A geostatistical framework for predicting variations in strontium concentrations and isotope ratios in Alaskan rivers

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ABSTRACT

Bataille and Bowen (2012) developed models to predict variations in the ratio of 87-strontium to 86-strontium ($^{87}Sr/^{86}Sr$) in rocks (bedrock model) and rivers (catchment water model) for regional provenance studies. Here, we revisit those models' formulation and calibration and apply them to predict Sr concentrations ([Sr]) and $^{87}Sr/^{86}Sr$ of Alaskan rivers. In a first step, we add several new components and/or improvements to resolve limitations of the model, including: 1) an independent siliciclastic sediment sub-model, 2) an explicit consideration of $^{87}Sr/^{86}Sr$ variability at the local scale, and 3) a fully-coupled assessment of prediction uncertainty. Tested against a compilation of 885 $^{87}Sr/^{86}Sr$ rock analyses across Alaska, the new bedrock model significantly improves $^{87}Sr/^{86}Sr$ prediction accuracy in both igneous and sedimentary settings. In a second step, we develop a fully independent Sr chemical weathering model calibrated using a database of 339 [Sr] analyses from rivers of Northern Hemisphere high-latitude and predicting spatial variations in the rate of Sr release from rocks as a function of lithology, permafrost cover and slope. We combine the bedrock and Sr chemical weathering models to predict [Sr] and $^{87}Sr/^{86}Sr$ in Alaskan rivers. Tested on a dataset of 61 water samples, the resulting catchment water model explains 82% of $^{87}Sr/^{86}Sr$ variations in Alaskan rivers. We compare the average [Sr] and $^{87}Sr/^{86}Sr$ of Alaskan runoff estimated with the catchment water model to observed data of the Yukon River. The estimated average [Sr] and $^{87}Sr/^{86}Sr$ of Alaskan surface runoff – 104.3 μg/L and 0.7098 respectively – differ significantly from those of the Yukon River — 139.3 μg/L and 0.7137 respectively. This result calls into question the assumption that [Sr] and $^{87}Sr/^{86}Sr$ values estimated only from large rivers are representative of the Sr weathering flux from the entire Earth surface. The data products from this work provide an alternative basis for estimating $^{87}Sr/^{86}Sr$ values in rocks and rivers for regional provenance and chemical weathering studies across Alaska.

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1. Introduction

Variations in the ratio of 87-strontium to 86-strontium ($^{87}Sr/^{86}Sr$) in seawater have been used for decades as a proxy to reconstruct the interplay of mantle processes and continental weathering on the Earth's surface at timescales of millions of years (Peterman et al., 1970; Veizer and Compston, 1974; Brevart and Allegre, 1977; Burke et al., 1982; Chaudhuri and Clauer, 1986; Veizer, 1989; Shields, 2007). However, interpreting $^{87}Sr/^{86}Sr$ variations in seawater remains challenging and a multitude of hypotheses have been advanced to explain diagnostic features of the seawater $^{87}Sr/^{86}Sr$ curve. For instance, it has been argued that the rapid increase in $^{87}Sr/^{86}Sr$ in seawater over the last 40 Ma could be associated with climatic changes enhancing high latitude denudation rates (Armstrong, 1971; Zachos et al., 1999) or with tectonic

factors such as Himalayan orogenesis or decreased subduction, and seafloor spreading rates (Raymo et al., 1988; Edmond, 1992).

The interpretation of $^{87}Sr/^{86}Sr$ variations in seawater relies heavily on our understanding of the modern strontium (Sr) budget in seawater. The modern Sr budget in seawater is thought to be primarily controlled by the input of Sr from two isotopically distinct Sr fluxes: a radiogenic Sr flux from continental runoff and a poorly constrained non-radiogenic Sr flux from the mantle, which includes island arc weathering (Allègre et al., 2010), ophiolite weathering (Davis et al., 2003), and hydrothermal alteration at oceanic ridges (Spooner, 1976; Coogan and Gillis, 2013). The magnitude and isotopic signature of each of these fluxes in the modern seawater Sr budget have been estimated by compiling global datasets documenting Sr concentrations ([Sr]) and $^{87}Sr/^{86}Sr$ from rivers and fluid samples recovered from oceanic ridges (Brass, 1976; Palmer and Edmond, 1992; Peucker-Ehrenbrink et al., 2010). However, current estimates of the non-radiogenic and radiogenic Sr fluxes do not balance each other, feeding a vivid debate about the accuracy of the empirically-

