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 δ^{34}S = -1.8 ± 2.4 ‰), and an inland saline lake (S derived entirely from rainwater, δ^{34}S = 21.4 ± 0.8 ‰). We use these two end member δ^{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 run off 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 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 across southern New Zealand, at a number of economically and ecologically important sites. In addition, we present paired sulfur and oxygen isotope data for aqueous sulfate from run-off 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 run-off 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. δ^{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.

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

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, δ^{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., 2000; 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 oxidized Fe^{3+} minerals (e.g. hematite). Fractionation during weathering is minimal (<1 ‰; Balci et al. 2007; Heidel & Tichomirowa 2011), and so the oxidized 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 ±0.8 ‰ (2σ), 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 metabolized, resulting in a wide range of sulfur isotope signatures depleted by as much as 70 ‰ compared with starting sulfate (Canfield 2001; 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., 2004; Goldhaber and Orr, 1995; Machel et al., 1995).

Anthropogenic signatures can originate from atmospheric sources, such as the burning of coal, and surface run off from fertilizer or sewage. These two sources tend to have overlapping signatures around 0 ‰ (Samborska et al., 2013). In a case study from Pennsylvania, animal manure ranges from 3-5 ‰ and fertilizer between 2-9 ‰ (Cravotta and Protection, 2002). In England, fertilizer ranges from 0-6 ‰ (Moncaster et al., 2000), and in Spain, -2 to +7 (Otero and Soler, 2002). The δ^{34}S of fertilizer and sewage will vary depending on local farm practice, but we exclude anthropogenic sources for our sampling areas (See section 2.1).

The major complication when interpreting sulfur isotope data is the fractionation effect during authigenic sulfide mineral formation, as bacterial sulfate reduction (BSR) can produce a wide range of fractionations depending on the environmental conditions. Fractionations from BSR may overprint any information about the original source of sulfate. Paired δ^{34}S- δ^{18}O measurements can help constrain mixing models in sulfate, but this is not possible for sulfide minerals, which are the focus of our study (Turchyn and Schrag, 2006).

The $\delta^{18}O_{SO4}$ of marine sulfate is 9.3 ‰ (Lloyd, 1968), and this signature should be preserved in marine aerosols. $\delta^{18}O_{SO4}$ is set when the sulfate molecule forms, and does not subsequently exchange oxygen with water at ambient temperatures and pH (Rennie and Turchyn, 2014). During BSR, sulfate with light oxygen is preferentially selected, leaving residual sulfate pools heavy in both sulfur and oxygen isotopes. During sulfate reduction and subsequent sulfide reoxidation, the sulfate-oxygen is lost and replaced with new oxygen atoms. The new oxygen atoms in sulfate are derived from a mixture of dissolved atmospheric oxygen ($\delta^{18}O_{O2}$ = 23.5 ‰, Kroopnick and Craig, 1972) and meteoric water ($\delta^{18}O_{H2O}$ is typically around -15 ‰ in New Zealand, Bowen and Wilkinson, 2002; Terzer et al., 2013). Under anoxic conditions, pyrite oxidation occurs via Fe(III) minerals, and the oxygen is derived from water with a fractionation of +2.3 ‰ (ε_{SO4-02})(Heidel and Tichomirowa, 2011). Regardless of the pyrite oxidation pathway, most of the oxygen atoms incorporated into sulfate are derived from water (Rosso and Vaughan, 2006). Under oxic conditions, around 10 % of the oxygen atoms will be derived from dissolved atmospheric oxygen, with a fractionation of -8.4 ‰ ($\varepsilon_{SO4-H20}$) (Heidel and Tichomirowa, 2010). Thus, we solve for an average $\delta^{18}O$ for sulfate derived from pyrite weathering using equation 2:

$$\delta^{18}O_{SO4} = x(\delta^{18}O_{H20} + \varepsilon_{SO4-H20} + (1-x)(\delta^{18}O_{O2} + \varepsilon_{SO4-O2}) \qquad (2)$$

For New Zealand, $\delta^{18}O_{SO4}$ is likely around -10 ‰. This value may vary considerably given the pathway for pyrite oxidation and the meteoric water $\delta^{18}O$, but should always remain negative compared with marine sulfate. If meteoric water is around -5 ‰, as reported for some New Zealand water bodies, $\delta^{18}O_{SO4}$ may be as heavy as -1 ‰.

We use a dual isotope linear mixing model to distinguish between fluxes from basement weathering ($f_{basement}$), direct contributions from rainwater (f_{rain}), and weathering of sulfide minerals derived from ancient rainwater ($f_{Sediment}$) in aqueous sulfate samples. In this simple model, we assign both sedimentary sulfide weathering and rainwater a $\delta^{34}S$ of 21 ‰ ($\delta^{34}S_{marine}$), and basement weathering a distinct $\delta^{34}S$ of -1.8 ‰ ($\delta^{34}S_{basement}$). We then assign both basement and sedimentary sulfide a $\delta^{18}O$ of -10 ‰ ($\delta^{18}O_{py\text{-}ox}$), and rainwater a distinct $\delta^{18}O$ of +9 ‰ ($\delta^{18}O_{rain}$). Through a series of three equations, the mixing of three components can be resolved for aqueous sulfate with a known $\delta^{34}S_{SO4}$ and $\delta^{18}O_{SO4}$ (Samborska et al., 2013).

$$f_{rain} = 1 - \left[\frac{(\delta^{18}O_{SO4} - \delta^{18}O_{rain})}{(\delta^{18}O_{py-ox} - \delta^{18}O_{rain})}\right] \qquad (3)$$

$$f_{basement} = 1 - \left[\frac{(\delta^{34}S_{SO4} - \delta^{34}S_{basement})}{(\delta^{34}S_{marine} - \delta^{34}S_{basement})}\right] \qquad (4)$$

$$f_{Sediment} = 1 - f_{rain} - f_{basement} \qquad (5)$$

1.2 Geological background

The basement rock across southern New Zealand is the Otago Schist, a Jurassic - Early Cretaceous metamorphic complex, which includes a range of metasediments and metavolcanics. The Otago Schist contains Au-bearing quartz veins, where metamorphic fluids have mobilised and concentrated Au and sulfur from marine sediments into narrow zones within the resulting metasediments (Large et al. 2011; Pitcairn et al. 2010; Scott et al. 2009). During this process sedimentary Au-bearing sulfide minerals recrystallize, releasing precious metals, and new authigenic Au-bearing sulfide minerals form from high temperature hydrothermal fluids (Large et al. 2012). The Otago Schist is overlain by unconformable marine and marginal marine sediments in eastern Otago, deposited during the Late Cretaceous submergence of New Zealand (Landis et al., 2008), and the following marine transgression (Figure 1). In central and western Otago, the basement is overlain by Mesozoic lithic conglomerates which terminate in a regional unconformity.

