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Improved in-situ δ^{7}Li analysis of synthetic glass by LA-MC-ICP-MS with 10^{13} Ω amplifier technology

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Keywords

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Abstract

The application of 10^{13} Ω amplifier technology to lithium isotope ratio analysis by LA-MC-ICP-MS is demonstrated to improve precision at typical lithium concentrations for geological materials.

Introduction

Lithium (Li) has two stable isotopes, ^{6}Li (7.5% natural abundance) and ^{7}Li (92.5%). The large mass difference between the two isotopes leads to a large (>60‰) observed isotopic fractionation in nature. As such Li isotope analysis is a useful environmental tracer of a variety of low (e.g. surface weathering) and high temperature (e.g. crust-mantle recycling) geochemical processes.

Multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS) is used to measure the Li isotopic composition of prepared solutions which are however, time consuming to produce. The in-situ measurement of Li isotopic compositions by coupling laser ablation (LA) to MC-ICP-MS[1-3] not only reduces sample preparation, but allows spatial resolved analysis. However, as Li is only present in trace amounts (typically a few µg/g) in many geological materials, LA-MC-ICP-MS measurements are challenging due to the low measured intensity (1-20 mV, 63-1250 kcps) of ^{6}Li. Amplifiers incorporating 10^{13} Ω resistors, a recent development in MC-MS,[4-5] extend the operating range of Faraday cup detectors to cover such small ion intensities. Compared to the standard 10^{11} Ω amplifier, the signal to noise ratio of the 10^{13} Ω amplifier is improved by 4 to 5 fold,[6] which is reflected in the precision achieved at low signal intensities. The ^{7}Li/^{6}Li analysis of synthetic glasses by LA-MC-ICP-MS demonstrates the improvements in accuracy and precision for low intensity ion beams afforded by 10^{13} Ω amplifiers.

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Method

The Thermo Scientific™ Neptune Plus™ MC-ICP-MS was coupled to a Teledyne Photon Machines Analyte G2™ excimer laser with 193 nm wavelength. The laser was equipped with a HelEx™ II two-volume ablation cell. Operating conditions for both the Neptune Plus MC-ICP-MS and Analyte G2 are given in Table 1. Li isotope ratio analysis ($^{7}Li/^{6}Li$) was performed on six synthetic MPI-DING glasses (T1-G, ATHO-G, GOR132-G, StHs/680-G, KL2-G and ML3B-G). A seventh MPI-DING glass, GOR128-G was used as the external standard. 5 individual spot ablations were made on each glass, bracketed by 2 spots on the external standard. A 60 s on-peak baselines was measured between each ablation. The analysis was performed twice, once with 10^{11} Ω and once with 10^{13} Ω amplifiers.

Li isotope ratios are typically reported in delta notation relative to the National Institute of Standards and Technology (NIST™) reference material SRM®8545.

$$\delta^{7}Li_{SRM8545} = \left(\frac{^{7}Li/^{6}Li_{sample}}{^{7}Li/^{6}Li_{SRM8545}} - 1 \right) \times 1000$$

A wide range of $\delta^{7}Li_{SRM8545}$ values have been reported for the MPI-DING glasses (e.g. ATHO-G, 3.9 – 17.1‰), hence $\delta^{7}Li$ values were calculated relative to the external standard GOR128-G only and not related back to $\delta^{7}Li_{SRM8545}$.

Results

Data analysis was performed within Iolite™ v3.4, built on the software platform Igor Pro™ v6.37 (WaveMetrics, Inc., USA), using a custom data reduction scheme. Five seconds were cropped from the start and end of each 30 s ablation.

The measured ^{6}Li sample signal ranged from 2.1 – 13 mV and was 5.3 mV for the external standard GOR-128-G (Li concentration 10.4 ppm).[7] The baseline was approximately 200 µV for ^{6}Li. For all six MPI-DING glasses using the 10^{13} Ω amplifiers resulted in significant improvements in both internal and external precision (Table 2). KL2-G and ML3B-G, with the lowest concentrations of Li,[7] observed a four to fivefold reduction in both internal and external 2SD. At 28.0 – 30.4 ppm ATHO-G had the highest concentration of the MPI-DING. Even at this elevated concentration and signal the 10^{13} Ω amplifiers resulted in at least a threefold improvement in precision.

Table 1. Experimental configuration of the laser ablation and MC-ICP-MS systems. ^{6}Li was measured in the L5 cup position, and ^{7}Li in the H4 cup position. A dummy mass of 6.512 was placed in the center cup.

