Stable chlorine isotopes in arid non-marine basins: Instances and possible fractionation mechanisms

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ARTICLE INFO

ABSTRACT

Stable chlorine isotopes are useful geochemical tracers in processes involving the formation and evolution of evaporitic halite. Halite and dissolved chloride in groundwater that has interacted with halite in arid non-marine basins has a $\delta^{37}Cl$ range of $0 \pm 3‰$, far greater than the range for marine evaporites. Basins characterized by high positive ($+1$ to $+3‰$), near-0‰, and negative (-0.3 to $-2.6‰$) are documented. Halite in weathered crusts of sedimentary rocks has $\delta^{37}Cl$ values as high as $+5.6‰$. Salt-excluding halophyte plants excrete salt with a $\delta^{37}Cl$ range of -2.1 to $-0.8‰$. Differentiated rock chloride sources exist, e.g. in granitoid micas, but cannot provide sufficient chloride to account for the observed data. Single-pass application of known fractionating mechanisms, equilibrium salt-crystal interaction and disequilibrium diffusive transport, cannot account for the large ranges of $\delta^{37}Cl$. Cumulative fractionation as a result of multiple wetting-drying cycles in vadose playas that produce halite crusts can produce observed positive $\delta^{37}Cl$ values in hundreds to thousands of cycles. Diffusive isotope fractionation as a result of multiple wetting-drying cycles operating at a spatial scale of $1-10$ cm can produce high $\delta^{37}Cl$ values in residual halite. Chloride in rainwater is subject to complex fractionation, but develops negative $\delta^{37}Cl$ values in certain situations; such may explain halite deposits with bulk negative $\delta^{37}Cl$ values. Future field studies will benefit from a better understanding of hydrology and rainwater chemistry, and systematic collection of data for both Cl and Br.

1. Introduction

Over the last three decades, stable chlorine isotopes have emerged as useful geochemical and forensic tracers (e.g. Philp, 2007; Eggenkamp, 2014). In low-temperature geochemistry, they are useful is systems where halite is crystallized or dissolved, and where diffusion operates on chloride ion. Stable chlorine isotope studies of Phanerozoic marine evaporites (Eggenkamp et al., 1995; Eastoe et al., 2007 and references therein) have demonstrated a narrow range of $\delta^{37}Cl$ in marine halite facies salt, predominantly $0 \pm 0.5‰$, with a few outliers to $\pm 1.0‰$. The narrow $\delta^{37}Cl$ range results from the probable constancy of $\delta^{37}Cl$ in Phanerozoic seawater (Eastoe et al., 2007) and the small isotope fractionation (0.30‰, averaged from Eggenkamp et al., 1995 and Eggenkamp et al., 2016) between halite and its aqueous solution. Eastoe et al. (2007) pointed out that the range of mean $\delta^{37}Cl$ values for marine halite facies of a variety of ages in the Phanerozoic exceeds the

range predicted on the basis of the halite fractionation factor by a factor of 4 or 5.

Evaporites in continental closed basins present a very different isotope spectrum. Available data (reviewed below) indicate a $\delta^{37}Cl$ range of $0 \pm 3‰$ in lacustrine/closed basin halite, and a range that extends to $+5.5‰$ in other kinds of continental halite occurrence. The detailed fractionation mechanisms involved in generating the more extreme $\delta^{37}Cl$ values have remained unclear. Available mechanisms discussed in the literature to date include equilibrium fractionation occurring on crystallization of salts from aqueous solution (Eggenkamp et al., 1994; Eggenkamp and Coleman, 2009; Luo et al., 2014) and disequilibrium fractionation attending the diffusion of chloride ion across concentration gradients (Eggenkamp et al., 1994; Eggenkamp and Coleman, 2009). Ion filtration is a special case of diffusion (Phillips and Bentley, 1987). These, with the possible addition of isotope fractionation associated with chloride uptake in halophytic plants, to be discussed below, and atmospheric fractionation of chloride eventually incorporated into rainwater (Sun et al., 2004; Kohler and Wassenaar, 2010; Liu et al., 2008), appear to be the only available

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mechanisms at the earth surface. In addition to fractionating isotopes, a viable mechanism for continental basins must lead to a persistent spatial separation of isotopically enriched and depleted fractions of chloride.

The aims of this article are to review the published data for lacustrine and associated halite in arid and semiarid continental basins, to add unpublished data from the archives of the Environmental Isotope Laboratory at the University of Arizona, and to present and discuss some ways in which diffusion and halite crystallization might generate the observed range of $\delta^{37}Cl$ under specialized conditions.

2. Previous work

Liu et al. (1997) and Xiao et al. (2000) presented chlorine isotope data for fourteen lakes in Qaidam Basin, western China. Ranges of $\delta^{37}Cl$ were as follows: for halite -0.6 to $+1.2‰$ (n = 14); for coexisting brine -2.1 to $+1.6‰$ (n = 10). The $\delta^{37}Cl$ values of brine were less than or equal to those of coexisting halite. In saline lake water without coexisting halite, $\delta^{37}Cl$ values were -0.7 to $-0.1‰$ (n = 6). River water in the area had a $\delta^{37}Cl$ range of $+0.7$ to $+2.2‰$ (n = 6). Other potential source water for the lakes included oil-field brines with a $\delta^{37}Cl$ range of -1.2 to $0.0‰$ (n = 4), and a hot-spring water, $\delta^{37}Cl = +2.9‰$. Citing low Na:Cl ratios as evidence, the authors determined that the lacustrine brines with lowest $\delta^{37}Cl$ values resulted from the presence of oil-field brines in certain lake basins. Brines with Na:Cl ratios near 1 had a range of $\delta^{37}Cl$ from -1.1 to $+0.5‰$.

In the Tarim Basin of western China, Tan et al. (2006) studied evaporite deposits in Cretaceous strata. On the basis of non-marine sulfur isotope signatures in gypsum, they determined that the evaporites of the Kuqa sub-basin were of non-marine origin, and reported a range of $\delta^{37}Cl$ values of 0.9 to $+3.3‰$ in halite from that sub-basin.

Meng et al. (2014) measured $\delta^{37}Cl$ in halite of Eocene age from the Jianghan Basin of central-eastern China. They determined that the halite was of non-marine origin on the basis of bromide content, fluid inclusion ion ratios, and $\delta^{37}Cl$ values ranging from -0.1 to $+2.5‰$ (n = 8, with 5 results greater than 1.7‰).

Safford Basin, Arizona, USA is a half-graben of the Basin and Range Province of western North America. Basin-fill sediments include large volumes of evaporite and salty lacustrine clay of Pliocene age, overlain by younger fluvial and alluvial deposits (Houser et al., 1985, Houser, 1990). Harris (1999), in a study addressing the origins of salinity in river water, presented a small set of $\delta^{37}Cl$ data for salty clay sampled from drill core from the Safford Basin, Arizona, USA. The range was -0.3 to $+0.3‰$. In addition, river water had a $\delta^{37}Cl$ range of -0.4 to $+0.6‰$ (n = 9), and groundwater -0.7 to $+0.7‰$. A single measurement of $+2.9‰$ was obtained from weathered salty clay. Changes in $\delta^{37}Cl$ in Gila River surface water indicated discharge of saline groundwater with net positive $\delta^{37}Cl$ into the river as it passes through the basin (Harris and Eastoe, 2002). Additional data for Safford Basin are presented below.

Arcuri and Brimhall (2003), in a study designed to identify the sources of chloride sources in atacamite from northern Chile, listed $\delta^{37}Cl$ data for salty mudstone of Lower Jurassic age in the Quebrada Chug Chug (QCC), about 30 km northwest of Calama, and San Salvador, about 7 km west of Calama. The range of $\delta^{37}Cl$ was -2.5 to $-0.3‰$ (n = 14). In five cases, $\delta^{37}Cl < -1.5‰$; Cl/Br for these five samples ranges from 744 to 1080, while Cl/Br has a range of 334–4040 in samples with Cl/Br $> -1‰$ (Fig. 1). At QCC, the samples were taken along a strike-length of 16 km, and $\delta^{37}Cl$ may be zoned; $\delta^{37}Cl$ values $<-1.5‰$ in the easternmost 5 km, and $>-0.8‰$ over the remainder. The authors considered the mudstone to be of
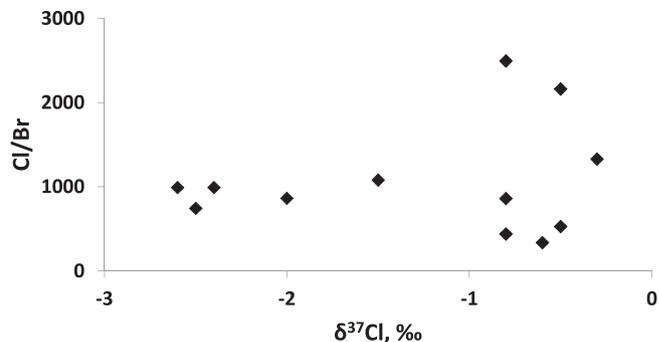
Fig. 1. Cl/Br (weight ratios) vs. $\delta^{37}Cl$ for salt from mudstone at Quebrada Chug Chug, Chile (data from Arcuri and Brimhall, 2003).

marine origin, and the low $\delta^{37}Cl$ values to have resulted from diffusion of chloride ion. An alternative interpretation will be discussed below.

