JAAS

Accepted Manuscript

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www.rsc.org/jaas

Journal of Applied Atomic Spectroscopy

ARTICLE

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Direct Determination (without Chromatographic Separation) of Lithium Isotopes in Saline Fluids using MC-ICP-MS: Establishing Limits on Water Chemistry

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Produced waters from petroleum and geothermal reservoirs contain large amounts of cations including lithium, and while lithium isotopes are time-intensive to measure in the traditional way, they have the potential to reveal information about fluid and solute origins and diagenesis. We tested the effect of added cations that dominate in produced waters (Na, Ca, Mg) on accuracy and precision of lithium isotope measurements by MC-ICP-MS in Li-isotope standard solutions without chromatographic separation. Repeated measurement of Li-isotope standards with no added matrix demonstrate high 2s reproducibility: LSVEC (RM8545) had δ^7Li of 0.04±0.74‰ (n =19); IRMM16 had δ^7Li of 0.07±1.2‰ (n =11); Li7N had δ^7Li of 30.07±0.12‰ (n=11); Li6N had δ^7Li of –8.04±0.58‰ (n=8). Replicates of standards with matrix and of diluted produced waters had 2s reproducibility smaller than ±1.8‰ and ±2.0‰, respectively. Results showed that Na/Li (weight ratio) up to about 500 (analysed aliquot < 20 mg kg^{-1} Na) and Ca/Li or Mg/Li up to about 250 (analysed aliquot < 10 mg kg^{-1} Ca or Mg) do not diminish δ^7Li accuracy or precision, so long as Li concentration in the measured solution is greater than 20 µg kg^{-1}. Because produced waters are chemically more complex than the added-matrix isotope standards we tested initially, we also compared δ^7Li in produced waters from which the Li was chromatographically separated, as is the convention, with diluted produced waters. Results show marked Li isotope fractionation occurred in those samples in which Na/Li ranged from 500 to almost 10,000. Geothermal waters and Na-Ca-Cl-type produced waters, therefore, are fluids that are most likely to have cation/Li ratios that will make them amenable to direct determination of δ^7Li with only sample dilution. We also found that two aliquots of the Li-isotope standard, LSVEC (RM8545), one obtained in 1985 and one in 2012, have δ^7Li that differs by about 2‰.

Introduction, Results and discussion

Lithium has two stable isotopes, mass 6 and 7, and is a common trace element in high-salinity water produced from hydrocarbon or geothermal wells. Measurement of Li isotope ratios in those types of waters, for simplicity here collectively referred to as produced water, began in the 2000's using thermal ionization mass spectrometry[1]. That and other work[2] have demonstrated the importance of using chromatography to separate Li from other ions in solution, and of collection of the entire Li-containing aliquot during the separation procedure. Recent work analysing Li isotopes on a multi-collector inductively-coupled plasma mass spectrometer (MC-ICP-MS) has shown that normal seawater can be analysed without separation from other dissolved components, using special equipment and operating conditions[3]. In the present study, a method of analysis is developed to measure normalized Li isotope ratios in diluted produced water, without chromatographic separation, using MC-ICP-MS. The isotope ratios are reported in the conventional way in delta

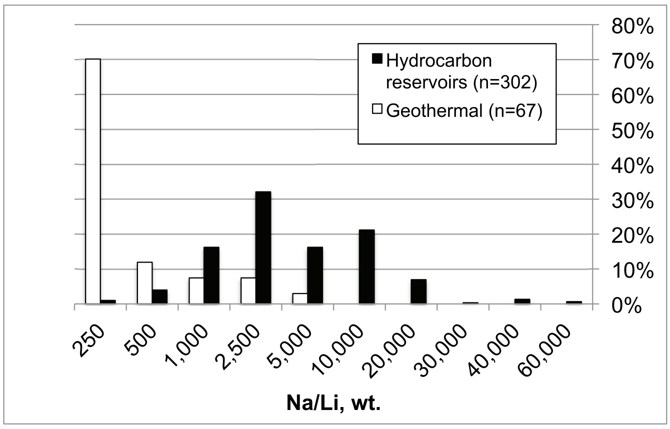

Fig. 1 Na/Li in selected produced waters§ demonstrate the high variability of produced-water cation chemistry, and the difference between geothermal and hydrocarbon-reservoir produced waters. Na, Ca, and Mg make up 96-100% of the cation mass in these samples, and Cl makes up 99-100% of the anion mass.

