Chemical Geology 393–394 (2015) 67–78

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Unravelling sources of solutes in groundwater of an ancient landscape in NW Australia using stable Sr, H and O isotopes

Shawan Dogramaci [a,b], Grzegorz Skrzypek [b,c,*]

[a] Rio Tinto Iron Ore, 152–158 St Georges Terrace, Perth, WA 6000, Australia
[b] West Australian Biogeochemistry Centre, School of Plant Biology, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia
[c] Ecosystems Research Group, School of Plant Biology, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia

ARTICLE INFO

Article history:
Received 24 July 2014
Received in revised form 21 November 2014
Accepted 24 November 2014
Available online 3 December 2014

Editor: David R. Hilton

Keywords:
Stable isotope
Strontium
Water
Arid
Western Australia

ABSTRACT

The Precambrian meta-sedimentary fractured rock aquifers of the Hamersley Basin in northwest Australia are some of the oldest water-bearing formations on the planet and host enormous iron ore deposits. Groundwater is the only permanent source of water in the basin, therefore understanding the hydrological processes that effect water quality and quantity is a pre-requisite for sustainable water management. We used a combination of major dissolved ion concentrations, including Sr and Ca, in combination with δ^{2}H, δ^{18}O and δ^{87}Sr in flood water and groundwater as tracers to constrain the processes affecting groundwater chemistry. The δ^{87}Sr composition of groundwater in three major aquifer types ranges from 11.8‰ to 40.6‰ and reflects the mineralogy of altered Precambrian dolomite (15.1‰ to 55.4‰) rather than the host iron ore formations (22.5‰ to 46.5‰ >95% iron oxides) or highly radiogenic shale bands and clay minerals (200‰ to 2322.5‰). Groundwater in the terminal Fortescue Marsh wetland of the basin has a rather constant δ^{87}Sr signature of 36.6 ± 1.4‰ irrespective of variations in TDS, δ^{18}O and Sr concentration. This groundwater is considered to be mature in a geochemical sense, representing the final stage of water evolution on a basin scale. Mixing calculations utilising δ^{87}Sr and Ca/Sr data demonstrate contributions of salts from three major sources: on average >92% from precipitation, ~7% from carbonate rocks and <1% from rocks with highly radiogenic signatures (shales and clays). These results demonstrate groundwater evolution from a recharge area to discharge area at the regional scale, but more importantly that water quality in the terminal wetland is primarily driven by rainfall chemistry in floodwaters rather than water–rock interactions in the catchment.

1. Introduction

Groundwater resources provide the only reliable source of water for environmental and economic purposes in arid zones throughout the world (Zektser and Everett, 2004). Quantifying the volume of available resource and understanding the physical and chemical controls on water quality in these regions are therefore of paramount importance for ensuring sustainable development and management practices. However, due to the complex hydrological characteristics, arid regions and more specifically arid subtropical regions quantitative assessment can be highly uncertain (English et al., 2012).

Previous research in arid environments has demonstrated that using major ion chemistry alone is often inconclusive or ambiguous (Bullen and Kendall, 1998). Major ion chemistry and stable hydrogen (H) and oxygen (O) isotope compositions generally span very large ranges, which means the processes effecting major dissolved ions and water molecules need to be decoupled. This is especially critical in terminal basins, where salt retention times can be very long compared to the quick turnover of water molecules (Skrzypek et al., 2013).

Strontium (Sr) isotopes have been widely used to trace the origin and evolution of solutes in groundwater and surface water (McNutt, 1987; McNutt et al., 1990) and to provide important clues on the groundwater flow paths and overall water balance (Bullen et al., 1996, 1997). However, until relatively recently, literature demonstrating the applicability of Sr isotopes in arid environments with very old geology (and thus highly radiogenic δ^{87}Sr signature) was limited. For example, Vengosh et al. (1999) used Sr isotopes, in conjunction with boron and O isotopes, to identify the sources of salinity in a coastal aquifer of Israel. Harrington and Herczeg (2003) used ^{87}Sr/^{86}Sr ratios in groundwater to determine the relative importance of weathering old silicate-rich minerals in comparison to relatively less radiogenic carbonate minerals in the arid Ti Tree Basin of Central Australia. Most recently, Paces and Wurster (2014) used Sr isotopes in conjunction with uranium isotopes to determine water balance contributions from different aquifers to a wetland habitat in arid Nevada, USA.