3. Methods

The previously unpublished $\delta^{37}Cl$ data presented in the following sections are from reports and the records of the Environmental Isotope Laboratory at the University of Arizona. Most were collected between 1995 and 2005. Chloride was precipitated as AgCl, and purified to remove sulfate. Values of $\delta^{37}Cl$ were measured on CH_3Cl gas on a modified VG602C mass spectrometer. The CH_3Cl was prepared from the AgCl by reaction with CH_3I, and was purified by gas chromatography. The analytical precision, estimated on the basis of repeated analyses of newly-prepared samples of seawater chloride, was 0.075‰ (1σ). Details of the method are given in Long et al. (1993).

4. Results

Sample locations corresponding to new data are shown in Fig. 2. The data are listed in Table 1.

4.1. China lake, California

Naval Facilities Engineering Command (2003) presented a set of O, H and Cl isotope data for groundwater representing the entire basin at Indian Wells Valley (IWV), which is arid, and includes small playas near Ridgecrest. The following summary of the basin geohydrology is from that report. The basin is one of several supplied with water from the Owens River at times of wet climate. At present, little surface water reaches the basin, and evaporite formation is limited to thin halite crusts in the playas. The salient features of the basin geohydrology are three aquifers termed the Shallow, Intermediate and Deep Hydrologic Zones (SHZ, IHZ, DHZ respectively). The SHZ consists of highly permeable alluvial sand and gravel, and contains unconfined groundwater. The IHZ consists principally of lacustrine clay and silt, within which continuous sand layers bear semiconfined groundwater. The DHZ also consists of highly permeable alluvial sand and gravel, and groundwater is confined where it occurs beneath lacustrine sediment of the IHZ. Groundwater appears to move between the zones, driven upwards by confining pressure, and downwards possibly by high density due to solute content. Groundwater from IWV appears to discharge slowly through fractures in solid rock to the Salt Wells Valley, to the east (Fig. 2, panel C).

The main control on stable O and H isotope data is an evaporation trend originating near a $\delta^{18}O$ value of $-14.5‰$ on the global
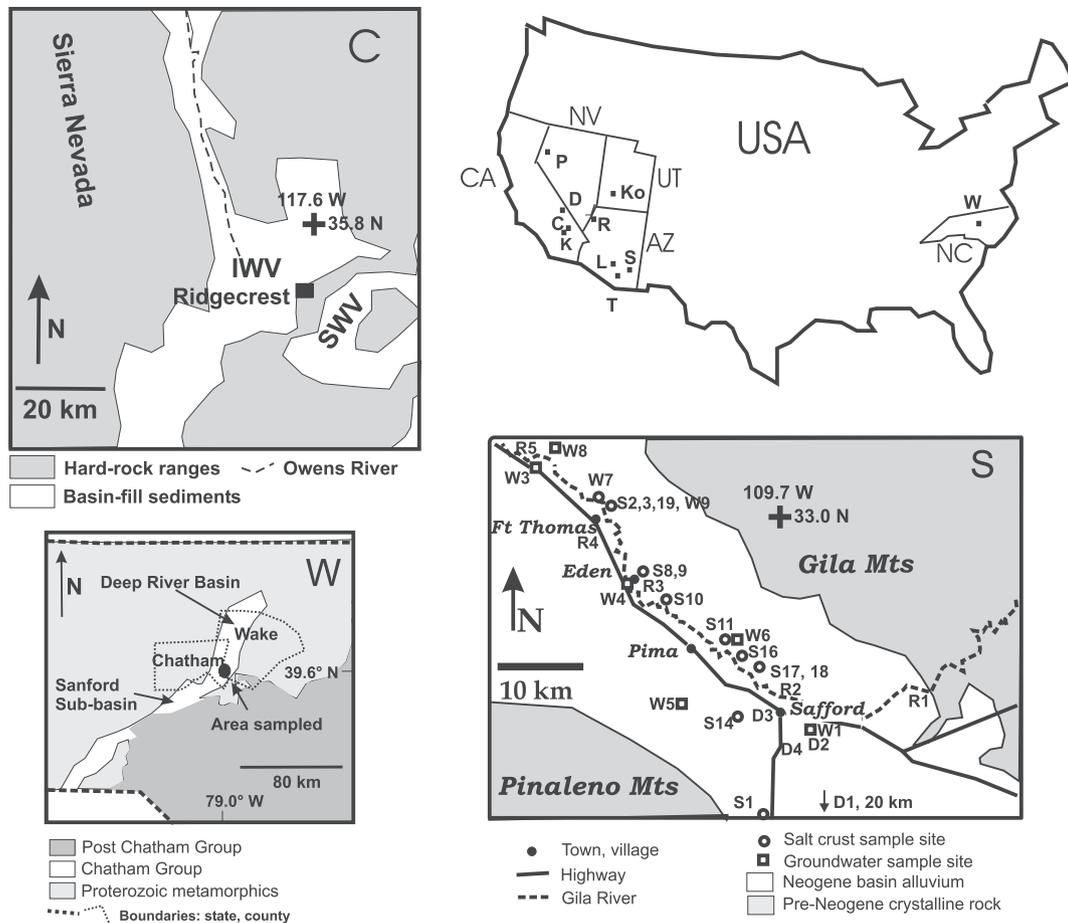
Fig. 2. Maps of sample sites for which new data are reported. State names are: AZ = Arizona, CA = California, NC = North Carolina, NV = Nevada and UT = Utah. Site and corresponding inset names are: C = China Lake, D = Death Valley, K = Kelso, Ko = Kodachrome State Park, L = Luke Salt, P = Pyramid Lake, R = Red Lake Salt, S = Safford Basin, T = Tucson Basin.

meteoric water line (Fig. 3A), consistent with a water origin at high elevation in the Sierra Nevada Mountains, largely a granitoid batholith, to the north. The scatter of the data about the trend may indicate mixing between meteoric waters of remote and local derivation. The most evaporated sample is a brine within the IHZ, probably a preserved lacustrine brine, with the highest observed chloride and boron contents (13,900 ppm and 425 ppm respectively), but otherwise there is no simple relationship between chloride content and degree of evaporation. The O and H stable isotope data are consistent with infiltration of variably evaporated surface water that acquired solutes in the subsurface by dissolution of salt and mixing with preserved lacustrine brine.

The most evaporated sample also has the highest value of $\delta^{37}Cl$, +2.6‰. This and other IHZ samples indicate mixing between high-salinity water with $\delta^{37}Cl$ values between 0.2‰ and 2.6‰ (or higher) on the one hand, and low-salinity water with $\delta^{37}Cl$ near −1‰ on the other (Fig. 3B). High-salinity water with $\delta^{37}Cl$ between −0.7 and + 1.0‰ is found in the SHZ and DHZ, where a second mixing trend between these and the high-$\delta^{37}Cl$ brine from the IHZ may be present.

4.2. Deep River Basin, North Carolina

The Deep River Basin is a failed-rift graben at the boundary of Wake and Chatham counties, southwest of Raleigh, North Carolina. The following description of the geology is from Smoot and Olsen (1988) and Olsen et al. (1991). The graben is one of a series of Triassic age extending along the Atlantic coast of North America, both onshore and offshore, and originally continuous with a belt of analogous structures in northwest Africa. Thick halite sequences fill the graben adjacent to Newfoundland and Morocco, indicating an arid, mid-latitude climate. At the lower latitude of the Deep River Basin in the Triassic, the climate appears to have been moist during the deposition of much of the thousands of meters of basin-fill strata, which include lacustrine beds, coal measures, shale and arkosic arenites and rudites. However, certain sedimentary features point to transient arid conditions at the time of deposition, e.g. mudstone with mud cracks and evaporite casts, redbed sandstone and conglomerate, preserved soil carbonate deposits, and a gypsum bed in the Sanford sub-basin, the southern part of the Deep River Basin.

In the mid-1990s, a set of groundwater samples (representing groundwater within 15 m of the surface, in an area within a radius of 1500 m of 35.6185°N, 78.9850°W) was analyzed for stable isotopes of O, H and Cl as part of an evaluation of the area as a disposal site for low-level radioactive waste. Red-bed sandstone and conglomerate crop out in the area. The data (Table 1) appear to be available now only in an original report of the Laboratory of Isotope Geochemistry at the University of Arizona. The stable O and H isotopes, which are not from exactly the same set of samples as the Cl isotope data, are consistent with long-term average local precipitation at the nearest station of the Global Network of Isotopes in Precipitation (Hatteras, North Carolina; International Atomic Energy Agency, 2015), with two evaporated outliers (Fig. 4A). The

Table 1
Cl isotope data.

