



## Research paper

## River solute fluxes reflecting active hydrothermal chemical weathering of the Yellowstone Plateau Volcanic Field, USA

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## ABSTRACT

In the past few decades numerous studies have quantified the load of dissolved solids in large rivers to determine chemical weathering rates in orogenic belts and volcanic areas, mainly motivated by the notion that over timescales greater than ~100 kyr, silicate hydrolysis may be the dominant sink for atmospheric CO<sub>2</sub>, thus creating a feedback between climate and weathering. Here, we report the results of a detailed study during water year 2007 (October 1, 2006 to September 30, 2007) in the major rivers of the Yellowstone Plateau Volcanic Field (YPVF) which hosts Earth's largest "restless" caldera and over 10,000 thermal features. The chemical compositions of rivers that drain thermal areas in the YPVF differ significantly from the compositions of rivers that drain non-thermal areas. There are large seasonal variations in river chemistry and solute flux, which increases with increasing water discharge. The river chemistry and discharge data collected periodically over an entire year allow us to constrain the annual solute fluxes and to distinguish between low-temperature weathering and hydrothermal flux components. The TDS flux from Yellowstone Caldera in water year 2007 was 93 t/km<sup>2</sup>/year. Extensive magma degassing and hydrothermal interaction with rocks accounts for at least 82% of this TDS flux, 83% of the cation flux and 72% of the HCO<sub>3</sub><sup>-</sup> flux. The low-temperature chemical weathering rate (17 t/km<sup>2</sup>/year), calculated on the assumption that all the Cl<sup>-</sup> is of thermal origin, could include a component from low-temperature hydrolysis reactions induced by CO<sub>2</sub> ascending from depth rather than by atmospheric CO<sub>2</sub>. Although this uncertainty remains, the calculated low-temperature weathering rate of the young rhyolitic rocks in the Yellowstone Caldera is comparable to the world average of large watersheds that drain also more soluble carbonates and evaporates but is slightly lower than calculated rates in other, less-silicic volcanic regions. Long-term average fluxes at Yellowstone are likely ~20% higher than those in the abnormally dry water year 2007, but the protocol used in this study can be easily adaptable to track future changes in low-temperature weathering and hydrothermal flux components, which could provide better monitoring of magmatic unrest.

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## 1. Introduction

Chemical weathering of large watersheds (>100 km<sup>2</sup>) is a major process influencing landscape evolution, nutrient supply to soils and streams, and global geochemical cycles. In the past few decades research on chemical weathering has mainly focused on using the load of dissolved solids in rivers as a proxy for rock weathering (e.g. Drever and Clow, 1995; White and Blum, 1995; Gaillardet et al., 1999; Dupré et al., 2003; Meybeck, 2003; Tipper et al., 2006; Hren et al., 2007). A primary motivation for many of these studies relates to the notion that over timescales greater than the residence time of bicarbonate (HCO<sub>3</sub><sup>-</sup>) in seawater (~100 kyr), silicate hydrolysis may be the dominant sink for atmospheric CO<sub>2</sub>, thus creating a feedback

between climate and weathering (Berner et al., 1983; Raymo and Ruddiman, 1992; Kump et al., 2000; Gislason et al., 2009).

While weathering of silicate rocks from the world's major rivers has been shown to play a strong role in global consumption of CO<sub>2</sub>, global compilations (Gaillardet et al., 1999) did not include data from rivers draining active magmatic provinces, where silicate hydrolysis is likely induced to some degree by acid gases emanating from a deep magma (e.g. Giggenbach, 1984, 1988; Chiodini et al., 1991; Christenson, 2000; Taran, 2009) rather than by atmospheric CO<sub>2</sub>. Several studies have quantified chemical weathering rates in volcanic systems (Gislason et al., 1996; Louvat and Allègre, 1997, 1998; Varekamp and Thomas, 1998; Stefánsson and Gislason, 2001; Dessert et al., 2003; Rad et al., 2006, 2007; Goldsmith et al., 2008; Gislason et al., 2009; Goldsmith et al., 2010), but only recently, the role of magmatic gases and high-temperature water-rock interactions were incorporated into the calculations (Dessert et al., 2009). In all these studies, the flux of major elements originating from high-temperature reactions was calculated based on the assumption that most, or all of the chlorine in

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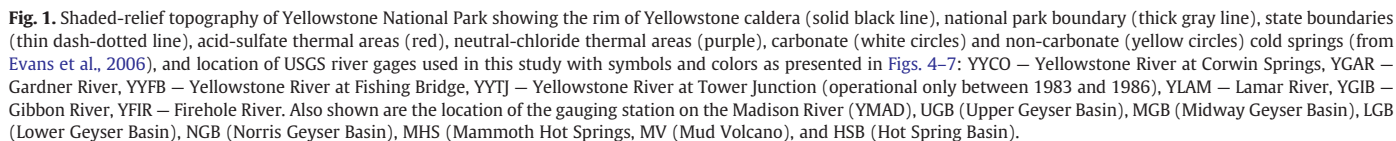
E-mail address: [shaulh@usgs.gov](mailto:shaulh@usgs.gov) (S. Hurwitz).

This study was carried out with the objective of characterizing and quantifying water-rock interaction and chemical weathering rates and riverine fluxes of major ions in the Yellowstone Plateau Volcanic Field (YPVF) (Fig. 1). More specifically, our goals are to: (1) determine the magnitude of chemical weathering induced by atmospheric CO<sub>2</sub> relative to that induced by high-temperature rock interaction with magmatic gases, (2) estimate the denudation rates across Yellowstone Caldera, and (3) provide a baseline against which fluxes during periods of increased magma degassing and volcanic unrest can be compared.

The YPVF is a prime location to address the above goals because (1) all the major rivers have gages (Fig. 1) (U.S. Geological Survey National Water Information System) and a well established sampling protocol (Friedman and Norton, 2007; Hurwitz et al., 2007a,b) providing high quality water discharge records and precise solute flux determinations, characterization of spatial patterns, and quantification of temporal trends (2) high emission rates of magmatic gases,

mainly CO<sub>2</sub> (Werner and Brantley, 2003; Werner et al., 2008) imply that the underlying magmatic system is active and extensively degassing; (3) geochemical and thermodynamic models of thermal fluid composition (Truesdell and Fournier, 1976; Fournier, 1989; Lowenstern and Hurwitz, 2008) and detailed descriptions of hydrothermal alteration minerals from research drill holes (e.g. Keith and Muffler, 1978; Sturchio et al., 1986) provide constraints on the high temperature water–rock interaction (4) Corrections for atmospheric deposition of major elements are not required because precipitation in the area is extremely dilute and the contribution of precipitation-derived solutes to the river load is negligible (Miller and Drever, 1977; Zelt et al., 1998; Kharaka et al., 2002; Hurwitz et al., 2007a).

The YPVF hosts Earth's largest "restless" caldera (Newhall and Dzurisin, 1988; Christiansen, 2001; Lowenstern et al., 2006), containing over 10,000 thermal features (Fournier, 1989) and covering about 6500 km<sup>2</sup> at an average elevation of approximately 2400 m above sea level (Fig. 1). It has been a center for rhyolitic volcanism during the



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