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Sources of environmental sulfur in the groundwater system, southern New Zealand

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ABSTRACT

Sulfide minerals commonly occur in sediments and basement rocks in southern New Zealand, as authigenic precipitates from groundwater below the oxygenated surface zone. There are two principal potential sources for sulfur in the groundwater system: weathering of sulfide minerals in the metamorphic basement and rainwater-derived marine aerosols. We present data for these two key sulfur sources: metamorphic sulfide and associated hydrothermal Au-bearing veins within the Otago Schist (average $\delta^{34}S = -1.8 \pm 2.4$‰), and an inland saline lake (S derived entirely from rainwater, $\delta^{34}S = 21.4 \pm 0.8$‰). We use these two end member $\delta^{34}S$ values to estimate the contributions of these sources of sulfur in authigenic groundwater sulfide minerals and in waters derived from oxidation of these sulfide minerals, across a range of environments. We show that authigenic groundwater pyrite along joints in the Otago schist is derived primarily from metamorphic basement sulfur. In contrast, authigenic groundwater pyrite cementing Miocene-Recent aquifers shows a substantial marine aerosol component, and represents a distinct hydrogeological system. We suggest that marine aerosols represent a significant flux to the terrestrial sulfur cycle that has been present through the groundwater system in Otago over the past 20 million years.

1. Introduction

Sulfur is ubiquitous in surface and ground waters, and can have a wide variety of both natural and anthropogenic sources. Common sources include rainwater, (which may derive from marine aerosols, atmospheric pollutants or volcanic gases), geological weathering of sulfide and evaporite minerals, and surface runoff from fertiliser or sewage (Chivas et al., 1991; Moncaster et al., 2000; Otero et al., 2008; Turchyn et al., 2013; Wadleigh et al., 1996). The relative contribution from each of these sources varies regionally, depending on the geology, climate and land use, and can be affected by anthropogenic processes such as mining and groundwater extraction (Bottrell et al., 2008; Otero and Soler, 2002; Samborska and Halas, 2010). The abundance and speciation of sulfur in groundwater has important implications for redox and pH balance, ecology and drinking water quality. Sulfur is intimately linked with the recycling of organic matter, as sulfate reducing bacteria respire sulphate in the absence of oxygen, producing sulfide (Jørgensen, 1982).

Marine aerosols are generated from sea spray along coastlines, and can be transported inland and enter surface waters via precipitation (Beck et al., 1974; Chivas et al., 1991; O'Dowd et al., 1997; Stallard and Edmond, 1981). As much as 50% of the total salts have been attributed to marine aerosols in some coastal rivers (Beck et al., 1974; Berner and Berner, 1996; Stallard and Edmond, 1981). The presence of marine aerosols is anticipated in surface waters across southern New Zealand, as even the most inland areas are <120 km from the coastline (Barker et al., 2004; Craw and Beckett, 2004; Kusakabe et al., 1976; Robinson and Bottrell, 1997). As a result of the sparse population and strong winds, atmospheric sulfur emissions are low in areas outside of major cities and volcanic regions. In contrast to Europe, the eastern United States and China (Jådrysek, 2000; Jenkins, 2005; Mayer et al., 1995; Xiao and Liu, 2002), rainwater in southern New Zealand is dominated by marine aerosols (Craw and Beckett, 2004; Craw and Nelson, 2000; Jacobson et al., 2003; Litchfield et al., 2002). Aerosols are transported from the Tasman Sea by the Prevailing Westerly winds, with the occasional influence of the Southerlies from the Pacific east coast. Atmospheric sulfur is deposited over the Southern Alps

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mountain range, and is episodically washed into the semi-arid central Otago basin during periods of heavy rainfall (Craw et al., 2013).

Sulfide minerals are readily oxidised when exposed to atmospheric oxygen, and as groundwater circulates through shallow aquifers, leaching of sulfur-bearing minerals adds to the dissolved sulfur load. These sulfur-bearing minerals may include evaporites, sedimentary sulfides or magmatic sulfides, depending on the regional geology. The mineral leaching processes that add sulfur into surface waters and rivers, ultimately delivering sulfur to the world's oceans, vary regionally and remain poorly constrained on a global scale (Calmels et al., 2007; Karim and Veizer, 2000; Martin and Meybeck, 1979; Otero et al., 2008; Turchyn et al., 2013; Yuan and Mayer, 2012). Local basement rocks across southern New Zealand are rich in metamorphic sulfide minerals, and these minerals dominate the weathering addition to terrestrial waters (Litchfield et al., 2002; Pitcairn et al., 2010). Hence, surface and ground waters in the Otago Basin contain dissolved sulfur from two dominant sources, basement weathering and marine aerosols, in a proportion that will be defined by local geological, climatic and anthropogenic processes.

Deep groundwater is typically relatively reduced, and as such, dissolved sulfur occurs as various sulfide ions (Grenthe et al., 1992; Jakobsen and Postma, 1999), which can lead to deposition of secondary authigenic sulfide minerals in the hosting aquifers. These authigenic sulfide minerals should record information about ancient groundwater sulfide. Shallower groundwater, and surface waters in river and lakes, are typically oxidising, and contain sulfur as dissolved sulfate ions. Here, oxidation of geological sulfide minerals and mixing with atmospheric sulfur may occur. Oxidation of sulfide minerals may continue in deep anoxic groundwater, via reduction of Fe(III) minerals. Evaporitic sulfate minerals may precipitate from surface waters where the dissolved sulfur load is sufficiently high. The boundary between oxidising and reducing conditions is controlled primarily by the position of the water table and associated extent of the vadose zone (Sophocleous, 2002).