Map code	Site name	Lat. °	Long. °	δ37Cl ‰	Cl ppm
Tucson Basin					
23	B26	32.25693	−110.9102	0.1	8
26	B42	32.23875	−110.9102	0.0	4.5
27	B43B	32.24818	−110.9294	−0.1	7
28	B44	32.25134	−110.9351	−0.1	8.4
29	B45	32.2550	−110.9315	0.2	11.4
30	B46	32.25319	−110.9230	0.0	9.9
35	B54B	32.2357	−110.9240	0.2	5.1
36	B56a	32.23885	−110.9081	0.2	6.9
74	C85	32.23465	−110.7923	0.1	13.9
77	C114	32.23292	−110.8541	0.0	13.8
88	D16	32.20743	−110.8498	−0.3	4.8
89	D18	32.2165	−110.8435	−0.2	6.5
94	D35	32.220	−110.8050	−0.8	11.8
110	E7	32.2110	−110.8008	−0.8	11.6
146	SS15	32.16595	−110.9865	−0.1	13.8
175	Z1	32.29157	−111.0232	0.1	99.5
200	Cresta Loma	32.30137	−110.9801	0.1	
205	Horizon Hills	32.33413	−111.0460	0.5	
207	Ina/La Canada	32.33454	−110.9935	−0.1	
220	Tucson Natl E	32.3636	−111.0101	−0.3	
232	Davis-Monthan 2	32.1760	−110.8698	0.1	
233	Davis-Monthan 6	32.1453	−110.8296	0.1	
341	Almquist	32.25657	−110.6949	−0.3	
356	Deer Run Ranch	32.33653	−110.9445	−0.1	
387	Small	32.26075	−110.7814	−0.2	
391	Walden	32.23271	−110.7646	−0.2	
414	Agua Caliente Spring	32.28104	−110.7343	0.0	
419	Finger Rock Spring	32.34727	−110.9036	−0.4	
417	Bowes Rd. Dug Well	32.30756	−110.7898	−0.2	
422	Pontatoc Spring	32.34184	−110.8928	−0.3	
Salt lakes and Playas, western USA					
K	Kelso, California	35.0086	−115.651	0.5	
P	Pyramid Lake, Nevada	40.0409	−119.647	−0.1	
D	Death Valley, California	36.230	−116.780	0.0	
Red Lake Salt, Arizona					
R	DDH RLS-1 1570 ft	35.68	−114.06	0.5	
R	DDH RLS-2 2506 ft	35.68	−114.06	0.6	
R	DDH Unknown	35.68	−114.06	0.7	
Luke Salt, Arizona					
L	DDH 2531 2740 ft top	33.5275	−112.3698	0.3	
L	DDH 2531 3720 ft	33.5275	−112.3698	0.3	
L	DDH 2531 4470 ft base	33.5275	−112.3698	0.3	
Wake & Chatham counties, North Carolina					
	W3MC6	35.61	−79.00	1.9	150
	W3MC4C	35.61	−79.00	2.4	23
	W4MC1	35.61	−79.00	1.8	958
	W4MC2	35.61	−79.00	1.6	840
	W4MC3	35.61	−79.00	1.5	3100
	W6SW1	35.61	−79.00	1.9	1900
	W6MC35	35.61	−79.00	−0.5	362
	W8MC10	35.61	−79.00	0.4	13
	W8MC11	35.61	−79.00	0.5	16
	W10MC13	35.61	−79.00	−0.2	7.7
	W10MC15D	35.61	−79.00	1.5	80
	W11MC28	35.61	−79.00	1.1	1000
	W113MC19	35.61	−79.00	0.6, 0.5	2600
	W113MC20	35.61	−79.00	0.6	1500
	W16OW33	35.61	−79.00	1.3	440
	W16OW37	35.61	−79.00	1.6	290
	W16OW41	35.61	−79.00	2.0, 1.9	150
	W16OW44	35.61	−79.00	1.4	370
	W32MC41	35.61	−79.00	0.0	100
	W37SW17D	35.61	−79.00	1.5	1020

Map code	Site name	Lat. °	Long. °	δ37Cl ‰	Cl ppm	
Safford Basin Arizona						
Drill Core samples						
D1	Tenney #3 1300−1500 ft	32.60	−109.54	−0.1		#
D1	Tenney #3 1500−1700 ft	32.60	−109.54	0.2		#
D1	Tenney #3 1900−2100 ft	32.60	−109.54	0.1		#
D1	Tenney #3 2500−2700 ft	32.60	−109.54	−0.3		#
D1	Tenney #3 2900−3300 ft	32.60	−109.54	0.4		#
D2	Claridge 2045−2150 ft	32.81	−109.67	0.5		#
D2	Claridge 2150 ft	32.81	−109.67	0.5		#
D3	Whitmore #1	32.85	−109.72	0.3		#
D4	Unnamed well	32.80	−109.71	0.1		#
Salty weathered crust samples at Watson Wash						
S16	WW1	32.5977	−109.7683	3.9		
S16	WW2	32.5977	−109.7683	0.8		
S16	WW3	32.5977	−109.7683	3.8		
S16	WW4	32.5977	−109.7683	3.9		
S16	WW5	32.5977	−109.7683	4.2		
S16	WW6	32.5977	−109.7683	2.1		
S16	WW7	32.5977	−109.7683	3.0		
S16	WW8	32.5977	−109.7683	0.7		
S16	WW9	32.5977	−109.7683	4.8		
S16	WW10	32.5977	−109.7683	2.7		
S16	WW11	32.5977	−109.7683	4.4		
S16	WW12	32.5977	−109.7683	5.5		
S16	unnumbered	32.5977	−109.7683	2.9		#
Watson Wash horizontal profiles						
S16	Profile 1 15 cm from surface	32.5977	−109.7683	1.7		
S16	Profile 1 30 cm from surface[a]	32.5977	−109.7683	0.1		
S16	Profile 2 15 cm from surface	32.5977	−109.7683	1.4		
S16	Profile 2 30 cm from surface[a]	32.5977	−109.7683	0.2		
Other salty surface crusts						
S1	near Mt Graham Rd	32.73	−109.72	1.8		
S1	near Mt Graham Rd	32.73	−109.72	−2.3		
S2	Opposite Ft. Thomas	33.0526	−109.9512	0.8		
Safford Basin Arizona						
S3	Opposite Ft. Thomas	33.0544	−109.9527	1.3		
S8	Eden	32.9714	−109.8827	4.2		
S9	Bryce-Eden Rd, Markham Wash	32.9446	−109.8176	2.0		
S10	Peck wash/Bryce	32.3393	−109.8176	0.9		
S11	Pima, W of Watson Wash	32.9046	−109.7796	1.1		
S14	Foot of Frye Mesa	32.7935	−109.7646	0.8		
S17	Safford-Bryce Rd, Watson Wash	32.8931	−109.7649	1.6		
S18	Safford-Bryce Rd, Talley Wash	32.8854	−109.7534	2.4		
S19	Charlie Thompson salt	33.0457	−109.9478	1.8		
Gila River surface water						#
R1	Entrance, Safford Basin	32.93	−109.46	−0.4	150	#
R2	Safford	32.8469	−109.7157	0.2	161	#
R3	Eden	32.9616	−110.9149	0.1	432	#
R4	Fort Thomas	33.0497	−109.9664	−0.3	1190	#
R5	Geronimo	33.092	−109.9664	−0.1	1660	
Shallow groundwater						#
W1	Safford Ag. Center well	32.8147	−109.6805	0.7	435	
W2	Clay mine wash sprring	33.0514	−109.9478	0.0		#
W7	Tom Niece Spring			0.2	1265	#
W8	Salt Spring			0.4	1636	#
W9	Charlie Thompson Spring	33.0457	−109.9478	−0.1	1344	
Deep Groundwater						#
W3	Knowles well Geronimo	33.0771	−110.0340	0.5	9770	#
W4	Gila Oil Syndicate well bulk	32.99	−109.92	0.6	1170	
W4	Gila Oil Syndicate well, 430 ft	32.99	−109.92	−0.1		
W4	Gila Oil Syndicate well, deep	32.99	−109.92	0.7		
W5	Cluff Ranch pond	32.89	−109.77	−0.1		
W6	Watson Wash well	32.9013	−109.7643	0.7		

Data from Harris (1999).
Tucson Basin: locations refer to map in Eastoe et al. (2004); Cl concentrations from Tucson Water, listed in Kalin (1994).
[a] Unweathered salty clay.

spread of the stable O and H isotope data and the range of chloride concentrations are large for a relatively small volume of rock, suggesting groundwater of short, but different, residence times, localized mixing only, and compartmentalization of the aquifer(s).

