



Stable sulfur isotope dynamics in an acid sulfate soil landscape following seawater inundation



C.A. Maher^{a,*}, L.A. Sullivan^b

^a Southern Cross GeoScience, Southern Cross University, Lismore, NSW, Australia

^b Federation University, Ballarat, VIC, Australia

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ABSTRACT

In 2002 a tidally driven seawater exchange remediation strategy was successfully implemented on a severely acidified tropical coastal landscape dominated by acid sulfate soils (ASS) in northern Australia. This study examined changes in the stable sulfur isotope signatures in a range of sulfide and sulfate (SO₄) fractions at three sites with different levels of exposure to the tidally driven seawater exchange remediation. δ³⁴S in the acid soluble SO₄ fraction (e.g. jarosite) was less depleted in ³⁴S than the corresponding sulfide, indicating a degree of fractionation during sulfide oxidation and jarosite precipitation. The δ³⁴S of jarositic-SO₄ was similar at all three sites indicating the appreciable stability of jarositic-SO₄ even after extended exposure to seawater. δ³⁴S of the water soluble, exchangeable and schwertmannitic-SO₄ reflect conditions post remediation and indicate the relative contributions from two potential SO₄ sources – a lighter SO₄ derived from the oxidation of pyrite, and a heavier SO₄ derived from the seawater. The δ³⁴S of the contemporary surficial sulfide accumulations also reflect a SO₄ contribution from seawater used for remediation and were isotopically different from the relict sulfides found at depth at all sites. δ³⁴S of water soluble sulfate allowed the progress of the remediation to be traced down the soil profile. This study demonstrates the utility of stable sulfur isotope signatures in various sulfide and SO₄ fractions to trace the sulfur geochemical pathways occurring in soils, in this case as a result of the introduction of tidally driven seawater.

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1. Introduction

The CRC CARE National Acid Sulfate Soil Demonstration Site is located on the eastern side of Trinity Inlet, near Cairns in far north Queensland (145°48' E, 16°56' S). The site, referred to as 'East Trinity' (Fig. 1), comprises 9.4 km² of deeply stratified Holocene sediments down to 80 m overlying Pleistocene basement strata (Smith et al., 2004). This region has a tropical climate, with a summer wet-season, mean annual precipitation of 2000 mm and average daily maximum and minimum temperatures for all months exceeding 25 °C and 17 °C, respectively (Hicks et al., 2009).

In the early 1970s the East Trinity property was developed for sugarcane production. This involved the construction of a bund wall to prevent tidal entry and the installation of pumps to assist with drainage of the intertidal wetland (Smith et al., 2004; Powell and Martens, 2005).

The development of the site for agriculture by combined drainage and seawater exclusion severely degraded the environment. Firstly, the drainage of the land lowered the natural water table and allowed oxygen to enter the surface layers of the deep Holocene sediments

and oxidise the iron sulfide minerals. This initiated the acidification of the acid sulfate soil (ASS) materials, producing a variety of acidic iron precipitate minerals such as jarosite and schwertmannite (Russell and Helmke, 2002; Powell and Martens, 2005; Johnston et al., 2009a, 2009b). The exclusion of seawater from the site severely limited the supply of a readily available source of neutralisation namely bicarbonate (HCO₃⁻) in the tidally driven seawaters. Impacts associated with the oxidation of ASS at East Trinity as a result of this development include extremely low pH in the soil and surrounding creeks, mobilization of heavy metals (particularly iron and aluminium), diminished populations of aquatic biota, and significant fish kills (Russell and Helmke, 2002; Smith et al., 2004).

In May 2000 the Queensland State Government purchased the East Trinity property and implemented a remediation plan to address the environmental hazards posed by this severely degraded site. In general the remediation plan at this site was guided by two strategies: firstly, to neutralise any existing acidity generated from the oxidation of pyritic material, and; secondly, to prevent further pyrite oxidation by re-establishing a higher water table to limit the introduction of oxygen into the soil profile. At East Trinity these strategies were achieved by lime assisted tidal exchange although the effect of the lime additions was negligible on the remediation of acidification compared to the

* Corresponding author.

E-mail address: crystal.maher@scu.edu.au (C.A. Maher).

