In Situ Sr Isotope Analyses of Plagioclase: An Effective Tool in Undertsanding Lunar Magmatic Evolution.
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Introduction: A laser ablation (LA)-MC-ICP-MS method was first developed for in situ $^{87}Sr/^{86}Sr$ determinations in plagioclase with <1000 ppm Sr [1,2], and later refined and applied to other magmatic minerals, such as apatite and carbonate [3], clinopyroxenes from mantle peridotites [4], and plagioclase with <1000 ppm Sr (e.g., [5]). The University of Notre Dame hosts the Midwest Isotope and Trace Element Research Analytical Center (MITERAC), which houses a Nu Plasma II multicollector (MC)-ICP-MS coupled with a NWR193 Excimer laser ablation (LA) unit. The versatile detector array of the Nu Plasma II allows for in situ $^{87}Sr/^{86}Sr$ ratios to be determined as all the significant interferences can be measured and corrected for [3-8]. **Table 1** shows all potential interferences in determining $^{87}Sr/^{86}Sr$ isotopic ratios via LA-MC-ICP-MS (adapted from [3,6-8]). Here, we focus on determining Sr isotopic compositions from plagioclase, which contains low abundances of Fe, Zn, REE, and Hf, meaning that interferences reported for these elements will be negligible, although the invariant ratios need to be constantly monitored to insure this is the case (cf. [3]). In fact, Vroon et al. [8] concluded that plagioclase represents a reliable material for Sr isotope analysis by LA-MC-ICP-MS because Rb levels are usually low (<0.5 ppm) and Sr abundances are relatively high (>150 ppm), which results in low Rb/Sr ratios (<0.05).

The major interferences that could affect Sr isotopic determinations in plagioclase by MC-LA-ICP-MS are highlighted in red in **Table 1**. These are isobaric interferences from Kr (contamination in the Ar gas) and Rb, possibly from doubly charged REE, and Ca-Ca dimers. Oxide, doubly charged ion, and dimer interferences can be minimized through careful tuning of the machine prior to analysis, as well as through analysis of known reference materials; the only potential major oxide interference could be ArO_3 (**Table 1**). Argide interferences have proven to be negligible because, if present, they involve only the minor Ca isotopes. For this method, the corrections include: the monitoring of ^{85}Rb ion signal in order to correct for the ^{87}Rb; any interferences from ^{84}Kr, ^{86}Kr and ArO_3 can be eliminated with a 30 s on-peak baseline measurement prior to ablation, and monitoring of doubly charged REE ion signals at half-mass positions with additional Faraday detectors (e.g., [6,8,9]).

		MASS	82	83	84	85	86	87	88
		Sr			$^{84}Sr_{0.56\%}$		$^{86}Sr_{9.9\%}$	$^{87}Sr_{7\%}$	$^{88}Sr_{82.6\%}$
INTERFERENCE	Isobaric	Rb				^{85}Rb		^{87}Rb	
		Kr	^{82}Kr	^{83}Kr	^{84}Kr		^{86}Kr		
	Doubly Charged Species	Er^{2+}		^{166}Er	^{168}Er	^{170}Er			
		Yb^{2+}			^{168}Yb	^{170}Yb	^{172}Yb	^{174}Yb	^{176}Yb
		Lu^{2+}							^{176}Lu
		Hf^{2+}						^{174}Hf	^{176}Hf
	Oxides	^{40}Ar							$^{40}Ar^{16}O^{16}O$
		^{54}Fe					$^{54}Fe^{16}O^{16}O$	$^{54}Fe^{16}O^{17}O$	$^{54}Fe^{18}O^{18}O$
									$^{54}Fe^{17}O^{17}O$
		^{56}Fe							$^{56}Fe^{16}O^{16}O$
		^{66}Zn		$^{66}Zn^{17}O$					
		^{67}Zn		$^{67}Zn^{16}O$					
		^{68}Zn			$^{68}Zn^{16}O$	$^{68}Zn^{17}O$	$^{68}Zn^{18}O$		
		^{70}Zn					$^{70}Zn^{16}O$	$^{70}Zn^{17}O$	$^{70}Zn^{18}O$
		^{69}Ga				$^{69}Ga^{16}O$	$^{69}Ga^{17}O$	$^{69}Ga^{18}O$	
		^{71}Ga						$^{71}Ga^{16}O$	$^{71}Ga^{17}O$
	Ca Dimers			$^{40}Ca^{43}Ca$	$^{40}Ca^{44}Ca$	$^{42}Ca^{43}Ca$	$^{40}Ca^{46}Ca$	$^{43}Ca^{44}Ca$	$^{40}Ca^{48}Ca$
							$^{42}Ca^{44}Ca$		$^{42}Ca^{46}Ca$
							$^{43}Ca^{43}Ca$		$^{44}Ca^{44}Ca$
	Ca Argides			$^{43}Ca^{40}Ar$	$^{48}Ca^{36}Ar$		$^{48}Ca^{38}Ar$		$^{48}Ca^{40}Ar$
					$^{46}Ca^{38}Ar$		$^{46}Ca^{40}Ar$		
					$^{44}Ca^{40}Ar$				

Table 1: List of potential interferences when determining Sr isotopes in plagioclase by LA-MC-ICP-MS. Those highlighted in red are the most serious interferences that must be monitored and corrected for (if needed).

