

Strontium isotopic composition as tracer of weathering processes, a review with respect to James Ross Island, Antarctica

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Abstract

Strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) are routinely used to determine sources and mixing relationships in geochemical studies. They have proven to be useful in determining weathering processes and quantifying end-member mixing processes. A number of studies highlight that Sr isotopes represent a powerful tool helping to constrain weathering reactions, weathering rates, flow pathways and mixing scenarios, even when inherent differences in weathering rates of different minerals, and mineral heterogeneity in natural environments may cause difficulties in defining the weathering component of different geochemical systems. Nevertheless, Sr isotopes are useful when combined with other chemical data, to constrain models of water–rock interaction and mixing as well as geochemical processes such as weathering. This paper presents basic information about Sr isotopic system, new analytical developments, summary of recent published studies in constraining the weathering processes, and indicates studies similar to weathering in polar regions. The aim of this paper is to present rationale of using Sr isotopes as tracer of weathering processes on James Ross Island, Antarctica.

Key words: Strontium, isotopes, chemical weathering, Antarctica

Introduction

Strontium isotopes have proven to be an important and powerful tool in investigations of many aspects of weathering and hydrology. Their isotopic variations provide natural fingerprints of rock-water interactions and have been widely utilized in studies of weathering and hydrology. Their first applications to weathering processes were based on studies that sought to understand the effects of chemical weathering on the geochronology of whole rock samples and geochronologically important minerals (Goldich et Gast 1966, Dasch 1969, Blaxland 1974, Clauer 1979, 1981; Clauer et al 1982). Since these pioneering works strontium isotopes have unquestionably become the most commonly used radiogenic isotope

tracer because of the large variability in isotopic composition and the interest in tracing sources and cycling of the analog element calcium. The mechanisms controlling differences in strontium isotope ratios in the environment and the hydro-geochemical behavior of strontium have become reasonably well understood and as a result, strontium has been increasingly used as tracer in weathering and hydrologic studies.

Studying of weathering has important implications in a diverse range of geochemical issues. Among them are the linkage between weathering rates and CO_2 draw-down and long-term climate change, and the rates of release of macronutrients such as K and Ca.

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Sr isotopes as a tracer

Strontium has four stable natural isotopes, ^{84}Sr , ^{86}Sr , ^{87}Sr and ^{88}Sr . However, the isotopic abundances in rocks are variable because of the formation of radiogenic ^{87}Sr by the β decay of naturally occurring ^{87}Rb with a half-life of 4.88×10^{10} y (Faure 1986). The increase in isotope ratio is proportional to the Rb/Sr ratio, forming the basis of dating rocks using the isochron method. Hence older rocks, particularly those with high Rb/Sr ratios tend to have larger variations between different minerals and higher $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than younger rocks. Individual mineral phases of silicate rocks, such as biotite or feldspars, exhibit charac-

teristic $^{87}\text{Sr}/^{86}\text{Sr}$ ratios due to different Rb/Sr initial ratios in silicate minerals and decay of ^{87}Rb to ^{87}Sr . This allows tracing the weathering of individual mineral phases by measuring $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in soils and in the dissolved and suspended load of runoff water samples. A complete review of Sr isotope system fundamental characteristics for tracing geochemical reactions is given in Bullen and Kendall (1998). In addition, the two non-radiogenic isotopes, ^{88}Sr and ^{86}Sr , could provide a new, unexplored stable isotope tool to trace mass-dependent fractionation effects (Mavris et al. 2010).

Radiogenic Sr isotopes

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is extremely useful because it is not fractionated by low temperature geochemical reactions (*e.g.*, mineral dissolution and precipitation) or biotic processes, and may thus be used to investigate mineral weathering reactions (Shand et al. 2007). The advantage of using Sr isotopes over major elements as proxies of chemical weathering is that Sr-isotopic ratios are not sensitive to the processes that may concentrate or dilute concentrations of solutes, and therefore can be used as a conservative tracer to determine water-flow paths, mixing relations, and groundwater ages (*e.g.* Shand et al. 2007, Pett-Ridge et al. 2009).