The stable Cl isotope data (Fig. 4B) indicate mixing between water with a range of chloride concentration and δ37Cl values near 0.0‰ on the one hand, and water with high chloride concentration and δ37Cl values near +2‰ on the other.
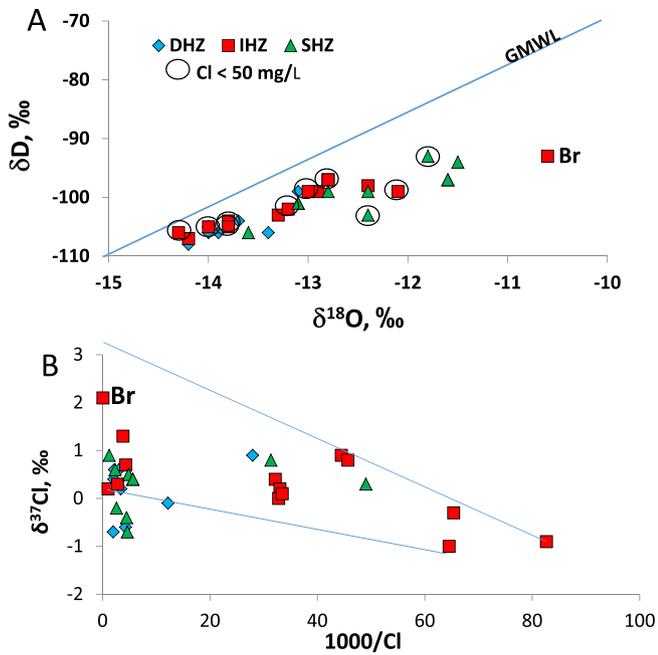
Fig. 3. Isotope data for groundwater samples from Indian Wells valley, China Lake, California. A: δD vs. δ18O; B: δ37Cl vs. 1000/Cl (concentrations in mg/L). GMWL = global meteoric water line. Br = brine sample. DHZ, IHZ, SHZ = deep, intermediate and shallow hydrologic zones, respectively. Data from Naval Facilities Engineering Command (2003).
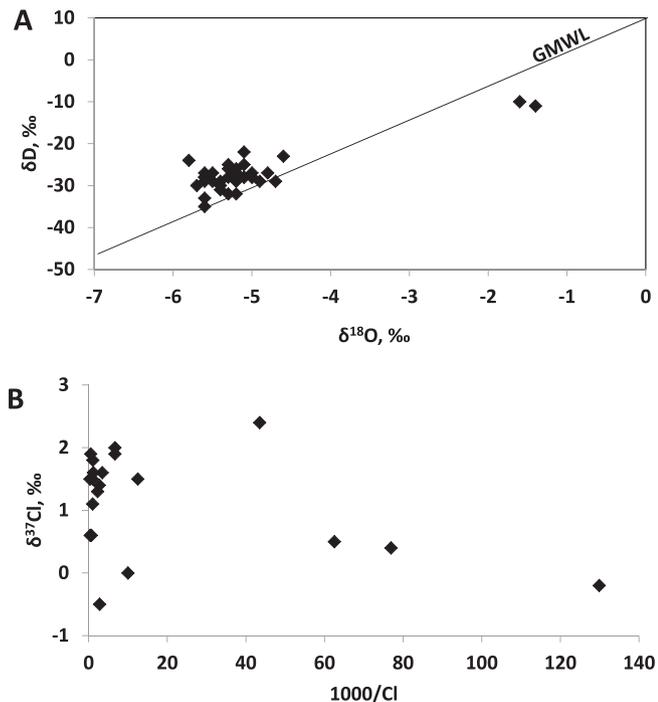
Fig. 4. Isotope data for groundwater samples from the Wake-Chatham site, North Carolina. A: δD vs. δ18O; B: δ37Cl vs. 1000/Cl (concentrations in mg/L). GMWL = global meteoric water line.

4.3. Tucson Basin, Arizona

Tucson Basin is a typical fault-bounded Neogene basin of the semiarid Basin-and Range Province of western North America. It is at present an open basin, part of the Santa Cruz River catchment.

The upper 300 m of basin-fill sediment, from which the groundwater samples reported here were collected, consist of poorly-consolidated alluvial and fluvial sands and gravels. Gypsum/anhydrite evaporite is present at depths of 240−750 m in the central western part of the basin, but no halite was reported (Anderson, 1987). The isotope hydrology of the basin was described in Eastoe et al. (2004). Measurements of $\delta^{37}Cl$ were made on 29 of the samples used in that study. The data are presented here (Table 1) as an example of the distribution of $\delta^{37}Cl$ in a non-marine basin with groundwater that has dissolved little halite. The $\delta^{37}Cl$ data show no apparent relationship to other isotope parameters (listed in Eastoe et al., 2004). The average $\delta^{37}Cl$ for the sample set is 0.1 ± 0.3 (1σ). Soil chloride from the vadose zone away from major washes (Kayaci, 1997) has a mean $\delta^{37}Cl$ value of -0.4 ± 0.5 (1σ, n = 7).

4.4. Safford Basin, Arizona

Safford Basin is another semiarid basin of the Basin and Range Province. New Cl isotope data, along with data from Harris (1999), are listed in Table 1. Sample locations are shown in Fig. 2, panel S. The samples may be classified into three broad groups: 1. surface water in the Gila River; 2. chloride samples originating from un-weathered sediment (groundwater samples, and salty clay from drill core or from unweathered sediment excavated at the surface); and 3. halite collected from weathered surface crusts.

A surface crust at Watson Wash was sampled in detail because of a single high $\delta^{37}Cl$ value discovered at the site during the initial sampling of Harris (1999). The new sampling provided 12 samples spanning the vertical extent (approximately 10 m) of the horizontally-bedded outcrop, and two horizontal profiles into the surface crust, at 15 and 30 cm from the surface; the 30 cm sample in each case was in unweathered material. The unweathered material consists of dense, bedded, expandable, salty clay that expands energetically when placed in water. The weathered crust is the result of gradual hydration of the clay exposed to rainwater. It has a rough, somewhat porous surface texture, and contains cavities in which bladed halite crystals up to 1 cm long occur. Other weathered-crust halite samples come from salty patches on silici-clastic and carbonate units of the basin fill, and in one case (site S1) a thin ochre bed.

Surface water and chloride from unweathered basin sediment have a relatively narrow range of $\delta^{37}Cl$, $0.0 \pm 0.7‰$, in stark contrast to the range for weathered crusts, namely $+0.7$ to $+5.5‰$, with a single outlier, $-2.3‰$ at the ochre occurrence (Fig. 5).

4.5. Closed basins, western USA

The Red Lake salt mass, of volume up to 400 km³ on the basis of gravity data (Peirce, 1972), occurs in non-marine sediment of Pliocene or earlier age in the Hualapai Valley, Arizona (Peirce, 1976). The mass consists almost entirely of halite. Another large halite body, the Luke Salt of possible volume 60−120 km³, underlies a mantle of alluvial-fluvial sediment in the Salt River Valley about 27 km west-northwest of Phoenix, Arizona. The age is Pliocene or earlier. Low Br concentrations indicate a non-marine origin, and much of the salt may have been subject to halokinesis (Eaton et al., 1972). In both cases, the source of such large amounts of salt in a continental setting is problematic. Three samples from the Red Lake salt gave $\delta^{37}Cl$ values of 0.5, 0.6 and 0.7‰. Three samples from the Luke salt had $\delta^{37}Cl$ values of 0.3‰.

Single samples from closed basins gave the following values of $\delta^{37}Cl$: water from Pyramid Lake, Nevada (a permanent water body fed by springs and a perennial river), $-0.1‰$; halite from a small playa near Kelso, California, $+0.5‰$; halite from the Badwater salt flat at the lowest point of Death Valley, California, 0.0‰. A salt crust
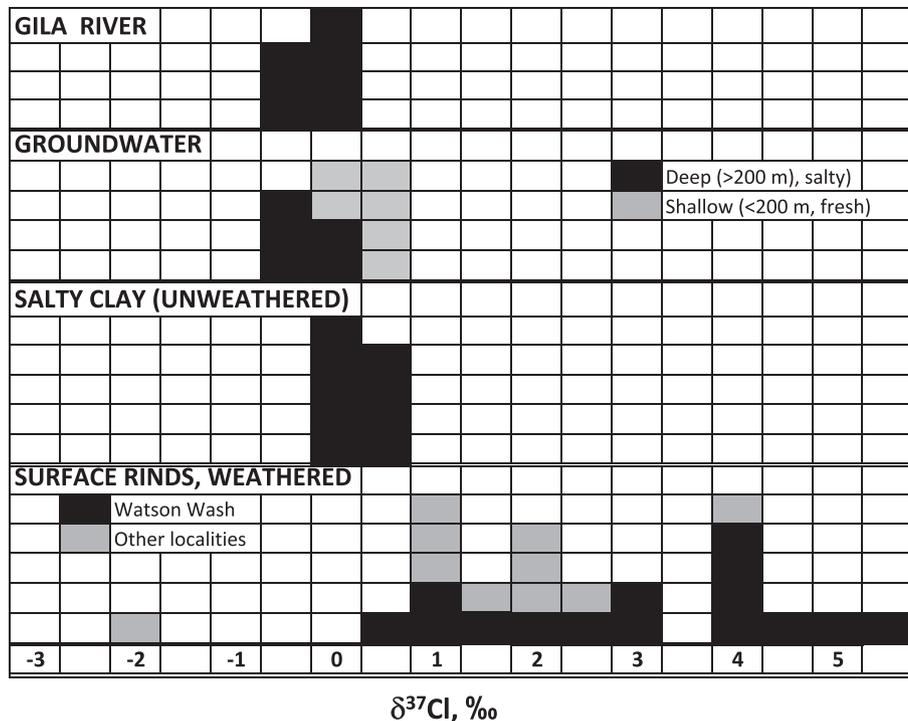
Fig. 5. Frequency histogram of δ^{37}Cl data for water and halite samples from Safford Basin, Arizona, including data from Harris (1999).

from weathered Jurassic Entrada Sandstone near Kodachrome State Park, Utah, gave a δ^{37}Cl value of $+3.3$‰.