Eocene Quartz pebble conglomerates transition into Oligocene marine and marginal marine sediments, terminating in a regional unconformity. This unconformity is overlain by fluvial and lacustrine sediments hosting alluvial fans and quartz rich channels, that range from Miocene (20 million years ago, Ma) to late Quaternary (Figure 1). Gold has been fluvially reworked from quartz veins within the schist into placer deposits that occur at erosional breaks in the sediment pile during uplift and erosion. This placer gold was then further recycled into overlying Pliocene and Pleistocene gravel sediments. During this series of uplift and erosional cycles, sulfur was also mobilized (Youngson, 1995). These resulting quartz gravel sediments are often cemented by authigenic groundwater pyrite.

1.3 Hydrogeological background

Rainwater falls over the southern Alps, bringing associated sulfur into the Otago Basin. The groundwater in the Otago basin is reducing and acidic, and so the sulfur is initially precipitated as sulfide in fan sediments along the range margins (Rosen and Jones, 1998). Evaporation rates are high within the basin, bringing mineral charged groundwater to the surface, and evaporitic saline soils and an ephemeral salt lake have developed within the rain shadow (Craw and Beckett, 2004). These salts may be remobilized and flushed into the river system during periods of heavy rainfall, and ultimately delivered to the ocean.

2. Methods

2.1 Sampling

Weathering has oxidised much of the sulfide exposed at the surface, making it difficult to obtain fresh samples. We commonly sampled in active or recently active mine environments where fresh rock with unoxidised pyrite is exposed. This approach limited the availability of suitable sites. Moreover, there may be additional processes operating in mine environments that affect the local surface waters, and do not reflect widely occurring natural processes. However, mine environments are the only localities where it is possible to extensively sample unweathered sulfide minerals in this region.

Pyrite and arsenopyrite are almost ubiquitous as accessory minerals in orogenic gold mines, and so interaction with these sulfide minerals affects the compositions of mine waters and nearby surface waters and groundwaters. Exposure of fresh mineral surfaces is normally the rate limiting factor for sulfide oxidation, but mine excavations rapidly expose fresh surfaces from below the oxygenated surface zone, as well as dramatically altering the geometry of the local vadose zone. While this wouldn't affect mineral samples from veins and joints at Macraes pit, which formed prior to the onset of mining activity, it may have affected sulfate in the pit lake and recent run-off waters.

We sampled evaporitic salt accumulations, and associated run-off waters, but these soils have been modified by human agricultural activity over the past 100 years, and remaining sites are limited (Rogers et al., 2000). Some of our terrestrial gravel aquifer sediments come from historical placer mines, where sluicing activity has left behind gentle slopes that encourage pooling and evaporation of rainwater. This may have increased the marine component in surface waters compared with surrounding sediments and waters. We also sampled an ephemeral saline lake. Some of these environments represent important ecological and geographical sites that harbor unique flora and fauna (Allen et al., 1997; Bayly, 1967; Patrick, 1989; Rogers et al., 2000).

Possible contaminant anthropogenic sulfur sources include fertiliser, industrial emissions, and the burning of coal. However, the studied areas in southern New Zealand are sparsely populated, and the region is strongly affected by prevailing westerly winds in the vast Southern Ocean, with negligible sources for S contamination. Our water samples were obtained from sites removed from local anthropogenic influences and farm run-off (aside from mine activity). Further, the majority of samples are sulfide minerals precipitated from the ancient groundwater system prior to human settlement of New Zealand. Volcanic emissions represent an additional potential contaminant sulfur source. While this may be significant on the North Island, we discount this source for southern New Zealand.

2.2 Analytical methods

Sulfide mineral concentrates were extracted from schist using a tungsten carbide chisel. Mineralized lumps were subsampled across layers using a diamond tipped drill. Where grains were visible, pyrite and arsenopyrite were hand-picked using an optical microscope. All samples were ground to a flour-grade powder using an agate pestle and mortar. Multiple sub-samples were taken from within a single mineralized piece to analyse internal variability, which may be large in sulfide minerals (e.g. Kohn et al., 1998).

Water sampling was undertaken in June 2015. Water samples were collected in clean plastic bottles, rinsed three times in ambient water before being filled from >10 cm beneath the surface and acidified. Samples were filtered through 0.45 μm filter papers within 24 h of collection. Excess 10 % $BaCl_2$ solution was added, and samples were filtered after >48 h to collect solid $BaSO_4$ precipitates, which were rinsed once in 10 % HCl and three times in Milli-Q water before being dried at 50°C for >24 h.

The weight percentage S for each sample was measured to determine the purity, before 200 μg of sulfur was weighed for isotopic analysis on an element analyser attached to a mass spectrometer at the Iso-trace Laboratories, Department of Chemistry, University of Otago. V_2O_5 was added to aid combustion. Data here are reported in permil (‰) relative to the Canyon Diabolo Troilite. Silver sulfide reference materials IAEA-S1 and IAEA-S2 were used to calibrate measurements, and control samples (IAEA-S1 and NBS-127) are accurate to within 1 ‰ for all runs. Samples were run in duplicate or triplicate, and most give a standard deviation <1 ‰ (table 1).

$\delta^{18}O_{SO4}$ was analysed for six barite samples derived from aqueous sulfate. Samples and standards were weighed in triplicate into tin capsules (0.8 mg), and vacuum dried for 18 hours at 50 degrees. V-SMOW-2 water sealed in silver tube was used as a standard and the samples were transferred to a sealed autosampler after brief contact with the atmosphere. $\delta^{18}O$ was measured by thermolysis to CO gas at 1450 degrees in a Thermo TC/EA, followed by measurement of the CO in a Thermo Delta V IRMS.

3. Sample sites

Metamorphic pyrite from schist basement was collected from a deeply-incised river gorge at Fiddlers Flat (figure 2; Large et al. 2012). The pyrite is coarse grained (up to 1 mm) and aligned with the foliation in pumpellyite-actinolite facies rocks exposed in the floor of the gorge. Hydrothermal pyrite and coexisting arsenopyrite occur in a late metamorphic gold-bearing shear zone, the Hyde-Macraes Shear Zone, in lower greenschist facies schist basement. These minerals are exposed in the walls of open cut pits of the Macraes mine (figure 2), and were sampled for this project in the Golden Bar pit (Large et al., 2012). In addition, detrital pyrite and arsenopyrite derived from this gold-bearing shear are preserved in Late Pleistocene to Holocene sediments at the Macraes mine (Chappell and Craw, 2002), and individual grains were hand-picked from a heavy mineral concentrate from these sediments. Pyrite deposited by groundwater on joints and foliation-parallel fractures was sampled from the Golden Bar pit at Macraes mine, and from a quarry developed for paving stones in the uplifted scarp of an active fault at Pennyweight Hill (figure 2 and 3; Craw 2013).

Sulfate-bearing saline water derived from evaporation of rainwater was collected from the Sutton Salt Lake (figure 2; Craw & Beckett 2004). Salt encrustations derived by complete evaporation of similar waters were collected from an abandoned placer gold mine in Miocene non-marine quartz gravels at Chapman Road (Druzbicka et al., 2014). These encrustations contain evaporative sulfate minerals, including gypsum and bloedite ($Na_2Mg[SO_4]_2.2H_2O$), and possibly epsomite, thenardite, and ferricopiapite (Druzbicka et al., 2014).

