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

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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 are a pre-requisite for sustainable water management. We used a combination of major dissolved ion concentrations, including Sr and Ca, in combination with $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{87}\text{Sr}$ in flood water and groundwater as tracers to constrain the processes affecting groundwater chemistry. The $\delta^{87}\text{Sr}$ 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 $\delta^{87}\text{Sr}$ signature of 36.6 ± 1.4 ‰ irrespective of variations in TDS, $\delta^{18}\text{O}$ 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 $\delta^{87}\text{Sr}$ 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.

Keywords: stable isotope; strontium; water; arid; Western Australia;

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 is 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 et al., 1990; 1987) 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 $\delta^{87}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 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 $\delta^{87}\text{Sr}$, $\delta^2\text{H}$, $\delta^{18}\text{O}$ 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 $\delta^{87}\text{Sr}$ calculation (Coplen, 2011):

$$\delta^{87}\text{Sr} = \frac{[^{87}\text{Sr}/^{86}\text{Sr}]_{\text{sample}}}{0.70920} - 1 \quad (\text{Eq. 1.})$$

where the 0.70920 represents the $^{87}\text{Sr}/^{86}\text{Sr}$ 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 later 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 (1.13Å compared to Ca 0.99Å) allows Sr to replace Ca selectively in Ca-bearing minerals. The ancient rocks of the Archean Hamersley group have a wide spectrum of $\delta^{87}\text{Sr}$ 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 reflect a marine signature ($\delta^{87}\text{Sr} = 0\text{‰}$; $^{87}\text{Sr}/^{86}\text{Sr} \sim 0.7092$), $\delta^{87}\text{Sr}$ values of runoff generated from rainfall events reflects 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 $\delta^{87}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $^{87}\text{Rb} \rightarrow ^{87}\text{Sr}$, (with decay constant λ of $1.42 \times 10^{-11} \text{ yrs}^{-1}$ 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 $\delta^{87}\text{Sr}$. 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $\delta^{87}\text{Sr}$ 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 $^{87}\text{Sr}/^{86}\text{Sr}$ 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 $\delta^{87}\text{Sr}$ 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.

Figure 1. The evolution of stable Sr isotope composition over 2.7 Ga in five rock types with different initial Rb/Sr ratio. Note that the rock characterised by a higher Rb/Sr ratio results in significantly more radiogenic $\delta^{87}\text{Sr}$ values. The labels show (e.g., for green line), initial Rb/Sr = 50, final Rb/Sr = 20.4 after 2.7 Ga and $\delta^{87}\text{Sr} = 2744\text{‰}$.

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 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 Indian Ocean (Fig. 2). The rivers and creeks in the basin are ephemeral, only flowing after intense rainfall events (Grootemaat, 2008).

The Hamersley Basin is part of the Precambrian crustal unit of Pilbara Craton that was stabilised and composed of two major units: 1) granite-greenstone terrain 2) overlain unconformably by the younger Mt Bruce Supergroup (Myers, 1993). The latter volcanic and sedimentary sequence occurred ~2.8 to 2.4 Ga and presently outcrops in the Hamersley Basin (Arndt et al., 1991). The Mt Bruce Supergroup is composed of three major subgroups, the oldest being the Fortescue group (2.7 Ga) which is overlain by the Hamersley group (2.4 Ga), the subject of this study, and the relatively younger Turee Creek group respectively (Fig. 2).

The Hamersley group is a 2.5 km thick stratified sequence of Banded Iron Formation (BIF), shale, chert, dolomite and tuff. It contains numerous sills of dolerite and rhyolite up to

1 km thick (Taylor et al., 1991; Myers, 1993). The BIF has been the subject of numerous investigations because it contains some of the world's largest iron ore deposits (Morris 1993; Harmsworth et al., 1990). An important feature of the BIF in the Hamersley Basin is the apparent absence of lateral facies changes (Morris and Kneeshaw, 2011). Over the last 2.4 Ga some parts of BIF has gone through significant uplift and structural extension as well as diagenesis and chemical alteration resulting in the development of significant iron ore bodies controlled by fault systems (Taylor et al., 1991). The Hamersley group is comprised of three main water-bearing formations: the iron oxide dominated Brockman Iron Formation, overlying the dolomite and shale dominated Wittenoom Formation, upon the iron oxide dominated Marra Mamba Iron Formation (Fig.2) (Hickman, 1983).

Figure 2. Geological map showing the stratigraphy of the Hamersley Group within the Hamersley Basin. Note the mafic igneous rocks surrounding Paraburdoo region. The insert shows the location of CID aquifer and the north, south (A-A') hydrogeological transect. The red circles denote groundwater-sampling points.

The ore formation resulted from a multistage, sequential removal of gangue minerals from the host BIF, giving rise to residual concentration of iron ore (Taylor et al., 2001; Morris and Kneeshaw, 2011). The formation of ore from parent BIF has been subject of many studies but it is not yet fully explained (Morris and Kneeshaw, 2012; Taylor et al.,

2001). The formation of iron ore must have started with the removal of silica residual enrichment of iron oxides. This may have occurred due to the interaction of highly saline and alkaline bicarbonate-saturated fluids, derived from relatively deep dolomite-shale (Wittenoom Formation), which leaked upward along fault zones into the ore body. The circulation of meteoric water through the ore resulted in further oxidation and a second stage of gangue removal, stripping carbonates and leaving highly porous and permeable iron ore zones (Taylor et al., 2001).

4.2. *Hydrogeological setting, aquifer types and recharge*

The long geological history of the Hamersley Basin and millennia of erosion have exposed the Archean bedrock of Hamersley group over most of the basin (Fig. 2&3). The soil covering most of the basin is minimal, with shallow stony soils on hills and ranges and sands on sand plains (Van Vreeswyck et al., 2004). The lower floodplains have clay soils and duplex soils on alluvial plains (Van Vreeswyck et al., 2004).

