Sustained sulfide oxidation by physical erosion processes in the Mackenzie River basin: Climatic perspectives

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ABSTRACT

The chemical weathering of rocks with sulfuric acid is usually not considered in reconstructions of the past evolution of the carbon cycle, although this reaction delivers cations and alkalinity to the ocean without involvement of atmospheric CO_2. The contribution of sulfuric acid as a weathering agent is still poorly quantified; the identification of riverine sulfate sources is difficult. The use of $\delta^{34}S$ and $\delta^{18}O$ of dissolved sulfate allows us to demonstrate that most of the sulfate in surface waters of the Mackenzie River system, Canada, derives from pyrite oxidation (85% ± 5%) and not from sedimentary sulfate. The calculated flux of pyrite-derived sulfate is 0.13×10^{12} mol/yr, corresponding to 20%–27% of the estimated global budget. This result suggests that the modern global ocean delivery of sulfide-derived sulfate, and thus chemical weathering with sulfuric acid, may be significantly underestimated. A strong correlation between sulfide oxidation rates and mechanical erosion rates suggests that the exposure of fresh mineral surfaces is the rate-limiting factor of sulfide oxidation in the subbasins investigated. The chemical weathering budget of the Mackenzie River shows that more than half of the dissolved inorganic carbon discharged to the ocean is ancient sedimentary carbon from carbonate (62%) and not atmospheric carbon (38%). The subsequent carbonate precipitation in the ocean will thus release more CO_2 in the atmosphere-ocean system than that consumed by continental weathering, typically on glacial-interglacial time scales.

Keywords: carbonate weathering, sulfide oxidation, mechanical erosion, Mackenzie River, atmospheric CO_2.

INTRODUCTION

Chemical weathering of rocks at the Earth's surface acts as a giant neutralization reaction wherein protons are consumed to transform the primary minerals into secondary ones and soluble ions (Ebelmen, 1845). Because most of these protons come from carbonic acid produced by the dissolution of atmospheric and/or soil CO_2 in surface waters, the weathering of silicate minerals followed by carbonate deposition in the ocean acts as a global climate regulator, removing greenhouse gases from the atmosphere, on geological time scales (Walker et al., 1981; Berner et al., 1983; François and Walker, 1992). To assess the effect of rock weathering on climate, studies of river chemistry have estimated the global CO_2 consumption associated with the chemical weathering of different lithologies (Garrels and Mackenzie, 1971; Meybeck, 1987; Gaillardet et al., 1999; Dessert et al., 2003). However, the dissolution of atmospheric and/or soil CO_2 is not the unique weathering agent in surface waters, and the fraction of sulfuric acid produced by the oxidative weathering of pyrite (OWP) in rocks (Equation 1) could be significant:

$$FeS_2 + 15/4O_2 + 7/2H_2O \rightarrow Fe(OH)_3 + 2H_2SO_4. \quad (1)$$

This reaction is important on a global scale, consuming atmospheric oxygen as well as participating in the global carbon cycle. The involvement of sulfuric acid in weathering reactions rather than CO_2 reduces the alkalinity input to the ocean and thus affects carbonate precipitation rates. Although numerical models of climate evolution have incorporated increasingly sophisticated parameterizations of CO_2 consumption (Donnadieu et al., 2004), the influence of rock weathering with sulfuric acid on climate is unknown because quantifying the origin of sulfate in large rivers remains difficult. To date, the fraction of acidity generated by OWP as sulfuric acid is still not well quantified. Current estimates of pyrite-derived sulfate in river waters range from 0.48×10^{12} to 0.65×10^{12} mol/yr (François and Walker, 1992; Berner and Berner, 1996), but this contribution has not been directly measured from river chemistry data and results from a forward calculation based on the composition of continental crust. Whereas acid rains and fertilizers may be significant anthropogenic sulfate sources to rivers, sedimentary sulfate dissolution (gypsum in further discussion) and OWP are the main natural sources. Because only OWP affects the global C cycle, recent efforts attempted to develop isotopic tracing to distinguish between the different sulfate sources (Galy and France-Lanord, 1999; Karim and Veizer, 2000; Pawellek et al., 2002; Spence and Telmer, 2005), because the major element concentration alone does not allow such a distinction. The combined use of S and O isotopes would be a particularly powerful technique for constraining the origin of sulfate in rivers (Karim and Veizer, 2000; Pawellek et al., 2002) and we pursue this approach for the rivers of the Mackenzie basin.