based estimates of those Sr fluxes. Some scientists argue that the current seawater Sr budget is inaccurate and/or missing some fluxes (Allègre et al., 2010; Jones et al., 2012; Beck et al., 2013; Coogan and Gillis, 2013; Jones et al., 2014); whereas others argue that the modern Sr budget is not at steady-state in post glacial periods (Davis et al., 2003; Vance et al., 2009). Models able to predict [Sr] and $^{87}Sr/^{86}Sr$ in rivers at regional scale could provide a more robust framework to improve the estimates of the Sr flux and $^{87}Sr/^{86}Sr$ from continental runoff and island arcs and contribute to resolving this debate.

A pre-requisite for developing models predicting $^{87}Sr/^{86}Sr$ in rivers is to develop a model to predict $^{87}Sr/^{86}Sr$ in rocks, because bedrock is the dominant source of Sr in the Earth's surface. In previous work, Bataille and Bowen (2012) (referred to as BB12) developed a bedrock model that predicts $^{87}Sr/^{86}Sr$ variations in rocks as a function of rock type and rock age. This model showed promising results when applied to the conterminous US and circum-Caribbean regions (Bataille and Bowen, 2012; Bataille et al., 2012), but suffered from: 1) a poor representation of $^{87}Sr/^{86}Sr$ heterogeneity within and between rock units across a range of spatial scales, 2) the absence of consideration of key sedimentary processes influencing the $^{87}Sr/^{86}Sr$ of siliciclastic sedimentary rocks, and 3) the absence of explicit uncertainty assessment for model prediction.

Another critical step to predict $^{87}Sr/^{86}Sr$ in river water is to develop models predicting the release of Sr by chemical weathering, which account for the variable contribution of different rock units to the dissolved Sr in rivers. BB12 developed a chemical weathering model accounting for differential weathering rates and Sr content of different rock types. BB12's chemical weathering model only predicts chemical weathering variations as a function of geological variables and does not account for environmental controls. Bataille et al. (2012) took a different approach and applied an adapted version of a multi-linear regression model (Hartmann, 2009), predicting solute concentration in rivers as a function of lithological proportion and mean runoff of catchments. While Bataille et al.'s (2012) chemical weathering model attempted to account for environmental controls, their chemical weathering model is not calibrated for application at high-latitudes and does not account for Sr-specific weathering processes.

Here, we develop new components and improvements to our previously published models that enhance their power to predict $^{87}Sr/^{86}Sr$ in bedrock and water. We apply the models to predict [Sr] and $^{87}Sr/^{86}Sr$ in Alaskan rivers. Alaska is an ideal area to extend our modeling work because i) human impact on Alaskan rivers is limited ii) a wealth of geochemical and geological data exists for this region and, iii) a new spatially extensive dataset documents solute concentrations and $^{87}Sr/^{86}Sr$ in 61 rivers of Alaska (Brennan et al., 2014–this issue). Alaska is also an interesting location to test the sensitivity of the high-latitude Sr budget to geologic and physiographic factors because it displays varied geology, topography, and climate. We focus on testing the influence of geology (age and lithology), topography (slope), climate (temperature and runoff), and glacial processes (permafrost and alpine glacier cover) on the [Sr] and $^{87}Sr/^{86}Sr$ variations of Alaskan rivers.

2. Material and methods

2.1. Bedrock model

The formulation and calibration of this new bedrock model are standardized to make use of the new global lithological map (GLiM) (Hartmann and Moosdorf, 2012). The GLiM divides rock of the Earth surface into 16 major lithological classes including plutonic and volcanic acid (pa and va), basic (pb and vb), intermediate rocks (pi, py and vi); metamorphic rocks (mt); and siliciclastic (ss), unconsolidated (su), mixed (sm), carbonate (sc) and evaporite sedimentary rocks (ev). The GLiM represents the geology of Alaska by 57,714 polygons with an average area of 48 km², based on polygons (Moll et al., 1997) and lithology

descriptions (Moosdorf et al., 2010) from previous maps. The median age of those polygons is 57 Myrs.