The long process of iron ore formation has had significant effect on the hydraulic properties of the ore bodies in terms of increased fractures and a subsequent increase in overall porosity. The impact of these processes on the hydraulic characteristics of the Hamersley group formations depends mainly on topography and local structural geology. Therefore, the degree of evolution and development of the fractured rock aquifers are not uniform throughout the basin. For example, areas that fall outside iron ore zones are characterised by fewer fractures and much lower porosity, and rarely contain groundwater (Dogramaci et al., 2012). Inside the ore zone, the water table in the three water-bearing formations (hitherto called Brockman Iron Formation, Wittenoom Formation and Marra Mamba Iron Formation aquifers respectively) is generally deep ranging from 20 m below ground level (bgl) to 130 m bgl. The hydraulic conductivity (k) of the Brockman and Marra Mamba Iron Formation aquifers range from 10 m/d to 100 m/d (KBR, 2008). The Wittenoom Formation aquifer also demonstrates relatively high k values ranging from 50 to 100 m/d (KBR, 2008). In addition to fractured rock aquifers, groundwater also resides in the sedimentary aquifers of Tertiary palaeo-channel iron deposits (CID) and Tertiary and Quaternary alluvium and colluvium (hitherto called creek alluvium aquifer) along major rivers and most of the creeks. Groundwater depths in these aquifers are shallower and range from 0 m to 30 m bgl (Fig. 3 and 4). Within the Ore zone, groundwater levels demonstrate sufficient continuity to suggest a well-connected hydraulic system between the aquifers (Fig. 3 and 4).

Figure 3. Three dimensional conceptual model showing the main aquifer types surrounding the Fortescue Marsh (Refer to Figure 2 for the location).

Figure 4. Conceptual model showing the hydraulic connection in dry and wet periods between fractured and alluvium aquifers in the Hamersley Basin.

The groundwater hydraulic gradient is relatively low ranging from 0.001 to 0.01. Therefore, the maximum lateral flow velocity would not exceed ~ 10 m/d (e.g. CID aquifer- Kirkpatrick and Dogramaci, 2010). The fractured aquifers are invariably connected to the adjacent alluvium aquifers, along the major creeks and tributaries (Fig. 4). The hydraulic gradient varies seasonally, depending on rainfall intensity and the subsequent recharge rates during the wet summer season. Generally, the groundwater levels are closest to the surface in alluvium aquifers after major flood events. The relatively high water level results in recharge to the adjacent fractured aquifers. With the onset of the dry season the water table in the

alluvium aquifers is lowered. This is due to evapotranspiration, which may reverse the hydraulic gradient, resulting in discharge from fractured to the alluvium aquifers (Fig. 4). The alluvium aquifers therefore act as a transitory conduit to transmit groundwater to the ultimate discharge area of the Fortescue Marsh.

Recharge to the exposed fractured rock aquifers is via preferential pathways with minimal evaporation (total dissolved solids (TDS) can be as low as 100 mg/L, see Fig 3). The alluvium aquifers on the other hand, are invariably recharged from run-off after intense rainfall events (Dogramaci et al., 2012). Recharge up to 10 mm/d has been recorded for the CID aquifer underlying Weelli Wolli creek which discharges directly to Fortescue Marsh (Dogramaci, 2014). Recharge of the regional Wittenoom Formation may also occur where erosion has removed the overlying formations (Fig. 4). Similarly, recharge to the Fortescue Valley aquifers occur during major flooding events through the Fortescue River and smaller tributaries draining the Hamersley and Chichester range catchments (Fig. 3; Skrzypek et al., 2013). The large volume of flood water saturates the centre of the valley causing surface water to pond in the Fortescue Marsh. This results in the recharge of the alluvial and underlying Wittenoom Formation aquifers. Periods of inundation and evaporation in the Marsh has led to significant salt build up, and highly saline groundwater (Skrzypek et al., 2013).

4.3. *Methods*

Groundwater from 76 production and monitoring bores at various depths from 57 locations, covering most of the Hamersley Basin, were sampled in May 2011 (Fig. 2). All groundwater samples were collected after pumping out at least three casing volumes of a bore. EC, pH, Eh, dissolved oxygen and temperature were measured in situ using a portable multimeter (INSITU Inc. Multi parameter Water Quality TROLL[®] 9500, Ft. Collins, CO, USA). Water samples were collected in 0.5 L plastic containers for major ion analysis (acidified for cations and metals) and in 40 mL sealed glass vials for stable isotope analysis, following filtration using a sterile syringe microfilter (0.21 µm). The groundwater samples were analysed for stable isotope composition ($\delta^{87}\text{Sr}$, $\delta^2\text{H}$, $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ -DIC) and water chemistry (Na, Ca, Mg, K, Si, Fe, HCO_3 , SO_4 , Cl, Sr and Br). In addition to water samples, a total of 31 rock samples representing typical fractured and alluvium aquifer matrix were selected from un-mineralised and mineralised BIF, alluvial sediments, shales and carbonate

rocks from Paraburdoo, Tom Price, Yandicoogina, Koodaideri and Fortescue Marsh areas (Fig.2 and 3).