4.6. Halophyte plants

Seven measurements of δ^{37}Cl in chloride, representing four halophyte species belonging to four different plant families, have a range of -2.1 to -0.8‰ (Table 2). The sample set includes mangroves that extract water from seawater assumed to have a δ^{37}Cl value of 0.0‰.

5. Discussion

5.1. Implications of available data

Lacustrine brine and halite have a natural range of δ^{37}Cl values of about -1 to $+3$‰. Lower values in brine from the Qaidam Basin appear to result from a human-caused perturbation, the discharge of oilfield brine into some of the lake basins (Liu et al., 1997). The examples described above include several lake basins in which higher positive values of δ^{37}Cl ($+1$ to $+3$‰) are characteristic, but in other cases, near-0‰ values or lower negative values (<-1‰) are the rule. The higher and lower δ^{37}Cl values represent large

fractionations for natural chloride-dominated systems. An adequate explanation of these observations must allow for the occurrence of large Cl isotope fractionation in certain basins, but not in others.

In the IHZ at China Lake, California, the highest δ^{37}Cl values appear to be characteristic of the brine and evaporitic salt associated with an ancient playa, not of the groundwater of the broader catchment basin. The latter is largely water conveyed from the Sierra Nevada in the Owens River, evaporated to different degrees, and exposed to soluble salts in the playa vicinity. An alternative explanation, that the high δ^{37}Cl values represent a basin-wide average of high δ^{37}Cl values in catchment bedrock or in rain, is not supported by δ^{37}Cl data for groundwater in the playa catchment, because all of the δ^{37}Cl values in the sample set are more negative than that of the most concentrated brine. The role of diffusion in generating the range of δ^{37}Cl in the high-chloride SHZ, IHZ and DHZ samples must be minor, first, because most of the range is present in samples with high chloride content (Fig. 3B) and second, because the high-δ^{37}Cl samples in the IHZ are from thin sand aquifers separated by thicker clay aquicludes that would inhibit rapid diffusion away from the sandy aquifers, and are most likely the source of any dissolved salt. Values of δ^{37}Cl value in the IHZ range down to -1‰, this value appearing in dilute

Table 2
Chlorine isotope data, halophyte plants.

Date	Common name	Species	Family	Location	Latitude	Longitude	Fraction	δ^{37}Cl, ‰
1995	Black mangrove	*Avicenna germinans*[a]	Aviceniaceae	El Sargento, Sonora, Mexico	29.3246	−112.3416	Excreted halite	−1.4
1998	Black mangrove	*Avicenna germinans*[a]	Aviceniaceae	El Sargento, Sonora, Mexico	29.3246	−112.3416	Excreted halite	−1.3
1998	White mangrove	*Laguncularia nucemosa*[a]	Combutaceae	El Sargento, Sonora, Mexico	29.3246	−112.3416	Excreted halite	−1.0
1998	Saltbush	*Sarcobatus vermiculatus*[a]	Sarcobataceae	Pima, Arizona, USA	32.89	−109.82	Sap	−1.5
1998	Salt cedar	*Tamarix* sp.	Tamaricaceae	Clifton, Arizona USA	33.0617	−109.3006	Excreted halite	−1.2
1998	Salt cedar	*Tamarix* sp.	Tamaricaceae	Eden, Arizona, USA	32.95	−109.90	Excreted halite	−2.1
1998	Salt cedar	*Tamarix* sp.	Tamaricaceae	Tucson, Arizona, USA	32.2473	−110.9542	Excreted halite	−0.8

[a] Indentifed by L.J. Toolin.

groundwater (<15 mg/L Cl). Low values of δ^{37}Cl in water of low chloride content could result either from diffusion, or from dissolution of salt with low δ^{37}Cl. These observations imply a fractionation mechanism in some way associated with lacustrine processes and responsible for the high δ^{37}Cl, rather than high δ^{37}Cl chloride being leached from rock in the catchment or generated by diffusive loss of ^{35}Cl.

At the Deep River Basin site, low-salinity water with δ^{37}Cl values near 0.0‰ may contain precipitated marine aerosol. The most saline groundwater, with 150−3125 mg/L of Cl, has a δ^{37}Cl range of −0.5 to +1.8‰, with most values greater than 1‰. There is no indication from O and H isotope data of systematic evaporation to explain the high salinities (Fig. 4A), and no systematic relationship between δ^{37}Cl and Cl concentration (Fig. 4B). A rock source of chloride is required, and such a source is most unlikely to lie in the permeable, well-flushed sandstone and conglomerate redbeds. If the suggestion of a source in salty mudstone units is correct, then the high salinities reflect a combination of advective and diffusive transport of chloride away from the rock sources. In that case, the higher δ^{37}Cl values in groundwater will be close to those of the rock source, while lower δ^{37}Cl values, particularly those in more dilute groundwater, may be influenced by diffusion. The data set suggests a chloride source with a range of δ^{37}Cl, mainly +1 to +2‰, within the sedimentary rocks of the basin.

The higher values of δ^{37}Cl in halite (>+3‰) are limited to the specialized environment of weathered crusts on salty sedimentary rock, a point that is emphasized by comparing the different kinds of salt in Safford Basin, where all sampled chloride that has not been subject to weathering has a narrower δ^{37}Cl range of 0.0 ± 0.7‰. This observation calls for a fractionation mechanism that operates in the weathering environment. Diffusion under specialized circumstances may be the mechanism, and will be discussed below.

Arcuri and Brimhall (2003) proposed that the original salt in the Quebrada Chug Chug (QCC) and San Salvador mudstones was marine, and that diffusion could explain the low observed δ^{37}Cl values. Such an explanation is problematic for the following reasons. 1. In a diffusing system, the fugitive chloride has lower δ^{37}Cl values and concentrations than those of the salty reservoir from which it diffuses (Fig. 5). If diffusion, operating on near-0‰ marine chloride, were responsible while the mudstone still contained pore water, then only fugitive chloride has been preserved. This is an unlikely circumstance, because it would require selective expulsion of the pore water that was most concentrated in chloride. 2. It is difficult to introduce large amounts of salt into mudstone after deposition. 3. Lateral diffusion at a scale of kilometers (in the case of QCC) within an argillaceous stratum is difficult; more probable is diffusion at a scale of meters to tens of meters, normal to the stratum boundaries, leading to loss of fugitive chloride into more permeable enclosing strata. An alternative, and simpler, interpretation is that the salt is evaporitic, was deposited with the mudstone in a non-marine basin in which earlier halite was reworked (leading to the high Cl/Br values, Fig 1B), and has been preserved with zoned δ^{37}Cl and Cl/Br values close to those at deposition.

All of the data reviewed and discussed above pertain to continental basins that are at present arid or semiarid, or more ancient basins in which the geology (particularly the formation of halite or salty sediment) implies arid climate. Strong Cl isotope fractionation, leading to both positive and negative δ^{37}Cl values, has been observed in many of the basins with halite, but not in the low-salinity groundwater of Tucson Basin, where no halite has been reported. The rest of the Discussion will center on possible isotope fractionation processes related to the formation and evolution of halite in interior basins.

5.2. Cl isotope fractionation: watershed source effect, or lacustrine process?

Two possible explanations for lacustrine basins with higher positive δ^{37}Cl values can be considered. On the one hand, certain watersheds may contain rock sources of chloride with δ^{37}Cl > +1‰, while others do not. On the other hand, a process associated with the formation of lacustrine halite may lead to Cl isotope fractionation in certain basins, but not in others.

Marine evaporite strata and granitoid containing Cl-bearing silicate minerals are likely to be common rock-chloride sources in lacustrine basins. The former cannot provide bulk chloride with δ^{37}Cl > +0.5‰ or < −0.5‰. A granitoid source could provide bulk chloride with δ^{37}Cl near +2‰ (Eastoe and Guilbert, 1992; Arcuri and Brimhall, 2003), but is unlikely to do so in quantity sufficient to match the supply of chloride dissolved in rainwater, as shown by the following calculation.

Consider a 1 km^2 area of granitoid outcrop in a basin receiving 250 mm of rain annually, making a total rainwater volume of 25×10^{10} cm^3. If average rainwater contains 1 mg/L of Cl (as in Tucson, Arizona; Gu, 2005), the annual supply of Cl is 2.5×10^5 g.

