

ION MICROPROBE MASS ANALYSIS OF PLAGIOCLASE FROM "NON-MARE" LUNAR SAMPLES. C. Meyer, Jr., D. H. Anderson and J. G. Bradley, NASA Johnson Space Center, Houston, TX 77058.

The highly cratered surface of the lunar highlands and the dominantly metaclastic texture of the samples returned from these regions indicate that these samples have had a very complicated history. If lunar scientists are to understand the origin of the lunar crust then it is important to know if these "non-mare" samples represent chemical systems set by endogenous igneous processes or if instead their bulk chemistry is the accident of some extensive mixing processes. Comparison of detailed analyses of the clasts in these complicated "non-mare" samples with their bulk composition can provide important criteria for deciding which "non-mare" samples may represent true rock types. A common feature of many of the metaclastic "non-mare" samples is the occurrence of abundant small grains (50-500 μm) of calcic plagioclase (An95-98). Trace element analyses of these grains can be important criteria for deciding whether they are phenocrysts which at some time crystallized from a magma with the composition of the bulk rock or if they are instead xenocrysts which somehow got thoroughly mixed into the sample without being reequilibrated with it.

Analytical Method

We have used the ARL Ion Microprobe Mass Analyzer (IMMA) to measure the abundance of Li, Mg, Ti, Sr and Ba in small spots (10-20 μm diameter) on the surface of plagioclase grains in polished thin sections. An ion beam of 20 kV negative oxygen is used to sputter the sample (sample current $5\text{--}15 \times 10^{-9}\text{A}$). We have used the abundances of the major elements (Ca, Al, Si) as internal standards for the computerized data reduction procedure known as CARISMA (1). We have found that it is important to make corrections for interferences by atomic and molecular ions and have also applied a correction factor to the CARISMA output derived by analyzing terrestrial plagioclase standards with the same instrumental operating conditions. Table I gives the comparison of CARISMA reduced IMMA analyses with values obtained by isotope dilution. Lake County (2) is our most homogeneous standard, and we have used the calibration factors derived from it to adjust all our lunar data. Limited mass resolution (~ 300) prevents accurate measurement for those elements whose masses are nearly the same as molecular ions formed from the major elements. For example, Al^+ , CaO^+ and CaOH^+ interfere with the Fe^+ isotopes and CaSiO^+ and CaAlO^+ interfere with Rb^+ . For this reason we are not able to accurately measure small amounts of Rb and/or Fe in plagioclase. Such molecular ion interferences are also the reason why our instrument cannot be used for age determinations by the Rb-Sr technique. We have carefully studied these interferences for which we do not make specific interference corrections to show that they are less than 5% of the count rate. For example, Si_2O_2^+ is less than 3% of the $^{88}\text{Sr}^+$ at 200 ppm Sr. $^{24}\text{Mg}^+$ is corrected for $^{48}\text{Ca}^{++}$ by measuring $^{40}\text{Ca}^{++}$. Our maximum sensitivities in cps per ppm are on the order of 250 for Li, 50 for Mg, 45 for K, 3 for Ti, 20 for Sr, and 10 for Ba.

Results

Our results are given in Table I. The Li, Sr and Ba values for plagioclase from 15415 and 67075 are in fair agreement with previous analyses of

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bulk samples by isotope dilution (5,6). 68415 - Helz and Appleman (3) describe probable relict inclusions of low Fe plagioclase in 68415. Our analysis of similar inclusions (Grains A and B) did not differ significantly from our analyses on the large phenocryst and we were not able to establish further evidence for the origin of these interesting grains. Zoning in trace elements in the large phenocryst was found to be irregular. 14310 - The trace element content of plagioclase from 14310 shows that the lowest Ba is in the most calcic plagioclase with zoning towards higher Na_2O . The increase in Sr at the margin is caused by coprecipitation of other phases which select against Sr forcing it to go into the liquid faster than the plagioclase can use it up. The relatively high Mg and Ti values are typical of plagioclase crystallizing from basaltic melt. We have also used the ion probe to establish upper limits for Y <6, Zr <2 and Ce <6 ppm. These values are more nearly consistent with partition coefficients than the previously published analyses for these elements in plagioclase mineral separates because of the unavoidable contamination in these separates. No relict plagioclase inclusions were found in 14310,23. 15022,2,9 - The plagioclase in this sample of KREEP basalt (4) is zoned in Ba, Li and Sr similar to 14310. 65015 and 62235 - These samples of metaclastic "KREEP basalt" from the Apollo 16 site have abundant grains of calcic plagioclase referred to as xenocrysts in Table 2. Their low contents of Ba distinguish them from the plagioclase in 14310. Small grains of plagioclase rich in trace elements are also present in this rock but are hard to analyze by ion probe because the beam overlaps on surrounding material. 61156 - This sample is an example of "VHA Basalts" (6) which has relict clasts of large plagioclase. 12033,85C and 14321,17E - These unusual "anorthosites" were first described by Meyer (4) and Hubbard et al. (5). Their extremely high content of Ba, Sr and K indicates they formed from a magma very rich in trace elements.

Discussion

Calcic plagioclase is commonly the most abundant mineral of samples from the lunar crust and is also one of the first-forming phases in melts of highland composition. The wide range in trace element composition which we have found in the plagioclase in these samples indicates that there was a wide variety of rock types in the lunar crust before it was brecciated and sintered to its present state.

The distribution of Ba, Li and Sr between basaltic liquid (represented by the composition of the bulk rock) and the first forming plagioclase can be calculated using our data for the concentration of these elements in the (Ca-rich) centers of the largest phenocrysts of 14310 and 68415.

