Insights into combined radiogenic and stable strontium isotopes as tracers for weathering processes in subglacial environments

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ABSTRACT

This study reports stable and radiogenic strontium isotope behaviour in the dissolved load and suspended sediments from the subglacial outflow of the Lemon Creek glacier (Juneau Ice Field, Alaska) over a single melt season. *In situ* measurements (discharge, total alkalinity, pH and conductivity) are combined with elemental concentrations, X-ray diffraction (XRD) analysis and radiogenic strontium isotope measurements to interpret the variations observed in stable strontium isotopic ratios.

The stable Sr isotope composition ($^{88}Sr/^{86}Sr$ ratio expressed as $\delta^{88/86}Sr$, ‰) of the dissolved load averages 0.31 ± 0.05‰, and is heavier than both the suspended sediment 0.18 ± 0.03‰, as well as local bedrocks ~0.20 to 0.26‰. We attribute the enrichment of heavier isotopes in the dissolved load to the uptake of lighter Sr isotopes by secondary weathering minerals, driving the dissolved load to heavier values. X-ray diffraction (XRD) analysis confirms the presence of clays in the suspended sediments and thermodynamic modelling suggests the presence of iron oxy-hydroxide phases. Although it is not possible to completely rule out the effect of dissolution of primary minerals in controlling Sr isotopic compositions of the dissolved load, our data indicate that the extent of secondary mineral formation likely plays a significant role. The preferential weathering of minerals such as biotite (consistent with the mineralogical assemblages found in the suspended sediments), as well as the potential presence of radiogenic calcites from metacarbonates (derived from the Yukon-Tanana terrain), may be driving the small seasonal shifts in $^{87}Sr/^{86}Sr$ of the dissolved load to more radiogenic compositions, from $^{87}Sr/^{86}Sr_{(DL)} = 0.71048$ to 0.710647.

Using the combination of stable and radiogenic strontium isotopes to investigate weathering processes shows that radiogenic Sr isotopes provide information regarding weathering of primary phases. While the stable Sr isotope data appear to record information regarding the extent of secondary mineral formation, where secondary minerals incorporate the light isotopes, driving the dissolved load to heavy values.

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1. Introduction

Glaciers are one of the most effective agents of erosion on Earth, generating vast quantities of fine particles with fresh reactive mineral surfaces that are susceptible to chemical weathering (Fairchild et al., 1994; Tranter et al., 1993). Sediment–water interactions are crucial to understanding glacial meltwater chemistry (Brown et al., 1994a; Fairchild et al., 1999; Tranter et al., 1993), as the rapid flow of water over these reactive surfaces maximizes both rates of chemical weathering and erosion. Glaciated outflows are dominated by high calcium, potassium and sulphate concentrations (Anderson et al., 1997; Tranter, 2003), reflecting high physical and low chemical weathering

rates occurring in the subglacial environment, and resulting in incongruent and non-stoichiometric chemical weathering processes (Anderson et al., 1997; Tranter, 2003).

Stable isotope variations in group I and II metals have been successfully investigated as tracers of weathering processes in proglacial environments, for example lithium (δ^7Li, e.g. Pogge von Strandmann et al., 2006; Wimpenny et al., 2010) magnesium ($\delta^{26}Mg$, e.g. Tipper et al., 2012; Wimpenny et al., 2011), and calcium ($\delta^{44}Ca$, e.g. Hindshaw et al., 2008, 2011). Stable strontium isotopes have also emerged as an additional proxy for tracing chemical weathering (Chao et al., 2015; de Souza et al., 2010; Pearce et al., 2015; Wei et al., 2013). The traditional radiogenic strontium ($^{87}Sr/^{86}Sr$) system has been applied to glacial outflow waters as a proxy for mineral weathering reactions and processes (e.g. Anderson et al., 2000; Arn et al., 2003; Hagedorn and Hasholt, 2004; Sharp et al., 2002), and also to further understand connections between Sr isotope ratios in glacial runoff and the variation in the Sr isotope composition preserved in marine biogenic carbonates,

which are widely regarded as the most well understood proxy of continental Sr fluxes to the ocean (Hagedorn and Hasholt, 2004). Chemical weathering associated with glaciers has attracted much attention due to the possible link between increased chemical weathering during glacial retreat and control of the marine radiogenic strontium (^{87}Sr/^{86}Sr) ratios (e.g. Armstrong, 1971; Capo and Depaolo, 1990; Mokadem et al., 2015; Vance et al., 2009) and the potential for negative feedbacks to global climate through the carbon cycle (Anderson et al., 2000; Blum and Erel, 1995).