Prior to stable Sr isotope analysis, water samples were evaporated to dryness in ultraclean Teflon vessels, redissolved in distilled HCl and centrifuged in order to separate any undissolved precipitate. The whole rock samples for bulk analyses were totally digested in sealed Teflon vessels using distilled HF and HNO₃ and quartz distilled HCl. The rock samples were also analysed for the most mobile fraction as leaches after crushing and soaking in 0.05 M acetic acid for 24 hrs. Strontium in extracted and concentrated solutions from water and rock samples was separated from other ions using a standard cation exchange column procedure. The stable strontium isotope analysis ($\delta^{87}\text{Sr}$) was carried out on a Finnigan MAT 262 thermal ionization mass spectrometer (TIMS), operated in dynamic measurement mode in Mawson Laboratories at The University of Adelaide, South Australia. Results of measurements of at least 10 blocks of 10 (8 second) scans, for a minimum of 100 replicated measurements, were normalized to $^{88}\text{Sr}/^{86}\text{Sr} = 8.375209$. The mass spectrometer measurement precision and reproducibility (two standard deviations, 2σ) were determined by analysing Strontium Carbonate Isotope Standard SRM987 from the National Institute of Standards and Technology, USA. The average $^{87}\text{Sr}/^{86}\text{Sr}$ ratio for 31 individual measurements of 0.71024 ± 0.00017 was in good agreement with the certified value of 0.71034 ± 0.00026 . The reproducibility of ± 0.00017 for $^{87}\text{Sr}/^{86}\text{Sr}$ ratio corresponds to $\pm 0.24\%$ for the $\delta^{87}\text{Sr}$ value.

The stable H and O isotope composition of water samples was analysed using an Isotopic Liquid Water Analyser Picarro L1102-i (Picarro, Santa Clara, California, USA) at the West Australian Biogeochemistry Centre (WABC), The University of Western Australia. The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values were normalized to the VSMOW scale (Vienna Standard Mean Ocean Water) following a three-point normalization (Skrzypek, 2013) based on three laboratory standards and are reported in permil (‰). All laboratory standards were calibrated against international reference materials determining the VSMOW-SLAP scale (Coplen, 1996), provided by the International Atomic Energy Agency ($\delta^2\text{H}_{\text{VSMOW}}$ and $\delta^{18}\text{O}_{\text{VSMOW}}$ equals 0‰ and $\delta^2\text{H}_{\text{SLAP}} = -428.0\%$ and $\delta^{18}\text{O}_{\text{SLAP}} = -55.50\%$). The analytical uncertainty (one standard deviation) was determined as $<1.0\%$ for $\delta^2\text{H}$ and $<0.1\%$ for $\delta^{18}\text{O}$.

Water samples were also analysed for $\delta^{13}\text{C}$ -DIC in the WABC at The University of Western Australia using a GasBench II coupled with a Delta XL Mass Spectrometer (Thermo-Fisher Scientific). The obtained δ -values were normalized to the international VPDB scale (Bellemnitella Americana from the Pee Dee Formation in South Carolina) using

L-SVEC, NBS19 and NBS18 reference materials with values as determined by Coplen et al., (2006) and the combined analytical uncertainty was determined as $\leq 0.10\%$ (Skrzypek et al., 2010).

The concentration of major ions in water were analysed by SGS laboratories Australia Pty. Ltd. in Perth, Western Australia, using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) for Ca, Mg, Na, and K cations, Ion Chromatography for Br⁻, Discrete Analyser in Water by Aquakem DA for SO₄ and Cl anions and HCO₃ alkalinity by acid titration (Skrzypek et al., 2013). Rock samples for elemental concentration were finely ground and fused with standard type 1.2:2.2 X-ray flux in a platinum crucible at 1050°C for 30 minutes. The melt was dissolved in 10% HCl and elemental concentrations were determined against matrix matched calibration solutions using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) PE 5300DV ICP-OES (Perkin Elmer, Norwalk, CT, USA) at The University of Western Australia.

5. Results

5.1. Geochemistry and $\delta^{87}\text{Sr}$ signatures of aquifer mineralogy

The results of the elemental concentrations and $\delta^{87}\text{Sr}$ values of rocks (electronic supplementary material Tab. S2.) allow the characterisation of five major sources of Ca and Sr ions that may contribute to the current chemical characteristics of groundwaters in the basin (Fig. 5);

1. Dolomite of the Wittenoom Formation has the lowest measured $\delta^{87}\text{Sr}$ value of -5.9% for whole rock, reflecting the original Precambrian marine $\delta^{87}\text{Sr}$ values (Veizer et al., 1992) and suggesting little change due to post depositional alteration. The whole rock leachates extract (-5.3%) has a very similar $\delta^{87}\text{Sr}$ value to the whole rock value. The Ca/Sr ratio of 529 typically reflects a high relative concentration of Ca to Sr (0.072%) in carbonate rocks.

2. Various carbonates partially altered by diagenesis with radiogenic Sr-sources, such as clays and shales, have δ -values slightly higher than unaltered carbonates -0.5% to 8.2% (mean 5.0% , $n = 6$) and leachates (-0.4% to 12.6%). The Ca/Sr ratios are higher and vary over a wide range from 426 to 1701 (hydrothermal calcite has $\text{Ca/Sr} > 13,000$).

3. In contrast to the two previous groups of marine carbonates, the secondary calcrete, of the Fortescue Marsh alluvium and colluvium sequence, are characterised by high $\delta^{87}\text{Sr}$, 46.4 – 55.4% and highly variable Ca/Sr ratios of 180–3935 (electronic supplementary material Tab. S1, Fig. 5). These calcrete samples within the alluvium of the Fortescue valley were sampled

from various depths below the water table (up to 20 m) and most likely precipitated from groundwater saturated with respect to calcite (Skrzypek et al., 2013). The relatively high $\delta^{87}\text{Sr}$ values of the carbonate samples reflect the signature of the source groundwater during precipitation.

4. CIDs dominated by hematite (up to 60% of Fe_2O_3 .) have variable $\delta^{87}\text{Sr}$ values ranging from 22.5‰ to 46.5‰ and low Ca/Sr ratios of 40-434. However, both Ca (<8%) and Sr (<0.02%) were present in very low concentrations.

5. The most radiogenic $\delta^{87}\text{Sr}$ signature was typical for the fifth group of aquifer rock samples representing chloritic, carbonaceous and pyritic shale from Mt McRae shale, and varied between 114.8‰ to 2322.5‰ (n = 9).

