Supplemental Information

Lithium and strontium isotope dynamics in a carbonate island aquifer, Rottnest Island, Western Australia

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Key words: lithium isotopes; groundwater; karst; carbonate; aeolianite; Rottnest Island

A.1 Appendix

A.1.1 Groundwater Types

Fresh groundwaters are shallow, (0 to -1 m AHD), have low TDS values (<1 g/L) and younger groundwater age estimates (^{3}H and ^{14}C$_{DOC}$ values of >0.6 TU and >89 pMC, respectively), whereas T2 groundwaters are deeper (-5 to -15 m AHD), more saline (7 to 30 g/L) and have older groundwater age estimates (^{3}H and ^{14}C$_{DOC}$ values of <0.3 TU and <67 pMC, respectively). The T1 groundwaters have a composition that is intermediate between the fresh and T2 groundwaters, probably due to groundwater level fluctuations and subsequent mixing.

A.1.2 Column calibration experiments for Li

Three experiments were conducted to ensure the 100% recovery of Li in column chromatography procedures following the one-step procedure from Van Hoecke et al. (2015) (Table A.1). Experiment 1 was conducted with ~0.4 mL seawater (2% resin capacity), Experiment 2 was conducted with ~0.8 mL seawater (4% resin capacity), and Experiment 3 was conducted with ~0.4 mL seawater with 0.1 mL of a 10.5 ppm Li spike added (2% resin capacity). After loading the sample, column cuts were retained following the elution of 5, 10, 12.5, 15, 20, 25, 30, 35, 37.5, 40, 45 and 50 mL of 0.5 HCl. According to Van Hoecke et al. (2015), it was expected that 100% of Li should be eluted in the 15 to 37.5 mL fractions. In all experiments, Li was 100% recovered in the anticipated Li fraction (15 - 37.5 mL) and successfully separated from Na (Figure A.1). As an additional check when processing samples, the columns were also eluted with a further 10 mL of 0.5 M HCl after eluting the Li fraction and this solution was retained. These solutions were then screened prior to MC-ICPMS analyses, evaporated and redissolved in 2% (v/v) HNO$_3$. The Li signal intensities for these retained cuts of the non-Li fractions from column chromatography could not be distinguished from the background signal (ca. 2 mV for ^{7}Li) during MC-ICP-MS analyses.

A.1.3 Ion enrichment and depletion calculation method

Transition zone reactions can be revealed by comparing the measured water composition with the composition calculated for conservative mixing of freshwater and seawater. The seawater fraction (f_{sw}) is calculated from the Cl$^-$ concentration, assuming that it acts conservatively and that there are no additional Cl$^-$ sources (Appelo and Postma, 2005):

$$f_{sea} = \frac{m_{Cl^-,sample} - m_{Cl^-,fresh}}{m_{Cl^-,sea} - m_{Cl^-,fresh}} \qquad \text{(Equation A.1)}$$

where $m_{Cl^-,sample}$, $m_{Cl^-,fresh}$ and $m_{Cl^-,sea}$ are the Cl$^-$ concentrations in a sample, fresh groundwater and seawater respectively. The Cl$^-$ concentration of the freshest groundwater sample (2-94), which was determined according to its low TDS value (474 mg/L), was used as the $m_{Cl^-,fresh}$ value.

The conservative mixing concentration ($m_{i,\,mix}$) for other dissolved species is then calculated from (Appelo and Postma, 2005):

$$m_{i,mix} = f_{sea} \cdot m_{i,sea} + (1 - f_{sea}) \cdot m_{i,fresh} \qquad \text{(Equation A.2)}$$

where $m_{i,\,sea}$ and $m_{i,\,fresh}$ are the concentrations in seawater and freshwater of the species i. The enrichment or depletion (m_{react}) of the species i is then obtained by (Appelo and Postma, 2005):

$$m_{react} = m_{i,sample} - m_{i,mix} \qquad \text{(Equation A.3)}$$

A positive m_{react} indicates that the groundwater is enriched for species i, and a negative m_{react} indicates that the groundwater is depleted for species i, compared to conservative mixing.

A.1.4 Rainfall data

There was no correlation between Li and Sr concentrations, or Li and δ^7Li values for rainfall samples (Figure A.2).

