Ge/Si and $^{87}\text{Sr}/^{86}\text{Sr}$ tracers of weathering reactions and hydrologic pathways in a tropical granitoid system

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Received 5 April 2005; accepted 19 August 2005
Available online 27 December 2005

Abstract

Ge/Si and $^{87}\text{Sr}/^{86}\text{Sr}$ data from primary and secondary minerals, soil waters, and stream waters in a tropical granitoid catchment quantitatively reflect mineral alteration reactions that occur at different levels within the bedrock–saprolite–soil zone. Near the bedrock–saprolite interface, plagioclase to kaolinite reaction yields low Ge/Si and $^{87}\text{Sr}/^{86}\text{Sr}$. Higher in the regolith column, biotite weathering and kaolinite dissolution drive Ge/Si and $^{87}\text{Sr}/^{86}\text{Sr}$ to high values. Data from streams at base flow sample the bedrock–saprolite interface zone, while at high discharge solutes are derived from upper saprolite–soil zone. Coupled Ge/Si and $^{87}\text{Sr}/^{86}\text{Sr}$ can be effective tools for quantifying the importance of specific weathering reactions, and for geochemical hydrograph separation.

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Keywords: Germanium; Silica; Ge/Si; Strontium isotopes; Weathering reactions; Hydrograph separation

1. Introduction

Chemical weathering of a complex polymineralic substrate generally produces solutes derived from a number of simultaneous reactions. Traditional equilibrium mass balance models use the composition of the major primary and secondary minerals, and the composition of waters believed to be produced by the weathering transformation, to invert for the masses of primary minerals destroyed and secondary minerals produced (Garrels and Mackenzie, 1967). Isotope and trace element data can also be used to identify mineral or biogenic sources of solutes in soil waters, ground waters and stream waters. They can identify sources that may otherwise be overlooked by using only major element abundances (Blum et al., 2002). Here we present a combined approach from a well constrained weathering profile developed on a granitoid basement under wet tropical conditions. Detailed mineral and soil water composition data provide a mass balance constraint. $^{87}\text{Sr}/^{86}\text{Sr}$ and Ge/Si data provide tracer information that can complement and extend the results of the inversions. One goal of this research is to test the utility of the Ge/Si tracer to provide quantitative information on the sources of silica in a weathering system, by explicitly comparing the results from Ge/Si with the overall mass balance calculations. We find that the combined $^{87}\text{Sr}/^{86}\text{Sr}$ and Ge/Si tracer data allow the identification and quantification of the major mineral
sources of solutes. In particular we find that the tracer data from stream water samples over the course of hydrographic events provide information on how stream solute sources change as a function of hydrologic stage. This information is valuable both as a means of improving discharge weighted flux estimates, and as a tool for hydrograph separation, as different mineral sources dominate at different depths within the regolith–bedrock profile.

2. Study site and methods

Granitoid weathering processes have been the object of intense study at the Luquillo Experimental Forest, Puerto Rico (White et al., 1998; Schulz and White, 1999). Our study site is a soil and regolith complex developed on the early Tertiary Rio Blanco quartz diorite pluton. The current climate has a mean annual temperature of 22 °C and a mean annual precipitation of 420 cm, and weathering rates are high. We sampled soil waters from a network of installed tension lysimeters down to a depth of 8 m. Soil and mineral samples were obtained by hand coring of the regolith, or by sampling unaltered bedrock in a nearby road cut. Mineral samples were separated by a combination of density separation and hand picking. Stream water samples were taken by an event-triggered ISCO water sampler in polyethylene bottles. Major ions, dissolved silica, $^{87}\text{Sr}/^{86}\text{Sr}$ and Ge/Si ratios were measured by ion chromatography, colorimetry, TIMS, and HG-ICP-MS, respectively (Kurtz et al., 2002). Samples analyzed for Ge/Si and $^{87}\text{Sr}/^{86}\text{Sr}$ were taken several months apart, so there may be some temporal differences between them.