The Rb/Sr ratio of shale is much higher than that of carbonate minerals, particularly in the Wittenoom Formation. Generally, rock samples with a relatively low Rb/Sr ratio correspond to lower $\delta^{87}\text{Sr}$ values (less radiogenic) compared to those with high Rb/Sr ratios and higher $\delta^{87}\text{Sr}$ (more radiogenic). The $\delta^{87}\text{Sr}$ values of the leachates were highly enriched, although lower than whole rock samples, and vary from (74.6‰ to 841‰, Fig. 5).

5.2. *Hydrochemical, $\delta^{18}\text{O}$ and $\delta^{87}\text{Sr}$ signatures of surface and groundwater*

Based on $\delta^{87}\text{Sr}$, Ca/Sr ratio and major ion chemistry (electronic supplementary material Tab. S1.) groundwater in the Hamersley Basin can be divided into four groups (Fig. 5 and 6), each with distinct geochemical signatures reflecting the aquifer matrix and stage of evolution;

1. Groundwater in fractured rock aquifers of the Paraburdoo region that are characterised by the occurrence of numerous mafic rock outcrops (Fig. 2 and 3), contain relatively low Sr concentrations <1 mg/L (TDS 0.2-1.4g/L), Ca/Sr ratios that vary between 136 and 379 and relatively less radiogenic $\delta^{87}\text{Sr}$ signatures of $20.9 \pm 4.7\text{‰}$ (n=11). The $\delta^{18}\text{O}$ varies in a narrow range but is exceptionally ^{18}O -enriched ($-5.7 \pm 0.4\text{‰}$) compared to groundwater from other parts of the Hamersley Basin ($-8.22 \pm 0.70\text{‰}$, Dogramaci et al., 2012).

2. In contrast, the fresh groundwater (TDS 0.2-1.4 g/L) in the geochemically more homogenous CID aquifers (Fe_2O_3 dominated with minor pockets of clays and shales) is characterised by lower Sr concentrations (≤ 0.2 mg/L), therefore, higher Ca/Sr ratios of 242-438, and relatively more radiogenic $\delta^{87}\text{Sr}$ values $42.4 \pm 1.0\text{‰}$ (n=6). The stable O isotope compositions also vary in a narrow range, $-8.1 \pm 0.30\text{‰}$ ($\delta^{18}\text{O}$), but are less ^{18}O -enriched and similar to groundwater of the Hamersley Basin.

3. Fresh and brackish groundwater in alluvial aquifers along creek lines, in alluvial fans and under flood plains (TDS 0.2 to 6.5 g/L) have a relatively wider range of Sr concentrations (0.1 to 1.4 mg/L) and Ca/Sr ratios (91 and 645), and $\delta^{87}\text{Sr}$ values fall between the previous two groups, 27.2‰ to 40.2‰ (n=29). The narrow range of $\delta^{18}\text{O}$, -8.0 ± 0.9 ‰, is similar to that of the CID aquifer and recent recharge (Dogramaci et al., 2012).
4. The highly saline groundwater occurs in the alluvium and colluvium and Wittenoom Formation aquifers under the Fortescue Marsh. Despite the wide range of Sr concentrations (0.1 to 1.4 mg/L, n = 29), salinity (TDS 11 to 185 g/L) and $\delta^{18}\text{O}$ (-8.2 to $+2.5$ ‰), the range of $\delta^{87}\text{Sr}$ and Ca/Sr ratio are narrow (35.3 ± 3.2 ‰) and (52-148) respectively, suggesting a hydrochemically homogenous group.

Figure 5. Stable Sr isotope composition of aquifer matrix and groundwater in the Hamersley Basin. The bulk rock and leachates are represented by symbols B and L respectively (for details refer to section 4.1). Flood water is represented by four water samples collected from the Fortescue Marsh three weeks after cyclone Heidi (January 2012).

Figure 6. Selected dissolved ion distribution in groundwater in the Hamersley Basin. The saline end member (FM saline) is characterised by relatively lower Ca/Sr and Ca/Mg ratios with increasing Cl concentrations, suggesting the removal of Ca and enrichment of Sr and Mg ions in groundwater.

The five surface water samples collected from separate pools on the Fortescue Marsh after cyclone Heidi (>200 mm rainfall event in 24 h, on 13th January 2012) are characterised by a wide range of Sr concentrations (0.06 mg/L to 1.83 mg/L) and a narrow range of $\delta^{87}\text{Sr}$

values (33.5‰ to 36.8‰). Despite a low salinity range (TDS 136-2332 mg/L), and relatively high Ca/Sr ratios (149-241), their $\delta^{87}\text{Sr}$ values resemble that of saline groundwater under the Fortescue Marsh (Fig. 5).

Similar to $\delta^{87}\text{Sr}$ composition, the chloride concentration (Cl) in groundwater, varies over three orders of magnitude ranging from fresh (15 mg/L) at Paraburdoo, to brine (96,000 mg/L) under the Fortescue Marsh. Except for deep groundwater under the Marsh, most of the groundwater in the fractured rock aquifers across the basin is characterised by Cl concentrations < 1,000 mg/L (Fig. 6A). This is also reflected in Sr and Ca concentrations where the groundwater from the latter group contains < 2 mg/L of Sr whereas the brine groundwater under the Marsh contains much higher Sr ranging from 3.7 to 10.5 mg/L (Fig. 6A&B). The ratio of Ca/Sr and Ca/Mg also decreases with increasing Cl concentration (Fig. 6C&D) by two fold from 0.001 to 0.020, suggesting the addition of Sr to groundwater at the more saline end of the spectrum (Fig. 6C&D). The decreasing trend of Ca/Sr corresponds to a general increasing trend in $\delta^{13}\text{C}$ values of Dissolved Inorganic Carbon (DIC) in groundwater from -1.9 to -15.3‰; the more saline groundwaters under the Fortescue Marsh are characterised by more positive $\delta^{13}\text{C}$ DIC values (Fig. 6E).