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notation, δ^7Li, with units of ‰, calculated as 1000 * (R_{sample} – $R_{standard}$)/$R_{standard}$, where R is the atomic ratio of ^{7}Li to ^{6}Li, and the standard is the certified LSVEC. Because the chemistry of produced waters is not uniform (Fig. 1), the effects of several compositional variables are investigated, including Li concentration, and Na/Li, Ca/Li and Mg/Li matrix effects. Results are used to develop optimum dilutions for analysis of produced water. The tests were also run on a variety of materials for which δ^7Li is certified, in order to cover a large range of δ^7Li. Finally we compare the results of δ^7Li measured in 15 produced-water samples and one manufactured brine, with and without chromatographic separation of Li from other cations.

Methods

Li isotope ratios were measured on a Neptune Plus MC-ICP-MS (Thermo Scientific, Bremen, Germany) at a DOE-NETL/University of Pittsburgh facility. Table 1 shows the instrument setup and data acquisition scheme; 40 µg kg^{-1} total Li in solution resulted in a ^{7}Li signal of 1 volt. The cones were cleaned before each analytical session and the spray chamber was cleaned approximately monthly. The instrument was tuned before the start of each analytical session. The bracketing method was used for data collection, with each sample bracketed by a standard and every sample and standard bracketed by blanks. The bracketing standard was LSVEC, (RM8545; obtained from the National Institutes of Standards and Technology). It has a reported atomic ^{6}Li/^{7}Li ratio of 0.08215±0.00023. In δ notation, this is 0.0±2.8‰.

Table 1 MC-ICP-MS settings for Li isotope data acquisition

Instrument settings, Neptune Plus	
Forward power (W)	1300
Coolant gas flow rate (l min^{-1})	15
Auxiliary gas flow rate (l min^{-1})	0.85
Nebulizer gas flow rate (l min^{-1})	1.15
Mass resolution	Low
Sample delivery	Peristaltic pump, 50 µL min^{-1}
Sampler cone	Ni, standard
Skimmer cone	Ni, X-type

Cup configuration

L4: ^{6}Li	C: mass 6.5	H4: ^{7}Li

Data acquisition parameters

Sample type	Blocks	Cycles/block	Integration time
Blanks	3	45	4 sec
Standards, unknowns	3	15	4 sec

Solutions spiked with cations for the matrix tests were made by adding aliquots of purchased, single-element solutions (Na, Ca, Mg from Spex Certiprep through Thermo Fisher Scientific) to 4 lithium isotope standards while matching the acid strength of the solution (2% v/v HNO_3) to that of produced-water samples. A manufactured brine also was made using purchased salts (NaCl and $CaCl_2$•$2H_2O$) and a stock solution (Li) (purchased from Spex CertiPrep through Thermo Fisher Scientific). The manufactured brine, similar to Na-Ca-Cl type produced waters, contained Li (50.5 mg kg^{-1}), Na (19.1 gm kg^{-1}), Ca (16.7 gm kg^{-1}) and Cl (58.9 gm kg^{-1}) as well as HNO_3 (2% v/v).

The authors, DOE-NETL personnel, USGS personnel and graduate students and faculty from the University of Pittsburgh, Bucknell University, and the University of Texas collected produced-water samples previously according to standard methods[4]. Li isotope ratios for some of these samples have been published previously[5].