A.1.5 Error propagation for estimated proportions of cations from various reservoirs

The proportions of Li and Sr sourced from atmospheric input, carbonate weathering and silicate weathering for fresh groundwaters were constrained by considering the concentrations of Ca, Cl, Li and Sr in rainfall and groundwater samples. The propagated error ($\sigma_{propagated}$) was then calculated by using the following equation:

$$\sigma_{propagated} = \sqrt{\left(\frac{\sigma_x}{x}\right)^2 + \left(\frac{\sigma_y}{y}\right)^2 + \left(\frac{\sigma_z}{z}\right)^2} \tag{A.4}$$

Where σ_x, σ_y, and σ_z represent the individual uncertainties associated with the input parameters x, y and z. The parameters for our calculations are given in Table A.4. The individual and propagated uncertainties for all parameters are given in Table A.4.

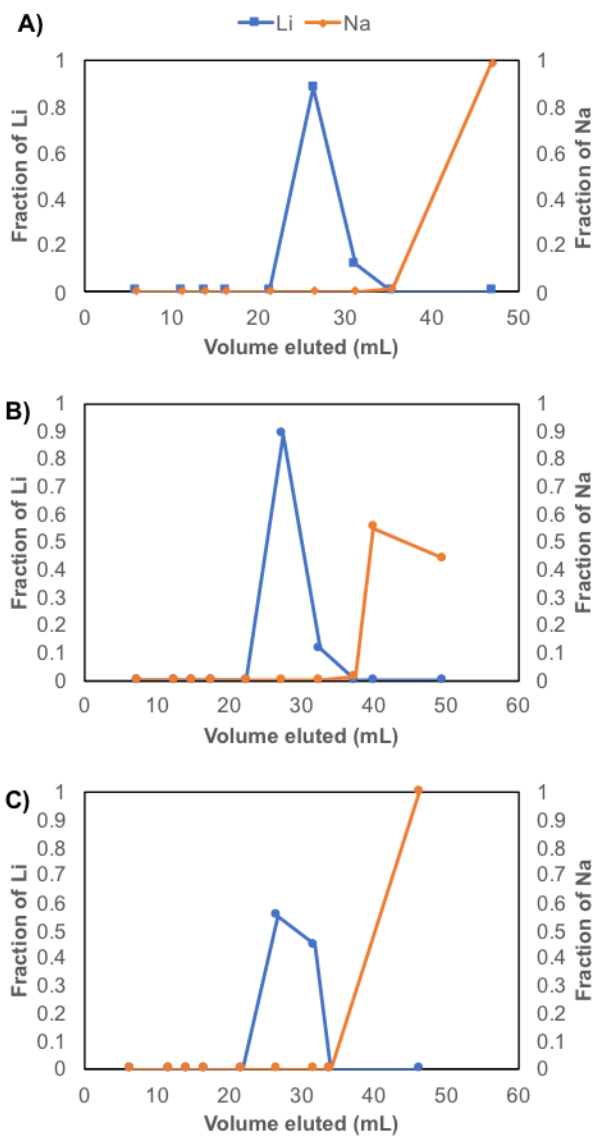# Figures for Supplemental Information

Figure A.1 Fractions of Li and Na eluted during column calibration experiments using A) 0.433 mL seawater (Experiment 1); B) 0.866 mL seawater (Experiment 2); and C) 0.433 mL seawater plus 0.1 mL of a 10 ppm Li spike (Experiment 3).
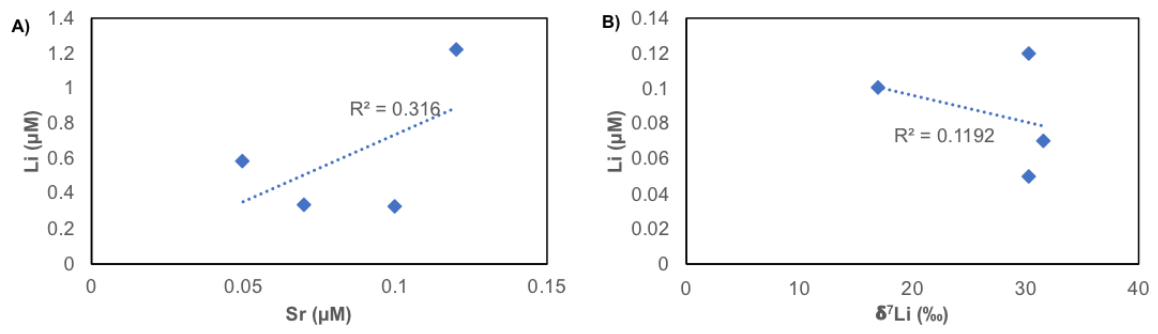
Figure A.2 Lithium concentrations in rainfall samples as a function of A) Sr concentrations and B) Li isotope values.