Sulfur derived from Miocene non-marine quartz gravels was collected as evaporative Fe sulfate minerals at Blue Lake (figure 2), an abandoned placer gold mine (Barker et al., 2004; Craw, 2013; Youngson, 1995). These encrustations have formed under overhangs in cliffs of quartz gravels, where groundwater containing sulfate derived from oxidation of authigenic pyrite has evaporated (Youngson, 1995). In addition, we collected water from Blue Lake itself, which receives groundwater discharging from the same sediments, and from the underlying pyrite-bearing basement rocks, as well as surface runoff from the same rocks (Barker et al., 2004; Youngson, 1995). Similarly, we collected a sample of water derived from Miocene quartz gravels and the pyrite-bearing basement rocks at Pennyweight Hill (figure 2; Craw 2013). A placer gold mine developed in Pleistocene river gravels that were derived from adjacent schist basement at Glenore (figure 2 and 3) contained abundant authigenic pyrite, particularly in association with detrital woody material. We collected several nodules of this authigenic pyrite that are up to 1 cm across.

Authigenic marcasite nodules, similar to those described by Falconer et al. (2006), were collected from a placer gold mine developed in Pliocene quartz-rich gravels at Belle Brooke to the south of our main study area (figure 2), for comparison to the terrestrial gravels that were the focus of this study. Similarly, some pyrite from older marine and marginal marine sediments was collected for comparison to the terrestrial sulfur. These latter samples include partially-oxidised authigenic sulfides in basement immediately underlying Eocene marginal marine sediments at Tirotiti; authigenic pyrite in marginal marine

Cretaceous coal measures at Wangaloa coal mine (Black and Craw, 2001) and marcasite from the adjacent Kai Point coal mine; and nodules of pyrite from joints in Oligocene marine sediments at Matanaka.

4. Previous geochemical results

The concentration ratios of major ions can be used to constrain weathering processes, as the addition of elements from the leaching of various minerals drives elemental ratios away from seawater values. A compilation of data for groundwater and surface waters from around southern New Zealand is shown in figure 4. The rainwater presented in figure 4A is from north of our study area, close to Lake Tekapo and Lake Pukaki, and is enriched in sulfate compared with marine SO_4/Cl ratios, suggesting some sulfate addition from anthropogenic input (Jacobson et al., 2003). SO_4/Cl ratios are consistent with the salinity at Sutton Salt Lake, within our study area, being entirely derived from unpolluted rainwater. The SO_4/Cl falls slightly below seawater, suggesting some sulfur has been lost, possibly through the formation of DMS (Craw and Beckett, 2004). Elevated SO_4/Cl ratios show that there are highly variable excess sulfur contributions from the dissolution of sulfide minerals in different environments.

SO_4/Cl ratios for boreholes from within the Otago Schist suggest highly variable degrees of basement leaching, with sulfate concentration ranging from 3 to 140 mg/L. Additional Schist groundwater data is shown on Figure 4B, some of which comes from sites close to Macraes mine, which tend to have more elevated SO_4/Cl ratios due to excess mineral leaching in the vicinity of hard rock mines (Craw and Chappell, 1999). The maximum recorded sulfate concentration is 540 mg/L, more than double the safe limit for drinking water (>250 mg/L). SO_4/Cl ratios for leachates from salt encrustations at Chapman Road suggest a minor basement component, of 5-10%. Elevated SO_4/Cl ratios for the waters at Blue Lake suggest as much as 90% of sulfur is derived from mineral leaching (Barker et al., 2004). Major element ratios can detect addition of sulfur from weathering sources, but cannot be used to distinguish between alternate excess sulfur sources, and cannot provide historical information about groundwater from authigenic pyrite precipitated along its flow path.

There is limited δ^{34}S data for sulfides around southern New Zealand, partly due to difficulty in obtaining unoxidised samples in surface environments (section 2.1). Existing δ^{34}S data for sulfides in metasediments and metavolcanics across the Otago Schist fall into a narrow range, -6 to +1 ‰ (Ashley and Craw, 1995; Craw et al., 1995), suggesting metamorphic homogenisation, or an original igneous source for all the rocks that now make up the schist belt. Existing data for Bellebrooke show a large range of δ^{34}S, from -45 to +18 ‰, with pyrite and arsenopyrite showing distinctly higher values than marcasite (Falconer et al., 2006). While some of these sulfide minerals may be detrital, transported from surrounding basement rock and sediments, the marcasite is thought to be an authigenic groundwater precipitate. This is based on independent constraints from morphology and Co:Ni ratios, but is supported by the wide range of negative δ^{34}S, suggesting a diagenetic origin via BSR (Falconer et al., 2006). The Chatton Marine Formation is stratigraphically equivalent to Matanaka, sampled in this study, and pyrite has elevated δ^{34}S that overlaps with seawater sulfate (+15 ‰ to + 21 ‰; Kusakabe et al., 1976). Sulfur in modern soils across southern New Zealand (Kusakabe et al., 1976; Martin et al., Accepted; Rogers et al., 2015)) show an almost ubiquitous marine δ^{34}S signature, except where influenced by localised agricultural run-off. Measurements of riverine sulfate from the north of the South Island show contributions from marine aerosols and local bed rock (Robinson and Bottrell, 1997). Limited $\delta^{34}S$ data for rain water show that in pristine catchments the majority of salts are derived from marine aerosols (Mizutani and Rafter, 1969).

5. Results of this study

Figure 5 shows a summary of all data, and the range of δ^{34}S for each locality. Our data is grouped into different environments, including metamorphic basement rock, pyrite along joints in the Otago schist, Tertiary marine transgression sediments, and terrestrial gravel aquifers. The data fall into distinct ranges that we ascribe to three broad categories: marine influenced, basement-derived or bacteriogenic (indicated on figure 5 by blue, grey and green zones, respectively). These zones provide guidance for a first order interpretation of δ^{34}S, but sulfide minerals often have complex histories that integrate contributions from multiple sources with sometimes overlapping δ^{34}S.

Table 1: All sulfur isotope data and uncertainties. Asterisk indicates triplicate analyses are not available, and so there is no calculated standard deviation. Abbreviations used: py = pyrite; conc. = concentrate; marc = marcasite

Locality	Sample ID	Sample description	δ^{34}S (‰)	Stdev (triplicate)
Rainwater-derived				
Sutton Salt Lake	SSLW	Dissolved sulfate	21.4	0.8
Marine sulfate		(Paytan et al., 1998)	21.0	
Metamorphic basement and orogenic Au-bearing quartz veins (average = -1.8‰)				
Macraes Frasers detrital	MFD-a	arsenopyrite grains	0.4	0.2
	MFD-p	pyrite grains	-3.1	0.1
Fiddlers AH 2B/03/12	AH2b	pyrite concentrate	1.1	0.1
Fiddlers T22B a	T22b	pyrite concentrate	-7.1	0.4
Fiddlers AH 3B/03/12	AH3b	pyrite concentrate	0.5	0.2
Macraes Golden Bar (Vein)	MGBV-1	arsenopyrite conc.	0.9	0.9
	MGBV-2	pyrite concentrate	1.2	0.5
	MGBV-3	pyrite concentrate	0.7	0.0
	MGBV-4	pyrite concentrate	-1.1	0.2
	MGBV-5	pyrite concentrate	-1.7	1.0
	MGBV-6	pyrite grains	-0.9	0.5