2.1.1. Igneous sub-model

2.1.1.1. Igneous sub-model formulation. For igneous rocks, we keep the model formulation described in Bataille and Bowen (2012) (BB12), but we develop new calibration steps to assess the uncertainty and represent within-unit $^{87}Sr/^{86}Sr$ variability. Based on the tectonic history of the Earth, BB12 made the simplifying assumption that the modern $^{87}Sr/^{86}Sr$ of silicate rocks can be approximated based on a three stage history. Before the onset of plate tectonics and the beginning of recycling and chemical differentiation of crustal material (Dhuime et al., 2012), ^{87}Sr was produced in the chemically quasi-undifferentiated Earth until $^{87}Sr/^{86}Sr$ reached 0.701 at 3 Ga (an approximation of the age of the onset of plate tectonics, t_1). After 3 Ga, geochemical differentiation between crust and mantle accelerated and $^{87}Sr/^{86}Sr$ evolved independently in the mantle and multiple crustal rock reservoirs having different Rb/Sr ratios. In the third stage, extant rock units were formed from one of these rock reservoirs at times corresponding to the rock unit ages (t_2) as documented in geological map data. From this theoretical framework, BB12 derived the following equation:

$$\left(\frac{^{87}Sr}{^{86}Sr}\right)_{rock} = 0.701 + \left(\frac{^{87}Rb}{^{86}Sr}\right)_{parent}\left(e^{\lambda(t_1-t_2)}-1\right) + \left(\frac{^{87}Rb}{^{86}Sr}\right)_{rock}\left(e^{\lambda t_2}-1\right), \quad (1)$$

where λ is the decay constant of the parent isotope ($1.42 * 10^{-11}\,yr^{-1}$), $(^{87}Rb/^{86}Sr)_{parent}$ is the $^{87}Rb/^{86}Sr$ of the parent material, and $(^{87}Rb/^{86}Sr)_{rock}$ is the $^{87}Rb/^{86}Sr$ of the modern rock.

$^{87}Rb/^{86}Sr$ can be expressed as:

$$\frac{^{87}Rb}{^{86}Sr} = \frac{Rb\left(w^{87}Rb\right)(mSr)}{Sr\left(w^{86}Sr\right)(mRb)} = k\frac{Rb}{Sr} \approx 2.8936\frac{Rb}{Sr}, \quad (2)$$

where m refers to the atomic mass of an element, w to the abundance (%) of an isotope, and k to the conversion factor. $w^{86}Sr$ and mSr depend on the abundance of ^{87}Sr and hence on the $^{87}Sr/^{86}Sr$ of each sample. When using the modern abundance of ^{87}Rb (27.8346%) and $^{87}Sr/^{86}Sr = 0.70916$ (seawater), k equals 2.8936 (Faure, 1977). k only increases by a negligible amount when $^{87}Sr/^{86}Sr$ increases from 0.7 to 1. To simplify our calculations, we neglected changes in $w^{86}Sr$ and mSr and assumed a constant k value of 2.8936.

2.1.1.2. Igneous sub-model calibration. In the t_2 calibration step (Fig. 1), we estimated the numeric minimum and maximum possible age of each rock unit of Alaska from the age descriptor given in the GLiM database using the USGS geological time scale (USGS, 2007).

In the $(^{87}Rb/^{86}Sr)_{parent}$ calibration step (Fig. 1), we proceeded as in BB12, using a global dataset downloaded from the Earthchem portal (www.earthchem.org; query by "chemistry": $^{87}Sr/^{86}Sr$ and Sr and Rb, "Age" = age exists) containing $^{87}Sr/^{86}Sr$, t_2 and Rb/Sr data for 31,421 samples. We grouped samples into 7 sub-datasets representing the major plutonic, volcanic and metamorphic GLiM lithological classes (mt, pa, pb, pi, va, vb, vi). We then back-calculated $(^{87}Rb/^{86}Sr)_{parent}$ for each igneous rock sample by solving Eq. (1). For each GLiM lithological class, the resulting distribution of $(^{87}Rb/^{86}Sr)_{parent}$ values was strongly positively skewed. To resolve this issue, we power-transformed $(^{87}Rb/^{86}Sr)_{parent}$ for each sub-dataset (R, car package, powerTransform function) to achieve a normal distribution and calculated the mean and standard deviation for each lithological class (Supplementary material, Appendix A, Tables A1 and A2).

In the $(^{87}Rb/^{86}Sr)_{rock}$ calibration step (Fig. 1), we used ordinary kriging to estimate within-unit patterns of $(^{87}Rb/^{86}Sr)_{rock}$ that lead to