Tables for Supplemental Information

Table A.1 Details of column calibration experiments for Li

Parameter	Experiment		
	Experiment 1	Experiment 2	Experiment 3
Sample volume (mL)	0.433	0.866	0.433
Sample [Li] (ppm)	0.203	0.203	0.203
Spike volume (mL)	n/a	n/a	0.1
Spike [Li] (ppm)	n/a	n/a	10.5
Li loaded (ng)	87.9	175.8	1137.9
Resin capacity (%)	2	4	2

Table A.2 Groundwater mixing types (Bryan et al., 2017)

Mixing type	Depth (m AHD)	TDS (g/L)	^{3}H (TU)	^{14}C$_{DOC}$ (pMC)
F (·)	0 to -1	<1	0.6-1.4	89-105
T1 (●)	-1 to -7	1-21	0.2-1.0	84-98
T2 (▲)	-5 to -15	7-30	0.0-0.3	47-67

Table A.3 Supporting geochemical parameters for groundwaters and a local seawater sample from Rottnest Island

ID	T^a	pH^a	Field Alkalinity^a	DO^a	Density^a	TDS^a	$K^{+,a}$	$Cl^{-,a}$	$Br^{-,a}$	$SO_4^{2-,a}$	$HCO_3^{-,a}$	CBE^a	DIC^b	$^{13}C_{DIC}^b$	$^{14}C_{DIC}^b$	DOC^b	$^{13}C_{DOC}^b$	$^{14}C_{DOC}^b$	$^3H^a$
-	°C	-	mg/L	mg/l	g/cm3	mg/l	mM	mM	mM	mM	mM	%	mM	‰	pmc	mg/L	‰	pmc	TU
RI_2-77	19	7.6	225.7	1.8	1.00	672	0.14	4.55	0.01	0.47	4.49	-1	4.72	-7	52.5	1.18	-24.96	NA	0.9
RI_3-77	16	7.5	261.6	1.5	1.00	776	0.13	5.06	0.01	0.65	5.21	-1.3	5.59	-8.2	56.64	1.13	-25.01	88.91	0.8
RI_1-83	17	7.5	233.6	1.6	1.00	789	0.13	6.13	0.01	0.64	4.65	-2.5	4.96	-8.6	66.53	1.96	-24.66	105.62	0.9
RI_4-83	17	7.8	216.8	4.2	1.00	674	0.13	4.44	0.01	0.66	4.29	-0.6	4.47	-5.9	45.32	1.24	-25.28	NA	1.1
RI_2-90	19	7.8	201.8	3.6	1.00	605	0.1	4.24	0.01	0.41	4	-1.4	4.16	-6.5	41.81	0.56	-26.51	NA	0.8
RI_6-90	19	7.7	232.4	3.4	1.00	799	0.13	6.75	0.01	0.46	4.61	-2.5	4.83	-8.6	67.68	1.02	-26.26	NA	0.6
RI_16-90	17	7.4	263	1.3	1.00	812	0.14	5.91	0.01	0.54	5.24	-1.6	5.65	-9.8	74.13	2.9	-26.09	99.78	0.9
RI_17-90	17	7.9	229.4	3.5	1.00	787	0.15	5.93	0.01	0.74	4.52	-1.4	4.68	-8.6	66.12	1.53	-25.49	93.73	NA
RI_3-93	19	7.6	210	2.9	1.00	833	0.13	7.52	0.01	0.66	4.17	-1.6	4.41	-5.9	44.45	0.83	-25.99	NA	NA
RI_6-93	17	7.6	229.8	4	1.00	713	0.12	5.48	0.01	0.42	4.57	-3.5	4.81	-5.8	46.39	0.78	-26.58	NA	NA
RI_1-94	19	7.7	231.4	4.6	1.00	667	0.11	4.55	0.01	0.37	4.58	-1.6	4.79	-9.7	85.76	0.6	-25.24	NA	1.1
RI_2-94	19	7.6	176.7	7.1	1.00	474	0.08	2.68	0	0.29	3.52	-1	3.72	-11	95.23	0.6	-25.33	NA	1.3
RI_1-90	16	7.5	254.5	2.5	1.00	2461	0.62	35.0	0.06	1.04	5.07	-4.6	5.39	-6.7	48.5	1.4	-26.92	NA	0.6
RI_8-90	19	7.4	311	1.9	1.00	1144	0.26	9.24	0.02	0.97	6.19	-0.5	6.67	-7.3	56.81	2.02	-25.86	97.5	
RI_7-90	22	7.4	185	3.3	1.01	2067	5.64	320.	0.51	16.35	3.65	0	3.86	-3.1	21.17	0.1	-30.3	NA	0.6
RI_13-90	20	7.2	197.5	0.5	1.00	4997	1.19	74.1	0.11	2.86	6.42	-3.3	7.23	-4.1	23.99	1	-28.6	NA	0.2
RI_21-90	19	7.4	325	0.3	1.00	3584	1.06	46.3	0.07	3.76	6.47	-3.3	7	-9	59.33	2.8	-25.9	91.48	0.6
RI_24-90	19	7.6	275.6	0.4	1.00	1211	0.28	11.8	0.02	1.11	5.48	-5.6	5.81	-7.4	56.31	2.2	-24.83	94.8	0.6
RI_28-90	20	7.5	245.7	1.1	1.00	1986	0.53	27.3	0.04	0.67	4.89	-4.4	5.23	-9.8	77.03	0.8	-26.59	83.97	0.9
RI_3-94	18	7.6	251.3	3	1.00	1244	0.25	13.6	0.02	0.73	4.99	-3.7	5.29	-11	97.21	0.8	-26.61	NA	1.0
RI_4-94	18	7.6	287.2	2.4	1.00	1075	0.2	8.9	0.02	1.04	5.69	-2.3	5.99	-6.7	54.68	1.3	-25.44	NA	0.6