	MGBV-7	pyrite concentrate	-1.8	0.3
	MGBV-8	pyrite concentrate	-1.4	0.6
Joint pyrite				
Pennyweight 1	PW1-1	pyrite concentrate	7.3	0.3
	PW1-2	pyrite concentrate	9.6	0.2
Pennyweight 2	PW2-1	pyrite concentrate	-5.1	0.4
Pennyweight 3	PW3-1	pyrite concentrate	-4.1	0.7
	PW3-2	pyrite concentrate	2.4	0.4
	PW3-3	pyrite concentrate	-0.8	0.3
Pennyweight 4	PW4-1	pyrite concentrate	2.8	0.1
	PW4-2	pyrite concentrate	-4.7	1.2
	PW4-3	oxidised py conc.	-6.5	0.8
	PW4-4	oxidised py conc.	4.2	1.3
	PW4-5	oxidised py conc.	1.7	*
	PW4-6	oxidised py conc.	4.0	0.5
	PW4-7	pyrite concentrate	-2.4	0.9
	PW4-8	pyrite concentrate	-5.9	0.2
	PW4-9	pyrite concentrate	-5.0	0.5
	PW4-10	oxidised py conc.	-1.9	0.8
Macraes golden bar (joints)	MGBJ-1	pyrite concentrate	-2.7	0.4
	MGBJ-2	pyrite concentrate	-2.6	0.3
	MGBJ-3	pyrite concentrate	-4.2	0.2
	MGBJ-4	pyrite concentrate	-1.0	0.1
	MGBJ-5	pyrite concentrate	0.2	0.5
	MGBJ-6	pyrite concentrate	-1.7	0.5
	MGBJ-7	pyrite concentrate	-0.9	0.0
	MGBJ-8	pyrite concentrate	-0.9	0.1
	MGBJ-9	pyrite concentrate	-8.5	0.3
	MGBJ-10	arsenopyrite grains	0.6	0.8
	MGBJ-11	pyrite concentrate	-1.6	0.1
	MGBJ-12	pyrite grains	-1.1	0.2
	MGBJ-13	pyrite concentrate	-3.0	0.1
	MGBJ-14	pyrite concentrate	-27.0	0.3
	MGBJ16	pyrite concentrate	-7.4	0.2
Macraes pit lake	MGBW-1	Dissolved sulfate	-7.1	0.2
Macraes run-off	MGBW-2	Dissolved sulfate	-14.8	0.5
Cretaceous-Oligocene marine trangression Sediments (for comparison)				
Matanaka	M1-a	Lump py (centre)	-37.4	0.8
	M1-b	Lump py (edge)	-44.5	0.1
	M1-c	Py grains along joint	-36.4	1.0
	M1-d	Lump py (centre)	-33.3	0.6
	M1-e	Lump py (edge)	-30.9	0.4

Wangaloa	WP-a	pyrite	-21.4	1.4
	WP-b	weathered pyrite	-7.6	0.3
	WP-c	pyrite	-10.7	0.6
	WP-d	pyrite	-12.1	0.1
Kai point	KP-a	Marcasite	31.2	0.3
	KP-b	Marcasite	36.0	0.4
	KP-c	pyrite grains	19.0	0.1
	KP-d	Marcasite	23.2	0.5
	KP-e	Marcasite	30.0	0.2
	KP-f	pyrite grains	11.4	1.2
Tirotiti Basement	TB	Fe sulfate mineral	-1.5	0.1
Terrestrial gravel aquifers				
Belle Brooke	BB2-a	Lump marc (centre)	-29.7	0.4
	BB2-b	Lump marc (mid)	-24.5	0.0
	BB2-c	Lump marc (edge)	-40.7	0.1
Glenore	G1-a	Pyrite concentrate	-0.4	0.6
	G1-b	pyrite concentrate	5.1	0.5
	G1-c	pyrite concentrate	13.8	0.1
	G1-d	oxidised py conc.	12.0	0.4
	G1-e	pyrite concentrate	13.1	0.4
	G1-F	pyrite concentrate	13.3	0.3
	G1-G	pyrite concentrate	19.7	0.1
	G1-H	pyrite concentrate	9.2	0.4
Blue Lake	BL-1	Evaporitic salts	22.8	0.2
	BL-2	Evaporitic salts	22.6	0.0
	BL-3	Evaporitic salts	22.9	0.0
Blue Lake water	BLW	Dissolved sulfate	14.4	0.3
Chapman Road	GG1	evaporitic salts	8.5	0.0
	GG2	evaporitic salts	8.6	0.5
	GG3	evaporitic salts	5.7	1.4
	GG4	evaporitic salts	7.8	0.3
	GG5	evaporitic salts	7.7	*
	GG6	evaporitic salts	8.7	*
Chapman run-off	GGW	Dissolved sulfate	5.7	0.1
Pennyweight water	PWW	Dissolved sulfate	8.9	0.4

5.1 Marine Aerosols (end-member 1)

Sutton Salt Lake is saline as a result of the buildup of rainwater-derived marine aerosols over thousands of precipitation-evaporation cycles. The lake is impounded by schist bedrock in a depression between two tors, (Craw and Beckett, 2004). Rainfall is lower than at the coast, ~500 mm/year (Allen et al., 1997; Bayly, 1967; Craw and Nelson, 2000), due to a rain shadow effect from the southern Alps. The barren landscape is subjected to strong westerly winds, and the lake surface can lose up to 700 mm/year of moisture via evaporation (Allen et al., 1997; Bayly, 1967; Craw and Nelson, 2000). The lake dries up in the summer, where a halite crust with trace gypsum develops across the dry surface, and then refills in the following winter, which is when we sampled (June 2015). Major element ratios indicate that there is negligible contribution to salinity in the lake from sulfur sources other than rainfall (Craw and Beckett, 2004). Therefore, the $\delta^{34}S$ should represent the end-member $\delta^{34}S$ for rainwater-derived sulfur (Jacobson et al., 2003). Since Sutton Salt Lake is the only emphemeral saline lake in New Zealand, the water chemistry presents an opportunity to constrain the long term $\delta^{34}S$ of rainwater input, as other water bodies likely contain mixed signatures. We report a $\delta^{34}S$ for dissolved sulfate of +21.4 ± 0.8 ‰, consistent with the accepted seawater value of 21 ‰, and derivation from rainwater. SO_4/Cl ratios for Sutton Salt Lake are slightly depressed compared with rainwater, suggesting some sulfur loss, likely via DMS formation. $\delta^{18}O_{SO4}$ is 7.8 ± 0.1 ‰. This is within the range of marine sulfate (9.3 ‰), but the lighter $\delta^{18}O$ may indicate a small proportion of the sulfate has been reduced and reoxidised.

