Chemical weathering processes in the Great Artesian Basin: Evidence from lithium and silicon isotopes

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ABSTRACT

Variations in lithium and silicon isotope ratios in groundwaters of the Great Artesian Basin in Australia, and the causes of these variations, have been explored. The chemistries of Li and Si in groundwater are influenced by the dissolution of primary phases, the formation of secondary minerals, and the reaction of solid phases with dissolved constituents, while isotopic variations are generated by uptake into clays, which preferentially incorporate the light isotopes. The lithium isotopic composition (expressed as δ^7Li) of the groundwaters ranges from $+9$ to $+16$‰, and clearly reflects changes in aquifer conditions. Reaction-transport modelling indicates that changes in Li concentrations are principally controlled by the ratio of the weathering rate of primary minerals to the precipitation rate of secondary minerals, whereas δ^7Li is affected by the extent of isotope fractionation during secondary mineral formation (which is dependent on mineralogy). The patterns of groundwater Si concentrations and δ^{30}Si values versus flow distance suggest that Si is at steady state in the aquifer. The δ^{30}Si value of most of the groundwater samples is close to -1‰, which is significantly lower than the δ^{30}Si value of the reservoir rocks (~ 0‰). Since precipitation of clays preferentially removes the light Si isotopes from solution, the most plausible explanation for these low groundwater δ^{30}Si values is addition of Si by dissolution of isotopically light secondary minerals. These data, together with model calculations, show that Li isotopes are extremely sensitive to changes in the chemical and physical conditions in the aquifer, whereas Si is not. Importantly, the model suggests that even in large aquifers with long fluid residence times, where steady-state would be expected to be reached, the concentrations and isotopic fractionation of trace elements are not controlled by Li adsorption. The model developed here provides a basis for using Li isotopes measured in groundwaters and surface waters to constrain weathering processes.

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1. Introduction

Chemical weathering, especially of silicate minerals, and the transport of dissolved material to the oceans via rivers and groundwaters, is thought to have a profound influence on Earth's climate, due to its sequestration of atmospheric CO_2 (Berner, 2003; Berner et al., 1983; Walker et al., 1981). Therefore, in order to understand the operation of the carbon cycle, the role of weathering processes must be quantified. Traditionally, radiogenic isotopes such as strontium have been used for this purpose, but the interpretation of these isotope systems can be ambiguous, because the isotope composition of the weathering products is primarily controlled by that of the host rock, and rarely provides any information on the weathering processes themselves (Oliver et al., 2003; Palmer and Edmond, 1989, 1992).

The stable isotopes of lithium (^{6}Li and ^{7}Li) are useful tracers of weathering processes, because the δ^7Li value of silicate rocks covers a very narrow range (MORB: 3–5‰; continental

crust $\sim 0‰$; Elliott et al., 2006; Teng et al., 2004; Tomascak et al., 2008), compared to that of rivers weathering the continental crust (6–42‰) (Huh et al., 2001, 1998; Kisakürek et al., 2005; Pogge von Strandmann et al., 2010, 2006a). Natural groundwaters tend to have δ^7Li that are lower than mean global rivers (Hogan and Blum, 2003; Meredith et al., 2013; Negrel et al., 2010, 2012; Tomascak et al., 2003). Studies have also shown that the Li budget of rivers is primarily determined by weathering of silicate rocks, even in carbonate-dominated catchments (Kisakürek et al., 2005; Millot et al., 2010). The Li cycle is not affected to any significant extent by biological activity: Li concentrations in plants are ~ 3–4 orders of magnitude lower than in soils or rocks, and plant growth appears to cause little isotope fractionation (Lemarchand et al., 2010). Congruent dissolution of rocks is also thought to cause negligible isotope fractionation; however, secondary minerals preferentially incorporate ^6Li, driving the isotope composition of residual waters to heavier values (Pistiner and Henderson, 2003; Vigier et al., 2008; Wimpenny et al., 2010). Thus the Li isotope composition of natural waters provides information on the balance of primary silicate dissolution (low δ^7Li, high [Li]) relative to secondary mineral formation (high δ^7Li, low [Li]) (Pogge von Strandmann et al., 2010). Also, because the elements involved in sequestration (C, Ca, Mg) must be transported to the oceans for long-term carbon storage to occur (assuming that storage in soil carbonates is not important), the information that Li provides on storage of material on the continents in secondary phases, relative to that transported to the oceans, can also be used to assess the links between weathering and CO_2 removal. For this reason, several studies have attempted to reconstruct past Li isotopic compositions of ancient seawater (Hall et al., 2005; Hathorne and James, 2006; Misra and Froelich, 2012; Pogge von Strandmann et al., 2013). However, in order for these records to be fully understood, Li behaviour in the weathering environment must be further examined.