Analytical advances have increased the potential utility of stable strontium isotopes because they permit the measurement of small, yet resolvable mass dependent fractionations in the ^{88}Sr/^{86}Sr ratios in natural materials (e.g. Fietzke and Eisenhauer, 2006; Krabbenhöft et al., 2009; Ohno et al., 2008; Rüggeberg et al., 2008. Whilst this proxy is still being developed, data for natural samples and rock standards indicate that $\delta^{88/86}$Sr ($\delta^{88/86}$Sr = ((^{88}Sr/^{86}Sr)$_{SAMPLE}$/(^{88}Sr/^{86}Sr)$_{NBS987}$) − 1) × 1000) preserves a broad range of values ranging between +0.1 to −0.3‰ for terrestrial carbonate rocks (Halicz et al., 2008; Ohno et al., 2008), +0.05‰ to +0.35‰ for biogenic marine carbonates (e.g. Fietzke and Eisenhauer, 2006; Halicz et al., 2008; Rüggeberg et al., 2008; Stevenson et al., 2014) and +0.2 to +0.3‰ for terrestrial silicate rocks (Charlier et al., 2012; Ma et al., 2013; Moynier et al., 2010). More recently barites have been shown possess values between +0.07 to +0.11‰ (Widanagamage et al., 2014). Measurable mass dependent fractionations of $\delta^{88/86}$Sr can occur during terrestrial exogenic cycling with lighter strontium isotopes preferentially incorporated into substrates including, but not limited to: biogenic and inorganic calcium carbonates (e.g. Böhm et al., 2006; Fietzke and Eisenhauer, 2006; Rüggeberg et al., 2008; Stevenson et al., 2014); other secondary minerals (Halicz et al., 2008) and terrestrial plants (de Souza et al., 2010). de Souza et al. (2010) measured $\delta^{88/86}$Sr in a glaciated granitic watershed, with results indicating no resolvable fractionation between bulk soils and bedrock. However the authors argued this was because of the chemical heterogeneity of the forefield, and that due to incipient silicate weathering the soils have thus far witnessed nominal net loss of Sr. In addition to potential source variation in stable strontium isotopes from the dissolution of bedrock in the glacial environment, natural and experimental studies have shown that during the crystallization of calcium carbonate Sr isotopes undergo mass dependent fractionation whereby the lighter strontium isotopes are preferentially incorporated into the carbonate phase and therefore have lighter $\delta^{88/86}$Sr values than the fluid phase (e.g. Bohm et al., 2012; Fietzke and Eisenhauer, 2006. Therefore, the stable strontium isotope composition of complementary bedrock, suspended sediments and the dissolved load accompanying glacial weathering may vary significantly due to (i) the intensity of physical and chemical weathering of source primary minerals, (ii) a change in rate or extent of secondary mineral formation, (iii) a change in the balance of these dissolution and precipitation reactions, and (iv) adsorption/desorption processes associated with clays or other secondary minerals.

Rates of subglacial chemical weathering vary with the timing of the melt season; at the onset of the melt season, surface derived meltwater begins to reach the ice–rock interface, which can result in an increase in water stored at the glacier bed, and promote longer water–rock contact times leading to an increase in chemical weathering (Benn and Evans, 2010). During peak melting, a well-developed hydrological network system will increase the meltwater flow-through speed, decrease the residence time within the glacier and lower the water–rock interaction times (e.g. Fountain and Walder, 1998; Tranter, 2003). Therefore we may see variations in the radiogenic and stable Sr isotope ratios associated with seasonal changes in the subglacial network caused by: (i) faster mineral dissolution kinetics due to the lengthening of subglacial channels over fresh unweathered bedrock; (ii) variations in bedrock composition and weathering rates of the minerals present, (iii) differing water–rock interaction times, and/or (iv) sediment residence times in discrete pockets of subglacial water.