Our data confirm that rainwater is dominated by marine sulfate, with only minor contributions from anthropogenic aerosols or DMS (Mizutani and Rafter, 1969). The salinity has developed via 20,000 annual cycles of evaporation and lake refilling. The $\delta^{34}S$ represents integrated rainwater over 20 kyr, during which time the aerosol concentration in rain may have varied widely, but will not have contained an anthropogenic component. Isotopic fractionation during evaporitic formation of sulfate minerals is thought to be minor, <2‰ (Raab and Spiro, 1991), but these cumulative changes could become significant over 20,000 cycles. The consistency of the $\delta^{34}S$ with marine sulfate suggests that precipitation-dissolution cycles of these minerals were quantitative, with minimal net fractionation each year.

5.2 Basement rocks (end-member 2)

Sulfide minerals along cleavage planes and in quartz veins within the Otago Schist have a narrow $\delta^{34}S$ range of -3.1 ‰ to +1.8 ‰. This includes data from hydrothermal pyrite in auriferous quartz veins within Macraes Golden Bar pit (n=8), detrital material derived from these veins at Macraes Frasers pit (n=2), and metamorphic pyrite from Fiddlers Flat (n=3), giving an average $\delta^{34}S$ of -0.9 +2.3 ‰. This range is consistent with previous data (Craw et al. 1995, n=17), and combining data from this study with Craw et al., (1995) gives an average $\delta^{34}S$ for the Otago Schist of -1.8 ±2.4 ‰ (n=30). There is one outlier value, -7.1 ‰, at Fiddlers Flat, which represents metamorphic pyrite that has not been remobilised into hydrothermal veins. Arsenopyrite at Macraes Frasers and Golden Bar pits are heavy (by around 2 to 4 ‰) compared with co-existing pyrite, consistent with Craw et al. (1995). This narrow range of values is consistent with derivation from hydrothermal fluids during regional metamorphism (Craw et al., 1995). The detrital material from Macraes Frasers is derived directly from fluvial weathering of sulfide in associated quartz veins, and the δ^{34}S is therefore consistent. Oxidative weathering of this basement sulfur represents an end-member component for the weathering contribution to groundwater sulfur reservoirs (figure 6). The boundaries of the basement δ^{34}S zone may change slightly as more data is collected.

5.3 Sulfide minerals along basement joints

Joints within the Otago Schist formed during a series of Miocene-Recent uplift events, and associated pyrite likely precipitated from low temperature fluids during preferential flow along joint planes. The majority of data for Pennyweight mine (n=16) fall within range of basement sulfide, from -6.5 ‰ to +4.2 ‰, but two values from the same surface are exceptionally high (+7.3 ‰ and +9.6 ‰). This may reflect the temporally limited influence of marine aerosols, or an evolving sulfur reservoir with increasing δ^{34}S due to fractionation during BSR. Sulfide minerals within joints at Macraes Golden Bar pit (n=15) are largely consistent with the surrounding basement rock, -8.5 ‰ to +0.2 ‰ (figure 6). This narrow range suggests that sulfur in groundwater circulating along joint planes was largely derived from the leaching of the surrounding basement rock. There is one outlier with a very negative δ^{34}S (-27.0 ‰), which may result from fractionations during BSR, or temporally limited influence from the leaching of bacteriogenic sulfides in local soils or sediments.

Groundwater sulfate in the Macraes pit lake has a δ^{34}S of -7.1 ‰, which is lighter than the average Schist value (-1.8 ‰), but within range of local minerals from veins and joints, confirming the absence of marine influence in local sulfide minerals. However, the local groundwater in the pit lake may be affected by enhanced leaching rates in the vicinity of the mine, and be inconsistent with regional groundwater. A recent run-off puddle gave more negative δ^{34}S (-14.8 ‰), considerably lower than local basement sulfide minerals. This surface run-off may contain S from an additional source with a light signature, such as easily leachable bacteriogenic sulfur in surface soils. $\delta^{18}O_{SO4}$ for the pit lake and recent run off waters are -5.1 ± 0.6 ‰ and -7.1 ± 0.1 ‰, respectively. These negative values are consistent with sulfate derivation entirely from sulfide oxidation, with little contribution from rainwater. Given the inconsistency between δ^{34}S for aqueous sulfate and surrounding rocks, the dissolved sulfate in the groundwater may point to a modern, uncharacterized sulfur reservoir.

5.4 Marine transgression sediments

Early Cenozoic marginal marine sequences overlying basement rocks include marine sediments (Matanaka and Tirotiti), as well as fluvial quartz conglomerates and lignites (Wangaloa and Kai Point). Although we don't expect these sediments to be a significant source of sulfur to groundwater in southern New Zealand, we present new data for comparison (figure 7). δ^{34}S for pyrite at along joints in Matanaka marine sediments (n=5) ranges from -44.5 ‰ to -30.9 ‰, indicating bacteriogenic formation. This depleted signal may be inherited from formation within pore waters on the ancient seafloor, or secondarily acquired during remobilisation along joint planes. The δ^{34}S of the weathering products of pyrite in Tirotiti sediments is -1.5 ‰, so there is no clear bacteriogenic signal. Underlying quartz pebble conglomerates and lignites have less depleted signals. Sulfide minerals in lignite likely formed from groundwater sulfate introduced during early burial. At Wangaloa (n=4), δ^{34}S ranges from -21.4 ‰ to -7.6 ‰, consistent with a bacteriogenic origin. Lump marcasite with pyrite grains on the outer surface from Kai Point (n=6) shows much heavier δ^{34}S, +11.4 ‰ to +36.0 ‰. The upper end of this range is highly unusual, and exceeds modern and Cenozoic (~15 ‰) marine sulfate δ^{34}S (Claypool et al., 1980). We note that pyrite grains have lower δ^{34}S, in line with seawater sulfate, whereas lump marcasite has δ^{34}S enriched above seawater sulfate. The marcasite may have formed from an evolved sulfate pool enriched via precipitation of sulfide minerals at shallower depths (Bottrell et al., 2000b).

5.5 Plio-Pleistocene Au-placer deposits

δ^{34}S values from Belle Brooke marcasite (n=3) range from -40.7 ‰ to -24.5 ‰, within a single mineralized chunk. This large range of negative values suggests marcasite formed via BSR, consistent with previous work (Falconer et al., 2006). Glenore sits directly within basement rocks, and pyrite samples (n=8) show a wide range of δ^{34}S, from -0.4 ‰ to +19.7 ‰ (figure 7). We suggest this range reflects variable mixing between basement and marine end-members, with multiple generations of sulfide formed from groundwater through time. Sulfide minerals at Glenore are commonly found replacing wood, and so some bacteriogenic signal would be expected. It is possible that there has been some BSR with fractionation factors <20 ‰ from starting sulfate with marine composition. This would result in a δ^{34}S close to 0 ‰, which is equivocal and overlaps with the basement signal.