6. Discussion

6.1. *Strontium isotope signatures derived from groundwater aquifer matrix*

The age of major formations constituting the majority of rocks in the Hamersley Group range from 2.4-2.7 Ga (Buick et al., 1995); even the age of most of the younger volcanic units range between 2.2-2.6 Ga (Geosciences Australia, Australian Stratigraphic Names Database http://dbforms.ga.gov.au/www/geodx.strat_units.int). The age of these formations is reflected in the Sr isotopic signature developed by the addition of radiogenic ^{87}Sr from the decay of ^{87}Rb over billions of years, to the initial ^{87}Sr signature of aquifer rocks. Because of the relative similarity of the age of all Hamersley group forming minerals, the simplified $^{87}\text{Rb} \rightarrow ^{87}\text{Sr}$ decay model (Fig. 1) suggests that $\delta^{87}\text{Sr}$ signatures for minerals developed over 2.4-2.6 Ga are mainly dependent on the initial Rb/Sr ratio. The $\delta^{87}\text{Sr}$ value for rocks with Rb/Sr < 0.1 (typical for carbonate rocks) will not significantly change over time as the ^{87}Rb decay over 2.7 Ga from a small Rb concentration will not produce a significant mass of radiogenic ^{87}Sr to substantially alter the original ^{87}Sr concentration. On the other hand, the measured range of Rb/Sr ratios (2 to 50) in shales from different formations in the basin will produce $\delta^{87}\text{Sr}$ signatures between 115‰ and 2322‰, which are

within similar ranges to those measured in shales and clay mineral samples from various aquifers in the basin (Fig. 5). In addition to the decay of radiogenic Rb, alteration by a radiogenic source, such as isotope equilibrium with clay minerals, will tend to increase $\delta^{87}\text{Sr}$, while alteration by fluids affected by interaction with volcanic or carbonate rocks will tend to decrease the original $\delta^{87}\text{Sr}$ depending on the signature of the fluid (e.g., Stuckless and Ericksen, 1976).

The overall $\delta^{87}\text{Sr}$ signature of groundwater in each aquifer depends on the type of minerals and the Rb and Sr concentrations in the aquifer matrix. Based on Sr concentrations, the carbonate-rich rocks of the Hamersley group, can potentially deliver a significant amount of Sr with a relatively low radiogenic $\delta^{87}\text{Sr}$ signature (Fig. 5 and 7). In contrast, there is no significant correlation between Ca and Sr in CID aquifer minerals that are characterised by low concentrations of Ca and Sr and a more radiogenic $\delta^{87}\text{Sr}$ signature (Fig. 5 and 7). This suggests that Sr concentrations in the groundwater from CID aquifers are not associated with carbonate minerals and it originates from clay minerals.

Figure 7. The association of Sr ions with Ca ions in aquifer matrix. Colours of the symbols correspond to the colours of description.

Despite the similarity of the range of Sr concentrations in groundwater from fractured and palaeo-channel CID aquifers at Paraburdoo and Yandicoogina, the $\delta^{87}\text{Sr}$ values for groundwater from the fractured aquifers are significantly lower compared to that of the CIDs, in both locations. The relatively lower $\delta^{87}\text{Sr}$ in fractured aquifers of Paraburdoo (Fig. 8, yellow points) suggests that low Rb concentrations in mafic igneous intrusions and dolerites are the dominant influence on Sr concentration, rather than highly radiogenic shale and clay minerals.

The fractured rock aquifers of Paraburdoo are located adjacent to Pirrburdu and Seven Mile creeks' catchments draining 480 km² and 170 km², respectively. Mafic igneous rocks that are low in Rb concentration intrude most of these catchments (Fig. 2). The weathering of plagioclase during erosion of mafic igneous rocks, and minor carbonates, progresses more rapidly than the dissolution of other mafic minerals, such as pyroxene and biotitic micas, which contain a relatively higher concentration of Rb (Lasaga, 1984). Therefore, the $\delta^{87}\text{Sr}$ value of groundwater in Paraburdoo falls within the range of Sr isotope ratios defined by mafic igneous minerals and altered Precambrian dolomite. The mechanism responsible for groundwater $\delta^{87}\text{Sr}$ therefore, is mainly determined by the signature of recharge water that originates from runoff and flooding rather than interaction with aquifer matrix. The runoff and surface water draining the catchments that ultimately recharges the aquifer reflects the signature of more soluble plagioclase feldspar and minor carbonates rather than dissolution of the whole host rock (Franklyn et al., 1991; McNutt et al., 1987, 1990).

The deep groundwater from the carbonate Wittenoom Formation under the Fortescue Marsh are characterised by relatively high Sr concentration and high $\delta^{87}\text{Sr}$ (33.5‰). This is a far more radiogenic signature than the unaltered dolomite of the Wittenoom Formation (-5.9‰; Fig. 5). However, the relationship between the Sr and Ca concentrations, and the progressive decrease in Ca/Sr, and Ca/Mg suggest that the high Sr concentrations are derived from dolomite dissolution. The relatively radiogenic Sr isotope composition in groundwater is likely to be due to the moderate contribution of Sr from highly radiogenic shale and clay minerals.

The complex structural setting of the catchment, and metamorphism, results in wide-scale fluid transport and resetting of Rb/Sr isochrones of the aquifer rocks throughout the catchment (e.g., Taylor, 2001). This relatively late metamorphic and structural activity has

led to an increase in the $\delta^{87}\text{Sr}$ of the carbonate minerals within the Wittenoom Formation due to the influx of radiogenic Sr from local high Rb/Sr shale bands and clay minerals (Myers, 1993; Bekker et al., 2010) and isotopic equilibrium of clays within the carbonate rock. This is evident from altered dolomite $\delta^{87}\text{Sr}$ values (Fig. 5). The Sr concentration and $\delta^{87}\text{Sr}$ of groundwater under the terminal Fortescue Marsh therefore is largely defined by mixing of two major sources; (i) carbonates and to a lesser extent mafic igneous rocks with high Sr contents but low $\delta^{87}\text{Sr}$ and, (ii) shale and clay minerals with low Sr concentrations but high $\delta^{87}\text{Sr}$.