The granitoid has a density of 2.7 g cm^{-3}, and contains 0.022% Cl (Kuroda and Sandell, 1953), so that 1 cm^3 of rock contains about 6×10^{-4} g of Cl. Therefore the amount of rock containing the same amount of Cl as a year's rainwater is 4×10^8 cm^3, corresponding to a layer 0.04 cm thick over the 1 km^2 area of interest. Matching the rate of Cl supply in rainwater would therefore require an erosion rate averaging 0.04 cm/a, or 400 m/Ma, a value about 1 order of magnitude higher than erosion rates proposed for the Sierra Nevada batholith, a granitoid occurrence of very high relief and therefore high erosion rate (Riebe et al., 2001).

Granitoid chloride is therefore unlikely to be available in sufficient amount to dominate the chloride supply to a playa in a granitoid terrain, and thereby account for evaporitic halite with δ^{37}Cl near +2‰. This is consistent with data from two catchments in which granitoids are abundant: China Lake, where background chloride in groundwater appears to have δ^{37}Cl near −1‰, and Tucson Basin, where δ^{37}Cl in groundwater is near 0‰. A fractionation mechanism associated with the formation of lacustrine halite is therefore required to explain high δ^{37}Cl values. Note, however, an opposite indication in the Qaidam basin, where a single stream water sample was found to have high δ^{37}Cl (Liu et al., 1997). In that case, dust from playas cannot be excluded as a source of chloride in the stream water.

5.3. Geological fractionation mechanisms

Known mechanisms for fractionating Cl isotopes in water-salt systems under near-surface conditions include equilibrium fractionation between crystalline halite and its solution (Eggenkamp et al., 1995, 2016; Luo et al., 2014), and kinetic fractionation associated with diffusion (Eggenkamp et al., 1994; Eggenkamp and Coleman, 2009).

Starting with near-0‰ chloride, a single application of halite-solution fractionation is incapable of producing the extreme δ^{37}Cl values reviewed here, given a Cl isotope fractionation factor of +0.30 ± 0.05‰ (the variance-weighted mean of two statistically-consistent estimates from Eggenkamp et al., 1995 and Eggenkamp et al., 2016).

The time required to generate a diffusion gradient and extract low-δ^{37}Cl in a single diffusion event can be estimated from the linear case of Fick's second law of diffusion, for which the solution (Senftle and Bracken, 1955) is:

$$C_x/C_o = 1 - \text{erf}(n) \tag{1}$$

where c_o is the initial chloride concentration of a reservoir of chloride, and c_x is the chloride concentration at distance x along a diffusion gradient emanating from the reservoir. "Erf" is the error function (Harvard University Computation Laboratory, 1952), and

$$n = \frac{x}{2\sqrt{Dt}} \tag{2}$$

D is the Fick's Law diffusion coefficient, and t is time. Values of D, designated D^{35} and D^{37} for the Cl isotopes of mass 35 and 37, differ slightly. As has been shown elsewhere (e.g. Eastoe et al., 2001), the isotope fractionation

$$\Delta^{37}Cl = \delta^{37}Cl_x - \delta^{37}Cl_o \tag{3}$$

at (x, t) due to diffusion, with $\delta^{37}Cl_o = 0‰$, can be expressed

$$\Delta^{37}Cl = 1000\left(\frac{1 - \text{erf}(n, 37)}{1 - \text{erf}(n, 35)} - 1\right) \tag{4}$$

where $(n, 35)$ and $(n, 37)$ denote the values of n for isotopes of mass 35 and 37, respectively. Using D^{35} (diffusion coefficient for mass 35) = 1.0017×10^{-9} m^{2}s^{-1} and $D^{35}/D^{37} = 1.0017$ (values for surface temperatures, near 21 °C, based on the gel diffusion experiments of Eggenkamp and Coleman, 2009), the diffusion profiles in Fig. 6A were calculated. Neglecting small corrections for tortuosity, these show that diffusion of chloride ion in aqueous solution can remove low-δ^{37}Cl chloride from a source reservoir over distances of a few cm over periods of 1–10 days, a time scale that will be useful in the following discussion. Similar diagrams in Eastoe et al. (2001) give diffusion profiles for longer time scales.
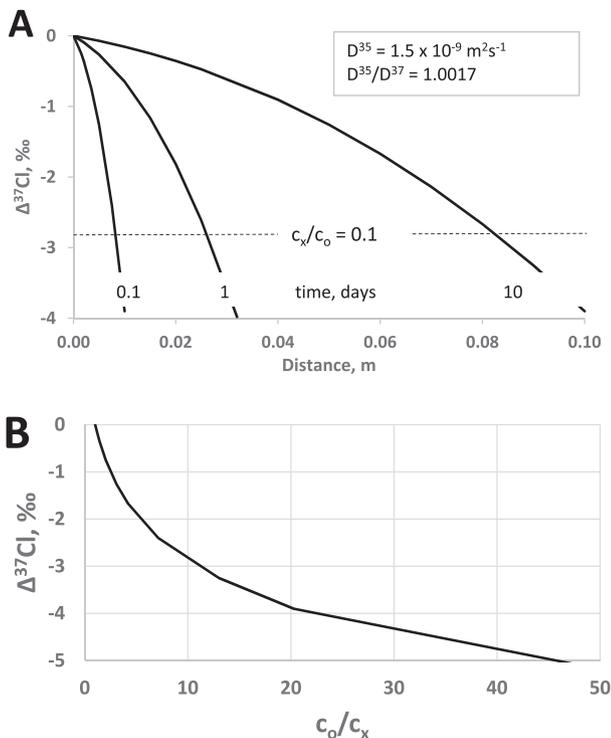
Fig. 6. Calculated diffusion profiles of δ^{37}Cl into pure water next to a source reservoir with δ^{37}Cl = 0.0‰. A: Δ^{37}Cl as a function of distance from the reservoir; B: Δ^{37}Cl as a function of c_o/c_x.

Starting with a source reservoir of near-0‰ chloride, diffusion can produce negative values of δ^{37}Cl in fugitive chloride, and positive values in the residual source chloride. However, fugitive chloride with strongly negative δ^{37}Cl is commonly produced in small quantity relative to the source reservoir (Fig. 6B). A small source reservoir may evolve to higher values of δ^{37}Cl as a result of diffusion of chloride out of the reservoir, but a large source reservoir undergoes only a small increase in δ^{37}Cl in a single application of diffusion.

Ion filtration, or ultrafiltration, is a special case of diffusion in which back-diffusion of chloride excluded on the upgradient side of a filtering membrane (e.g. a clay aquiclude in the geological context) generates high δ^{37}Cl values in concentrated chloride solution near and within the membrane (Phillips and Bentley, 1987). A large pressure difference across the membrane is required to drive ultrafiltration.

To these mechanisms may be added fractionation of chloride species in acidified marine aerosol in the atmosphere. Values δ^{37}Cl in rainwater chloride may reflect a complicated set of interactions between marine aerosol, which has a δ^{37}Cl range from −0.9 to +2.4‰, depending on particle size (Volpe et al., 1998), HCl evolved from acidified aerosol and residual HCl in water droplets. Δ^{37}Cl$_{\text{HCl (gas)-HCl (aq)}}$ is about +1.4 at sub-boiling temperatures (Sharp et al., 2010). Under some circumstances, rain with δ^{37}Cl values between −3.5 and −1.2‰ is observed at inland sites (Kohler and Wassenaar, 2010; Liu et al., 2008). Positive values, near +1.5‰ have been reported for single samples from Xi'ning, Xiamen and Nanhai in China (Sun et al., 2004).

Processes associated with igneous intrusion and the expulsion of magmatic volatiles as complex salt-water mixtures are capable of producing chloride with δ^{37}Cl up to +2‰ in phyllosilicates from granitoids in porphyry copper deposits (Eastoe and Guilbert, 1992; Arcuri and Brimhall, 2003). As explained above, such chloride sources are unlikely to predominate in arid basins.

In the absence of alternatives, one or more of the known mechanisms must act to generate each of the instances of extreme fractionation. Single−pass applications of the crystallization and diffusion mechanisms are inadequate, but cumulative incremental changes resulting from multiple passes can be considered. For the crystallization mechanism, an analogous effect is known in sulfate-(S, O) isotope systems, e.g. where cyclic dissolution and partial recrystallization of gypsum produce increases in the δ^{34}S and δ^{18}O of sulfate in the final gypsum (Lu et al., 2001; Gu, 2005). To be efficacious in producing a fractionated reservoir such as the halite in a dry lake, the mechanism must succeed not only in fractionating the isotopes, but also in effecting an enduring spatial separation of the enriched and depleted fractions.

5.4. The mechanism of fractionation in halophyte plants

Halophyte plants are common in areas where salt accumulates in closed basins. The following account is based on Krishnamurthy et al. (2014) and Scholander et al. (1962). Uptake of water in salt-excreting halophytes is accompanied by partial exclusion of salt in their roots. Any salt intake is counteracted by excretion of salt on leaves or in dead tissue. The mechanism of exclusion is not fully understood, but in mangroves appears to involve the presence of biopolymers within endodermal root tissue. The biopolymers are porous at molecular scale, and permit the passage of water molecules while greatly limiting the passage of Na$^+$ and Cl$^-$ ions. The biopolymer layers are strengthened by mangroves in response to increased salt stress under experimental conditions. A pressure gradient exists across the biopolymer layer, but is too low to drive ultrafiltration. The exclusion of salt leads to formation of halite crystals in the root cortex, sandwiched between the exodermal and

endodermal layers of the root. This process superficially resembles the ion filtration (ultrafiltration) mechanism for Cl isotope fractionation (Phillips and Bentley, 1987), but in addition to lacking a cross-membrane pressure difference sufficient for ultrafiltration, it also lacks the possibility of back-diffusion upgradient of the membrane, as indicated by the trapping of salt and the formation of crystals within the cortex. Isotope fractionation in this case appears consistent with diffusion, driven by the concentration gradient between concentrated cortical salt solution and the relatively dilute root sap, and producing negative values of $\delta^{37}Cl$ in plant sap.