In this study, we compile SO_4/Cl ratios for groundwater and evaporitic salts around southern New Zealand. We present new sulfur isotope data to investigate the sources of sulfur that contribute to widespread authigenic sulfide minerals precipitated from groundwater at a number of economically and ecologically important sites. In addition, we present paired sulfur and oxygen isotope data for aqueous sulfate from runoff waters and lakes. We focus on the relative importance of basement and marine aerosol sources, which may have varied between the Miocene and the present day as a result of marine regression and intermittent periods of tectonic uplift (Youngson, 1995). Our study is mainly directed at the origins of authigenic groundwater sulfides that locally cement young (Miocene-Holocene) terrestrial sediments. Disturbance of these sediments, by uplift and erosional processes in a dynamic tectonic environment can result in exposure and oxidation of these sulfides, and we aim to characterise the dissolved sulfur that arises in runoff waters in these settings. These results are of direct interest for assessing influences on groundwater prior to anthropogenic impacts, to enable comparison with modern aquifers. We also consider the impact of mining operations on local sulfur fluxes. The high air quality, coastal environment and schist dominated geology generate a simple system whereby sulfur isotopes can provide useful constraints on sources of environmental sulfur in different hydrogeological environments.

1.1. Isotopic signatures of environmental sulfur

Sulfur isotope ratios provide a sensitive means to determine the source of environmental sulfur in waters and minerals. $\delta^{34}S$ is a measure of the relative abundance of the two common stable isotopes of sulfur, ^{32}S and ^{34}S, expressed in delta notation relative to the Vienna Canyon Diabolo Troilite (VCDT) standard.

$$\delta^{34}S = \left[\frac{{}^{34}S/{}^{32}S_{sample} - {}^{34}S/{}^{32}S_{standard}}{{}^{34}S/{}^{32}S_{standard}}\right]*1000 \quad (1)$$

Different possible sources of sulfur have characteristic isotope signatures. While some of these signatures may cover wide ranges that partially overlap, and a single sample may reflect an integrated and complex history, $\delta^{34}S$ has been used to distinguish between marine, metamorphic and bacteriogenic sources of sulfur in terrestrial environments (Bottrell et al., 2008; Bottrell et al., 2000a,b; Calmels et al., 2007; Karim and Veizer, 2000; Otero et al., 2008; Pawellek et al., 2002; Robinson and Bottrell, 1997; Samborska et al., 2013; Turchyn et al., 2013; Tuttle et al., 2009; Xiao and Liu, 2002; Yuan and Mayer, 2012).

Geological sulfide sources include magmatic and sedimentary sulfides, both of which may be homogenised or fractionated during metamorphism, and evaporite minerals. Magmatic sulfide $\delta^{34}S$ can range from $-10‰$ to $+10‰$, and metavolcanics should fall within this range. Metasediments may show a wider $\delta^{34}S$ range, depending on the $\delta^{34}S$ of any original bacteriogenic sulfide, but metamorphism tends to homogenise $\delta^{34}S$ (Canfield, 2004; Garrels and Lerman, 1984). Oxidative weathering of metamorphic pyrite may occur directly in the presence of oxygen, or via reduction of oxidised Fe^{3+} minerals (e.g. hematite). Fractionation during weathering is minimal ($<1‰$; Balci et al., 2007; Heidel and Tichomirowa, 2011), and so the oxidised products should reflect the $\delta^{34}S$ of the leached minerals. Additionally, weathering of evaporite minerals may be a significant geological sulfur source in some regions (Stallard and Edmond, 1983). Marine sulfate $\delta^{34}S$ has ranged between ~15 and ~25‰ over the Mesozoic and Cenozoic (Claypool et al., 1980; Paytan et al., 1998), and any evaporitic source rock in New Zealand would likely fall within this range. However, there is no significant evaporite source in southern New Zealand.

The concentration and $\delta^{34}S$ of marine sulfate is globally homogeneous. The traditional accepted value for the $\delta^{34}S$ of marine sulfate is $20.3 \pm 0.8‰ (2\sigma)$, but Rees (1978) demonstrated that there is a bias towards lighter values when measuring $\delta^{34}S$ via combustion to sulfur dioxide, and that $\delta^{34}S$ is closer to 21‰ (Paytan et al., 1998; Tostevin et al., 2014). Marine sulfate is the main source of atmospheric sulfur in coastal areas (Wadleigh et al., 1996), but organic sulfur compounds, such as dimethyl-sulfide (DMS), may constitute an additional minor source in regions of excess productivity, including saline mud flats and marine upwelling zones (Gibson et al., 1991; Warneck, 1999). DMS is typically depleted by as much as 3‰ compared with marine sulfate, but remains heavy compared with terrestrial sulfur sources (Amrani et al., 2013; Calhoun et al., 1991).

In anoxic environments, sulfate is reduced to sulfide, and in the presence of reactive Fe^{2+} this sulfide may be preserved as iron sulfide minerals (Berner, 1970). When sulfate reduction is biologically mediated, the light isotope is preferentially metabolised, resulting in a wide range of sulfur isotope signatures depleted by as much as 70‰ compared with starting sulfate (Canfield, 2001a,b; Canfield et al., 2010; Detmers et al., 2001; Habicht et al., 2002; Leavitt et al., 2013; Sim et al., 2011). In contrast to these bacteriogenic signatures, inorganic thermochemical sulfate reduction (TSR) from groundwater below the oxygenated zone is accompanied by smaller isotope fractionations, 0–20‰, that may be positive or negative (Ohmoto and Goldhaber, 1997; Watanabe et al., 2009). TSR is limited to high temperature environments rarely found in groundwater reservoirs (Claypool and Mancini, 1989; Cross et al.,