	Ba	Sr	Li
14310	649/89=7.3	188/216=0.87	27.5/13.5=2.0
68415	76/11 =6.9	182/177=1.03	5.7/1.5 =3.8
Terrestrial (5)	7.1-4.6	0.84-0.66	

Although these rocks have compositions similar to lunar soils (14163 and 67601), they appear to have been completely melted. They apparently crystallized slowly enough to partition Ba and Li, but rapidly enough to not have

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initially partitioned Sr.

On the other hand, our analysis for Ba in the xenocrysts in 65015 and 62235 are more than an order of magnitude too low for these grains to ever have been in equilibrium with a melt the composition of the bulk rock. Thus these KREEP-rich metaclastic rocks must be mechanical mixtures of at least two types of material. The observation that these clasts are rather small and evenly distributed throughout the matrix indicates that the preexisting lithology for these rocks was an early regolith derived by comminution and mixing of both KREEP and anorthositic materials. Some lunar anorthosites (67075) apparently have relatively lower Sr contents than others (5). Our analyses of the plagioclase clasts in 65015, 62235 and 61156 also show low Sr content which is a partial explanation for the low Sr of Apollo 16 and VHA basalt materials (6). However, the relatively high Li content of these xenocrysts distinguishes them from 67075. Possibly Li has diffused into these clasts from the surrounding matrix during the lithification of these samples.

Table 1. I.M.M.A. Plagioclase (weight percent and ppm)

		# Analyses	Na ₂ O	Li	Mg	K	Ti	Sr	Ba
Lake County ^a	Standard	13	3.38	2.8 ± 0.5 (4.1 ± 0.2)	650 ± 20 (822 ± 66)	1800 ± 300 (986 ± 16)	210 ± 10 (230 ± 14)	710 ± 30 (582 ± 6)	94 ± 7 (63 ± 2)
i.d. ^c		1		0.68	0.79	1.83	0.91	1.22	1.49
Correction Factor ^d									
Pacaya ^e	Standard	5	0.83	0.46 ± 0.09 (0.68 ± 0.19)	350 ± 80 (398 ± 12)	180 ± 80 (147 ± 15)	100 ± 22 (134 ± 11)	820 ± 70 (942 ± 9)	30 ± 5 (28.8 ± 0.9)
i.d. ^c									
15415,15	Anorthosite	8	0.41	1.6 (2)	280	190 (127)	90	177 (178)	9 (6.2)
i.d. (5)									
67075,48	Anorthosite	6	0.43	1.6	210		63	154 (145)	10 (8)
i.d. (6)									
68415,131	Large Grain	27	0.29	1.5	790	110	75	177	11
	Small Grains	3	0.22	1.0	490	55	83	180	17
	Grain A	4	0.31	1.8	570	100	68	192	13
	Grain B	6	0.27	1.5	680	71	62	188	11
14310,23	Phenocryst	9	0.75	14	1000	670	150	216	80
	Margin	1	1.48	24	810	4000	370	325	420
	2nd Phenocryst	2	0.75	13	1400	400	170	238	98
	Small Grains	5	0.53	9.3	1050	300	140	238	94
	Small "	1	0.90	15	980	600	140	250	120
	Small "	1	1.18	19	1090	720	360	270	200
14063,26	Clasts	8	0.63	8	300		190	290	84
	Small Grain	1	1.80	24	260		450	370	182
15022,2,9 (4)	KREEP Basalt								
	Center of grain	8	1.32	22	1200	-	350	280	150
	Margin	1	1.55	16	1020	-	470	350	340
	2nd Grain	4	1.74	27	1900	1200	380	285	170
65015,79	Xenocrysts	12	0.45	6	570	320	87	161	7
	Small Grains	6	0.43	5	380	400	78	170	35
	Small Grain	1	1.36	20	600	1000	360	450	133
62235,65	Xenocrysts	6	0.42	5	600	240	97	162	9
	Small Grain	1	0.76	10	360	500	130	270	30
61156,6	Xenocrysts	3	0.39	5	400	760	110	150	18
	Anorthosite	3	0.33	1.4	560	110	90	155	8
64422,A ^f	Troctolite	2	0.50	3	-	500	--	173	70
76535	Large Grain s	8	0.30	3	970	200	76	165	46
76502	Anorthosite	1	0.82	16	439	1200		500	1200
14321,17i	Anorthosite	1	1.01	31	315	4000		490	600
12033,85C	Anorthosite	1							

(a) Labradorite (An 67) (2) Large clear crystal, Oregon USNM 115900. (b) Data reduction by modified CARISMA (1). Ca, Al and Si used as internal standards. (c) Isotope dilution by H. Weismann + C. Shih, NASA-JSC. (d) Calibration factor derived from Lake County which is used in this paper as an external standard. (e) Anorthite (An 92) clear center of large phenocryst, Central America, USNM 122261. (f) Small polygonal anorthosite from 2-4 mm coarse fines.

References - (1) C. Anderson and Hinthorne 1973, *Analy. Chem.* 45, 1421. (2) Steward et al. 1966, *Am. Min.* 51, 171. (3) Helz and Appleman 1973, *Proc. Fourth Lunar Science Conf.* Vol. 1 p643. (4) Meyer 1973, (abs.) *Proc. Third Lunar Science Conf.* p542. (5) Hubbard et al. *EPSL* 13, 71. (6) Hubbard et al. *Science* 181, 339.