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

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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 ± 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 ± 0.5‰, with a few outliers to ± 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 ± 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

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
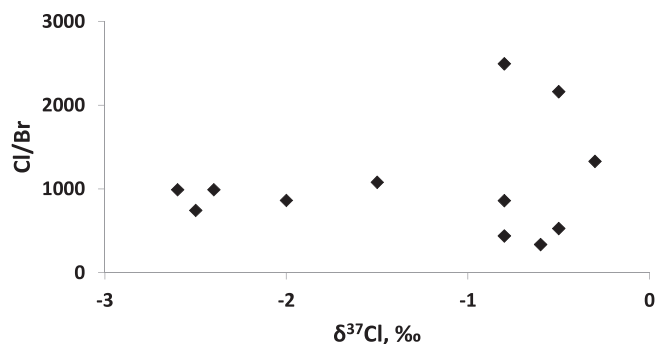

Fig. 1. Cl/Br (weight ratios) vs. $\delta^{37}Cl$ for salt from mudstone at Quebrada Chug Chug, Chile (data from Arcuri and Brimhall, 2003).

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