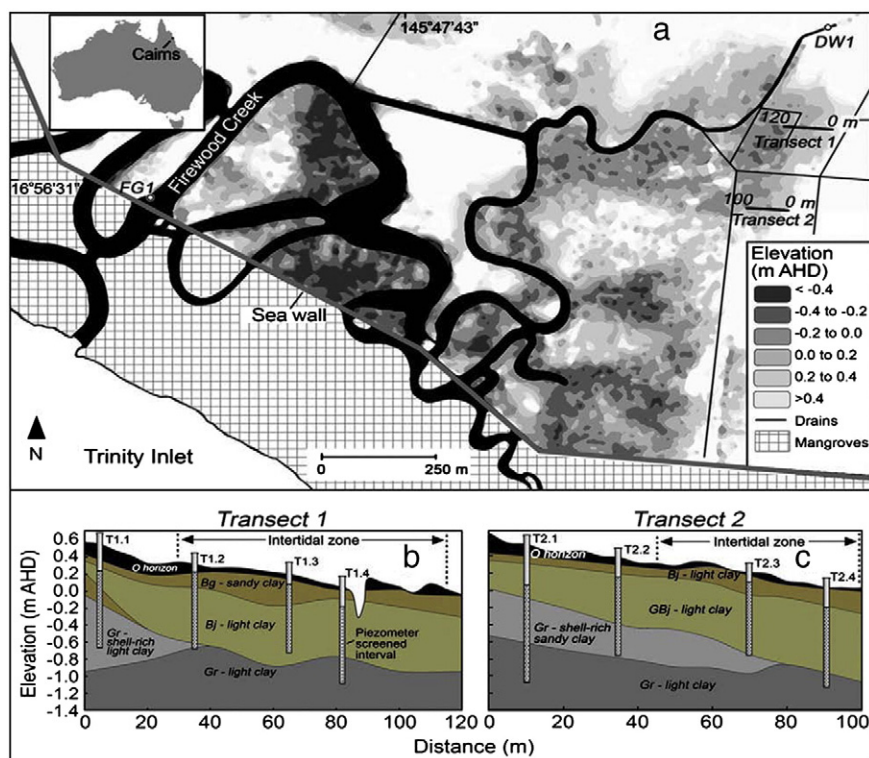


Fig. 1. Location of the East Trinity site in northern Queensland, Australia. Sampling Sites 1, 2 and 3 in this study correspond to Sites T2.1, T2.3 and T2.4 respectively (Johnston et al., 2011b).

contribution of the seawater (Johnston et al., 2012). The ongoing remediation also provided an excellent opportunity to investigate the likely response of a severely degraded ASS during climate change induced sea level rise.

There have been several studies examining the consequent geochemical changes. Some of these studies examined the hydrology and water chemistry of the site (Johnston et al., 2009a, 2011a), contemporary pedogenesis (Johnston et al., 2009b) and the abundance and reactivity of aluminium, iron and trace metals (Johnston et al., 2010; Keene et al., 2010; Burton et al., 2011a, 2011b; Claff et al., 2011).

Although stable sulfur isotope geochemistry has been investigated previously in field and experimental studies, only a few preliminary studies having been undertaken to date in ASS, and none in relation to the likely response of these sediments to climate change impacts. For example, Johnston et al. (2009b) used sulfur isotopes solely to help identify the depth that seawater inundation was impacting the soil profile and consuming acidity at the East Trinity site. Their results indicate that tidal inundation was only affecting the surficial sulfuric horizon and not the underlying sulfidic material. Boman et al. (2008) used sulfur isotopes to identify the possible sources and causes of sulfate and acidity in waters draining from Finnish ASS. Fractionation of stable isotopes occurs because the strength of the chemical bonds varies slightly with the mass of the isotope. The principle reaction in the formation of sulfide minerals is the reduction of SO_4 to produce H_2S (Rees, 1973; Dent and Pons, 1993; Sammut et al., 1996; Burton et al., 2011a, 2011b). This bacterially mediated process results in isotopic fractionation because the rate at which $^{34}\text{SO}_4^{2-}$ transforms to H_2^{34}S is significantly slower than the rate at which $^{32}\text{SO}_4^{2-}$ transforms to H_2^{32}S . Thus the result of sulfidation is lighter sulfide and heavier SO_4 (Fry et al., 1995; Brownlow, 1996; Wijsman et al., 2001; Fry, 2006; Hatzinger et al. 2012).

Some of the factors that can affect the degree of isotopic fractionation include SO_4 concentration, SO_4 reduction rates, substrates, depositional environment, temperature, pH, bacterial species and growth conditions (Kaplan and Rittenberg, 1964; Chambers and Trudinger, 1979; Habicht and Canfield, 1997; McConville et al., 2000; Farquhar et al., 2007; Stam et al., 2011). The aim of this study is to examine the

utility of sulfur isotopes in examining the geochemical processes occurring in ASS landscapes, using a formerly severely degraded ASS landscape that has been subject to varying degrees of remediation by tidally driven seawater inundation.

2. Methodology

2.1. Sampling site

Three sites were examined across the East Trinity property with varying surface elevations. Site 1 has a surface elevation of 0.5 m AHD and has not been affected by seawater inundation. Site 2 is at a slightly lower elevation (0.1 m AHD) and receives intermittent seawater flushing (Johnston et al., 2011a). Site 3 is again topographically lower (−0.1 m AHD) and remains inundated by seawater for most of the time (Johnston et al., 2009b). Site 3 has been receiving tidal inundation with seawater since 2002. Sites 1, 2, and 3 in this study correspond to Sites T2.1, T2.3, and T2.4, respectively as described by Johnston et al. (2011b).

2.2. Sample collection and preservation

Soil samples were collected using a gouge auger to a depth of 1.5 m and sectioned into 0.1 m depth increments. At each site multiple cores were taken and these increments bulked. Soil samples were placed in thick plastic bags, squeezed to exclude oxygen, sealed to reduce oxidation, and immediately frozen. Samples were kept frozen and analysed within 2 years of collection.

2.3. Chemical analysis

Subsamples were oven dried at 105 °C for 7 days, then reweighed for gravimetric moisture content determination (0g) (Rayment and Lloyds, 2011). Where applicable, results are reported on an oven-dried basis. pH and electrical conductivity (EC) were measured immediately after thawing of the samples, in a 1:5 soil:water suspension (Rayment and

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