Parameter	Value	Parameter	Value
Analyte G2™ Laser Ablation		**Neptune Plus MC-ICP-MS**	
Fluence (J cm^{-2})	2.36	Cool Gas (L min^{-1})	16
Repetition Rate (Hz)	10	Auxiliary Gas (L min^{-1})	0.95
Spot Shape	Circle	Sample Gas (L min^{-1})	0.915
Spot Size (µm)	85	Power (W)	1200
Duration (s)	30	Skimmer Cone	X
He Outer Cell (L min^{-1})	0.60	Sample Cone	Jet
He Cup Flow (L min^{-1})	0.4	Resolution	Low
N_2 Addition (mL min^{-1})	0.0	Integration Time (s)	0.524

Using the better $^{7}Li/^{6}Li$ precision achieved with the 10^{13} Ω amplifiers, the two Komatiite glasses, GOR128-G and GOR132-G, could be distinguished from each other (Figure 1). StHs6/80-G and ATHO-G could now also be identified as having different Li isotopic compositions by using 10^{13} Ω amplifier technology.

For the smallest intensity ion beams, KL2-G and ML3B-G, using the 10^{13} Ω amplifier introduced a large shift (≈ 5‰) in the measured mean $\delta^{7}Li$ value (Table 2; Figure 2). Smaller shifts were detected with T1-G and GOR132-G. It is concluded that the high uncertainty at low count rates with the 10^{11} Ω amplifiers introduced a positive bias to the measured ^{6}Li signals and therefore changing the calculated mean ratio.

Table 2. Li isotope ratio analysis of 6 reference MPI-DING glasses. GOR128-G, was used as the external standard (δ^7Li = 0.0). Operating conditions are given in Table 1, n = 5. Five seconds were cut from the beginning and end of each ablation, resulting in 40 cycles per ablation.

Sample		Li conc.[7]	^6Li	$^7Li/^6Li$ - 10^{11} Ω	$^7Li/^6Li$ - 10^{13} Ω	$\delta^7Li_{GOR128-G}$ - 10^{11} Ω	$\delta^7Li_{GOR128-G}$ - 10^{13} Ω
ATHO-G	Mean	30.4 ppm	13 mV (812 kcps)	11.988	11.964	-14.99 ± 1.33	-16.93 ± 0.30
	Internal 2SD (‰)			1.38	0.44		
	External 2SD (‰)			1.35	0.31		
KL2-G	Mean	5.1 ppm	2.7 mV (169 kcps)	12.033	12.006	-11.25 ± 6.62	-13.46 ± 3.45
	Internal 2SD (‰)			6.13	1.43		
	External 2SD (‰)			6.69	3.50		
ML3B-G	Mean	4.5 ppm	2.1 mV (131 kcps)	12.062	11.979	-8.87 ± 9.00	-15.73 ± 1.16
	Internal 2SD (‰)			9.23	1.72		
	External 2SD (‰)			9.09	1.18		
StHs6/80-G	Mean	20.7 ppm	8.8 mV (550 kcps)	11.943	11.929	-18.65 ± 2.72	-19.82 ± 0.79
	Internal 2SD (‰)			2.18	0.48		
	External 2SD (‰)			2.77	0.81		
T1-G	Mean	19.9 ppm	8.9 mV (556 kcps)	11.967	11.945	-16.66 ± 2.98	-18.45 ± 1.58
	Internal 2SD (‰)			2.02	0.55		
	External 2SD (‰)			3.03	1.61		
GOR132-G	Mean	8.9 ppm	4.7 mV (294 kcps)	12.129	12.121	-3.34 ± 2.64	-4.06 ± 0.91
	Internal 2SD (‰)			3.54	0.78		
	External 2SD (‰)			2.65	0.91		

Conclusion

Due to the low abundance of Li in geological materials, more precise δ^7Li values can be obtain for LA-MC-ICP-MS by employing 10^{13} Ω amplifiers. The ± 0.31‰ (2SD) precision achieved for MPI-DING silicate glass ATHO-G represents an approximately fourfold improvement over both the 10^{11} Ω amplifiers (± 1.37‰) and published values (± 1.2‰).[3] Similar enhancements in precision were observed for all the MPI-DING glasses.