Figure 8. Stable Sr and O isotope composition and Ca/Sr ratios in groundwater from major aquifers.

6.2. Hydrochemistry of groundwater in alluvial and fractured rock aquifers

6.2.1. Stable hydrogen and oxygen isotope composition

The stable H and O isotope compositions of groundwater samples (Fig. 9) vary in the general range observed earlier in the Hamersley Basin, and the surface flood water on the Fortescue Marsh after cyclone Heidi (01/2012) closely follows the regional evaporation line (Dogramaci et al., 2012; Skrzypek et al., 2014). The narrow range and negative $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values for the basin (alluvial aquifers $\delta^{18}\text{O}$ $-8.02 \pm 0.83\text{‰}$, $\delta^2\text{H}$ $-55.6 \pm 6.0\text{‰}$, $n=65$; fractured rock aquifers $\delta^{18}\text{O}$ $-8.22 \pm 0.70\text{‰}$, $\delta^2\text{H}$ $-56.9 \pm 5.0\text{‰}$, Dogramaci et al., 2012) suggests relatively low evaporative losses prior to recharge ($<20\%$, Skrzypek et al., 2013). These low evaporative losses likely result from rapid vertical recharge after large cyclonic events only. The low intensity events with substantial under-cloud base evaporation do not contribute to groundwater recharge (Skrzypek et al., 2013; Dogramaci et al., 2012). In light of the current study, this observed earlier pattern is confirmed along with two exceptions from the general principles: the Paraburdoo area and the Fortescue Marsh (Fig. 9).

Figure 9. Stable H and O isotope composition of groundwater showing the distinct signature of fractured rock aquifers in the Paraburdoo region and brines in the Fortescue Marsh.

Significant deviations from the local meteoric water line (LMWL) of groundwater in the Paraburdoo area and the Fortescue Marsh may indicate modification of the groundwater initial isotope signature by three potential processes: 1) evaporation, 2) mixing or 3) mineral–water reactions, to a lesser extent. The fresh groundwater in the fractured aquifer in the Paraburdoo region has consistently higher $\delta^{18}\text{O}$ values by 2‰ and $\delta^2\text{H}$ values by 20‰, compared to fresh groundwater from other parts of the basin (Fig. 9). However, these $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are distributed along the groundwater line between regional LMWL and LEL (Local Evaporation Line). Therefore, evaporation alone cannot explain this ^{18}O and ^2H enrichment (Fig. 9). Furthermore, there is no apparent relationship between Cl concentration and $\delta^{18}\text{O}$ values which suggests a lack of substantial mixing of two end members with different stable isotope compositions and salinity (Fig. 6F). Paraburdoo is located at the south-eastern edge of the Hamersley Basin that is characterised by distinct landform elevation (Beard, 1990) and rainfall regime (Charles et al., 2013). Unlike the eastern part of the basin, rainfall in the south-eastern edge of the basin is influenced by southern cold fronts that originate from the Southern Ocean and extend to this region in late autumn, winter and early spring, bringing rain to the region. In addition, the thermal uplift associated with heat lows that influence the formation of convective thunderstorms is also more common in this part of the basin (Charles et al., 2013). The isotopic signatures of rainfall from both of these systems are more enriched in heavy isotopes compared to the high rainfall events generated from tropical cyclones that dominate recharge processes in the basin. The contribution of rainfall from these two sources to the groundwater budget can explain the higher $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values at the south-eastern edge of the Hamersley Basin. In contrast to Paraburdoo, the significant correlation between Cl concentration and stable isotope composition was observed for saline groundwater under the Fortescue Marsh and are significantly different from groundwaters that occur up gradient in the Hamersley Basin. The slope of the regression for the saline groundwater line (3.69) is significantly lower than for LEL (5.16) therefore, the line does not reflect direct evaporation but mixing between two end-members that are characterised by different δ -values and salinity (i.e. fresh rain/flood water and highly saline deep groundwater, Skrzypek et al., 2013).

6.2.2. Major ion chemistry

The groundwater hydrochemistry is characterised by the dominance of Ca, Mg and HCO_3 in the alluvial, fractured and CID aquifers and of Na and Cl in the saline alluvium aquifer under the Fortescue Marsh (Fig. 6AB&C). The range of Sr, Ca and Mg concentrations in fresh groundwater are narrow and do not correspond to the increase in Cl concentration. In contrast, these ion concentrations are much higher in the saline groundwater. This may be attributed to the so called “drying and wetting” process that occurs in arid and semi-arid zones (Drever and Smith, 1978). The gradual drying of surface water pools and shallow groundwater at the end of wet season results in precipitation of evaporite salts such as calcite, gypsum and halite. This process results in the removal of Ca from the liquid phase and the exclusion of Sr and Mg ions from the calcite lattice during precipitation, leading to a progressive decrease in Ca/Sr and Ca/Mg ratios in the remaining water (Fig 6c). A general decreasing trend of Ca/Sr ratio is also observed with increasing $\delta^{13}\text{C}(\text{DIC})$ values and the relatively lower Ca/Sr ratio corresponds to the more enriched $\delta^{13}\text{C}(\text{DIC})$ values (Fig. 6F). Although the increase in Ca concentration by evaporation is controlled by calcite saturation and dependent on pH, temperature and ion activity product of Ca and HCO_3 , the increase in Sr and Mg concentration are not bounded by the “drying and wetting” process. The decrease in Ca/Sr and Mg/Ca ratios therefore, could be due to the fact the groundwater attained calcite saturation, and evaporation beyond this point results in the precipitation of calcite and the removal of Ca ions from solution. The continuous evaporation and increase in Cl concentration therefore should increase both Sr and Mg relative to Ca. However, the general association of lower Ca/Sr ratios with more enriched $\delta^{13}\text{C}$ values suggest additional processes that change the concentration of ions as well as $\delta^{13}\text{C}$ values. The dissolution of Precambrian carbonate within the shale bands and dolomite from the Wittenoom Formation ($\delta^{13}\text{C}$ values $\sim 2\text{‰}$ to 2‰ , Becker and Clayton, 1972) will result in the addition of Ca, Mg, Sr and HCO_3 as well as enrichment in $\delta^{13}\text{C}$ values. However, this process would not change the ratio of the Ca/Sr ions because they will be added to the solution reflecting their ratio in the rocks (for Wittenoom dolomite Ca/Sr is 529). In addition, the dissolution process can only be initiated if groundwater was under saturated with respect to carbonate minerals. The only process that combines dissolution of carbonate minerals and precipitation of another is dedolomitisation, where dolomite dissolves and releases Mg and Sr into the solution phase and concurrent precipitation of calcite. This process results in the decrease of Ca/Sr and Ca/Mg ratios, as well as enrichment in $\delta^{13}\text{C}$ values due to addition of ^{13}C -enriched carbon from Precambrian dolomite. The Ca/Sr and Mg/Ca ratio that we observe therefore, is the result of