Differences in solute Sr isotope ratios are controlled by variations in initial inputs, differences in mineralogy along flowpaths, mineral dissolution characteristics and residence time. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio in waters will therefore be a function of the “weatherable Sr” and the efficiency of the exchange between rock and solution (Åberg et al. 1989). One of the main problems for Sr isotope tracer studies lies in defining the isotope composition of this

weathering-derived Sr. Complete rock or soil dissolution does not give a fair representation of the weathering $^{87}\text{Sr}/^{86}\text{Sr}$ ratio because of the different weathering rates and stabilities of minerals in the weathering environment. The whole rock $^{87}\text{Sr}/^{86}\text{Sr}$ is, therefore, of little relevance in determining weathering rates because the weathering-derived ratio will be dominated by those mineral phases with the highest dissolution kinetics. A range of leachate and extraction techniques, usually employing organic acids, has therefore been used to determine the weathering component of Sr in soils (Åberg et al. 1989, Wickman et al. 1992, Miller et al. 1993, Sharp et al. 2002). The presence of different mineral phases and different water flowpaths necessitates a strict consideration of isotope data in conjunction with solute chemistry.

Radiogenic Sr isotope data have been recently successfully utilized to discriminate between carbonate and silicate weathering sources (*e.g.* Jacobson et al. 2002, Chamberlain et al. 2005, Tipper et al. 2006a, Jin 2012), for the investigation

of relative mineral weathering rates as well as for the identification of the sources of base cations in streams (*e.g.* Blum et al. 2002, Blum et Erel 1997, Bullen et al. 1997, White et al. 2001, Bullen et Bailey 2005, Pett-Ridge et al. 2009). Recent case studies from Antarctica or terrains with retreating glacier demonstrated that Sr isotopes are powerful tool helping to constrain weathering reactions in these environments. Lyons et al. (2002) used radiogenic Sr isotopes as a tool to help discern the proportions of the geologic material undergoing chemical weathering in the Taylor Valley, Antarctica. The data provided a detailed picture of present-day sources of solutes to the streams and lakes of Taylor Valley and strongly support the notion that chemical weathering is a major process in determining the overall aquatic chemistry of these lakes in polar environment. Anderson et al. (2000) utilized Sr isotopes to discriminate between carbonate and silicate weathering in streams in the foreland of the retreating Bench Glacier in

south-central Alaska. They have shown that chemical denudation rate and strontium isotope ratios decline with sediment exposure age in the proglacial streams and dominant weathering reactions in the young sediments are of carbonate and sulfide rather than silicate minerals. Hindshaw et al. (2011) highlighted the importance of long-term catchment monitoring. Study of a glacial catchment (Damma Glacier, Switzerland) improved our understanding of the spatial and temporal controls acting on stream water chemistry and silicate weathering processes. Mavris et al. (2010) showed in a study of proglacial area (Upper Engadine, Switzerland) that immediately after deglaciation, physical and chemical weathering as well as mineral transformation started at high rates. The results document a series of time dependent processes related to the weathering of rock-forming minerals and evidence that climate warming directly influences the biogeochemical cycles in cold areas.

Stable Sr isotopes

An additional constraint on the exogenic Sr cycle can be the stable isotope composition of Sr. It is now known that a wide variety of elements, such as boron, lithium, silicon, magnesium, calcium, iron and zinc, experience mass-dependent stable isotope fractionation during continental weathering (Rose et al. 2000, Huh et al. 2001, Pistiner et Henderson 2003, Schmitt et al. 2003, Fantle et DePaolo 2004, Ziegler et al. 2005, Georg et al. 2006, Tipper et al. 2006b, Viers et al. 2007). It has been tacitly assumed that the stable isotope composition of Sr (expressed as $\delta^{88/86}\text{Sr}$) exhibits negligible variation during weathering because of the small relative mass differences between Sr isotopes. Pioneering work of Patchett (1980) demonstrated that Sr isotopes were fractionated by up to 1.5%/amu in CAIs and chondrules of the meteorite Allende.

