Highly depleted Colorado Plateau gypsum deposits attributed to multiple episodes of redox cycling

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Introduction

The Department of Energy's Old Rifle site is a former uranium mill site situated along a floodplain of the Colorado River in western Colorado. The aquifer underlying the site consists of 6-7 m of Quaternary alluvium overlying the Tertiary Wasatch Formation. Sulfate concentrations in Old Rifle groundwater are elevated (8-10 mM), with unusually low sulfur isotope ratios ($\delta^{34}S$ values from -6 to -10‰). The source of the low $\delta^{34}S$ sulfate in groundwater appears to be gypsum veins within the Wasatch Formation, which outcrops above the site and through which regional groundwater recharges the Old Rifle aquifer. Veins of gypsum sampled from the upper Wasatch have $\delta^{34}S$ values lower than any previously reported in the literature (as low as -56‰). The veins are associated with Fe-oxide minerals and visible iron staining and are in close proximity to fossilized plant material within the Wasatch sediments (Figure 1). The low $\delta^{34}S$ gypsum is inferred to result from oxidation of ^{34}S-depleted sulfide minerals that formed in reducing zones associated with organic matter. Subsequent oxidation of the isotopically light sulfides mobilized low $\delta^{34}S$ sulfate that precipitated as gypsum infillings within high permeability fractures. Modern analogs of such naturally reduced zones occur within the alluvial sediments at Old Rifle, which are characterized by lignitic organic carbon and framboidal pyrites having low $\delta^{34}S$ values (as low as -70‰). Associated with these pyrites are greatly elevated concentrations of uranium [1]. Oxidation of such reduced zones within the alluvium and Wasatch Formation could lead to mobilization of reduced metals, such as uranium, that may explain the high background concentrations of metals in the Rifle groundwater outside of the tailings-impacted area.

Figure 1: Petrified branch or root in upper Wasatch Formation replaced with quartz, Fe-oxides and gypsum ($\delta^{34}S$ = -55.4‰).

[1] Qafoku *et al.* (2009) *Environmental Science & Technology* **43**, 8528-8534.

Recycling of crust in Proterozoic convergent margins : evidences from Sm-Nd isotopes and trace elements of mafic-ultramafic plutonic rocks from the Grenville Province

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Nearly 50 mafic and ultramafic rocks were sampled for a Sm-Nd isotopes study in 6 plutons coeval to the La Bostonnais complex, each <1 to 3 km^2 of surface and spread over 100 km within a north-south belt called the Portneuf-Mauricie Domain (PMD). Results show Nd T_{DM} ages that range from 1400 to 1970 Ma and $\varepsilon_{Nd}(t)$ mostly between +2.5 and +4.3. Trace element patterns of these 6 plutons normalized to the primitive mantle show strong negative Ta anomaly and moderate to strong negative Zr, Hf, and Ti anomalies. Two mafic lithologies within two plutons from the PMD (Lac Nadeau, Rochette West) with TIMS U-Pb zircon ages respectively of 1.396 and 1.386 Ga that are interpreted to represent crystallization ages [1]. A regression of 18 samples from the Nadeau and Lac-à-la-Vase plutons provide a Sm-Nd isochron age of 1423 ±28 Ma (MSWD=4), similar within error to the U-Pb ages. The Lac-à-la-Vase pluton is compatible with derivation from a near-depleted mantle reservoir whereas the other plutons suggest a mantle separation time of 100 to 400 millions years earlier than 1.39 Ga. Pyroxenites hosting the Lac Edouard Ni-Cu deposit show the lowest ε_{Nd} of the 6 PMD plutons with values between +0.85 and +2.6.

A second region of interest is the Renzy Terrane (RT), identified over an area covering at least 50 km^2, where sub-kilometric pyroxenites lenses have REE and HFSE ~1x to 10x primitive mantle contents with strong negative Ta anomaly and moderate to strong negative Zr, Hf (±Ti) anomalies. Coeval mafic gneisses have REE and HFSE ~5x to 50x primitive mantle contents and were divided in 3 distinct groups, although a majority have trace element signatures akin to subduction zone processes [2]. Both RT and PMD ultramafic rocks have 15-30 ppm Zr rendering them difficult to date by U-Pb zircon methods. A regression of 14 pyroxenites and 4 mafic gneisses samples from the RT provided a Sm-Nd isochron age of 1504 ±67 Ma (MSWD = 2.5) in agreement with U-Pb zircon ages of 1457 ±15 Ma obtained by ion microprobe on 3 different mafic to intermediate rocks. A Sm-Nd isochron including pyroxenites, mafic gneisses and felsic gneisses yields an age of 1508 ±47 Ma, and these rocks have a range of $\varepsilon_{Nd}(t)$ between +1.7 and +3.9, an average Nd T_{DM} age of 1.77 ±0.14 Ga (n=32) and therefore ~300 millions years older that their crystallization age.

Most of the trace element chemistry of the DMP and RT mafic and ultramafic rocks indicate that they probably originated from arc and back-arc magmatic activity. The RT was probably accreted to Laurentia as a thrust sheet over the Paleoproterozoic belt of the Grenville Province.

[1] Sappin et al. (2009) *Can. J. Earth Sci.* **46**, 331-353.
[2] Montreuil, Constantin (2010) *Prec. Res.* **181**, 150-166.