To separate Li from other cations in the produced water samples and the manufactured brine, we followed a procedure modified from James and Palmer[6]. The HCl eluent was Optima (Thermo Fisher Scientific) grade, diluted with 18.2 megaohm deionized water to ~0.18N. The 5 mL aliquots before and after the Li-containing aliquot were always checked for Li and Na concentrations using a Perkin-Elmer NexION 300X quadrupole ICP-MS at the University of Pittsburgh. The Li-containing aliquot was dried in a Class-100 space and then dissolved into Optima-grade HNO_3 (Thermo Fisher Scientific), diluted with 18.2 megaohm deionized water to 2% acid (v/v).

Results and discussion

Reproducibility of standards analysis

Repeated analysis over a five-month period of the dissolved and diluted LSVEC Li_2CO_3 salt purchased in 2012 (LSVEC-2012) resulted in δ^7Li of 0.04±0.16‰ (2 standard deviations of the measurements; n = 19). The average of 2 times the standard error of each measurement (average internal reproducibility) on the MC-ICP-MS was 0.17. Another aliquot of LSVEC Li_2CO_3 salt was purchased in 1985 (LSVEC-1985) and stored in a Teflon® screw-top beaker in a class-100 space. After dissolution and dilution, repeated measurements using LSVEC-1985 (corrected[7]) resulted in a different value of δ^7Li from LSVEC-2012. Replicate analyses of LSVEC-1985 (n=7), as well as 3 other Li isotope standards and 4 produced waters (n=14) show that LSVEC-1985 is 2‰ lighter than LSVEC-2012 (Fig. 2a). This difference is within the certified range for LSVEC, but much larger than the reproducibility possible using MC-ICP-MS. For this reason, δ^7Li of samples for which LSVEC-1985 was the bracketing standard were adjusted, using the best-fit equation (Fig. 2b), to values that would have been calculated if LSVEC-2012 were the bracketing standard.

Analysis of IRMM-16 (purchased from Sigma-Aldrich) over a five-month period resulted in δ^7Li of 0.07±0.35‰ (n=11, 2 SD); the reported δ^7Li of IRMM-16[7] is 0.35±1.41‰ (2 SD). Analysis of Li7-N[8] (n=11) and Li6-N[8] (n=8) (purchased from CPRG-CNRS, France) over the same period resulted in δ^7Li of 30.07±0.16‰ (reported value is 30.4±1.1‰[8]; 2 SD) and –8.04±0.20‰ (reported as –8.9±0.9‰[8]; 2 SD), respectively.