The salt exclusion mechanism described here has been proposed for mangroves, and an isotope effect has been observed in salt excluded by mangroves from the Gulf of California (Table 2). Mangroves do not occur in arid interior basins. The same chloride exclusion mechanism operates in other plant families (Krishnamurthy et al., 2014), and is likely in the genera *Tamarix* and *Sarcobatus* that were sampled in southern Arizona and show similar fractionation of Cl isotopes (Table 2). Halophyte salt exclusion cannot effect a long-term spatial separation of different fractions of chloride, because excreted chloride continually returns to the soil around the plant in rainwater that rinses salt from leaves, or in fallen dead plant matter.

5.5. Cumulative fractionation in vadose playas

Hibbs and Darling (2005) re-examined the concepts of open and closed continental drainage basins, noting that a basin that appears closed from the standpoint of surface topography can discharge groundwater to a neighboring basin, given appropriate hydrogeology. If the bottom of a playa lake in a closed basin lies above the local water table, the lake can potentially lose water into the local regional aquifer, resulting in permanent removal of the infiltrated water from the basin. Such downward discharge of water from playas has been documented (Scanlon and Goldsmith, 1997). This type of playa is termed vadose, in contrast to phreatic playas, in which the lake bottom lies below the water table, and groundwater discharges into the lake. A phreatic playa can discharge water only by evaporation, so that the bulk $\delta^{37}Cl$ value remains the same as the bulk $\delta^{37}Cl$ of the water sources, whether or not crystallization of salt occurs. In a vadose playa that forms a halite crust in summer, there is Cl isotope fractionation between the halite and the underlying pool of brine, so that loss of part of the brine to the regional aquifer during the summer leaves the remaining salt in the playa very slightly enriched in ^{37}Cl (Fig. 7). Repetition of the cycle can gradually change $\delta^{37}Cl$ of the salt remaining in the playa.

To estimate how long this cyclic process might take to arrive at a playa with a bulk $\delta^{37}Cl$ of $+2$‰, let us suppose the following. A lake basin ceases to discharge surface water at a time of change from wet to dry climate. Water entering the lake and lake water both have $\delta^{37}Cl = 0$‰.

In the new regime, rain occurs in winter only. Progressive desiccation eventually causes the water table to fall below the lake bed, and the lake water to reach saturation in NaCl each summer, forming a halite crust with brine beneath. The lake, which has become a vadose playa initially containing 1 mass unit of salt, passes through one summer cycle, during which:

The fraction of the NaCl in the brine beneath the halite crust = f, so that the fraction in the halite is $1-f$.

The fraction of underlying brine lost by discharge into the underlying aquifer = q.

The fraction of NaCl remaining in brine at the end of summer = $f(1-q)$.

During the following winter cycle, an amount A of NaCl, with $\delta^{37}Cl = 0$‰, is added to the lake. It is assumed that all of A arrives in the first winter runoff. A is larger than the amount of NaCl lost annually to vadose-zone discharge; otherwise, the lake water will gradually become fresh.

All NaCl is in solution during the winter, so that winter vadose discharge does not change the bulk $\delta^{37}Cl$ of the lake. In early winter, the lake contains this amount of halite:

$$f(1-q) + (1-f) + A$$

Considering isotope balance:

$$\delta\prime[f(1-q) + (1-f) + A] = \delta_{brine}(f)(1-q) + \delta_{halite}(f) + \delta_A(A)$$

Where.

$\delta\prime$ is $\delta^{37}Cl$ of bulk NaCl in the lake in early winter, after one annual cycle

$\delta_{brine} = \delta^0 + \varepsilon\ln(f)$ is $\delta^{37}Cl$ of brine after formation of salt crust, according to Rayleigh fractionation

δ^0 is the starting value of $\delta^{37}Cl$ in the lake water in each cycle

$\delta_{halite} = \frac{1}{1-f}[\delta^0 - f(\delta^0 + \varepsilon\ln(f))]$ is $\delta^{37}Cl$ of the bulk salt crust formed during each cycle

$\delta_A = 0$‰ is $\delta^{37}Cl$ of the annual addition of NaCl to the basin

and ε is the Cl isotope fractionation between halite and its solution, $+0.30 \pm 0.05$‰.

Fig. 8 shows values of $\delta\prime$ - δ^0, the annual increment of $\delta^{37}Cl$, as a function of $(1-f)$, the fraction of salt in the halite crust, for chosen
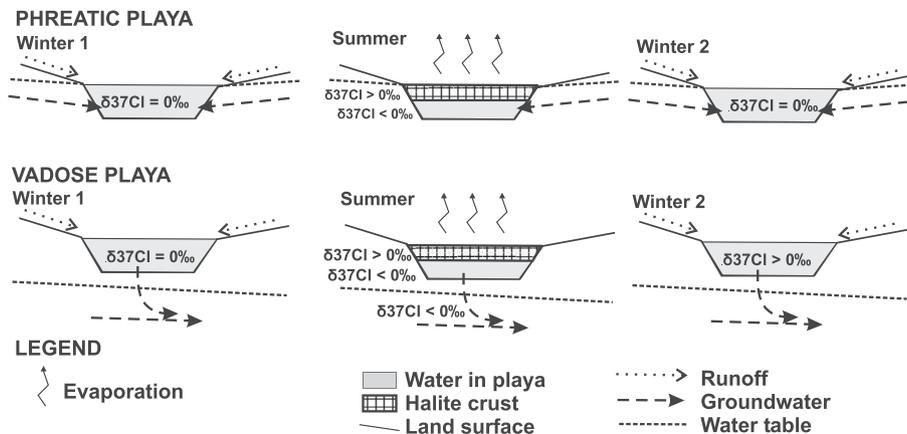
Fig. 7. Schematic cross-sections of phreatic and vadose playas, illustrating the effect of one cycle of seasonal change (as discussed in the text) on playas with initial $\delta^{37}Cl = 0.0$‰.

values of q, with A set at 2q in each case. Larger values of A lead to smaller increments. For the chosen conditions in the figure increments of up to 0.005‰ are possible in a year, and the calculated increments do not depend on the value of δ^0. Higher increments are possible for large values of (1−f) and q. Similar increments over hundreds to thousands of cycles of wetting and drying could generate $\delta^{37}Cl$ values of +2 to +3‰ in salt or brine in a vadose playa. Such time scales are reasonable in basins that have undergone annual wetting and drying since the early Holocene. The scenario adopted for the calculation above is relatively simple; more complicated scenarios and equations can be envisaged, e.g. overlap of addition of salt from the catchment with formation of halite. This simple scenario demonstrates approximately the magnitude of an annual increment and the time required to effect the observed changes in $\delta^{37}Cl$.

This mechanism can generate a spatial separation of chloride fractions differing in $\delta^{37}Cl$. The high-$\delta^{37}Cl$ chloride fraction may persist for tens of millions of years (e.g. Meng et al., 2014). Even though a corresponding bulk fugitive chloride fraction with negative $\delta^{37}Cl$ must be generated, it is unlikely to concentrate into a reservoir with low $\delta^{37}Cl$ because it is lost gradually from the playa into a groundwater system of regional extent.

Playas that discharge water only by evaporation would undergo no cumulative increase in $\delta^{37}Cl$. In the western USA, an example is in the lowest part of Death Valley, California, where groundwater flow to adjacent basins is precluded by the low elevation of the playa, below sea level in this case. Another example is Pyramid Lake, Nevada, which is also at the lowest point of the regional Lake Lahontan basin, and which does not at present form halite evaporite. An example of a playa with cumulative increase in $\delta^{37}Cl$ is Indian Wells Valley at China Lake, where halite evaporite appears to have formed in the past, and where subsurface groundwater flow into a downgradient basin has been postulated. In general, high values of $\delta^{37}Cl$ in closed basins appear to serve as indicators of the presence and the degree of vadose-zone discharge.

5.6. Cumulative fractionation in weathered rinds

The weathered rinds at Watson Wash in Safford Basin are the parts of the expandable-clay sediments that have been exposed to rainwater. While the rinds are up to 30 cm thick, the presence of halite at 10 or more cm beneath the outer surface indicates that rainwater seldom flushes the entire rind; rather, regular wetting to depths of a few cm is characteristic. Under such conditions, a concentration gradient between saturated solution deep in the rind

Fig. 8. Calculated annual increments ($\delta' - \delta^o$) in $\delta^{37}Cl$ in a vadose playa as a function of fraction (1 − f) of halite crystallized and fraction (q) of brine discharged during summer.

and low-chloride rainwater near the surface can be established. Chloride with $\delta^{37}Cl$ values lower than those of the salt deep within the rind can potentially be transported to the rind surface layer, where it can be flushed away in runoff. Salt remaining deeper in the rind will gradually become enriched in ^{37}Cl if the process of wetting and outward diffusion is repeated many times.