5.6 Terrestrial gravel aquifers

Salt derived from oxidation of pyrite within the sediments and subsequent deposition of evaporitic minerals from saturated run-off waters at Blue Lake (n=3) show a consistent δ^{34}S, +22.8 ± 0.2 ‰, whereas the sulfate present in the lake itself is less enriched, +14.4 ‰ (figure 8). These sediments formed around 20 Ma, and the δ^{34}S value suggests contemporary groundwater sulfur was derived from marine aerosols. The water in the lake has been present for only ~100 years, and if the δ^{34}S is considered alone, it is consistent with mixing between rainwater-derived marine sulfate (~70 %) and basement sulfur (~30 %) (Equation 4). This contrasts with SO_4/Cl ratios (figure 4), which indicate the addition of excess sulfate from weathering (~90 % weathering derived, Barker et al. 2004) compared with rainwater input. The excess SO_4^{2-} input may partly be derived from groundwater pyrite in the surrounding sediments, which have a marine δ^{34}S, and so this sulfur addition is not detected in the sulfur isotope signals.

δ^{18}O for sulfate in the lake water at Blue Lake is close to zero, -0.8 ± 0.1 ‰. This is likely the result of three component mixing between rainwater sulfate (δ^{18}O ~ +9 ‰), sulfide oxidation in sediments (marine δ^{34}S but δ^{18}O ~ -10‰) and sulfide oxidation in the basement (δ^{34}S ~ -1.8‰ and δ^{18}O ~ -10‰). If 30 % of the sulfate is basement derived, consistent with δ^{34}S constraints, we can further subdivide the remaining sulfate into sediment derived (20 %) and rainwater derived (50 ‰), using equations 3 and 5. The uncertainty in this calculation is large, as a result of poor constraints on the δ^{18}O of meteoric water. We used a δ^{18}O of -10 ‰ for sulfide oxidation here, which assumes meteoric water has a δ^{18}O of -15 ‰, but this values will vary regionally and is poorly constrained. If we instead use a δ^{18}O of -6 ‰ for meteoric water, we calculate that 60 % of the sulfate in the lake is sediment derived, with only a 10 % contribution from rainwater. This scenario is consistent with constraints from SO_4/Cl ratios.

δ^{34}S values for dissolved sulfate in recent surface run-off at Chapman Road, +5.7 ‰, result in a calculated rainwater component of ~30 %, with the majority of sulfate originating from basement leaching (Equation 4). δ^{34}S values for salts at Chapman Road (n=6) fall within a narrow range, around +7.8 ± 1.1 ‰, which is close to recent run-off waters, but it is possible that evaporative salts are elevated due to small fractionations during gypsum precipitation (<2 ‰, Raab & Spiro 1991). These evaporative salts occur directly on basement rock, where groundwater and surface run-off has pooled on shallow slopes and evaporated. Previous work, based on SO_4/Cl ratios in the salts, suggests sulfate is dominated by marine aerosols (80-95 %, Druzbicka et al. 2014). It is likely that there is differential mobility of salts (halite, bloedite, gypsum etc.) across the site, and so samples from Druzbicka et al. (2014) may not represent incoming groundwater. We suggest that isotope data from recent run-off is the most representative of the sulfur input at this site.

δ^{18}O for sulfate in surface run off at Chapman Road is 1.5 ± 0.1 ‰. If 70 % of aqueous sulfate is derived from basement sulfide, then isotopic mass balance constraints require basement derived sulfate to have a δ^{18}O of -1.5 ‰, implying meteoric water δ^{18}O is relatively heavy, -5 ‰. If a much higher proportion of sulfate were derived from marine aerosols (80-95%), as suggested by SO_4/Cl ratios, this would require the basement weathering source to have a δ^{18}O of -29 to -141 ‰. These values are below the δ^{18}O of meteoric waters in most environments and so support our inference that the proportion of basement sulfide was high.

Waters at the base of Pennyweight Hill represent run-off through Miocene sediments equivalent to those at Blue Lake, and have an enriched δ^{34}S that reflects a partial marine influence, +8.9 ‰. This value is consistent with around 55 % of the sulfur being derived from basement leaching, and the remaining 45 % either directly from marine aerosols, or from oxidation of pyrite in sediments derived from ancient marine aerosols (Equation 4). δ^{18}O for sulfate in surface run off is -9.0 ± 0.2 ‰. This negative value further constrains the source of aqueous sulfate with a marine δ^{34}S to derive from sedimentary sulfide oxidation. Combined δ^{34}S- δ^{18}O mass balance suggests no more than 5 % of sulfate derived directly from marine aerosols (Equation 3 and 5), regardless of the δ^{18}O of meteoric water.

6. Discussion

6.1 Sulfur isotopes as an environmental tracer

We present new sulfur isotope data to constrain the source of sulfur in sediments and waters around southern New Zealand (summarised in figure 9). The data for most localities fall into characteristic isotope ranges (figure 4), suggesting a common source and formation pathway for sulfur in each environment. We identify two key sulfur sources: leaching of basement sulfur, and delivery of marine aerosols via rainwater. The relative contribution of these two end-members varies depending on a number of geological, environmental and anthropogenic processes.

Bacterial processes commonly impart a strong fractionation on sulfide compared with the residual sulfate pool, $\Delta^{34}S_{SO4\text{-}H2S}$. This results in sulfide minerals with a light $\delta^{34}S$, as observed in some marine sediments in this study (Matanaka and Wangaloa). At Belle Brooke, bacteriogenic marcasite is present and often found replacing organic material (Falconer et al., 2006), with associated highly negative $\delta^{34}S$. However, authigenic groundwater sulfur minerals from terrestrial aquifers and along joint planes do not exhibit such depleted values, and are in line with probable source sulfur. This requires that either:

1. Authigenic pyrite formed via thermochemical sulfate reduction (TSR) with little fractionation,
2. Authigenic pyrite formed via bacterial sulfate reduction, but the fractionation was not expressed.

$\Delta^{34}S_{SO4\text{-}H2S}$ during TSR should be small compared with BSR, but can still reach 20 ‰ (Ohmoto and Goldhaber, 1997; Watanabe et al., 2009). TSR should be thermodynamically favourable at surface temperatures (>25 ˚C) (Worden and Smalley, 1996), but experimental and observational constraints suggest the reaction is kinetically inhibited at temperatures below <80 ˚C (Claypool and Mancini, 1989; Cross et al., 2004; Goldhaber and Orr, 1995; Machel et al., 1995). This is a result of the large activation energy for sulfate reduction, which can be overcome by the enzymatic processes during BSR. Metamorphic sulfide minerals and sulfide hosted in mineralised veins within the Otago Schist were precipitated from high temperature (300-400 ˚C) hydrothermal fluids via TSR (Craw et al., 1995). However, authigenic groundwater sulfide minerals in joints within the Otago Schist and within terrestrial gravel aquifers formed at low temperature, and so we infer that sulfide production must have been biologically mediated in these settings. Indeed, many reports of sulfide production in groundwater reservoirs report isotopic evidence for BSR, through depletions in sulfide $\delta^{34}S$ or complementary enrichments in the residual sulfate $\delta^{34}S$ (Bottrell et al., 2000a; Rye et al., 1981; Spence et al., 2001; Strebel et al., 1990; Yamanaka et al., 2007).