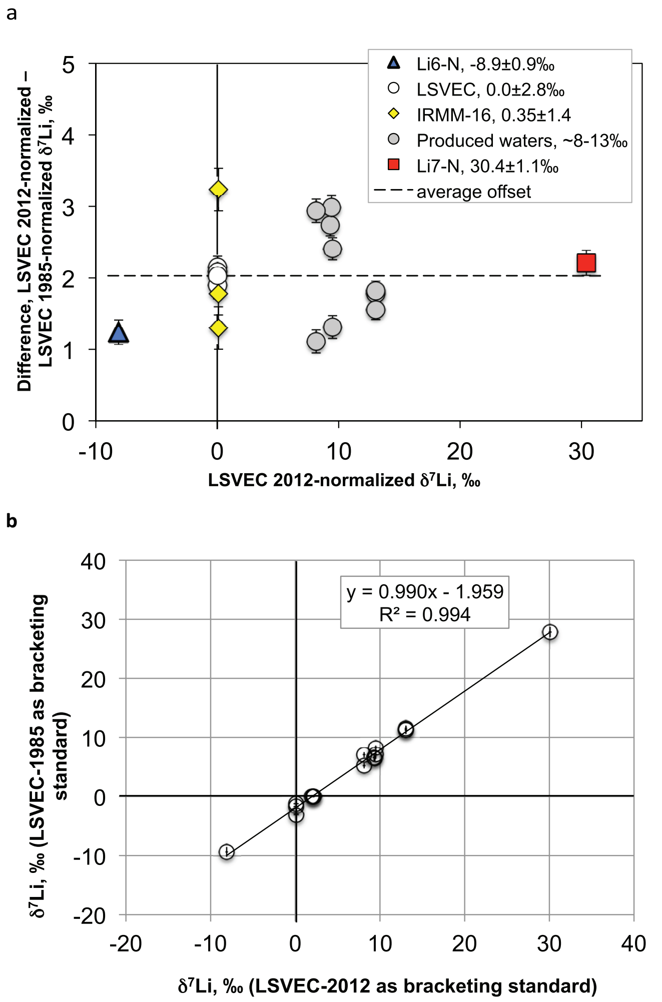

Fig. 2 a) Offset of samples and standards measured using different age aliquots of LSVEC as the bracketing standard. b) The equation shown was used to adjust early analyses where LSVEC-1985 was used as the bracketing standard to be consistent with later analyses using LSVEC-2012 as the bracketing standard.

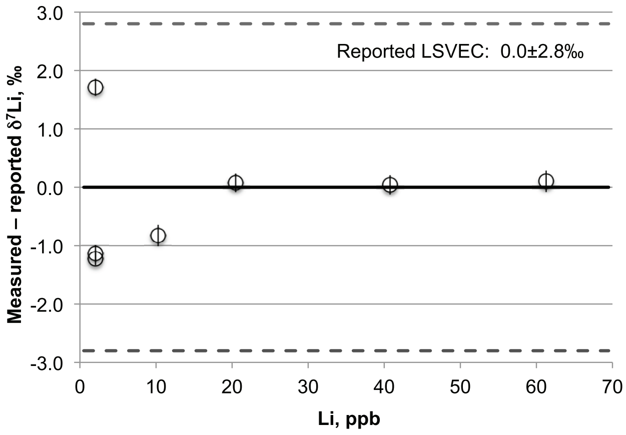

Fig. 3 Offset of δ^7Li measurements from reported value for LSVEC-2012 (0.0‰; solid black line) at different Li concentrations. Internal reproducibility (±2 SE) of each analysis is plotted as error bars (all less than 0.2). LSVEC 2σ uncertainty (±2.8‰) is shown as black dashed lines.

Effect of Li concentration on δ^7Li

For solutions of LSVEC-2012 containing 20 to 60 μg kg^{-1} Li, the δ^7Li is relatively constant (Fig. 3). At lower concentrations, corresponding to lower signal voltage, the measured δ^7Li is still within the reported error of the isotope standard, but outside the reproducibility of the measurement. Concentrations higher than about 80 μg kg^{-1} result in longer washout times with no added benefit to sample reproducibility or accuracy.

Effect of other cations on determination of δ^7Li

The effect of matrix cations most abundant in produced waters (Na, Ca, Mg) on measurement of δ^7Li was tested over most of the natural ranges of lithium isotope ratios in water by adding matrix cations to isotope standards (Fig. 4). Six of the seven

