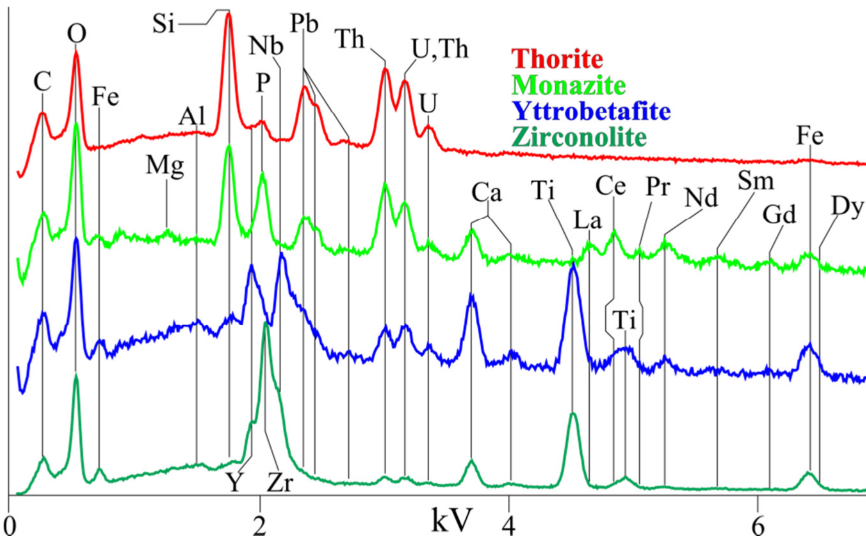

FIG. 1. EDS spectra of thorite (red), monazite (green), and yttrobetafite (blue) in sample 12023,147-10, and zirconolite (teal) in 12032,366-19. In the thorite spectrum, much of the Si peak is contributed by surrounding silica. Y is present but obscured between the Si and P peaks. P was confirmed via WDS wavescan. The monazite spectrum is strongly sampling hedenbergite surrounding it yielding additional Ca, Fe, and some Si. C is from carbon coating over the sample. In the zirconolite spectrum, Y and Nb peaks are shoulders on the Zr peak.

TABLE 1. Analyzed and model compositions of thorite, yttrobetafite, and monazite in 12023,147-10 and zirconolite in 12032,366-19.

	Thor	Thor[1]	Yβ	Mon	Zirc
SiO_2	46.5	17.3	<0.03	21.5	<0.01
P_2O_5	-	2.65	<0.03	11.5	-
Al_2O_3	1.66	0.15	0.11	0.15	0.18
ThO_2	0.03	51.0	5.95	21.9	2.40
UO_2	25.2	23.3	3.34	2.09	1.08
PbO	6.42	0	4.12	6.05	1.43
Y_2O_3	11.1	2.76	11.0	1.60	9.89
RE_2O_3*	1.62	2.01	11.3	21.1	8.89
FeO	-	0.76	6.35	7.00	9.35
CaO	0.46	0.13	7.19	4.98	4.28
TiO_2	-	-	23.1	0.22	24.3
ZrO_2	-	-	-	-	28.7
Nb_2O_5	-	-	17.5	<0.03	7.36
Total	93.02	100.0	90.1	98.1	97.9

Values are in wt%. RE_2O_3* is the concentration of rare earth oxides calculated from analyzed La_2O_3, Ce_2O_3, and Y_2O_3. Thor is an analysis of thorite in 12023,147-10 with the least beam sampling of adjacent phases. Thor[1] is an average of 10 analyses from which we "removed" SiO_2 to achieve thorite stoichiometry and calculated initial ThO_2 and UO_2. Yβ is the average of 4 yttrobetafite analyses (unanalyzed WO_3 is present in WDS wavescan). "Mon" is the average of 4 monazite analyses (includes contribution from adjacent hedenbergite). "Zirc" is the average of 2 zirconolite analyses.

TABLE 2. Age calculation results from samples 12023,147-10 and 12032,366-19.

Mineral	N	Age (Ga)	95% CI
Yttrobetafite	4	3.84	0.06
Thorite	5	3.87	0.03
Monazite	4	3.96	0.33
Zirconolite	4	3.87	0.28

Yttrobetafite, thorite, and monazite are from 120023,147-10. Zirconolite is from 12032,366-19. "95% CI" is the 95% confidence interval. "Pb_{Th}%" is the percent of Pb in the analyzed phase that was produced from the decay of Th. The remainder was produced from the decay of U.

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