Advances in multicollector mass spectrometry together with new methods developed for determining the mass discrimination effect on $^{88}\text{Sr}/^{86}\text{Sr}$ (Ohno et Hirata 2007, Fietzke et Eisenhauer 2006, Krabbenhöft et al. 2009) has shown that Sr also experiences mass fractionation during terrestrial exogenic cycling: lighter Sr isotopes are preferentially incorporated into biogenic and inorganic Ca-carbonates, and seawater has an isotopically heavy stable Sr isotope composition (Fietzke et Eisenhauer 2006), analogous to Ca isotopes (*e.g.* Skulan et al. 1997), even degree of stable Sr isotope fractionation is small in comparison with those observed in stable isotope studies of the lighter elements. Strontium is therefore virtually unique due to the fact that its isotope composition records analytically resolvable information both about the source of Sr

($^{87}\text{Sr}/^{86}\text{Sr}$) and mass-fractionating processes that it has witnessed ($\delta^{88/86}\text{Sr}$). The combined application of these data may thus lead to a uniquely well-constrained understanding of the exogenic cycle of Sr. To date, however, the understanding of stable Sr isotope fractionation in the weathering environment is extremely limited (Halicz et al. 2008), primarily due

to a paucity of data (De Souza 2010). First Sr stable isotope data study in a variety of geological materials in the weathering environment of Damma Glacier catchment, Switzerland (De Souza 2010) highlighted the potential of this tracer, but also points to the necessity of further development.

Chemical weathering

Chemical weathering of the continental crust is a key Earth System process critical to the global cycling of the elements, and through its coupling with carbonate precipitation in the oceans, the primary sink of atmospheric CO_2 on a geological timescale (Berner 2003). Furthermore, chemical weathering leads to the decomposition of rocks and the release of elements from continents into solution which controls the chemical composition of river waters, thus further influencing the composition of seawater (Edmond et al. 1979). The production of base cations due to chemical weathering is important because of their role as plant nutrients, in neutralizing acidity or generating alkalinity and in the replenishment of the soil ion exchange pool (Shand et al. 2007).

Historically, it has been accepted that climate (*i.e.* precipitation, temperature) exerts the principal control on chemical weathering. The feedback between climate and weathering has been attributed to a number of factors including the effect of temperature on i) silicate dissolution rates, ii) runoff, iii) mechanical weathering, and iv) glacial melting (*e.g.* Peters 1984, Sverdrup 1990, Bluth et Kump 1994, Meybeck 1994, Gibbs et Kump 1994, White et Blum 1995, Gislason et al. 1996, Gaillardet et al. 1999, Stefansson et Gislason 2001, Tranter et al. 2002, Dessert et al. 2003, Millot et al. 2003, West et al. 2005, Anderson 2007, Navarra-Sitchler et Brantley 2007, Gislason et al. 2009).

Although temperature may be an overriding factor in most environments, it may not explain weathering processes in all situations. For example, despite low temperatures and precipitation in Iceland, chemical denudation rates are higher than in Hawaiian catchments of similar geologic character (Bluth et Kump 1994). The high physical removal of material in Iceland continuously exposes fresh rock surfaces, whereas slow rates of material removal in Hawaii have allowed thick, highly weathered soils to build up. Similarly, frost action prevents accumulation of weathered material in Siberian river basins, resulting in aluminosilicate weathering rates equivalent to those in the tropical watershed of the Orinoco (Huh et Edmond 1997). Studies such as these suggest that chemical weathering is a function of several other physical factors beside the temperature that may potentially affect chemical weathering rates. Physical processes, such as frost action and glacial grinding, can increase mineral surface areas (Matsuoka 1995, Anderson et al. 1997). In deserts, salt weathering may enhance chemical weathering rates; this process has been also documented in the McMurdo Dry Valleys (Selby et Wilson 1971, Wellman et Wilson 1965, Matsuoka 1995). Most of the previous studies examining the control of climate on chemical weathering have focused on tropical and temperate watersheds, and comparisons between these. Few studies,