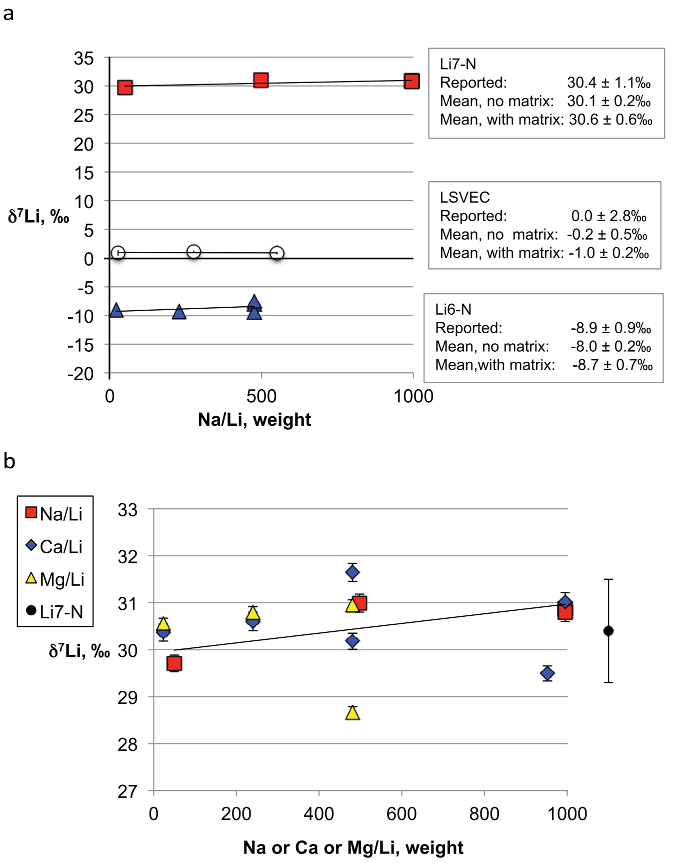

Fig. 4 Artificial matrix effect on determination of δ^7Li in spiked lithium isotope standards (LSVEC, Li6-N, and Li7-N). a) Effect of adding Na to standards with different δ^7Li shows little effect for Na/Li < 1000. One measurement in triplicate of LSVEC with Na/Li of 2500 and Ca/Li of 625 (not shown) averages –0.5‰, within the uncertainty of the standard. Error bars, ±2SE of each measurement are smaller than the symbols. b) Results of adding variable matrices of single-stock solutions (Na, Ca, Mg) to Li7-N show little difference from the reported value for each standard. Li7-N with uncertainty is shown on the right, for reference. Y-error bars are ±2SE. Solid line is best-fit line to Na/Li data set, and suggests little matrix effect with increasing Na.