In order to demonstrate the effectiveness of the LA-MC-ICP-MS method employed in this study for determining the Sr isotopic compositions in plagioclase, a pilot study was conducted using terrestrial plagioclases from the Detroit Seamount (Hawaiian-Emperor Seamount chain, NW Pacific). These plagioclases are similar in composition to those in lunar samples (e.g., Detroit plagioclases = An_{89-82} compared to An_{95-80} in the most lunar samples), Rb and Sr contents are ≤ 0.5 ppm and ≤ 300 ppm, respectively (both being similar to lunar plagioclases).

Preliminary Terrestrial Plagioclase Data: We report the in-situ Sr isotope ratios for plagioclase phenocrysts from various basaltic units at Detroit Seamount Site 1203 (Ocean Drilling Program). Optical and ompositional zonation is seen in most of the phenocrysts (**Fig. 1**). The plagioclases exhibit a limited variation in An (0.81-0.88). Whole-rock $(^{87}Sr/^{86}Sr)_I$ for the ~76 Ma Site 1203 basalts range from 0.703025 to 0.703204 [10]. Many of the plagioclase crystals analyzed via LA-MC-ICP-MS show isotopic disequilibri-

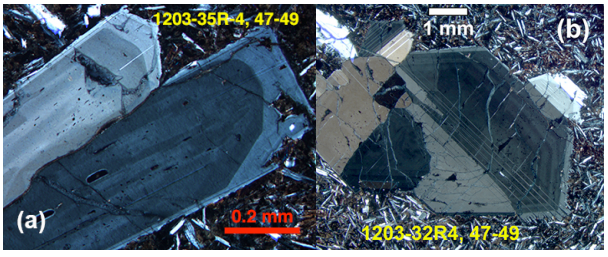

Fig. 1. Photomicropgraphs of plagioclase phenocrysts from Detroit seamount lavas that exhibit optical zonation.

um with the whole rock from the two flow units analyzed (Fig. 2). From Unit 3 at Site 1203, all analyzed plagioclase crystals have more radiogenic $^{87}Sr/^{86}Sr$ signatures than the whole-rock (Fig. 2a) – obviously more crystals need to be analyzed to reveal the full range of $^{87}Sr/^{86}Sr$ compositions. Plagioclases from Unit 11 are both more and less radiogenic that the whole-rock composition (Fig. 2b).

Lunar Plagioclase Sr Isotope Data – 12038. Apollo 12 basalts 12038 is a 746 g aluminous mare basalt (~12.5 wt.% Al_2O_3, e.g., [11,12]) with abundant plagioclase crystals (~44 modal% [13,14]). Plagioclases reach several mm in length with an average grain size of 0.6 mm [13]. Nine plagioclase crystals were analyzed from sample 12038 using a specially prepared to be 100 µm thick thin section (,254). A spot size of 150 µm, an energy density of ~11 mJ, and a repetition rate of 10 Hz were employed. The carrier gas was He that was mixed with Ar via a DSN-100 desolvating system before entering the torch. Results of the analyses are presented in Fig 3 and age corrected to 3.35 Ga [16] using a decay constant of 1.3968×10^{-11} Ga^{-1} [17]. The LA-MC-ICP-MS I(Sr) data presented here are compared with the ID-TIMS data from 12038 plagioclases [12,16]. Eight out of the nine LA-MC-ICP-MS analyses are within error of the ID-TIMS data (Fig. 3). Corrections for ^{87}Rb on ^{87}Sr are only significant for one analysis and the corrections have been made on the basis of $^{85}Rb/^{87}Rb$ ratios measured on the Nu Plasma II MC-ICP-MS.