however, have focused on extreme environments, such as polar deserts (Nezat et al. 2001). Data from the continental Antarctica published by Lyons et al. (1997) and Nezat et al. (2001) have shown, perhaps surprisingly, that the Taylor Valley streams had weathering rates (as determined by silica and bicarbonate fluxes) that were comparable to rates in far warmer climate regimes. The high weathering rates determined for the polar desert streams in Taylor Valley indicate, that chemical weathering is not primarily controlled by temperature and precipitation. In this case, high rates of physical weathering (*e.g.* frost action, salt weathering) contribute to the chemical weathering rate as a result of new rock surfaces exposed to weathering (Nezat et al. 2001).

Chemical weathering and physical erosion are coupled to the extent of mineral weathering rates which depend on the availability of fresh mineral surfaces with high reactivity (White et al. 1999, Jacobson et Blum 2003, Riebe et al. 2004). Weathering is kinetically limited in regions having young surfaces (West et al. 2005). Glaciers and periods of glaciation may have a significant impact on weathering, changing the interplay between physical and chemical weathering processes by putting large volumes of dilute melt waters and fine-grained sediment in contact with each other. Glaciers are significant agents of physical erosion; for example, the mechanical denudation of glaciated valleys in Alaska and Norway is an order of magnitude higher than that in equivalent non-glaciated basins (Hallet et al. 1996). Silicate weathering depends on the kinetic rate of mineral dissolution, the supply of material (*e.g.* by erosion) and the time available for reaction. Additionally, the weathering rate of a mineral or rock

decreases with the time (West et al. 2005) that the mineral spends in the weathering environment. Silicate weathering and transformation reactions should, consequently, be most intense in the initial stages of soil formation. The rates of reactions and their dependencies on environmental factors (such as climate) are of fundamental interest to understanding the soil system and its interaction with surrounding environmental conditions. In this context, the influence of climate is of growing interest with respect to landscape and soil evolution because of observed and predicted global climate changes. Due to climate warming, additional areas will become ice-free and subject to weathering and soil formation. Proglacial environments are important for the understanding of global CO₂ cycles on glacial/interglacial timescales as they made up a significant amount of the global land surface during the Quaternary due to the growth and retreat of glaciers and ice sheets (Gibbs et Kump 1994). The proglacial area is a potential zone of high geochemical reactivity due to the availability of freshly ground reactive material (subglacially derived), high water to rock ratios and contact times, high permeability and a high supply of dilute waters (meltwater and rain/snowmelt) percolating through the deposits. High silicate weathering rates have been measured in proglacial areas in the Alps (Arn 2002, Hosein et al. 2004) and the Rocky Mountains (Taylor et Blum 1995). Proglacial weathering intensities depend mainly on the lithology (*i.e.*, highly reactive minerals like carbonates and sulphates vs. crystalline rocks), the development of organic matter (Conen et al. 2007), the rate of supply of fresh rock material to the proglacial zone, the age of exposure and the character of the proglacial hydrological drainage system (Mavris et al. 2010).

