THORITE IN AN APOLLO 12 GRANITE FRAGMENT AND AGE DETERMINATION USING THE ELECTRON MICROPROBE. S. M. Seddio, B. L. Jolliff, R. L. Korotev, and P. K. Carpenter, Department of Earth and Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, Missouri 63130 (sseddio@levee.wustl.edu).

Introduction: We present the first quantitative analysis of lunar thorite. It contains a 12% xenotime component. We calculate an age of 3.88 Ga. Yttrobetafite and monazite, also present in the sample, yield similar ages. During routine petrographic investigation of lunar granite 12023,147-10 [1] by electron-probe microanalysis (EPMA), we identified three < 3 µm grains of thorite ($ThSiO_4$; Fig.1), several grains of yttrobetafite, $(Y,Ca,Th,U,Fe,REE)_5(Ti,Nb)_5O_{17}$, and one < 1 µm grain of monazite, $(LREE,Th,U)(P,Si)O_4$, qualitatively by energy-dispersive spectrometry (EDS). We then performed detailed analysis of these phases to confirm the presence of lunar thorite, to calculate the age of formation of the granite, and to obtain complimentary age calculations from yttrobetafite and monazite. Haines et al. [2] previously reported a single grain of thorite in sample 14259,97; however, no analyses (qualitative or quantitative) were included.

Terrestrial thorite is an accessory mineral found in felsic igneous rocks, often pegmatites [3]. It occurs in solid solution with zircon ($ZrSiO_4$), xenotime ($[Y,HREE]PO_4$), coffinite ($USiO_4$), and less commonly brabantite ($Ca[Th,U][PO_4]_2$) [4]. Thorite (tetragonal) has a monoclinic dimorph, huttonite, which can occur in solid solution with monazite ($[LREE]PO_4$).

Methods: Phases were identified using EDS and wavelength-dispersive (WDS) spectrometry on the Washington University EPS JEOL JXA-8200 Superprobe. WDS wavescans were used to confirm the elements present and identify background positions for use in all standards and samples. Phase compositions were determined by quantitative analysis performed at 15 kV accelerating voltage and 25 nA probe current. Probe for EPMA microprobe software [5] was used for analysis and data correction including peak interference corrections. Secondary and back-scattered electron (BSE) images were taken at 10 nA to achieve better resolution of small grains. Due to electron transmission through micron-sized grains as well as secondary fluorescence, all thorite analyses contain some component of adjacent or underlying phases (frequently silica but also plagioclase; Table 1; Fig. 1; the monazite grain is surrounded by hedenbergite.). Monte Carlo modeling using the Casino program [6] indicates that the electron interaction volume extends through the thorite into underlying phases if the thorite grains are less than ~0.75 µm thick. We modeled the actual thorite composition by iteritively subtracting amounts of the adjacent phase from the data and renormalizing until stoichiometry for thorite-xenotime solid solution was achieved. While we have not tried to use electron-backscatter diffraction

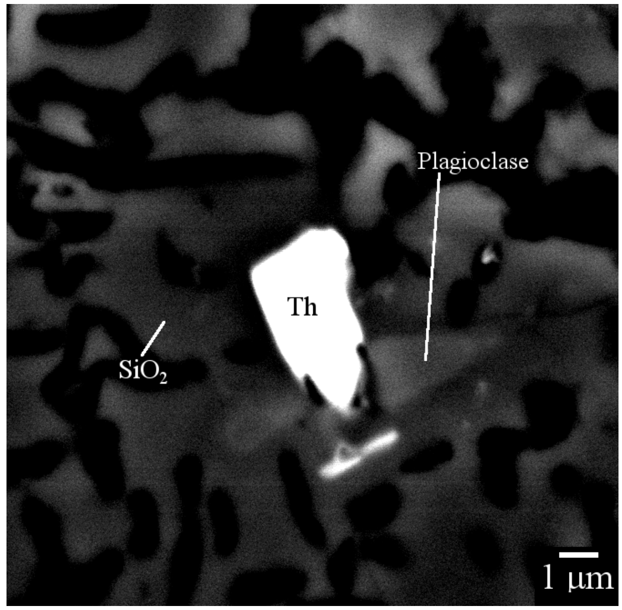

Figure 1. BSE image of the largest thorite grain (Th) in a matrix of SiO_2 and plagioclase. A second smaller, elongate grain of thorite is below and to the right of "Th."