Radiogenic strontium isotopes tend to behave conservatively during the short time period of a glacial melt season, with variation potentially resulting from reactive mineral dissolution, which reflects the subglacial lithology and weathering intensity. This study documents a seasonal record of both the radiogenic and stable Sr isotope compositions of the dissolved load (DL) and suspended sediments (SS) from a glaciated environment in southeast Alaska. Using a high precision double spike isotope technique (e.g. Krabbenhöft et al., 2009; Stevenson et al., 2014) we provide insights into the weathering of primary minerals such as biotite, using radiogenic Sr isotopes, and the formation of secondary weathering minerals, such as clays, using stable Sr isotopes.

2. Sample site and regional geology

The Lemon Creek glacier (LCG) is a small valley glacier forming the southernmost extension of the Juneau Icefield, ~6.5 km northeast of Juneau, Alaska (Fig. 1(a)). The Juneau Icefield is situated in the Tongass National Forest, part of the Coast Mountain Range of southeast Alaska, extending over an area of ~4000 km². The LCG is small, less than 11.7 km² in size, and thus exhibits simple alpine glacier dynamics (Criscitiello et al., 2010). The LCG is unbranched and is orientated generally in N–S direction except near the toe where it curves west, see Fig. 1 (b). Flow begins on the Northwest slope of Observation Peak (1512 m) and travels via an icefall between elevations of approximately 650 and 850 m (Heusser and Marcus, 1960). The LCG has undergone significant negative mass balance with a terminal retreat of over 700 m and a net surface height decrease of 24.7 m during the period 1953–1998 (Miller and Pelto, 1999). The LCG is situated within a maritime climate, and mass balance is strongly influenced by climatic parameters (temperature and precipitation), high winter snowfall, as well as the Pacific Decadal Oscillation (PDO), more so at the glacier terminus than in the accumulation zone (Criscitiello et al., 2010). The LCG covers approximately one third of the 32 km² Lemon Creek watershed, therefore seasonal fluctuations in discharge from this glacier can significantly impact the downstream Lemon Creek river which drains into Juneau.

Geologically, the LCG sits on the mid-Cretaceous central pluton-gneiss belt (Fig. 1 (b)), with the immediate area comprised of young tonalite sills (50–70 Ma) to the west, high grade pre-Tertiary metamorphosed sedimentary and volcanic rocks surrounding the sample site, and late-Permian metamorphosed sedimentary rocks (Greenschist facies) are found to the east (Kistler et al., 1993). The geological units underlying the LCG are predominantly biotite schist, biotite gneiss, marble and calc-silicate granofels, hornblende gneiss and granitoid rocks (mainly tonalite/migmatite and biotite/hornblende tonalite) with a general age range of 62–69 Ma and an overall younging of bedrock in a northeasterly direction (Brew and Ford, 1985; Gehrels et al., 1984).

An additional input into the LCG system is Lake Linda, a supraglacial lake at the head of the LCG. Lake Linda is located on the Juneau Icefield (N 58°21.000′, W 134°21.960′) and drains annually through a composite englacial cave ~450 m long and out through the LCG terminus each summer melt season. During 2012 a reconnaissance flight revealed that on calendar day (CD) 213, Lake Linda had not drained, however a field excursion on CD 230 to sample Lake Linda revealed the lake had by this time drained.

3. Methods

3.1. Sample collection

Prior to sampling, all sample containers and tubing were precleaned (see Supplementary information). Samples for Sr analysis were collected directly from the main subglacial outflow channel at the terminus of the Lemon Creek Glacier (Fig. 1 (c) site A: N 58°24.455′, W 134°22.296′) on a daily basis from CD 223–252 in 2012 between 9 and 10 am. For subglacial water and suspended sediment