Silicon isotopes (^{28}Si, ^{29}Si, ^{30}Si) can also be used as tracers of silicate weathering processes (Ding et al., 1996; Douthitt, 1982; Georg et al., 2006a, 2007; Ziegler et al., 2005). As for Li isotopes, secondary minerals preferentially take up light Si isotopes, driving residual waters to isotopically heavy compositions (De la Rocha et al., 2000) relative to the parental material (Savage et al., 2010). This fractionation is dependent on secondary mineralogy, as well as environmental conditions (Delstanche et al., 2009; Georg et al., 2009b; Opfergelt et al., 2009; Ziegler et al., 2005). However, unlike Li, Si isotopes in surface waters are also fractionated by biological processes, and the light isotopes are preferentially taken up by organisms such as diatoms (De la Rocha et al., 1997) and plant-forming phytoliths (Ding et al., 2005; Opfergelt et al., 2006). Consequently, while Si isotopes ratios have similar potential to Li isotopes for tracing weathering processes, both biological and weathering processes can generate heavy Si isotope signatures in waters.

Groundwaters are thought to transfer significant amounts of dissolved materials from the continents to the oceans, and can have a significant impact on the budgets of some elements and their isotopes in seawater. For example, it has been estimated that the groundwater Sr flux to the Bengal Basin is ~ 1.4 times the riverine flux (Basu et al., 2001), and in the same basin the Si groundwater contribution is $\sim 66\%$ of the riverine flux (Georg et al., 2009a). Geochemical processes occurring within groundwaters, including reactions with aquifer minerals, can also have a profound effect on water quality (Herczeg et al., 1991). The concentrations of trace elements and their isotopic ratios in groundwater are determined by inputs into the aquifer recharge zone and by water–rock reactions occurring within the aquifer itself. Thus, the examination of groundwaters can provide important information on aquifer chemical processes, such as weathering, secondary mineral formation, and groundwater transport times (Bethke et al., 2000; Burnett et al., 2006; Kenoyer and Bowser, 1992; Zektser and Loaiciga, 1993).

Here we report Li and Si isotope data for groundwaters and sediments from the Great Artesian Basin, Australia. This aquifer provides the opportunity to examine the behaviour of these isotope systems during fluid–rock interactions over very long distances (several hundred kilometres). The aim is to define the extent of Li and Si variations, and consider how changes in Li and Si concentrations and isotope compositions are coupled. This provides a basis for interpreting such data measured both in aquifers and surface waters. The aim is not to precisely constrain the processes occurring over the entire aquifer, requiring more intensive sampling and an analysis of an extensive set of geochemical parameters, but rather to establish how Li and Si isotopes behave in such groundwaters.

2. Field area and samples

The Great Artesian Basin (GAB), the world's largest confined aquifer, underlies an area of 1.7×10^6 km^2, which is $\sim 22\%$ of Australia (Mazor, 1995). The Basin extends beneath the arid and semi-arid regions of Queensland, New South Wales, South Australia and the Northern Territory, stretching from the Great Dividing Range to the Lake Eyre depression. The estimated total water storage of the GAB is 8.7×10^{15} l (Radke et al., 2000), which is $\sim 0.5\%$ that of the oceans. The aquifer consists of alternating layers of sandstone aquifers and relatively impermeable siltstones and mudstones. The proportions of these lithologies varies strongly within the aquifer, but the Hooray Sandstone has a composition of quartz of $90 \pm 8\%$, with remaining feldspar and lithics (Radke et al., 2000). The thickness of the Hooray Aquifer, the focus of this study, varies from less than 50 m at the Basin margins to over 800 m in the deeper parts of the Basin (Radke et al., 2000). There are Cenozoic volcanics in the Hooray Sandstone in the vicinity of Charleville (Collerson et al., 1988; Ewart, 1981, 1982).

Groundwater in the GAB flows generally westward to south-westward over most of the Basin but to the north-west and north in the north (Fig. 1). Average groundwater flow rates in the sandstones vary between 0.3 and 2.5 m/yr, and in the sampling area between 0.8–1.2 m/yr (Radke et al., 2000). Recharge by rainfall into the outcropping sandstone aquifers occurs mainly along the eastern margins of the Basin. Groundwaters from the GAB have been dated using a number of different techniques, including ^{81}Kr (Collon et al., 2000), ^{36}Cl (Love et al., 2000; Torgersen et al., 1991) and ^4He (Bethke et al., 1999; Lehmann et al., 2003). Water ages from the south-west of the Basin (near Lake Eyre) range between 230 and 890 kyr.

The field area for this study lies about 450 km east of Brisbane (Fig. 1). The sample sites extend for ~ 450 km on a northeast – south-west transect which approximately tracks the direction of groundwater flow (Radke et al., 2000). All samples, barring one, tap the artesian waters from the quartzose Jurassic Hooray Sandstone Formation (400–600 m deep in this area). The sample sites track the Augathella (near Charleville) to Eulo (near Cunnamulla) transect of the Hooray Aquifer conducted by the Bureau of Rural Sciences, Australia, which yields ^{36}Cl ages of ~ 100 kyr for every ~ 50 km flow (Radke et al., 2000). This area was chosen in order to obtain samples from close to the recharge zone, and then to examine flow over several hundred kilometres. Sampling locations and well names are given in Table 1. The sample from Charleville Bore #3 (830 m depth) is from a deeper aquifer level.

Samples of the Hooray Sandstone were obtained from core material recovered from the Wanaaring-1 stratigraphic test well,