Table 1. Quantitative analytical results and models.

	Thor	Thor*	Thor[1]	Thor[2]	Thor[3]	Thor[4]	Yβ	Mon
SiO_2	18.54	18.84	46.51	48.25	17.2	17.3	<0.03	21.5
SiO_2*	-	-	-	37.5	-	19-62	-	-
P_2O_5	-	0.12	1.66	1.72	2.75	2.65	<0.03	11.5
Al_2O_3	-	-	0.03	0.03	0.04	0.15	0.11	0.15
ThO_2	81.46	73.46	25.23	31.87	51.0	51.0	5.95	21.9
UO_2	-	5.90	6.42	14.75	23.6	23.3	3.34	2.09
PbO	-	0.43	11.09	0	0	0	4.12	6.05
Y_2O_3	-	0.35	1.62	1.68	2.69	2.76	11.0	1.60
$RE_2O_3^*$	-	0.31	-	1.23	1.96	2.01	11.3	21.1
FeO	-	-	0.46	0.47	0.76	0.76	6.35	7.00
CaO	-	0.13	-	-	-	0.13	7.19	4.98
TiO_2	-	-	-	-	-	-	23.1	0.22
Nb_2O_5	-	-	-	-	-	-	17.5	<0.03
Total	100.0	99.42	93.02	100.0	100.0	100.0	90.1	98.1

All values are in wt%. Thor is the composition of ideal thorite. Thor* is terrestrial thorite [8]. SiO_2* is the amount of SiO_2 contributed to the analysis from neighboring phases. $RE_2O_3^*$ is the concentration of rare earth oxides calculated from analyzed La_2O_3, Ce_2O_3, and Y_2O_3. Thor[1] is an analysis of the thorite in 12023,147-10 with the least beam sampling of an adjacent phase. Thor[2] is a model composition of Thor[1] in which all PbO has been calculated as either ThO_2 or UO_2 at the time of formation. Thor[3] is the modeled thorite composition of Thor[2] once the SiO2 has been "removed" from the analysis. Thor[4] is the average of 10 modeled thorite analyses. Yβ is the average of 4 yttrobetafite analyses (the low total is like due to unanalyzed WO_3 which is present in a WDS wavescan). "Mon" is the average of 4 monazite analyses (includes contribution from adjacent hedenbergite).