ID	T^a	pH^a	Field Alkalinity^a	DO^a	Density^a	TDS^a	$K^{+,a}$	$Cl^{-,a}$	$Br^{-,a}$	$SO_4^{2-,a}$	$HCO_3^{-,a}$	CBE^a	DIC^b	$^{13}C_{DIC}^b$	$^{14}C_{DIC}^b$	DOC^b	$^{13}C_{DOC}^b$	$^{14}C_{DOC}^b$	$^3H^a$
-	°C	-	mg/L	mg/l	g/cm3	mg/l	mM	mM	mM	mM	mM	%	mM	‰	pmc	mg/L	‰	pmc	TU
RI_5-94	19	7.7	252.7	1.1	1.00	1040	0.24	8.85	0.02	1.17	5.01	-1.7	5.24	-4.1	28.23	0.9	-24.66	NA	0.4
RI_5-90	17	7.3	377.5	0.4	1.00	6868	1.95	97.0	0.19	3.31	7.51	5.5	8.13	-2.3	8.71	1.2	-26.27	NA	0.1
RI_11-90	19	7.5	182.6	0.5	1.03	2967	8.04	473.	0.73	23.01	3.57	-2.8	3.75	-7.3	43.98	1.1	-24.84	57.78	0.0
RI_15-90	19	7.5	154.5	0.2	1.02	2297	6.55	380.	0.55	16.16	3.04	-6.4	3.21	-2.9	8.35	0.5	-25.51	NA	0.0
RI_18-90	18	7.4	191.6	0.3	1.02	2526	7.67	409.	0.62	20.45	3.78	-5.6	4.01	-5.9	35.12	0.2	-23.87	50.61	0.0
RI_25-90	18	7.5	208.6	0.3	1.01	1448	3.93	224.	0.38	11.19	4.11	-1.2	4.33	-2.2	13.18	0.2	-27.07	46.57	0.0
RI_27-90	19	7.3	244.8	0.9	1.02	2082	6.12	308.	0.6	17.47	4.85	3.3	5.22	-3	18.28	0.4	-26.03	66.99	0.2
RI_31-90	18	7.6	205.2	0.3	1.01	1634	4.55	244.	0.43	14.22	4.01	2	4.2	-9.4	52.47	0.9	-31.07	66.93	0.0
SW	21	8.1	109.8	6.7	1.02	3578	10.4	560.	0.85	31.35	1.95	-0.5	2.11	0.9	NA	0.4	-24.5	NA	NA

^{a}**Data sourced from Bryan et al. (2016). See Bryan et al. (2016) for measurement details and definitions of all parameters.**

^{b}**Data sourced from Bryan et al. (2017). See Bryan et al. (2017) for measurement details and definitions of all parameters.**

Table A.4 Individual and propagated errors for the mass balance calculations estimating the proportions of Li and Sr (X = Li or Sr) sourced from rainfall, and the weathering of carbonate and silicate minerals

Parameter	1σ relative standard deviation (%)
$X_{rainfall}$	6.2
$X_{groundwater}$	6.2
$Cl_{rainfall}$	6.2
$Cl_{groundwater}$	6.2
$Ca_{rainfall}$	6.2
$Ca_{groundwater}$	6.2
$X_{bedrock}$	6.2
$Ca_{bedrock}$	6.2
$X/Cl_{rainfall}$	12.0
$X_{rainfall\ corrected}$	15.0
$Ca_{rainfall\ corrected}$	15.0
$X_{carbonate\ derived}$	19.0
$X_{silicate\ derived}$	25.0