SETTING, MATERIALS, AND METHODS

The Mackenzie River basin (Fig. 1), northwestern Canada, is a large Arctic river system (1.78×10^6 km^2) with an annual water discharge of 310 km^3/yr. It yields the largest input of suspended material to the Artic Ocean and the second largest input of dissolved solids. From west to east, the Rocky and Mackenzie Mountains (Rockies), the interior platform (plains), and the Canadian shield (Precambrian granitic basement) form the basin. The Rockies are mainly composed of carbonate, dolomitic limestone, and shale, whereas extensive outcrops of carbonaceous black shale, sandstones, and a few evaporite layers form the plains (Reeder et al., 1972; Millot et al., 2003).

As defined by Millot et al. (2003), river samples are classified following their location (Rockies, plains, Western Cordillera) or their type (main tributaries) (Fig. 1). We measured

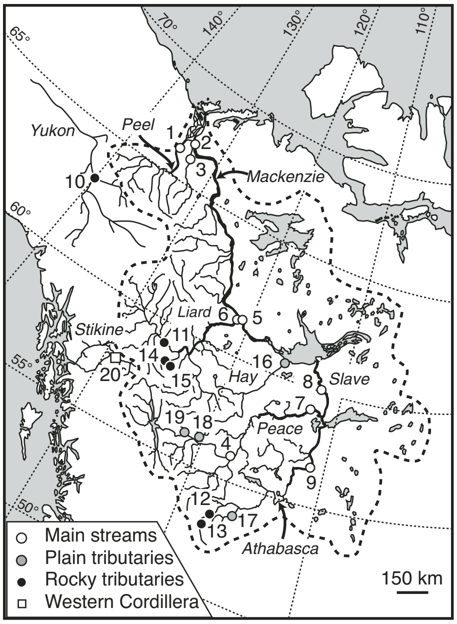

Figure 1. Map of Mackenzie basin showing locations of river samples. Numbers refer to sample numbers in Table DR1 (see footnote 1).

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Geology, November 2007; v. 35; no. 11; p. 1003–1006; doi: 10.1130/G24132A.1; 4 figures; Data Repository item 2007247.

the oxygen ($\delta^{18}O_{SO_4}$) and sulfur ($\delta^{34}S$) isotopic composition of dissolved sulfate and the $\delta^{18}O$ of water ($\delta^{18}O_W$) in 20 river samples. Data and details on analytical procedures are available in the GSA Data Repository.[1]

IDENTIFYING THE ORIGIN OF DISSOLVED SULFATE

Rivers in the Mackenzie basin have higher concentrations of SO_4^{2-} (200–300 μmol/L in rivers from the plains and Rockies; Millot et al., 2003) compared to the world average (~120 μmol/L). The low SO_4^{2-} in rivers draining the shield and Cl^- <6 μmol/L across the basin (Millot et al., 2002, 2003) demonstrate that atmospheric or anthropogenic input of SO_4^{2-} can be neglected. The high SO_4^{2-} in the Rockies and the plains is therefore of sedimentary origin, gypsum and OWP.

The proportion of SO_4^{2-} derived from OWP and gypsum can be inferred using $\delta^{18}O_{SO_4}$ and $\delta^{34}S$ (Fig. 2). Because S and O isotopic signatures are preserved during the congruent dissolution of gypsum, a Phanerozoic gypsum end member can be defined (Fig. 2) as having $\delta^{18}O_{SO_4}$ and $\delta^{34}S$ values ranging from 10‰ to 20‰ and from 10‰ to 30‰, respectively (Claypool et al., 1980; Strauss, 1997; Paytan et al., 2004; Turchyn and Schrag, 2006). None of the water samples is within the range of the gypsum end member, although two tributaries from the Rockies (stars in Fig. 2) and some of the main tributaries tend toward the gypsum end member. An alternative source of SO_4^{2-}, such as OWP, is therefore required.

Sulfate produced by OWP is expected to have $\delta^{34}S$ values similar to that of the pyrite source and $\delta^{18}O_{SO_4}$ resulting from a mixture between the $\delta^{18}O$ of atmospheric oxygen (+23.5‰) and the $\delta^{18}O$ of the meteoric water ($\delta^{18}O_W$) involved in the oxidation reaction. The good correlation between $\delta^{18}O_{SO_4}$ and $\delta^{18}O_W$ (Fig. DR1; see footnote 1) (except for the stars; Fig. 2), demonstrates that the oxygen of the water molecule influences the $\delta^{18}O_{SO_4}$ as a result of OWP (Equation 1). Consequently, the Mackenzie samples within the shaded area (Fig. 2) can be interpreted as a mixture between two pyrite-derived sulfate end members. The first has positive $\delta^{34}S$ (~10‰) and the lightest $\delta^{18}O_{SO_4}$ (−12‰ ± 3‰) while the second exhibits negative $\delta^{34}S$ (~−20‰) and heavier oxygen (−1‰ ± 3‰).