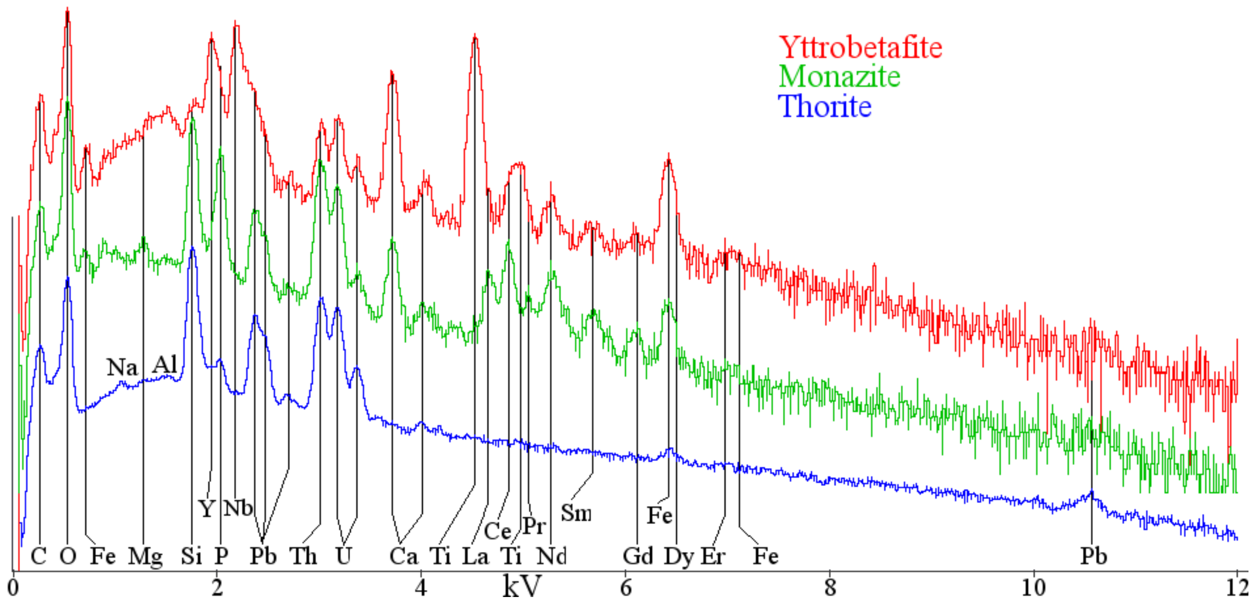

Figure 2. EDS spectra of the ~2 μm thorite grain of Fig. 1 (blue), the largest (~5 μm) yttrobetafite grain (red), and the monazite grain. In the thorite spectrum, Na, Al, and Ca are contributions from a nearby plagioclase grain. Much of the Si peak is likely a contribution of the surrounding silica. 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 comes from the carbon coating over the sample.

to further identify these phases, we expect that they are metamict and would not reveal a pattern for further confirmation of the mineralogy.

Age Calculation: Following the method of [7], we calculated the crystallization age of 12023,147-10 from our analyses of thorite. In doing so, we assumed that all Pb analyzed is radiogenic which is valid since Pb should not exist in thorite beyond trace concentrations. Given that assumption,

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

where Pb, Th, and U are in ppm and $\lambda^{232}, \lambda^{235}$, and λ^{238} are the decay constants for $\mathrm{Th}^{232}, \mathrm{U}^{235}$, and U^{238}, respectively. Solving for *t* yields the age of the analyzed grain along with the fraction of lead generated from each parent element (necessary for calculating the initial formula). Results (Table 2) from thorite are ~3.88 Ga. Yttrobetafite and monazite also contain several wt% of Th, U, and Pb (Table 1) and confirm the age calculated from the thorite.

Thorite Formula: An average of the 5 best thorite analyses yields the formula for thorite in the 12023,147-10 lunar granite:

$(\mathrm{Th, U})_{0.861}(\mathrm{Y,REE})_{0.110}(\mathrm{Fe,Ca})_{0.036}(\mathrm{Si,P,Al})_{1.009}\mathrm{O}_4$

The thorite is in solid solution with xenotime, $(\mathrm{Y,HREE})\mathrm{PO}_4$, and is composed of 88% thorite and 12% xenotime end members. There is no zircon component. Similarly, EDS spectra of the zircon in the 12023,147-10 granite do not reveal any Th or U.

Discussion: Lunar granites (pristine or otherwise) have crystallization ages between 3.88 and 4.32 Ga [9]. The 12023,147-10 crystallization age matches the low end of that range (3.88 Ga from sample 12033,507 [9]).

The upper limit of the age of crystallization of granite 12023,147-10 coincides with the formation if the Imbrium basin (3.90-3.92 Ga [10,11]). It is possible that this granite represents the end stage of fractional crystallization of the Imbrium melt sheet. Otherwise, it likely crystallized from a highly evolved magma tens of millions of years later.

Table 2. Age calculation results.

Mineral	N	Age (Ga)	95%CI	$\mathrm{Pb_{Th}}$%
Thorite	5	3.88	0.03	41.9%
Yttrobetafite	4	3.84	0.06	25.5%
Monazite	4	3.97	0.33	66.1%

N is the number of analyses for which the age was calculated. Ages are reported as the average age from all analyses on which the calculation was performed. $\mathrm{Pb_{Th}}$% is the average percentage of Pb atoms in the analyses produced by Th.

Acknowledgements: This work was funded by NASA grant NNG04GG10G (RLK).

References: [1] Seddio et al. (2012) *43rd LPSC* (this conference). [2] Haines et at. (1972) *1st LPSC*, 3, 350. [3] *Handbook of Mineralogy* (2001). [4] Förster (2006) *Lithos*, 88, 35. [5] Probe Software, Inc. [6] Hovington et al. (1997) *Scanning*, 19, 1. [7] Montel et al. (1996) *Chem.Geo.*, 131, 37-53. [8] Förster et al. (2000) *Can.Min.*, 38, 675. [9] Meyer et al. (1996) *M&PS*, 31, 370. [10] Nyquist et al. (2011) *42nd LPSC*, 1868. [11] Liu et al. (2011) EPSL (in press).