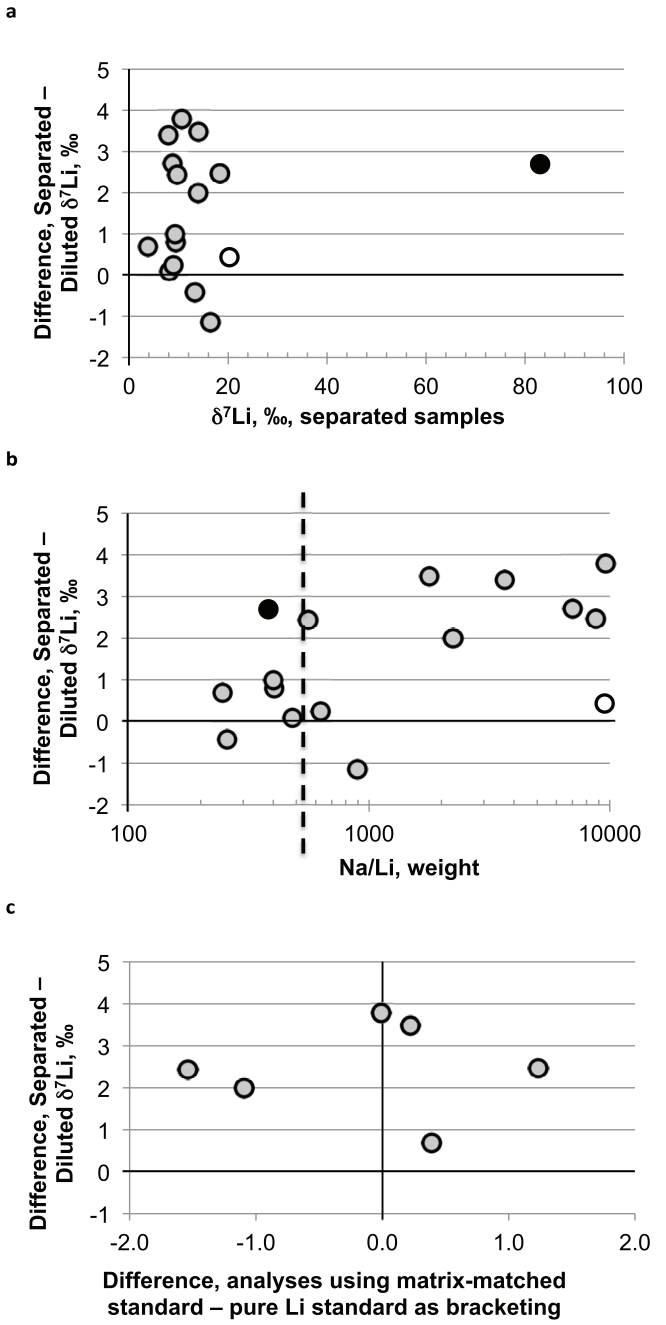

Fig. 5 Results of different methods of sample treatment and analysis for 15 produced waters (grey and white) and one manufactured brine (black). One produced water (white) contained 4 µg kg^{-1} Li, which is below our threshold of 20, and so does not follow the trends. a) Differences in δ^7Li between chromatographically separated Li and diluted samples without separation are not related to δ^7Li. The manufactured brine δ^7Li differences are calculated three ways: separated – diluted, separated – Li stock solution, and diluted – Li stock solution. b) Large differences between measurements of separated and diluted samples occurred for solutions with Na/Li greater than 500 (vertical dashed line). c) Using matrix-matched bracketing standard did not improve measurement precision.

sets of replicate analyses had 2s of ±0.2‰ to ±2‰; one of the replicate analyses had 2s of ±3.2‰. The effects of Na/Li ratios (by weight) on determination of δ^7Li were tested up to a ratio of 1000, which corresponds to a sample matrix containing 40 mg kg^{-1} Na in a solution with 40 µg kg^{-1} Li. This Na/Li range is significantly higher than that tested by Tomascak et al.[9] who showed negligible effect on δ^7Li with Na up to 0.5 mg kg^{-1} and Na/Li up to 5, and by Bryant et al.[10], comparing cool and hot plasma conditions, who showed little effect of Na on δ^7Li for Na concentrations of 0.05 to 5 mg kg^{-1} and Na/Li of 0.5 to 50. In contrast, Jeffcoate et al.[11] found depletion in δ^7Li with Na/Li ratios from 1 to 20 and Li of 2 ppb, possibly because of the markedly lower total Li. Choi et al.[3], using a fully-integrated inlet system under cool plasma conditions, found excellent correspondence between measurements of chromatographically separated seawater and diluted seawater, with Li of 10 µg kg^{-1} and presumed Na/Li of 57,000. In our experiments, the Li signal suppression was minimal for up to 20 mg kg^{-1} Na in the matrix, but at 40 mg kg^{-1} Na, the Li signal was 5% lower than in a matrix with Na <20 mg kg^{-1}.

The influence of Ca and Mg on measurement of δ^7Li in Li7-N, which has δ^7Li close to that of seawater, is small (Fig. 4). The reproducibility of δ^7Li in Ca and Mg matrices containing 10 or 1 mg kg^{-1} of either Ca or Mg (Ca/Li and Mg/Li up to 250) is high (30.48±0.33‰ 2s in Ca matrix, n=4; 30.67±0.33‰ 2s in Mg matrix, n=2). At 20 mg kg^{-1} Ca or Mg (Ca/Li and Mg/Li up to 1000 and 500, respectively), the data have wider variability (30.7±1.9‰ 2s in Ca matrix, n=2; 29.8±3.2‰ 2s in Mg matrix, n=2) than at 10 mg kg^{-1} or 1 mg kg^{-1}, although the averages of the replicates fall within the reported reproducibility of Li7-N. This suggests that modest alkaline earth metal concentrations that remain after chromatographic separation of Li in dissolved complex solids, such as igneous and metamorphic rocks, might not affect the measurement of δ^7Li, and that a second chromatographic separation, such as has been proposed[11], might not be necessary, although we did not test dissolved-rock matrices.