In order to reconcile our data, which mostly fall within range of our two proposed sulfur sources (-1.8 to +21.0 ‰), with generation via BSR, requires either that sulfide minerals record an integrated signal from closed system distillation, that BSR imparts little or no fractionation, or that small $\Delta^{34}S_{SO4\text{-}H2S}$ <20‰ has altered $\delta^{34}S$ within the given range. Sulfide minerals formed in closed systems, from an evolving sulfate pool that was eventually exhausted, record a progressive enrichment in $\delta^{34}S$ towards the outer margin (e.g. Ferrini et al., 2010; Kohn et al., 1998). Analysis of the whole mineral would produce an integrated signal that would be equivalent to the starting sulfate reservoir. Here we have analysed whole grains for some samples (see Table 1), which would homogenise any internal variability resulting from bacteriogenic fractionation.

Isotope fractionation during BSR is a kinetic effect associated with the rate limiting step during intracellular sulfur cycling, and so $\Delta^{34}S_{SO4\text{-}H2S}$ is dependent on sulfate concentrations. In general, $\Delta^{34}S_{SO4\text{-}H2S}$ is suppressed at very low sulfate concentrations, <0.2 mM (Habicht et al., 2002), but the expressed fractionation additionally depends on physiological factors, temperature and the organic substrate (Bradley et al., 2015; Canfield, 2001; Canfield, 2001; Detmers et al., 2001; Habicht et al., 2002). Present day sulfate concentrations in the Otago Schist range from 0.02 - 1 mM (figure 4A). Such low sulfate concentrations may have facilitated sulfide formation without significant isotope fractionation, and so sulfide minerals would reflect the $\delta^{34}S$ of groundwater sulfate. More complex fractionation may arise when sulfide is repeatedly cycled between reduced and oxidized species, as sulfide oxidation is also associated with a small negative $\Delta^{34}S_{SO4\text{-}H2S}$ (Fry et al., 1988; Kaplan and Rittenberg, 1964).

It is possible that some of our data have been affected by bacteriogenic fractionation, but have remained within the range -2 to +21 ‰. If small fractionations occur during BSR (<20 ‰), from starting sulfate with a marine composition, the resulting sulfide would have a $\delta^{34}S$ close to 0 ‰, overlapping with the range of basement sulfide values. Similarly, basement-dominated sulfur in waters may be driven to higher $\delta^{34}S$ by the precipitation of bacteriogenic sulfide minerals, resulting in a marine-like signature, which is then imparted on any later stage sulfide minerals. Sulfide minerals may record multiple generations of reduction, reoxidation and transport, particularly where sulfate has a long residence time in the groundwater system. δ^{34}S signals are somewhat equivocal, but can be more powerful when combined with constraints from SO_4/Cl ratios.

In some cases, δ^{34}S for aqueous sulfate is inconsistent with existing SO_4/Cl ratio data for the same water bodies. This discrepancy may arise via several mechanisms. Sulfate can be lost from waters (as DMS aerosols or solid phase sulfate or sulfide minerals) with no associated isotope fractionation. This process lowers SO_4/Cl, while δ^{34}S maintains the signature of the original sulfur source. Sulfate may also be added from a source with a similar isotope composition, increasing SO_4/Cl, without affecting δ^{34}S (e.g. leaching of sediments with a marine δ^{34}S at Blue Lake). While the use of elemental ratios is limited to modern water bodies, isotopic data enables reconstruction of ancient groundwater from associated sulfide and evaporite minerals. We are able to constrain sources of sulfur in the groundwater system since the Miocene using the δ^{34}S of authigenic groundwater sulfide minerals, both in joints throughout basement rock and cementing terrestrial gravel aquifers.

We make a first order interpretation of the isotope signatures in sulfide minerals, assuming that they record groundwater sulfate, where the δ^{34}S is predominantly affected by mixing between two sulfur sources. Marine aerosols fall into a very narrow range, consistent with the homogeneous nature of global marine sulfate. In contrast, $\delta^{34}S$ in basement sulfide ranges from -7 to +1 ‰. If the full range of basement $\delta^{34}S$ is considered (yellow area, figure 10), the uncertainty introduced in interpreting the proportion of weathered basement in mixed-source sulfate varies from 0-29 %, with the higher uncertainties introduced at high basement fractions. While individual sulfide crystals within basement rock exhibit a range of $\delta^{34}S$, weathering should be quantitative and produce a well-mixed signal. Sufficient analyses can provide a reliable average that can be used for accurate estimates in two-component mixing models (orange line, figure 10). We have used this average value in our mixing models.

We use combined $\delta^{34}S$-$\delta^{18}O$ to further constrain the origin of sulfur in aqueous sulfate samples. Rainwater sulfate should have a $\delta^{18}O$ close to +9 ‰, if sulfate-oxygen has not been enriched through fractionation during BSR, or replaced during sulfate reduction and subsequent re-oxidation. Distillation during water column sulfate reduction may enrich $\delta^{18}O$ compared with marine sulfate, but we do not observe such enrichment in any of our six sampled water bodies. The $\delta^{18}O$ of sulfate derived from sulfide oxidation will depend on both the $\delta^{18}O$ of meteoric water, as well as the source of oxygen (either dissolved atmospheric oxygen or molecular oxygen in water), but should always produce a distinctly negative $\delta^{18}O$ compared with marine sulfate. For samples with a marine sulfate $\delta^{34}S$, we use $\delta^{18}O$ to distinguish between direct input from marine aerosols, and sulfate derived from oxidation of ancient groundwater sulfide minerals. These calculations rely on an assumption about the $\delta^{18}O$ of meteoric water, which is poorly constrained in our field area. However, mixing models that require meteroic water to fall outside of the accepted range (-5 to -15 ‰) can be discounted. In some environments, dual isotopes of sulfate combined with SO_4/Cl ratios provide consistent and reliable constraints on the relative contributions from three different sulfur sources.

6.2 Geological and climatic controls on sulfur mobility

Sulfur contents are relatively low in the Otago Schist (<10 ppm, Craw & Chappell 1999), the area of exposed schist is very large (figure 2), and so there is potential for significant sulfur leaching into the central Otago Basin. This near-surface leaching process is supported by low sulfur contents at the surface compared with deep drill core samples (Youngson, 1995), as well as elevated SO_4/Cl ratios in schist aquifers (figure 4B, Barker et al. 2004; Craw & Beckett 2004; Rosen & Jones 1998). We show that in joint systems throughout basement rocks, the dominant source of environmental sulfur was metamorphic sulfide (figure 5 and 6). This is in stark contrast to terrestrial gravel aquifers, where rainwater is an important sulfur source (figure 5 and 8). Deep groundwater circulation in joint systems represents a deeper, and more restricted, groundwater system compared with circulation through terrestrial gravel aquifers. Sulfur may have been sourced from the immediately surrounding rocks and recrystallized in a closed system with little transport. In this case, sulfide minerals in basement joints would not be representative of fluxes into and out of surface environments. There is likely a continuum between local recystallisation, and open system flushing with regional groundwater. This may account for the range in our data, -8.5 to +9.6 ‰, with heavier values representing open system mixing with rainwater sulfate.