This paper further evaluates the benefits of using Sr isotopes as a hydrochemical tracer of mineral weathering reactions in a remarkably

---

[*] Corresponding author at: School of Plant Biology, The University of Western Australia, M090, 35 Stirling Highway, Crawley WA 6009, Australia. Tel.: +61 8 6488 4584.
E-mail addresses: shawan.dogramaci@riotinto.com (S. Dogramaci), grzegorz.skrzypek@uwa.edu.au, gskrzypek@yahoo.com (G. Skrzypek).

http://dx.doi.org/10.1016/j.chemgeo.2014.11.021

old, arid landscape. The Hamersley Basin in northwest Australia is characterised by Archean basement geology (~2.7 Ga) and an arid, subtropical climate of distinct wet and dry seasons, which give rise to pronounced cyclic wetting and drying. We demonstrate that the combination of δ^{87}Sr, δ^{2}H, δ^{18}O and major ion chemistry of surface water runoff and groundwater can provide improved constraints on recharge processes and enable decoupling of the origin of the water molecules from the origin of dissolved salts.

2. Sr isotope notations

Unlike stable isotopes of light elements (H, C, N, O, S), the relative difference in isotope mass between ^{87}Sr and ^{86}Sr is so small that mass dependent fractionation is usually negligible (Bullen and Kendall, 1998). Furthermore, Sr does not have a gaseous form and fractionation between solid and liquid phases is negligible at Earth surface conditions. The convention for Sr isotope reporting is as the ratio of ^{87}Sr to ^{86}Sr isotopes or as delta notation (δ). The small numerical differences in ^{87}Sr and ^{86}Sr is highly significant, therefore we express the Sr isotope compositions in permil (‰), as deviation from modern seawater. The following equation was used for δ^{87}Sr calculation (Coplen, 2011):

$$\delta^{87}\mathrm{Sr} = \frac{\left[{}^{87}\mathrm{Sr}/{}^{86}\mathrm{Sr}\right]_{\mathrm{sample}}}{0.70920} - 1 \qquad (1)$$

where 0.70920 represents the ^{87}Sr/^{86}Sr for modern seawater (Faure, 1986).

3. Background

3.1. Chemical controls on arid-zone groundwater

The primary sources of solutes to groundwater are generally aerosols of marine or terrestrial origin and weathering of minerals in the soil zone or host geology (Drever, 1988; Herczeg et al., 2001; Cartwright et al., 2012; Dogramaci et al., 2012). The composition of groundwater is then altered from these primary sources, due to mixing with other waters (e.g., localised recharge or deeper groundwater) and evapo-concentration. The latter process is commonly associated with hydrochemical evolution in arid and semi-arid regions, otherwise known as 'cyclic wetting and drying'. Infrequent rainfall and flooding events can re-mobilise the less soluble minerals that precipitated in dry periods.

The removal of solutes from solution during cyclic wetting and drying is dependent on the solubility of precipitated minerals and temperature of the solution phase. Due to its high solubility, calcite is one of the early minerals to precipitate, resulting in partial removal of calcium (Ca) and bicarbonate (HCO_3) ions from solution (Appelo and Postma, 2005). Gypsum and ultimately halite follow the precipitation of calcite, depending on the ion activity product of their relevant ions. Dissolution of precipitated minerals along the waterways in the wet season will result in addition of ions into the solution phase. Because Sr is geochemically associated with Ca ions, the relative ratio of Ca/Sr will change and can be traced to determine carbonate cyclic dissolution and precipitation processes.

3.2. Strontium isotope geochemistry

Strontium isotope composition is particularly useful for geochemical studies because of the strong association of Sr with Ca ions in carbonate and clay minerals, thereby providing an important insight into the dissolution and precipitation of these minerals. The similarity of chemical properties and the slightly larger ionic radius of the Sr ion (1.13 Å compared to Ca 0.99 Å) allows Sr to replace Ca selectively in Ca-bearing minerals. The ancient rocks of the Archean Hamersley group have a wide spectrum of δ^{87}Sr values developed over the past 2.7 Ga since its formation, which may lead to distinctive signatures of various Ca-bearing minerals such as carbonates and shales.

