Prediction and observation of dissolved geochemistry of the Fraser River, British Columbia

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The global correlation between bedrock age and the dissolved $^{87}Sr/^{86}Sr$ composition of continental runoff [1] suggests that sufficiently detailed knowledge of spatial distributions of lithological units and runoff fields may allow for more representative predictions of the geochemical nature of continental material exported to the ocean [2]. At the scale of individual drainage basins, however, variations in contributions from geochemically disparate portions of a basin over timescales of weeks to years can cause systematic shifts in the composition of dissolved material exported at different times. In such cases where variability in seasonal hydrology and geochemical "end-members" within a drainage area are significant, predicted geochemical properties must be compared with actual observations at high enough temporal frequency to determine if large-scale modeling approaches can reasonably be applied at the regional or catchment scale.

The Fraser River basin is of intermediate size (232,000 km^2) but possesses stark spatial variability in bedrock geology and precipitation patterns on account of its complex mountainous terrain. Conservative geochemical properties of dissolved constituents (including δD_{H2O} and $^{87}Sr/^{86}Sr$) measured over two years near the Fraser mouth demonstrate a stronger influence during the spring and summer from headwaters with radiogenic $^{87}Sr/^{86}Sr$ and depleted δD. $^{87}Sr/^{86}Sr$ ranges from 0.709 in late winter up to 0.714 in the summer. A mixing model is presented, in which a discharge-weighted average of tributaries is calculated to predict the values of these properties downstream. Strong agreement between the modeled and measured values suggests that such an approach adequately captures the spatial heterogeneity and temporal variability of the Fraser basin. The predicted $^{87}Sr/^{86}Sr$ based on gauging station discharge data agrees well with that based on discharge generated by a global hydrologic model [3], showing promise for extending such an approach to other river systems.

This study provides a framework for further work constraining fluxes and variability of nonconservative constituents (e.g. dissolved organic carbon, nutrients).

[1] Peucker-Ehrenbrink et al. (2010) *Geochem Geophy Geosy* **11(3)**. [2] Roelandt et al. (2010) *Global Biogeochem Cy* **24(2)**. [3] Vörösmarty et al. (1998) *J Hydrol* **207**.

In situ silicon isotope analysis of Archean cherts and BIFs by laser ablation MC-ICPMS

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We present results of in situ stable Si isotope measurements on Archean Cherts and Banded Iron Formations (BIFs) from the Pilbara (Western Australia) and Barberton (South Africa) greenstone belts. Samples were obtained from outcrops and drill cores. In this study we used: (1) a Microlas Geolas Laser ablation (LA) system equipped with a 193 nm Excimer laser at the VU Amsterdam (VUA) and an inhouse built LA system with a 193 nm Excimer laser at ANU. Both LA systems were connected to a Thermo Neptune MC-ICPMS. Molecular isobaric interferences of $^{12}C^{16}O^+$, $^{14}N^{2+}$, $^{14}N^{16}O^+$ that are present on masses ^{28}Si, ^{29}Si and ^{30}Si, were resolved with the aid of the medium resolution slit (RP=4000). An ablation pit size of 49 by 300um and with a 5-10 Hz repetition rate and 5 $J.cm^{-2}$ was used on both LA systems. The LA measurements on the VUA and ANU MC-ICPMS were performed with the same setup as described by [1]. To assess precision, accuracy and matrix effects of the LA technique, chert and BIF samples were analyzed that were previously characterized for silicon isotopes by micro-drilling and subsequent liquid chromatographic purification **[1].** A chemically homogenous chert sample that is well characterized for silicon isotopes by wet chemical techniques and has a $\delta^{30}Si$ of 0.50 ±0.20 (2sd, relative to NIST RM8546) was used as a standard at both the VUA and ANU.

LA silicon isotope results are significantly influenced by the matrix; e.g. in BIF layers with more than 50% Fe_2O_3, we observed a shift of more than 40‰ in $\delta^{30}Si$, compared to values obtained by micro drilling and chemical purification. This shift is highly dependant on the tuning conditions of lasers and MC-ICPMS. It is therefore necessary to carefully match standards and samples, and only if the chemical composition of the samples is relatively constant can accurate data be obtained.

BIFs display significant variations between iron poor and iron rich layers (maximum observed difference ~1.8‰). In all cases the iron rich layers have higher $\delta^{30}Si$ than the iron poor layers. Variations in $\delta^{30}Si$ of up to 1.2‰ were also observed within individual layers on a mm scale. Cherts display variation between black and white bands with a maximum $\delta^{30}Si$ difference of 1.2‰. The data of this study confirm that silicon isotope signatures are not altered by post depositional burial and metamorphism. Therefore, the laser ablation technique opens new possibilities to unravel the depositional mechanisms for Archean BIFs and cherts, provided samples are correctly matrix-matched with standards.

[1] Van den Boorn et al. (2006) J. Anal. At. Spectrom., 21, 734–742.