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NanoSIMS Pb/Pb dating of tranquillityite in high-Ti lunar basalts: Implications for the chronology of high-Ti volcanism on the Moon

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Analyses on the Phalaborwa baddeleyite

To cross-check the accuracy of our Pb/Pb dating procedure with the NanoSIMS 50, we analyzed fragments of a large baddeleyite crystal of about 2 cm from the Phalaborwa complex in South Africa. The large crystal was broken into smaller fragments by applying a gentle pressure with an agate pestle in an agate mortar. Subsequently, a few fragments were used to prepare a 10 mm epoxy mount. Repeated ID-TIMS measurements of 59 fractions from a single large baddeleyite crystal from Phalaborwa have previously yielded a $^{207}Pb/^{206}Pb$ age of 2059.6 ± 0.4 Ma (Heaman 2009), which is consistent with the $^{207}Pb/^{206}Pb$ ages of 2059.2 ± 2.2 and 2060.2 ± 2.1 Ma obtained on a different Phalaborwa baddeleyite by Reischmann (1995). The Pb concentrations of different Phalaborwa baddeleyite grains appear to be heterogeneous, ranging from 80 to 150 ppm in the crystal studied by Reischmann (1995) and averaging 194 ± 84 ppm (57 analyses) in the crystal studied by Heaman (2009).

For NanoSIMS analyses of Phalaborwa baddeleyite, the O^- beam was optimized using apertures D0-1 and D1-1, resulting in a current of ~ 250 - 300 pA on the sample surface. The sensitivity for Pb isotope measurements was ~ 1 to 3 cps/ppm/nA $^{16}O^-$. This compares well with Pb/Pb analyses carried out on other Zr-bearing minerals using the NanoSIMS 50: ~ 3 and 10 cps/ppm/nA $^{16}O^-$ for zircon and zirconolite, respectively (Stern et al. 2005), and ~ 4 cps/ppm/nA $^{16}O^-$ for both monazite and zircon (Sano et al. 2006; Takahata et al. 2008; Yang et al. 2012). Counting times were set to 4 s for ^{206}Pb and 10 s for ^{204}Pb and ^{207}Pb, with a 2 s waiting time between each isotope, resulting in a total analysis time of about 55 min for baddeleyite. The measured $^{204}Pb/^{206}Pb$ ratios in the Phalaborwa baddeleyite range between ~ 0.0002 and 0.0009 (Table S1), which are about an order of magnitude higher than the $^{204}Pb/^{206}Pb$ ratios measured by ID-TIMS (Reischmann 1995; Heaman 2009). This possibly indicates that our analyses on the Phalaborwa baddeleyite recorded some non-radiogenic ^{204}Pb counts. The measured $^{204}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$ ratios have been plotted in a $^{207}Pb/^{206}Pb$ vs. $^{204}Pb/^{206}Pb$ mixing diagram together with arrows pointing towards the compositions of the initial common-Pb at 2060 Ma, calculated using the Stacey and Kramers (1975) model, and of the Pb isotopic composition of Broken Hill galena, representing laboratory contamination (Fig. S1). Note that these two compositions are almost identical, which why the two arrows overlap with each other in Figure S1. In this diagram, the array defined by analyses on Phalaborwa analyses is close to horizontal, and does not fit with either contamination by initial common-Pb or by present-day common-Pb during sample preparation. Correcting the measured $^{207}Pb/^{206}Pb$ ratios using the measured $^{204}Pb/^{206}Pb$ and any Pb isotope composition would therefore result in an erroneous correction of the data. The weighted mean $^{207}Pb/^{206}Pb$ date calculated from the raw $^{207}Pb/^{206}Pb$ ratios measured from 15 analyses is 2065 ± 15 Ma (95% confidence level, Fig. S1). This date is associated with a MSWD of 0.81, and is consistent with the $^{207}Pb/^{206}Pb$ crystallization ages of ~ 2060 Ma determined by ID-TIMS (Reischmann 1995; Heaman, 2009), confirming the accuracy of $^{207}Pb/^{206}Pb$ ratio measurements in Phalaborwa baddeleyite using our NanoSIMS protocol. Correction of the $^{207}Pb/^{206}Pb$ ratios using the measured $^{204}Pb/^{206}Pb$ and a 2060 Ma terrestrial Pb and the Broken Hill galena Pb isotope compositions yield weighted mean $^{207}Pb^*/^{206}Pb^*$ dates of 2001 ± 32 and 1994 ± 35 Ma, respectively, indicating an overcorrection for the $^{207}Pb/^{206}Pb$ ratios. The origin of extra counts at mass 204 is unclear, but the accuracy of the measured $^{207}Pb/^{206}Pb$ ratios suggests that these extra counts do not have a significant effect on the measured ^{206}Pb and ^{207}Pb counts. As count rates for ^{206}Pb and ^{207}Pb were about an order of magnitude higher in tranquillityite analyses, the contribution of any extraneous 204 counts would be negligible compared to that in the case of Phalaborwa baddeleyite. Repeated mass scans in the region of mass 204 suggest that these extra 204 counts do not originate from an unresolved isobaric interference. They might be related to the instrumental background, which will need to be carefully monitored in future analyses, molecular ions generated from the Au coating, or even ^{204}Hg. One possibility in future analyses will be to monitor ^{202}Hg peak and the background counts to try to further assess this issue. In the present case, since ^{204}Pb background count does not have a significant effect on the measured $^{207}Pb/^{206}Pb$ ratios for Phalaborwa baddeleyite, it likely does not affect the $^{207}Pb/^{206}Pb$ ratios measured in lunar tranquillityite, considering that ^{206}Pb and ^{207}Pb count rates were about an order of magnitude higher.