mixing between recent recharge depleted in $\delta^{13}\text{C}$ (DIC) values ($\sim -15\text{‰}$ to -10‰) with old groundwater that perturbs dolomite equilibrium in the aquifer and results in de-dolomitisation.

6.3. Calculation of end member contribution to groundwater

The highly saline groundwater under the marsh is characterised by a large range of $\delta^{18}\text{O}$ (-8.2‰ to $+2.4\text{‰}$, Fig. 8A) and Sr concentrations (0.5 to 10.5 mg/L, Fig. 8B&D) reflecting mixing of two end-members: saline water and relatively fresh flood water (see 5.2). In contrast, these groundwaters are characterised by a narrow range $\delta^{87}\text{Sr}$ values $\sim 36.6 \pm 1.4\text{‰}$ and Ca/Sr ratios (51.9 and 147, Fig. 8C). These unique geochemical characteristics can only be explained if the source of water and salt are considered separately. The dissolved ions in groundwater under the Marsh have been accumulating and recycled over tens to hundreds of thousands of years (Skrzypek et al., 2013). The original geochemical source signature is consistent across the Marsh, and modified in situ only by two geochemical processes; wetting and drying and de-dolomitisation. Recent rainfall additions does not contribute significantly to the hydrochemical composition, due to low concentration of ions but does impact $\delta^{18}\text{O}$, reflecting dilution and different mixing ratios between fresh flood water and highly saline groundwater. The dilution changes the Sr concentration (Fig. 8B&D) but does not change the Ca/Sr ion ratio or $\delta^{87}\text{Sr}$ values (Fig. 8C). From this perspective the Ca/Sr and $\delta^{87}\text{Sr}$, along with other ionic ratios under the Marsh, can be considered as an “ultimate” composition for the basin, representing the last stage of regional groundwater evolution and reflecting mean contributions of all ion sources in the basin. All other waters that are characterised by a wider range of Ca/Sr and $\delta^{87}\text{Sr}$ values located around the Hamersley Basin outside the Marsh are not mature in a geochemical sense and represent localised geochemical signatures changing over time, depending on groundwater recharge and surface runoff.

The low and more variable $\delta^{87}\text{Sr}$ (from 11.8‰ to 26.7‰) values and variable Ca/Sr (136 to 379) ratios in groundwater of fractured rock aquifers around Paraburdoo (Fig. 8C) reflect various contributions from abundant mafic igneous rocks low in Rb (Fig. 2) outcropping in the area. On the other hand, the narrow range of $\delta^{18}\text{O}$ values and Sr concentrations (Fig. 8A&B), as well low TDS, suggest that all these geochemically variable waters originate from very recent rainfall (see also 5.2). In contrast, CID groundwater has high $\delta^{87}\text{Sr}$ (Fig. 8C) reflecting radiogenic origin from shales and clays pockets ($\delta^{87}\text{Sr}$ 115‰ to 2322‰) in iron ore deposits ($\delta^{87}\text{Sr} \sim 41.4 \pm 3.7\text{‰}$). The $\delta^{18}\text{O}$ signature ($-8.1 \pm 0.3\text{‰}$) also

reflects recent precipitation. Although this signature in Paraburdoo of the Eastern Pilbara is different from the central part of Pilbara. In the Eastern Pilbara groundwater $\delta^{18}\text{O}$ value reflects higher contribution from frontal systems than from cyclonic events. The $\delta^{87}\text{Sr}$ values of alluvial fresh and brackish groundwater (27.2‰ to 40.2‰) are spread between the signatures typical for CID and Paraburdoo but $\delta^{18}\text{O}$ values again reflects the most recent cyclonic rainfalls ($-8.0 \pm 0.9\text{‰}$) (Skrzypek et al., 2013).