Deformation of the Central Otago region has occurred almost continuously since the Miocene, but three distinct uplift phases can be distinguished. Initial uplift of Central Otago topography occurred in the middle Miocene (c. 10 Ma), but the rise of the high Southern Alps in the Pliocene was responsible for the development of the Otago rain shadow (Craw et al., 2013). A third uplift event in the Quaternary resulted in deposition of schistose alluvial fan gravels along the range margins. Each of these events is associated with elevated weathering rates and substantial sulfur mobility across the basin (Youngson, 1995). During later uplift events, recycling of sediments from previous deformation events would have mobilised additional sulfur. It is not clear if this temporal signal is reflected in the basement dominated sulfur preserved along joint planes. Although joint formation occurred during uplift events, sulfide minerals may have precipitated contemporaneous with joint formation, or later, as a result of preferential fluid percolation along joint planes. Any original sulfide minerals may have been remobilised, and undergone multiple cycles of dissolution and precipitation.

Sulfate concentrations are high in seawater, 28 mM, and sea spray produces an ongoing flux of sulfate into the atmosphere. The residence time of sulfur in the atmosphere is short, a few days, but during this time it may be transported a significant distance inland. Our data suggest that inland environments across southern New Zealand are heavily influenced by marine sulfate, even >100 Km from the coast. Environments such as Sutton Salt Lake make the distinction between marine and terrestrial evaporite deposits in the geological record difficult, as terrestrial environments may simply record marine sulfate δ^{34}S. Marine aerosols are delivered to surface waters via precipitation, but much of this sulfur is likely rapidly recycled back into the oceans. The effect of rapidly recycled marine aerosols has to be removed to determine the net transfer of new sulfate into the environment from the weathering of evaporite and sulfide minerals (Stallard and Edmond, 1981). Here, we are able to identify the prevalence of marine aerosol input, as the absence of a significant evaporite weathering source means there is no need to deconvolve fluxes with similar isotope signatures. In southern New Zealand, the net sulfate delivery to the ocean from rivers is largely derived from weathering of metamorphic sulfide, and so will have a $\delta^{34}S$ close to -2‰.

The flux of marine aerosols may have a seasonal or climatic component, due to variability in the wind stress on the surface ocean (to produce sea salt particles) and total rainfall delivery to inland areas. In the Miocene, the sub-tropical maritime climate in southern New Zealand was perpetually wet, giving way to a temperate sub-alpine climate in the Pliocene and Quaternary, interrupted by short periods of warm wet climate (Mildenhall et al., 1989; Pole, 2003; Youngson et al., 1998). This reflects both global climatic trends and the rise of the Southern Alps. The presence of marine aerosols has likely been important across Otago since before the Miocene, but absolute inputs may have decreased steadily over time as the distance from the coastline has increased with marine regression. In contrast to this, the input from oxidative pyrite weathering was likely not time-steady, and would have been highest during periods of uplift. The marked contrast between $\delta^{34}S$ for authigenic groundwater pyrite along joints and cementing terrestrial aquifers (figure 5) is consistent with a ~~strong~~ tectonic and geological control on fluxes of sulfur into different groundwater systems.

The recycling of marine aerosols and the weathering of basement sulfide have been ongoing for the past 20 Myr. Since the settlement and industrialisation of New Zealand, these natural processes have been accelerated by anthropogenic activities. Quarrying may increase sulfate concentrations and the fraction of basement sulfur in the groundwater system. We show an elevated basement flux into groundwater close to Macraes quarry, evidenced by elevated SO_4/Cl ratios (Figure 4B) and an absence of enriched isotope signatures (Figure 6). In contrast, placer mines that excavated shallow slopes, may have encouraged pooling and evaporation of rainwater, elevating the marine aerosol flux at sites such as Chapman Road.

7. Conclusions

Sulfur isotopes provide a sensitive means to determine the origin of dissolved sulfate in surface waters, and associated authigenic sulfide minerals precipitated from deep groundwater. We present new sulfur and oxygen isotope data for waters and minerals around southern New Zealand, from a number of ecologically and economically important saline water bodies and mines. We characterize the isotopic composition of the two end-member sulfur sources: oxidative weathering of metamorphic pyrite (-1.8 ‰) and rainwater-derived marine aerosols (+21.4 ‰), and show that these are the dominant sources of environmental sulfur across southern New Zealand. Sulfide minerals along joints in the Otago Schist formed from groundwater that was dominated by the products of oxidative pyrite weathering. In contrast to this, we present data for terrestrial gravel aquifers, which show a reduced basement-weathering component, with sulfur largely derived from marine aerosols. Joints within basement rock and terrestrial gravel aquifers represent two distinct hydrogeological environments, each dominated by different sources of environmental sulfur. Marine aerosols represent a significant sulfur flux to terrestrial environments, which we are able to deconvolve from geological sources because there is no large evaporite weathering source in southern New Zealand, to which elevated δ^{34}S may be alternately attributed. While both basement weathering and marine aerosols have been significant sulfur sources in southern New Zealand over the past 20 Myr, their relative contribution to groundwater likely varied with geological processes, and more recently, has been affected by anthropogenic activity.

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Figure Captions

Figure 1: Generalised stratigraphic column for Otago.

Figure 2: Map of localities around southern New Zealand. The limits of the Otago Schist bed rock are outlined in blue.

Figure 3: **A –** Pyritic growths on joint surfaces of the Otago Schist, Pennyweight Hill. **B** – Pyrite nodules from Glenore.

Figure 4: **A -** Cross plots of major elements for groundwater and surface waters around southern New Zealand, from (Craw, 2000; Craw et al., 2015, 2013; Jacobson et al., 2003). **B -** Boreholes in close proximity to mine environments show excess SO_4^{2-} leaching.

Figure 5: Summary of results for two end-member S sources: rainwater-derived marine aerosols (blue square), and metamorphic basement (yellow circles). Joint pyrite (red) shows a mostly basement signal, with one outlying sample denoted by a question mark. Terrestrial gravel aquifers and Au-placers (purple)

show a partly marine influenced signal. Marine transgression sediments (orange) are shown for comparison. Squares represent data from dissolved sulfate in surface waters, and circles represent sulfide minerals.

Figure 6: Summary of sulfur isotope data for auriferous quartz veins, pit waters and joints at Macraes mine. Orogenic Au (black squares) and joint pyrite (symbols) are present throughout the Otago Schist. The pit lake contains groundwater, and a puddle contains recent run-off waters.

Figure 7: Summary of geology and isotopic data for marine transgression sediments and Au-placer deposits, Glenore and Belle Brooke. Orogenic Au (black squares) and joint pyrite (symbols) are present throughout the Otago Schist.

Figure 8: Summary of geology for Blue Lake, and isotopic data for Miocene terrestrial gravel aquifers and associated run-off waters. Orogenic Au (black squares) and joint pyrite (symbols) are present throughout the Otago Schist.

Figure 9: Summary of fluxes and isotope composition of processes in the terrestrial sulfur cycle across southern New Zealand. Not to scale.

Figure 10: δ^{34}S of groundwater sulfate as a function of the proportion of basement sulfide, with the other single source being marine aerosols. The variability associated with the minimum and maximum recorded δ^{34}S in the basement is shown in yellow. The single orange line is the average δ^{34}S of the basement, which should be an appropriate estimation of the end member source.

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