We also tested the effect of a mixed-cation-spiked LSVEC solution containing 100 mg kg^{-1} Na, 25 mg kg^{-1} Ca and 40 µg kg^{-1} Li, a matrix similar to some (diluted) produced waters. Triplicate, longer-term measurements of δ^7Li in this mixture averaged –0.51±1.00‰, which is within the uncertainty of the LSVEC standard and our long-term reproducibility.

These findings suggest that complete separation of Li from Na during chromatography is not required so long as total Li concentrations are greater than 10 µg kg^{-1} in the analysed aliquot, and that cool plasma[12] or extra front-end devices such as desolvators[13] are not necessary to measure δ^7Li precisely and accurately. Use of samples as washout was not investigated[14], although for these high salinity samples, it is likely that salt build-up on the cones would create unreasonable reduction in signal voltage. It is more important to collect the entire aliquot containing Li during

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Table 2 Chemistry of produced water samples (in order of δ^7Li, separated aliquot).

Sample	Li mg kg^{-1}	TDS gm kg^{-1}	Na/Li wt. ratio	Ca/Li wt. ratio	Mg/Li wt. ratio	Average δ^7Li, ‰ separated	Average δ^7Li, ‰ diluted	2s (n) of replicates separated	2s (n) of replicates diluted
CHM-05	3.88	4.44	246	113	64	3.89	3.20	0.32(2)	0.47(3)
GC-W039	5	50.3	3660	187	31	7.98	4.58	0.36(2)	
AP-MD005	55	99	478	113	12	8.15	8.06	1.84(3)	
GC-M015	4.5	85.7	7022	400	102	8.79	6.09		
AP-MD004	74	168	626	238	26	8.94	8.69	0.98(4)	1.00(2)
AP-MD002	86.4	188	399	120	11	9.26	8.28	0.89(7)	
AP-MD003	123	158	402	114	14	9.42	8.63	0.89(6)	
GC-V007	80	70.4	557	1108	5	9.68	7.25	1.03(2)	2.01(3)
GC-O020	4.6	124	9587	848	261	10.7	6.90		0.05(3)
AP-MD001	118	110	258	52	5	13.3	13.8	0.22(4)	1.6(2)
AP-UD004	16.6	139	2235	669	84	13.9	12.0		
AP-UD003	20	137	1785	535	48	14.0	10.7		0.26(3)
GC-S001	80	286	898	351	18	16.4	17.6	0.33(2)	
AP-UD002	3.97	31.3	1788	2262	380	18.3	15.8		1.8(2)
AP-UD001	0.63	79.3	8476	2381	457	20.3	19.8	0.48(2)	0.03(2)

chromatographic separation, even if some Na is included, than risk excluding some Li, because ^{7}Li/^{6}Li is strongly fractionated in ion exchange columns[15].

Analysis of produced-water samples

Li in 15 produced waters of variable chemistry (Table 2) was separated from each matrix by chromatography and the samples analysed at least once for δ^7Li (separated samples); blanks for the full-procedural separations contained less than 0.04 ng Li, while aliquots of produced water aliquots put through the columns contained ~5 µg Li. The same produced-water samples were diluted to a Li concentration of 40 µg kg^{-1} and analysed without separation (diluted samples). For both separated and diluted samples, LSVEC-2012 at a concentration of 40 µg kg^{-1} was used as the bracketing standard, either as pure Li or, for a few samples, with an added matrix of 100 mg kg^{-1} Na and 25 mg kg^{-1} Ca (from diluted, purchased stock solutions and maintaining 2% HNO_3 v/v).