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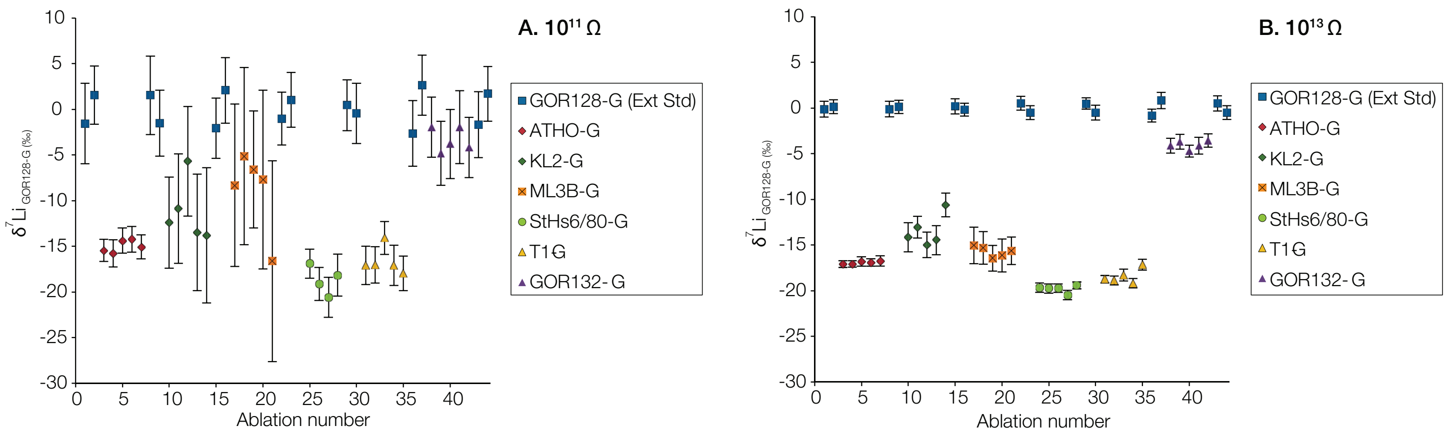

Figure 1. δ^7Li analysis of 6 reference MPI-DING glasses by LA-MC-ICP-MS. Another MPI-DING reference glass, GOR128-G, was used as an external standard (δ^7Li = 0.0). Error bars represent 2SE uncertainty (n = 40). (A.) δ^7Li measured on Faraday detectors connected to 10^{11} Ω amplifiers. (B.) δ^7Li measured on Faraday detectors connected to 10^{13} Ω amplifiers.

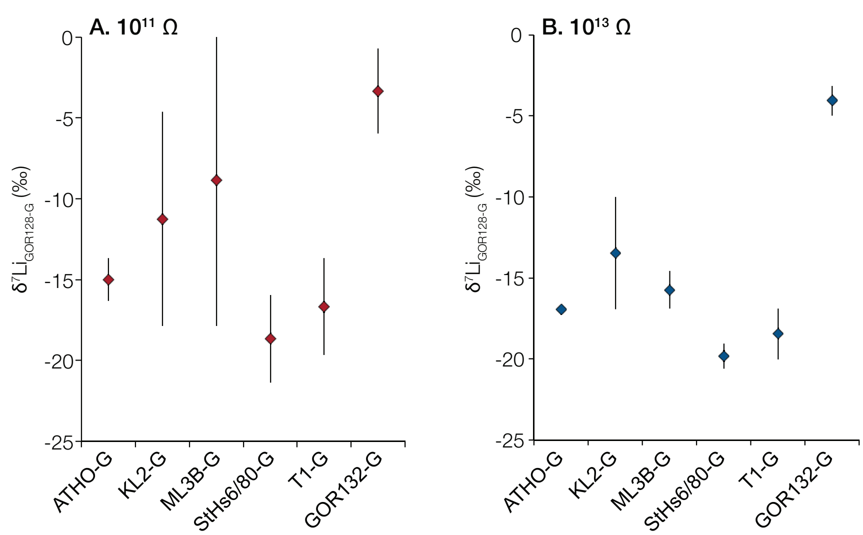

Figure 2. Mean δ^7Li of 6 reference MPI-DING glasses (n = 5). GOR128-G, was used as the external standard (δ^7Li = 0.0). Error bars represent 2SD. (A.) δ^7Li measured on Faraday detectors connected to 10^{11} Ω amplifiers. (B.) δ^7Li measured on Faraday detectors connected to 10^{13} Ω amplifiers.

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