3. Results and discussion

Primary and secondary minerals and pore waters from the site have a range of $^{87}\text{Sr}/^{86}\text{Sr}$ and Ge/Si ratios (Fig. 1). Plagioclase (0.7036) and hornblende (0.7058) have low $^{87}\text{Sr}/^{86}\text{Sr}$, while fresh biotite is quite radiogenic (0.7827). Altered biotite has a range of values between local pore water and fresh biotite, reflecting varying degrees of exchange of the interlayer cation site. Ge/Si is low in quartz (0.5), increasing in plagioclase (3.1), and high in hornblende (6.1) and biotite (6.8). Secondary kaolinite, primarily formed from plagioclase alteration, has high Ge/Si (5.9). The coupled $^{87}\text{Sr}/^{86}\text{Sr}$ and Ge/Si data provide a means to discriminate between mineral sources. For example, while quartz has negligible Sr content, it has a distinctly low Ge/Si ratio. Conversely, biotite and hornblende

3.1. Saprolite profiles

White et al. (1998) and Turner et al. (2003) suggest that the bedrock–saprolite interface zone is the locus of plagioclase to kaolinite conversion, driving large solute fluxes. Soil water samplers were not installed in this zone, and we take stream water at base flow conditions as an indication solute chemistry produced here. Base flow samples have $^{87}\text{Sr}/^{86}\text{Sr}$=0.7053 and Ge/Si=0.4. Using the mass balance calculations of White et al. (1998), we find that the predicted $^{87}\text{Sr}/^{86}\text{Sr}$ and Ge/Si are 0.7041 and 0.39, respectively. While the calculated Ge/Si is in excellent agreement with the observed value, the calculated $^{87}\text{Sr}/^{86}\text{Sr}$ is substantially lower than observed. However, the addition of only 1.5% biotite-derived Sr is sufficient to reconcile the observed and modeled data. The major element-mineral mass balance calculations are not sufficiently sensitive to identify this small but critical
contribution from biotite. Partial alteration of biotite may release radiogenic Sr from the interlayer site Sr while contributing little K and Ca and even less Si to solution (Derry and France-Lanord, 1996). With this input the mass balance and tracer data are highly consistent with one another and with plagioclase weathering to form kaolinite as the dominant reaction in this zone. The low (Ge/Si)w is produced by the formation of kaolinite with high Ge/Si at the expense of plagioclase. The bulk of the Sr released to solution is also derived from plagioclase, with a smaller contribution from hornblende. However, a small but important contribution of Sr from biotite is necessary to produce the observed base flow values.

In the middle saprolite Ge/Si and $^{87}\text{Sr}/^{86}\text{Sr}$ in lysimeter waters are higher, reflecting increased contributions of silica from biotite dissolution. Plagioclase to kaolinite conversion and some quartz dissolution provide low Ge/Si and keep the saprolite water Ge/Si near 2.5. In the shallow saprolite/soil region, biotite and plagioclase are mostly exhausted, and quartz and especially kaolinite dissolution dominate the silica flux, yielding high Ge/Si near 4.0. But soil solutions have high $^{87}\text{Sr}/^{86}\text{Sr}$, in excess of expected rainwater values. Because kaolinite contributes little Sr and quartz essentially none, the dissolution of a small quantity of altered biotite can influence the soil water Sr budget ad yet have no impact on the silica budget. The variability we observe in different samples of altered biotite in the saprolite profile makes estimation of the biotite contribution of Sr somewhat uncertain. We have not yet evaluated the role of mineral aerosol deposition as a source of radiogenic Sr in the shallow soil (Kennedy et al., 1998).

3.2. Storm water series

The storm water time series data show dilution of Si and Sr with rising water, while both $^{87}\text{Sr}/^{86}\text{Sr}$ and Ge/Si increase (Figs. 2 and 3). Both the dilution and ratio increases are consistent with derivation a component of the storm event water from higher in the regolith. While base flow conditions appear to reflect solute sources at the bedrock–saprolite interface, a substantial portion of storm water solutes must be derived form higher up in the profile. A best estimate concentration weighting of these components implies that 70% or more of the peak storm discharge is derived from saprolite water. Since discharge increases by a factor of 5–20 during these events they can contribute quantitatively to the total integrated export flux over time. This may be particu-
larly true for Sr, which shows less dilution during storm events than Si does.

4. Conclusion

The combination of mineral mass balance calculations and Ge/Si and $^{87}$Sr/$^{86}$Sr tracer data is a powerful combination for identifying and quantifying the processes that contribute solutes to soil and stream waters. The constraints are complimentary, with different sensitivities. The preliminary data we have obtained from the Luquillo site shows that the inferences from the combined $^{87}$Sr/$^{86}$Sr and Ge/Si data are both consistent with the mineral mass balance calculations, and provide additional information. They are sensitive to particular reactions, while the mineral mass balance calculations yield a “global” simultaneous solution that may over- or under-represent a given source. Furthermore, the tracer data permit ready evaluation of changing solute sources in streams as a function of discharge. Such calculations would be under-constrained with the mineral mass balance method.

Acknowledgements

This research was supported by NSF EAR-0208172 and the USGS WEBB Program.

References