Selection of study area, James Ross Island

The Antarctic Peninsula and adjacent islands hold some similarity to sub polar glacial systems (such as coastal Greenland, Svalbard, Patagonia, and Alaska), and are known to be more sensitive to atmospheric warming than the ice sheets covering the rest of the Antarctic continent (Vaughan 2006). Historical temperature records indicate that the Antarctic Peninsula region has been getting warmer much more rapidly ($3.7 \pm 1.6^\circ\text{C}$ per century) than the global mean of $0.6 \pm 0.28^\circ\text{C}$ per century (Houghton et al. 2001, Vaughan et al. 2003); it is the third-most warming site worldwide and the fastest warming in the Southern Hemisphere (King 1994, Thomas et Dieckmann 2002). Furthermore, a comparison of satellite data from 1979 to 1999 indicates that sea ice coverage has decreased significantly on both sides of the Antarctic Peninsula (Parkinson et al. 2002). Meanwhile, seven major ice shelves surrounding the Antarctic Peninsula have retreated over the last few decades, with the largest collapse occurring in March 2002 (Larsen B ice shelf; Scambos et al. 2003). Most glaciers in the Antarctic Peninsula region have been in retreat over the past half century (Cook et al. 2005). Retreating glaciers are leaving fresh rock surfaces preserved from an ancient ages exposed to extreme weather conditions. Global warming is not affecting only a retreat of glaciers but also the rate of rock weathering. Gíslason et al. (2009) reported results from the study at eight Icelandic glaciated and non-glaciated catchments. They declared 8–30% increase in the mechanical weathering rate and 4–14% increase in the chemical weathering rate for each degree C of temperature increase. Historically, it has been

accepted that climate represents the principal control on chemical weathering. It would imply that chemical weathering is the greatest in warm, wet climate regions whilst it is the lowest in cold and dry regions. However, recent studies from the continental Antarctica (Lyons et al. 1997, Nezat et al. 2001) indicate that in this environment chemical weathering is not primarily controlled by temperature and precipitation but rather by high rates of physical weathering, exposing new reactive surfaces to chemical weathering and can be as high as in warmer climatic conditions. Thus, there is an increasing recognition that physical geomorphologic processes are important drivers of chemical weathering. A detailed understanding of the connection between physical and chemical weathering rates is of vital importance to explain how landscape evolution, driven by tectonics, climate or anthropogenic activities, affects geochemical fluxes. These questions have applications to the long-term carbon cycle and nutrient availability to ecosystems. The observation that chemical weathering fluxes can be controlled by physical erosion rates needs to be explored from geochemical perspective (Anderson 2005). As far as we are concerned there is no such study within the region of Antarctic Peninsula.

James Ross Island, in particular the area of the Ulu Peninsula, with contrasting lithology and only recently uncovered from the ice and snow, with several remaining small-scale glaciers that are retreating, numerous permanent snowfields and a number of streams and small lakes is well suited for investigation of these weathering processes.

Summary

The recent case studies presented here highlight the use of $^{87}\text{Sr}/^{86}\text{Sr}$ as a tracer of weathering processes and flow pathways in surface and ground waters in Antarctica and terrains with retreating glacier. Strontium isotopes were used to estimate weathering rates, constrain flow pathways, identify sources of solutes, and distinguish between the carbonate and silicate weathering. A pre-requisite of using Sr isotopes as a tracer of weathering processes and determination of flow pathways is that the solid phase and potential end-member solution phases are characterized. Strontium isotopes generally provide additional evidence to that provided by solute concentrations alone and are routinely used in combination with other isotope and solute tracers, as well as physical measurements. Recent improvements in mass spectrometry lead to de-

velopment of additional constraints on the exogenic Sr cycle, the stable strontium isotope analysis. Applications of stable Sr isotopes on weathering processes constitute a new topic for future research.

A retreat of glaciers in remote polar regions belongs to the most serious consequences of global change of climatic conditions. Study of weathering processes after deglaciation and their influence on newly-established ecosystems is of particular interest because knowledge about weathering rates and mineral transformation processes is fundamental in analyzing the release of nutrients to ecosystems during primary succession. The Antarctic Peninsula and adjacent islands seems to be especially responsive to changing environmental conditions, which makes James Ross Island ideal area for such research.

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