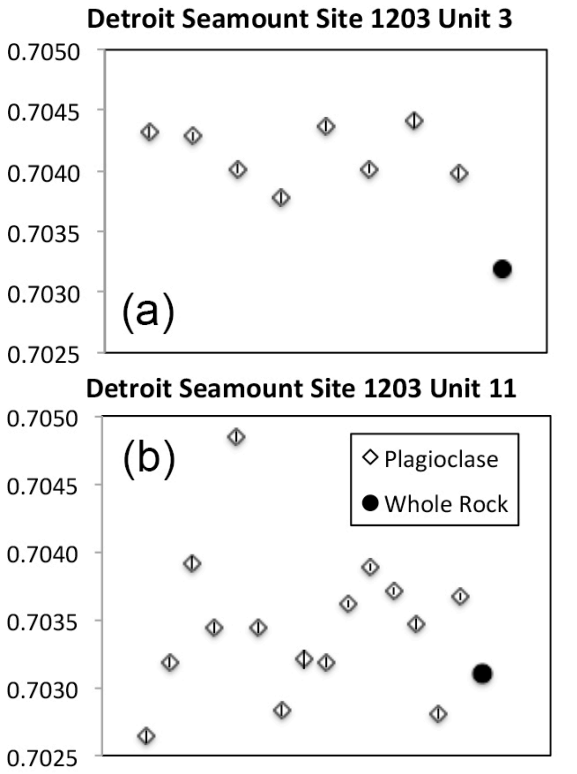

Fig. 2: Plagioclase (open diamonds) and whole rock (filled circles) I(Sr) from Units 3 and 11, Site 1203, Detroit Seamount. 2 sigma error bars are noted on each data point. A decay constant of 1.3968×10^{-11} is used [16].

Summary. The data presented here demonstrated that in situ Sr isotope determination in plagioclase is a valid tool for exploring the petrogenesis of both terrestrial and lunar igneous rocks. The 12038 data still contain relatively large errors, but slight modifications to the sampling protocol will be made to reduce these. Errors on the Detroit Seamount data are smaller because crystals were large and specific zones could be manually ratsered with the laser. Variations in Sr isotopes ratios across and between plagioclase crystals from lunar samples can now be explored using the method described here.

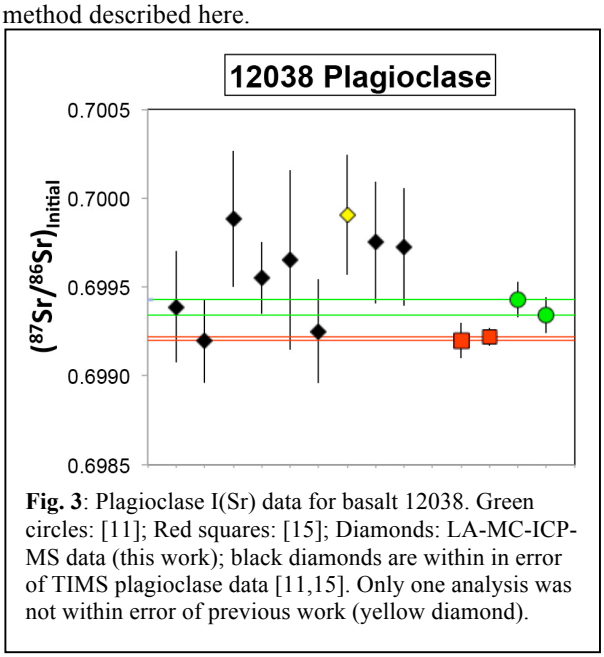

Fig. 3: Plagioclase I(Sr) data for basalt 12038. Green circles: [11]; Red squares: [15]; Diamonds: LA-MC-ICP-MS data (this work); black diamonds are within in error of TIMS plagioclase data [11,15]. Only one analysis was not within error of previous work (yellow diamond).

References: [1] Davidson J.P. et al. (2001) *EPSL 184*, 427-442. [2] Davidson J.P. (2002) *EOS Trans. AGU 83*, F1407. [3] Bizzaro M. et al. (2003) *GCA 67*, 289-302. [4] Schmidberger S.S. et al. (2003) *Chem. Geol. 199*, 317-329. [5] Alves A. et al. (2009) *J. Petrol. 50*, 2221-2247. [6] Ramos F.C. (2004) *Chem. Geol. 211*, 135-158. [7] Woodhead J. et al. (2004) *JAAS 20*, 22-27. [8] Vroon P.Z. et al. (2008) *Anal. Bioanal. Chem. 390*, 465-476. [9] Paton C. et al. (2007) *Geostds. Geoanal. Res. 31*, 321-330. [10] Huang S. et al. (2005) *G^3 6, doi:10.1029/2004GC000756*. [11] Compston W. et al. (1971) *PLSC 2*, 1471-1485. [12] Willis J.P. et al. (1971) *PLSC 2*, 1123-1138. [13] Beaty D.W. et al. (1979) *PLPSC 10*, 115-139. [14] Neal C.R. et al. (1994) *Meteoritics 29*, 334-348. [15] Nyquist L.E. et al. (1981) *EPSL 55*, 335-355. [16] Rotenberg E. et al. (2012) *GCA 85*, 41-57.