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Hydrochemical and stable isotope indicators of pyrite oxidation in carbonate-rich environment; the Hamersley Basin, Western Australia

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ABSTRACT

Sulphur (S) is a commonly occurring element in most aquifers, primarily in oxidised (sulphates) and reduced (sulphides) forms. Sulphides often constitute a risk to groundwater quality due to acid rock drainage, especially in catchments that are subject to mining excavations or groundwater injection. However, in semi-arid regions detection of the acid rock drainage risk can be challenging and traditional methods based on observations of increasing SO_4 concentrations or SO_4/Cl ratios in surface and groundwater, are not necessarily applicable. In addition, decreasing pH, usually accompanying pyrite oxidation, can be masked by the high pH-neutralisation capacity of carbonate and silicate minerals.

Analysis of 73 surface and groundwater samples from different water bodies and aquifers located in the Hamersley Basin, Western Australia found that most of the samples are characterised by neutral pH but there was also a large spatial variability in the dissolved sulphate (SO_4) concentrations that ranged from 1 mg/L to 15,000 mg/L. Not surprisingly, groundwater in aquifers that contained pyrite had high sulphate concentrations (>1000 mg/L). This was associated with low $\delta^{34}S_{SO4}$ values (+1.2‰ to +4.6‰) and was consistent with the values obtained from aquifer matrix pyritic rock samples (−1.9‰ to +4.4‰). It was also found that the SO_4 concentrations and acidity levels were not only dependent on $\delta^{34}S_{SO4}$ values and existence of pyrite but also on the presence of carbonate minerals in the aquifer matrix. The groundwater in aquifers containing both pyrite and carbonate minerals had a neutral pH and was also saturated with respect to gypsum and had high magnesium concentrations of up to 2200 mg/L suggesting dedolomitisation as the process buffering the acidity generated by pyrite oxidation.

Based on the findings from this study, a classification scheme has been developed for identification of the acid rock drainage contribution to groundwater that encompasses a myriad of geochemical processes that occur in aqueous systems. The classification uses five proxies (SO_4, SO_4/Cl, SI of calcite, $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$) to improve assessment of the oxidation of sulphide potential contribution to overall sulphate ion concentrations regardless of acidity levels of the aqueous system.

1. Introduction

Anthropogenic induced changes to natural hydrological regimes can change the hydrochemical equilibrium and significantly alter water quality of groundwater systems. Mining that occurs concurrent with the abstraction of groundwater associated with dewatering, exposes minerals previously located in an anaerobic or in an oxygen limited environment to oxidising conditions (Migaszewski et al., 2008; Tostevin et al., 2016). The water quality can degrade due to mobilisation of sulphur and subsequent acid generation along with significant increases in SO_4 concentrations. Similarly, reinjection or enhanced recharge arising from water-disposal into ephemeral creeks can alter the natural redox conditions through the introduction of oxygen-rich recharge water (Herczeg et al., 2004).

The traditional method of using SO_4 concentrations or SO_4 to Cl ratios in surface and groundwater to detect acid rock drainage, may not necessarily always be applicable. Sulphate minerals (e.g., gypsum) are ubiquitous in arid and semi-arid regions, are insoluble at concentrations over 2500 mg/L, and can effectively mask additional SO_4 inputs generated from pyrite oxidation. Also decreasing pH does not always accompany pyrite oxidation especially in aqueous systems containing materials with a high pH-neutralisation capacity such as carbonates. Carbonate dissolution results in the

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addition of bicarbonate ions into solution which acts to buffer the additional acidity generated by the pyrite oxidation.

Previous investigations have focused on the use of $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ values to study the sources of sulphur and hydrochemical processes in aqueous systems (Tostevin et al., 2016; Wang et al., 2014); tracing groundwater flow in regional aquifers (Dogramaci et al., 2001), sources of salinization in groundwater (Yamanaka and Kumagai, 2006), and groundwater pollution (Hosono et al., 2011). However little has been done to illustrate the usefulness of combining stable isotope and hydrochemical values to support increased understanding of subsurface geochemical processes, particularly acid rock drainage (e.g., Foster et al., 2008; Szynkiewicz et al., 2015). An integrated model combining SO_4 concentration, SO_4:Cl ratio, the saturation index for calcite, $\delta^{34}S\text{-}_{SO4}$ and $\delta^{18}O_{SO4}$ values enhance characterisation of particular processes and S-sources, enabling for the development of classification guidelines for the detection of sulphate contribution from acid rock drainage.

The dominant sources of SO_4 in semi-arid environments are atmospheric precipitation and weathering of rocks and minerals (Chivas et al., 1991; Herczeg et al., 2001). S-compounds associated with redox reactions are generally characterised by distinct sulphur isotope values ($\delta^{34}S$) which can largely be attributed to fractionation during biologically mediated SO_4 reduction (e.g., Chambers and Trudinger, 1979). Particularly the reduction of SO_4 to hydrogen sulphide (H_2S) accompanied by considerable isotopic fractionation that results in very low $\delta^{34}S_{H2S}$ values and relatively high $\delta^{34}S_{SO4}$ values in the residual SO_4 (Thode, 1991). In contrast, the subsequent inorganic formation of metal sulphide (e.g., pyrite) from H_2S is characterised by a relatively negligible stable isotope fractionation. Hence, sulphur in the reduced form of pyrite, is generally characterised by low $\delta^{34}S_{FeS2}$ compared to the dominant initial sulphate marine source ($\delta^{34}S_{SO4}$ ~21‰, Claypool et al., 1980). Also the oxidation of pyrite is characterised by relatively negligible fractionation between $\delta^{34}S$ of the parent pyritic rock and $\delta^{34}S$ of the dissolved sulphate by-product (Taylor et al., 1984). Therefore, dissolved SO_4 originating from pyrite oxidation will likely have low $\delta^{34}S_{SO4}$ values that reflect the signature of the parent pyrite. Also limited fractionation occurs during sulphate mineral formation, these minerals will have $\delta^{34}S_{SO4}$ values that reflect the signature of dissolved SO_4 in waters from which they derive.