Additional references

Stacey, J.C., and Kramers, J.D. (1975) Approximation of terrestrial lead isotope evolution by a two-stage model. Earth and Planetary Science Letters, 26, 207-221.

Table S1. NanoSIMS Pb/Pb data for Phalaborwa baddeleyite.

Analysis	$^{204}Pb/^{206}Pb$	1σ (%)	$^{207}Pb/^{206}Pb$	1σ (%)	f_{206} (%)	$^{207}Pb/^{206}Pb$ date (Ma)	1σ (Ma)
Phala@13	0.00092	13	0.1266	1.6	1.72	2052	28
Phala@14	0.00065	17	0.1283	1.8	1.21	2075	32
Phala@15	0.00077	17	0.1263	2.0	1.44	2047	34
Phala@23	0.00061	27	0.1248	2.9	1.14	2027	50
Phala@24	0.00071	24	0.1251	2.7	1.33	2030	48
Phala@25	0.00034	18	0.1290	1.4	0.64	2085	25
Phala@28	0.00036	21	0.1274	1.7	0.67	2062	29
Phala@29	0.00043	21	0.1264	1.8	0.80	2048	32
Phala@30	0.00030	25	0.1273	1.8	0.56	2061	32
Phala@31	0.00025	23	0.1247	1.5	0.46	2024	27
Phala@33	0.00017	28	0.1274	1.6	0.32	2062	28
Phala@34	0.00020	21	0.1309	1.3	0.37	2110	22
Phala@35	0.00028	25	0.1252	1.8	0.53	2031	31
Phala@36	0.00017	23	0.1283	1.3	0.31	2075	22
Phala@37	0.00023	25	0.1294	1.6	0.42	2090	28

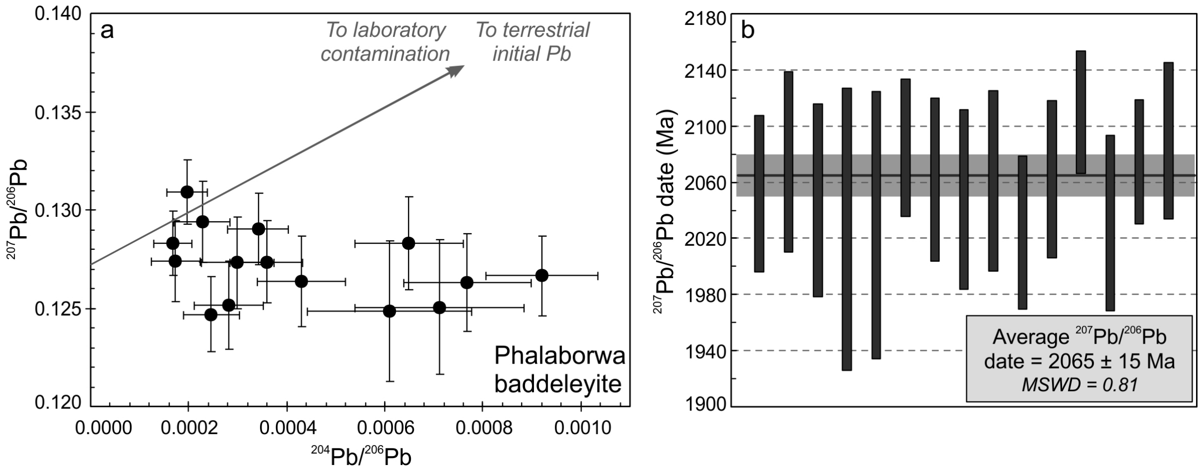

Figure S1. Pb/Pb data measured in Phalaborwa baddeleyite plotted as a $^{207}Pb/^{206}Pb$ vs. $^{204}Pb/^{206}Pb$ diagram (a), and weighted mean $^{207}Pb/^{206}Pb$ date (b). In $^{207}Pb/^{206}Pb$ vs. $^{204}Pb/^{206}Pb$ diagrams, uncertainties are portrayed at the 1σ level, whereas uncertainty bars in the weighted mean date diagram are at the 2σ level.