In addition to the small amount of Sr in rainfall <0.02 mg/L (Dogramaci and Herczeg, 2002) that reflects a marine signature (δ^{87}Sr = 0‰; ^{87}Sr/^{86}Sr ~0.7092), δ^{87}Sr values of runoff generated from rainfall events reflect a combination of inputs from multiple sources that include chemical weathering of silicates, carbonates and other minerals of the drainage basin as well as dissolution of salts precipitated during the previous dry spell (Drever and Smith, 1978). During recharge, Sr is also acquired from soil and unsaturated zones and along groundwater flow-paths, by interaction with aquifer matrix (Naftz et al., 1997; Veizer et al., 1997; Woods et al., 2000). Groundwater in equilibrium with Sr-bearing minerals will have δ^{87}Sr values that reflect the isotopic ratio of the minerals, leading to variation of the strontium isotopic ratio in groundwater from different lithologies (Bullen and Kendall, 1998; Dogramaci and Herczeg, 2002). The average ^{87}Sr/^{86}Sr of crustal rocks is dependent on their age and rubidium (Rb) content during formation. Subsequent geological activities may reset both isotopic composition and Rb content. Generally, crustal silicate rocks are more radiogenic and their isotopic composition is characterised by larger ^{87}Sr/^{86}Sr variability compared to carbonates rocks (Krishnaswami et al., 1992). This is particularly important when working in one of the oldest terrestrial landscapes such as that characterised by our study area, the Hamersley Basin (Buick et al., 1995). The age and chemical composition of various water bearing formations may be reflected in the Sr isotopic signature developed by ^{87}Rb radiogenic decay over ~2.7 Ga. These geo-chronological signatures may provide an opportunity to trace the major contributing sources to the ultimate geochemical composition of the groundwater (Skrzypek et al., 2013).

The radioactive decay of $^{87}\mathrm{Rb} \rightarrow {}^{87}\mathrm{Sr}$, (with decay constant λ of 1.42×10^{-11} yrs^{-1} and half-life of 48.8 Ga) has produced distinctly different ^{87}Sr abundances in different parts of the Earth over its 4.5 Ga history. Mean abundances of Sr isotopes are ^{88}Sr (82.53%), ^{87}Sr (7.04%), ^{86}Sr (9.87%), and ^{84}Sr (0.56%), of which ^{87}Sr is the only radiogenic isotope. Consequently, the Rb/Sr ratio varies substantially in various rocks resulting in variable δ^{87}Sr. Clay minerals which are weathering products of granitic rocks have some of the highest Rb/Sr ratios (Faure, 1996). The mafic igneous and carbonate sedimentary rocks that are usually characterised by very low Rb/Sr ratio (<0.01) will have ^{87}Sr/^{86}Sr signatures resembling that of the original rock signature at the time of crystallisation, regardless of their age, as decay of low concentrations of Rb will produce negligible amounts of ^{87}Sr. The Rb/Sr ratio of shale on the other hand, can be three to four orders of magnitude higher than that in mafic igneous rocks, resulting in significant ^{87}Sr enrichment and a radiogenic δ^{87}Sr signature. A theoretical example (Fig. 1) shows five rock samples with different initial Rb/Sr ratios (50, 20, 10, 2, 0.1) that formed with identical initial ^{87}Sr/^{86}Sr values (0.69). Based on the decay equation (Faure, 1996), the general principle is that a rock that is characterised by a high Rb/Sr ratio (e.g., shale) will have a much higher δ^{87}Sr value compared to a rock with a relatively low Rb/Sr ratio (e.g., dolomite). Both these end members are ubiquitous in the sedimentary sequence, volcanic sills and metasediments of the study area, the Hamersley group of 2.5–2.7 Ga age.

4. Materials and methods

4.1. Site Description

The Hamersley Basin is divided into ranges and floodplains. The elevation rises from 400 m a.s.l. at the lowest part of the basin (the Fortescue Marsh) to ~700 m a.s.l. along the ranges, with the highest peak at 1250 m a.s.l. at Mt. Meharry. The Fortescue and Ashburton Rivers form extensive floodplains on either side of the Hamersley Range, and extend as broad deltas toward the coast, draining into the