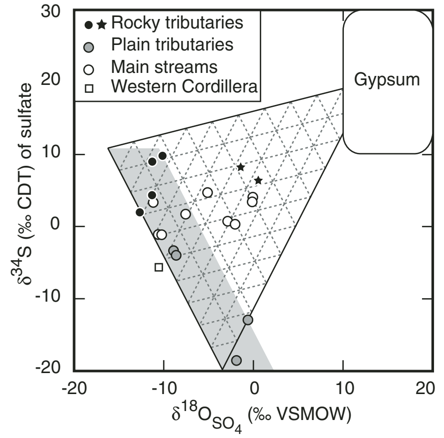

Figure 2. $\delta^{34}S$-$\delta^{18}O_{SO_4}$ mixing diagram of sulfate from rivers of the Mackenzie basin, between Phanerozoic evaporite (white rectangle) and a variable end member (shaded area) for pyrite-derived sulfate. Width of shaded area corresponds to range of expected $\delta^{18}O_{SO_4}$ assuming $\delta^{18}O_W$ (W is water) variation of 6‰ over the basin. Large triangle (drawn for $\delta^{18}O_W$ = −22.5‰) represents the field of possible isotopic composition. Dashed lines are equivalent mixing proportions between sulfate sources. Gypsum from western Canada has a mean isotopic composition of $\delta^{34}S$ = 20‰, $\delta^{18}O_{SO_4}$ = 13‰ (Hitchon and Krouse, 1972; Claypool et al., 1980; van Everdingen et al., 1982). Sample from Western Cordillera is out of triangle due to another lithological signature (Gaillardet et al., 2003; Spence and Telmer, 2005). VSMOW—Vienna standard mean ocean water; CDT—Canyon Diablo Troilite.

The range of $\delta^{34}S$ reflects different sources of sulfide between the Rockies and the plains, since no fractionation of S isotopes occurs during OWP and the $\delta^{34}S$ variations are related to the geographical location of the samples evolving from heavier $\delta^{34}S$ in the Rockies (first end member) to lighter $\delta^{34}S$ in the plains (second end member). Our data are consistent with sedimentary-sulfide $\delta^{34}S$ data from Paleozoic bedrocks of the Selwin Basin in the upper Rockies, –5‰ to 30‰ (Goodfellow and Jonasson, 1984), and the dominant Cretaceous lowland bedrocks (Strauss, 1997).

In contrast, the variability of $\delta^{18}O_{SO_4}$ may be explained by the involvement of two main oxidation pathways commonly used to represent the overall OWP process (Taylor et al., 1984a, 1984b; Van Stempvoort and Krouse, 1994):

$$\begin{gathered} FeS_2 + 7/2O_2 + H_2O \rightarrow \\ Fe^{2+} + 2SO_4^{2-} + 2H^+ \end{gathered} \tag{2}$$

and

$$\begin{gathered} FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow \\ 15Fe^{2+} + 2SO_4^{2-} + 16H^+. \end{gathered} \tag{3}$$

In Equation 2, where dissolved oxygen acts as the oxidant, the sulfate oxygen derives from both dissolved and water oxygen, whereas it only comes from water molecules when Fe^{3+} acts as the oxidizing agent (Equation 3). Consequently, Equation 2 is expected to produce heavier $\delta^{18}O_{SO_4}$ than Equation 3. The observed $\delta^{18}O_{SO_4}$ is most straightforwardly explained by these reactions acting in variable proportions and is also related to the geographical location of the samples, with lighter $\delta^{18}O_{SO_4}$ in the Rockies (first end member) to heavier $\delta^{18}O_{SO_4}$ in the plains (second end member). Given that part of this variation must also be driven by the variability of river $\delta^{18}O_W$ (−22.5‰ to −16.5‰) (Table DR1), we introduced the notation $\Delta^{18}O_{SO_4\text{-}H_2O} = \delta^{18}O_{SO_4} - \delta^{18}O_W$. The competing effects of oxidation pathways and $\delta^{18}O_W$ variability can be isolated using $\Delta^{18}O_{SO_4\text{-}H_2O}$, which also allows a direct comparison with natural or experimental data: $\Delta^{18}O_{SO_4\text{-}H_2O}$ is expected to vary as a function of oxidation pathways, hydrologic status of soils, or biology, because oxidation reactions are most probably controlled by microorganisms (Van Stempvoort and Krouse, 1994).