This study investigates the capacity of the stable isotope of sulphate ($\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$) to identify water affected by pyrite oxidation in a semi-arid environment and develops a classification system that can easily indicate acid rock drainage potential. Isotope and geochemical characterisation was conducted on waters from different hydrogeological units of varying mineralogy (pyritic and non-pyritic) in order to establish baseline data and constrain the various potential sources of sulphate in the Hamersley Basin of Western Australia. In addition, mass balance modelling of oxygen isotope values ($\delta^{18}O_{H2O}$ and $\delta^{18}O_{SO4}$) was used to distinguish differences in the oxidation pathways in natural groundwater systems relative to mining influenced waters.

2. Materials and method

2.1. Geological setting and S-bearing minerals in the Hamersley Basin

The Hamersley Basin covers an area of more than 100,000 km^2 containing a well-preserved supra-crustal succession of Archean to Lower Proterozoic rocks (Trendall and Blockley, 1970; Blake and Barley, 1992; Thorne and Trendall, 2001). Stratigraphically, the Basin can be divided into three major geological units; the upper Turee Creek Group (<2.2 Ga), the Hamersley Group (2.4 Ga); and the Fortescue Group (2.7 Ga) which unconformably overlies basement granite and greenstone of the Archean Pilbara Craton (Fig. 1). Stratigraphic deformation is observed throughout the Basin and is most pronounced in the southern part, where compression of the Pilbara Craton has resulted in the uplift of the underlying bedrock and formation of the Hamersley Ranges (Trendall and Blockley, 1970). Hence, in this region, both the pyrite containing shale units of the Hamersley and Fortescue Groups outcrop to surface. Minerals containing sulphur occur as sedimentary sulphides and sulphates produced over a wide range of geological eras. Sulphide minerals in reduced form occur as pyrite (FeS_2), in ancient sedimentary carbonaceous shale. Abundant pyrite has been identified in the Roy Hill Shale (RHS), the uppermost unit of the Fortescue Group (~2.7 Ga) and in the Mount McRae Shale (MCS) a unit of the Hamersley Group (~2.5 Ga). Total sulphur content from both of these shale units generally ranges between 0.1% and 10% (Ono et al., 2003). Pyritic rock samples from the MCS generally occur as finely grained disseminated pyrite or pyrite nodules (0.1–10 cm). Pyrite minerals from the RHS, however, are assumed to be predominately in the form of nodules (>1 cm). Pyrite has also been identified in lignitic detrital material in the eastern margins of the Basin.

The oxidised sulphur in the Hamersley Basin occurs in the form of sulphate (SO_4) contained in evaporite minerals such as anhydrite ($CaSO_4$) and the more hydrated gypsum ($CaSO_4{\cdot}2H_2O$). As there are no known massive deposits of ancient sedimentary sulphate in the Hamersley Basin, it is expected that sulphate minerals originate from relatively modern geochemical processes (Dogramaci and Skrzypek, 2015). Gypsum has been observed as both surface/near surface crystals in alluvial sediments within the internally draining Fortescue Marsh located on the eastern extent of the Basin; and in deeper sediments at Mount Tom Price where pyritic RHS outcrops (Kakegawa et al., 1998). Magnesium rich sulphates also occur as surface precipitates in the mine voids and adjacent to natural seepage in Karijini National Park (Hedley, 2009). The origin of surficial sulphate minerals can be attributed to the semi-arid environment where high evaporation rates cause evapo-concentration of water on the surface or capillary zone promoting evaporite mineral formation (Dogramaci et al., 2012). However, the occurrence of pyrite within deeper sediments of weathered pyritic RHS suggests the potential for formation of gypsum by diagenetic processes. Less common minerals containing sulphate identified in the Hamersley Basin include alunite ($KAl_3(SO_4)_2(OH)_6$ -Van Kranendonk, 2006) and jarosite ($KFe_3(SO4)_2(OH)_6$Webb et al., 2003).

2.2. Hydrogeological settings

Groundwaters investigated in this study occur in weathered and fractured rock aquifers of the Archean and Proterozoic Fortescue and Hamersley Groups; fluvial sediments deposited in Cenozoic palaeochannel (Channel Iron Deposits); and Tertiary/Quaternary valley-fill of unconsolidated detrital material (Fig. 2). Groundwater systems can be divided into four major aquifer types comprising unconsolidated sedimentary material; chemically-deposited carbonate rocks and minerals, iron-rich fluvial sediments and fractured rock aquifers (FRA).

Groundwater flow predominately occurs through the fractured rock aquifer via discontinuities in tight bedrock and shale units. Variable weathering during exposure and extensive deformation of the underlying bedrock has resulted in complex localised flow pathways. Recharge is predominately associated with high-volume rainfall (Dogramaci et al., 2012) and can be up to 13 mm/y estimated using Carbon-14 and catchment Cl mass balance calculations (Cook et al., 2016). Pyritic minerals are generally located below water table (BWT) with limited oxygen availability but also outcrop locally on the surface. An extensive investigation to date groundwater from the FRA using multiple tracer technique identified distinct age components in the groundwater. Most of the