The $\delta^{87}\text{Sr}$ values, in combination with the Sr concentrations, can therefore be used to construct a mass balance model (Fig. 10A) to estimate the contribution from three major end-members influencing the ultimate composition of the groundwater of the Marsh (Fig. 10A), following simultaneous equations (Eq. 2, 3 and 4):

$$\delta^{87}\text{Sr}_{\text{FMsaline}} = A \times \delta^{87}\text{Sr}_{\text{radiog}} + B \times \delta^{87}\text{Sr}_{\text{dolomite}} + C \times \delta^{87}\text{Sr}_{\text{precip}} \quad (\text{Eq. 2})$$

$$\text{Ca/Sr}_{\text{FMsaline}} = A \times \text{Ca/Sr}_{\text{radiog}} + B \times \text{Ca/Sr}_{\text{dolomite}} + C \times \text{Ca/Sr}_{\text{precip}} \quad (\text{Eq. 3})$$

$$A + B + C = 1 \quad (\text{Eq. 4})$$

where A (radiogenic), B (dolomite) and C (precipitation) are weighed contributions from different sources. $\text{FM}_{\text{saline}}$ - represents the Fortescue Marsh saline groundwater with mean $\delta^{87}\text{Sr}$ of 36.6‰ and mean Ca/Sr of 79.4. The mean signature for aquifer matrix rocks are adopted as on Fig. 4: radiogenic (radiog) signatures of shales and clays ($\delta^{87}\text{Sr} = 1085\text{‰}$, Ca/Sr = 681) and dolomite as measured in Wittenoom dolomite ($\delta^{87}\text{Sr} = -5.9\text{‰}$, and, Ca/Sr_{dolomite} = 530). The third end-member, precipitation (precip), is more difficult to estimate. The $\delta^{87}\text{Sr}$ signature was not measured directly in rainfall due to extremely low concentrations of Sr. Therefore, we adopted the signature of flood water ($\delta^{87}\text{Sr} = 33.5\text{‰}$) from the Fortescue River at the entry point to the Fortescue Marsh, collected immediately after cyclone Heidi (January 2012).

We used the precipitation end-member Ca/Sr, (ratio of 40) as observed in fresh groundwaters of fractured rock aquifers (Dogramaci et al., 2012), which closely reflects the rainfall Ca/Sr ratio. It is expected that the precipitation/flood water signature in the cyclone/flood driven hydrological regime will mainly reflect ratios in ocean water and to a lesser extent in atmospheric dust. This adopted value is also close to the 50.5 ratio, an ocean average for depths of 0-150 m. (Riley and Tongudai, 1967). Based on mass balance calculations (Fig. 10A), the contribution of A end member (radiogenic source) is <1%, B end member (dolomite) is ~7% and C end member (Sr from flood/precipitation) is > 92%. The Marsh represents a terminal location, where weathering products (i.e., major ions) from surrounding catchments are delivered (Fig. 10B).

However, the weathering from major rock bearing formations contributes a small percentage compared to ions in precipitation delivered by surface run off during flash-floods. This is consistent with the description of the Marsh as a flood water fed system, not a classical playa groundwater system, allowing accumulation of significant salt loads over millennia by rainwater evaporation.

Figure 10. Sr and $\delta^{87}\text{Sr}$ mass balance in groundwater of the Hamersley Basin. Note most of the groundwater signatures (red circles) resemble that of floodwater signatures (yellow circles). The three end-members are represented by $\delta^{87}\text{Sr}$ of clay minerals from shale band (Radiogenic), $\delta^{87}\text{Sr}$ of non-radiogenic carbonate from Wittenoom Formation and mafic igneous rocks (Dolomite) and recharge (Flood water). Mafic rocks have low Rb/Sr ratios and very low $\delta^{87}\text{Sr}$ (e.g., for Australia and New Zealand province 0.703-0.706‰, Johnson et al., 1989).

7. Conclusion

The Hamersley Basin is characterised by one of the oldest terrestrial landscapes on the planet. The interaction of an exceptionally old landscape with a semi-arid subtropical climate provides an opportunity for tracing the geochemical evolution of groundwater. The geochemical composition of deep groundwater of the terminal Fortescue Marsh represents the ultimate geochemical signature, reflecting mixing between major ions sourced from weathering of the basin and flood water. Groundwater hydrochemistry of fractured rock aquifers reflects the geochemical fingerprints of particular rock formations ranging from very high $\delta^{87}\text{Sr}$ values, characteristic of the CID aquifer that contains clays pockets and shale (115‰ to 2322‰), to low $\delta^{87}\text{Sr}$ values typical for mafic volcanic rocks, to very low $\delta^{87}\text{Sr}$

values typical for altered carbonates (-0.5‰ to 8.2‰) and the Wittenoom dolomite (-5.9‰). The saline and brine groundwater on the Marsh represents a fairly constant $\delta^{87}\text{Sr}$ signature of 36.6 ± 1.4 ‰ regardless of variations in TDS, $\delta^{18}\text{O}$ and Sr concentration. Waters with this signature can be considered as “mature” in a geochemical sense, representing the final stage of water evolution on a basin scale and reflecting contributions from three major sources: >92% from precipitation, ~7% from carbonates rocks and <1% from rocks with highly radiogenic signature (shales and clays). This implies that ion transport due to horizontal groundwater inflow to the terminal basin is very small compared to the vertical infiltration of direct precipitation and fresh flood water. The constant $\delta^{87}\text{Sr}$ of 36.6 ± 1.4 ‰ in the Marsh groundwater, along with variable TDS and $\delta^{18}\text{O}$, results from various mixing ratios of highly saline water and/or salt re-dissolution, governing ionic ratios, with fresh rain or flood water influencing ion concentrations. The locally significant geochemical processes influencing groundwater hydrochemistry in the terminal basin are dominated by cyclic wetting-drying and de-dolomitisation that have no significant influence on $\delta^{87}\text{Sr}$ values.

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881 Highlights

- 882 • $\delta^{87}\text{Sr}$ - clays and shale was 115 to 232‰, mafic volcanic rocks and altered
883 carbonates -0.5 to 8.2‰ and dolomite -5.9‰
- 884 • the ultimate $\delta^{87}\text{Sr}$ signature of water in the Hamersley Basin, one of the oldest
885 landscapes (2.7Ga), equals 36.6 ± 1.4 ‰
- 886 • waters with this signature can be considered as “mature” in a geochemical sense
- 887 • over > 92% of dissolved solutes originate from precipitation, ~7% from volcanic and
888 carbonates rocks and <1% shales and clays minerals
- 889 • vertical flow is the dominant mode compared to lateral groundwater flow
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