Diffusion occurring in a few days over distances of a few cm (Fig. 5A) is reasonable for the wetting/drying cycles affecting the weathered rinds at Watson Wash. Each rain event large enough to generate runoff would remove some low-$\delta^{37}Cl$ salt (remaining as halite near the dry rind surface, following the previous rain event and subsequent drying), and would wet the outer few cm of rind, initiating a new episode of surface-directed diffusion of chloride. A single application of the process is unlikely to change $\delta^{37}Cl$ of salt deeper within the rind by a measurable amount. However, repeated application of this process, many times per year over periods of decades to centuries, could eventually lead to measurable enrichment in ^{37}Cl in the salt deeper in the rind as a result of continual removal of chloride with low $\delta^{37}Cl$. Such enrichment will dominate the isotopic evolution of the rind salt, provided the growth of the rind (by wetting penetrating to its base, consequent hydration of salty unweathered clay, and addition of new near-0‰ salt to the rind) is slow relative to the operation of the diffusion effect within the rind. If a steady state is maintained with respect to the amount of salt in the rind (i.e. the amount of salt removed at each wetting is exactly balanced by an addition from unweathered rock), then the increases in $\delta^{37}Cl$ are self-limiting, for the following reason. Consider a volume of rind losing a fraction f of chloride with $\delta^{37}Cl$ n ‰ lower than the original bulk $\delta^{37}Cl$ of the volume, and then receiving an addition a fraction f of 0‰ chloride from unweathered rock. A small enrichment of the volume occurs at each wetting step until $\delta^{37}Cl$ of the volume reaches a value of n‰. At that point, the effects of losing chloride by diffusion and gaining an identical amount from unweathered rock cancel each other.

A process similar to this simple situation appears to occur in an uneven fashion at Watson Wash, resulting in $\delta^{37}Cl$ values of +0.7 to +5.5‰. To reach a particular value n of $\delta^{37}Cl$, it is necessary to remove small fractions of salt with $\delta^{37}Cl$ > n at each wetting step. Similar effects occur elsewhere in Safford Basin and near Kodachrome State Park in Utah, where salt crusts form on other sediment types (sandstone, siltstone), but where a discrete weathered rind is not visible.

The proposed cyclic diffusion mechanism is able to produce localized halite concentrations with high $\delta^{37}Cl$ values in the short term (years to centuries?), but it is not in general capable of effecting a long-term separation of chloride reservoirs differing in $\delta^{37}Cl$, or of supplying a sedimentary basin with chloride of low $\delta^{37}Cl$ value, even in the short term. Diffusion operating on the near-0‰ chloride in unweathered sediments of Safford Basin results in the separation of chloride with a bulk $\delta^{37}Cl$ value less than 0‰, but the separation is gradual, and the fugitive chloride is readily diluted by other sources of chloride, e.g. from dust, from saline groundwater and from erosion of salty sediment without any diffusive fractionation. In Safford Basin, where active Cl isotope fractionation is occurring in weathering rinds over much the basin, no $\delta^{37}Cl$ values lower than −0.4‰ have been observed in river water or groundwater. In the long term, the high-$\delta^{37}Cl$ chloride is certain to be eroded away and recombined with the fugitive chloride, either in a downstream basin or in the oceans.

5.7. Basins with negative $\delta^{37}Cl$

Neither the vadose playa mechanism nor the weathering-rind diffusion mechanism as presented here appears to be capable of generating the more extreme low $\delta^{37}Cl$ values ($\leq$−1‰) in the
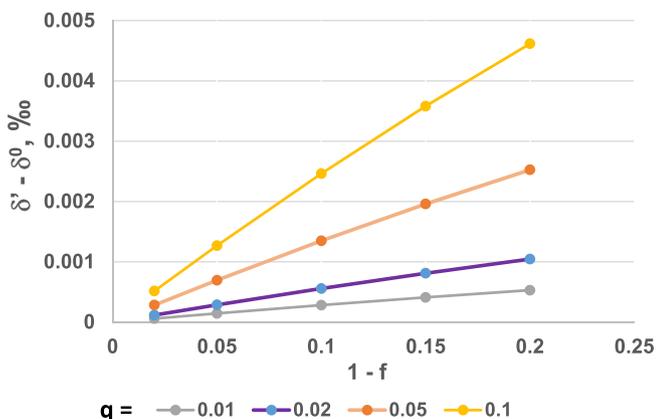
Qaidam Basin, at China Lake and in northern Chile. At present, possible mechanisms for generating large quantities of chloride with $\delta^{37}Cl < -1‰$ in continental basins appear to be: 1. the concentration of fractionated rainwater chloride, and 2. the expulsion to the surface of low-$\delta^{37}Cl$ formation waters. The fractionated chloride of mechanism 1 is not present in all interior basins without halite (e.g. Tucson Basin). Low-$\delta^{37}Cl$ formation waters are known in marine sedimentary basins (Eggenkamp, 1994; Eastoe et al., 2001), and similar formation waters are to be expected in sedimentary basins on land; however, mechanism 2 would require selective expulsion of low-$\delta^{37}Cl$ formation water that is generated locally by diffusion in the regional presence of higher-$\delta^{37}Cl$ formation water. In the continental setting, it might be possible to generate low-$\delta^{37}Cl$ formation water by passing fugitive chloride from a vadose playa through a series of hydrologically-connected vadose playas.

6. Conclusions

1. The range of $\delta^{37}Cl$ in lacustrine halite (including salty mudstone deposits) is broad, -3 to $+3‰$. Some halite deposits (e.g. western and central China) have only $\delta^{37}Cl$ values near 0‰, while others (western China, western USA) are characterized by more extreme positive $\delta^{37}Cl$ values ($>+1‰$), and, in two cases (western China and Chile), negative values.
2. The range of $\delta^{37}Cl$ in dissolved chloride in groundwater that has interacted with halite deposited in arid environments is also broad, -1 to $+2.4‰$. In two cases, the Deep River basin (North Carolina) and China Lake (California), values of $\delta^{37}Cl > +1‰$ are interpreted to represent halite-bearing mudstone and fossil evaporite brine, respectively.
3. Halite with $\delta^{37}Cl$ values ranging from $+0.7$ to $+5.5‰$ is present in weathered crusts of salty Neogene sedimentary rock in Safford Basin, Arizona. In chloride samples representing unweathered rock of Safford Basin, the $\delta^{37}Cl$ range is $0 \pm 0.7‰$.
4. Strongly fractionated rock sources of chloride are unlikely to explain extreme $\delta^{37}Cl$ values in continental lacustrine deposits.
5. Single-pass applications of known fractionating mechanisms (halite-solution equilibrium, diffusion) operating on ambient chloride with $\delta^{37}Cl$ near 0‰ are incapable of generating the more extreme ($>1‰$) observed $\delta^{37}Cl$ values reviewed here.
6. In vadose playas, small incremental changes in $\delta^{37}Cl$, repeated over hundreds to thousands of annual cycles of wetting and evaporation to form halite crusts, and resulting from downward discharge of evaporite brine, can generate lacustrine salt with $\delta^{37}Cl$ values of $+2‰$ or greater. Phreatic playas with no subsurface discharge will undergo no such isotope fractionation, whether or not halite is formed,
7. In the weathered crust of salty sedimentary rock, small incremental changes in $\delta^{37}Cl$ can result from outward diffusion of chloride depleted in ^{37}Cl, leaving an enriched salt reservoir at depth within the crust. Diffusion at a spatial scale of $1-10$ cm, and a time scale of days, is sufficient if repeated over many cycles of wetting and drying.
8. Cl isotope fractionation within halophyte plants that exclude salt during root uptake of water generates $\delta^{37}Cl$ values as low as $-2‰$ in salt excreted by the plants, but cannot lead to a lasting separation of distinct fractions of chloride.
9. Halite with negative $\delta^{37}Cl$ values ($\leq -1‰$) can at present be explained only by input of low-$\delta^{37}Cl$ chloride in precipitation.

This article serves as a review of existing chlorine isotope data for non-marine sedimentary basins. To date, the most significant data have emerged by accidental discovery in environmental and geological studies testing the general applicability of stable chlorine isotopes. Experimental replication of the cyclic fractionation mechanisms suggested here is feasible (by using a vessel with an outlet to represent a vadose playa, and by wetting and drying one side of a sample of salty sediment in the laboratory), but may be problematic in practice because of the number of cycles required to generate a measurable effect. Future advances in field studies are likely to result from (a) the careful selection of study sites, with attention to hydrology, (b) systematic collection of data for both bromine and chlorine, and (c) development of a better understanding of the behavior of chloride in the meteoric water cycle.

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