Samples were analysed at least once in each form (separated or diluted), and many were measured two or more times in the same day (short-term replicate) or on different days (longer-term replicate; Table 2). For the replicate sets, 2s ranged from ±0.03 to ±2.0‰. The measured δ^7Li ranged from about 0‰ to +20‰ in the produced waters and was about +80‰ in the manufactured brine (Fig. 5a). The differences in δ^7Li between the separated and diluted forms of the samples were less than ±1‰ when Na/Li was less than 500, but the increasing difference in the isotope ratios when Na/Li > 500 suggests non-spectroscopic interferences discriminate against ^{6}Li (Fig. 5b). No attempt was made to determine the cause of the fractionation, which might be attributed to space-charge effects, ion-beam clipping[16], expansion in the supersonic jet[17], or other effects. All analyses for each produced water fell within the analytical uncertainty of each group of analyses, and all of the uncertainties were less than the reported reproducibility of the LSVEC standard. In addition, the results did not vary whether a pure Li isotope or partially matrix-matched Li isotope standard (with added Na, Ca and Cl) was used as the bracketing standard (Fig. 5c); more work on understanding the effect of the more complex matrix of produced waters is needed. This work suggests that simple dilution of produced waters with Li greater than 20 µg kg^{-1} and Na/Li less than 500 is a quick and reliable method of δ^7Li determination by MC-ICP-MS. The types of produced waters that will most likely be amenable to δ^7Li determination on diluted samples are many geothermal fluids and most Na-Ca-Cl type fluids from petroleum reservoirs[18].

Conclusions

Determination of δ^7Li by hot plasma MC-ICP-MS in Li-isotope standards with no added matrix demonstrate high accuracy and 2s reproducibility: LSVEC (RM8545) δ^7Li was 0.04±0.74‰ (n =19); IRMM16 δ^7Li was 0.07±1.2‰ (n =11); Li7N δ^7Li was 30.07±0.52‰ (n=11); and Li6N δ^7Li was –8.04±0.58‰ (n=8). Direct determination of δ^7Li by hot plasma MC-ICP-MS in produced waters of variable salinity is robust for Li concentrations diluted to between 20 and 80 μg kg^{-1} total Li. Na/Li weight ratio up to 500 (Na < 20 mg kg^{-1} in analysed aliquot) and Ca/Li and Mg/Li weight ratios up to 250 (Ca or Mg < 10 mg kg^{-1}) do not significantly alter the measured δ^{7}Li (within ±1‰ δ^{7}Li in the chromatographically separated aliquot) and reproducibility of measurements is slightly worse than for aliquots with no matrix, but 2s was always smaller than ±2.0‰, which is smaller than the uncertainty of the bracketing standard. Further, although Na/Li ratios greater than 500 apparently exacerbate isotope fractionation, preliminary work shows there is no advantage to using a bracketing standard that is only partially matrix matched. There is a wide range (at least 16‰) in δ^{7}Li in produced waters, so that a slight reduction in measurement precision or accuracy does not compromise meaningful interpretation. The results of this investigation suggest that, especially considering the wide range in δ^{7}Li in produced waters, those samples with Na/Li and alkaline earth/Li weight ratios less than 500 and 250, respectively, that are diluted to Li concentrations greater than 20 μg kg^{-1} may be analysed directly by MC-ICP-MS (without chromatographic separation of Li from other cations), without reduction in δ^{7}Li accuracy or precision. This method can expedite screening of samples and can be applied for data interpretation where a large range in δ^{7}Li exists in the sample set.

Acknowledgements

This work was supported by the National Energy Technology Laboratory's ongoing research under the RES contract DE-FE0004000 at the University of Pittsburgh. We are grateful for generous support from the University of Kansas Department of Geology and the Geology Associates Fund of the KU Endowment Association, and for produced-water sample collection by the USGS, DOE-NETL personnel, Bucknell University, and University of Pittsburgh personnel. Dr. Karl Schroeder provided logistical support for the project. Dr. Andy Wall assisted with analytical procedures, and many students at the University of Pittsburgh assisted with laboratory tasks. Two reviewers helped improve this manuscript. The authors declare no conflict of interest.

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