The $\Delta^{18}O_{SO_4\text{-}H_2O}$ is strongly dependent on runoff (i.e., the effective amount of water flowing through catchments) (Fig. 3), which is as much as 15 times higher in the Rockies (1210 mm/yr) than in the plains (75 mm/yr). Schematically, this link between the mechanism of OWP and hydrologic conditions indicates that OWP occurs in more aerated environments of oxidation in the lowlands (or environments subjected to alternations of unsaturated and saturated conditions) than in the Rockies (water-saturated conditions). Aerobic experiments involving iron-oxidizing bacteria (Taylor et al., 1984a, 1984b) show that sulfate ions produced by oxidation in either water-saturated or alternatively wet and dry conditions exhibit $\Delta^{18}O_{SO_4\text{-}H_2O}$ ranging from 8.9‰ to 10.9‰ and from 17.6‰ to 18.1‰, respectively. These values are consistent with our extreme $\Delta^{18}O_{SO_4\text{-}H_2O}$ (Fig. 3). The above-reported experiments were conducted under pH 2–5 (soil conditions), but sulfide oxidation also occurs at higher pH (Moses and Herman, 1991) and gives similar $\delta^{18}O_{SO_4}$ values (Van Stempvoort and Krouse, 1994). However, the rate-limiting factor of OWP is the availability of Fe^{3+}, whatever the pH (Moses and Herman, 1991). As Fe^{3+} is usually not available in soil water, its production probably results from sulfide oxidation. Consequently, sulfide oxidation in the Mackenzie basin appears to be biologically mediated and may be self-catalyzed by creating local acidic environment favorable to the preservation of Fe^{3+}.

Our data (Figs. 2 and 3; Fig. DR1) and the consistency between our two expected $\delta^{18}O_{SO_4}$ end members of pyrite-derived sulfate and the results of Taylor et al. (1984b) demonstrate that most of the dissolved sulfate in tributaries of the Mackenzie River are derived from OWP.

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[1] GSA Data Repository item 2007247, Appendix DR1 (analytical methods), Appendix DR2 (calculations of the different sources of dissolved C), Figure DR1 ($\delta^{18}O_{SO_4}$ versus $\delta^{18}O_W$), and Table DR1 (chemical and isotopic data and physical erosion data), is available online at www.geosociety.org/pubs/ft2007.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

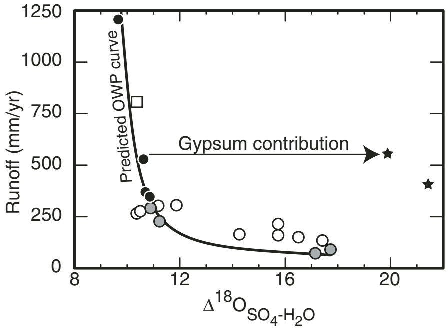

Figure 3. Relationship between hydrological conditions (runoff) and $\Delta^{18}O_{SO4\text{-}H2O}$. Except for samples out of the shaded area in Figure 1, all samples (even Western Cordillera sample) plot on curve that predicts the $\Delta^{18}O_{SO4\text{-}H2O}$ for a given runoff value. Observed negative trend can be explained by different oxidation pathways (see text for details). Horizontal distance from the predicted oxidative weathering of pyrite (OWP) curve gives the contribution of gypsum assuming that $\Delta^{18}O_{SO4\text{-}H2O}$ for gypsum dissolution ranges from 29.5‰ to 35.5‰, depending on $\delta^{18}O_W$ (W is water).

Furthermore, the oxidation of pyrite in natural systems does not necessarily lead to a well-characterized end member in a $\delta^{18}O_{SO_4}$ versus $\delta^{34}S$ diagram because S and O isotopic compositions depends on source effects ($\delta^{18}O_W$ and $\delta^{34}S$ of sulfide minerals) and on oxidation pathways associated with different hydrological conditions.

SULFIDE OXIDATION RATES AND THEIR LINK TO MECHANICAL EROSION

The origin of dissolved sulfate (OWP versus gypsum) can be quantified either from the mixing diagram (Fig. 2) or numerically, by combining the two mixing equations for S and O isotopes [i.e., for S, $\delta^{34}S = X\cdot(\delta^{34}S)_{OWP} + (1 - X)\cdot(\delta^{34}S)_{GYPSUM}$, where X is the proportion of total dissolved sulfate coming from OWP, and $(\delta^{34}S)_{GYPSUM}$ and $(\delta^{34}S)_{OWP}$ are the isotopic compositions for the gypsum dissolution end member and the calculated one for the OWP end member, respectively]. The variable OWP end member (shaded area in Fig. 2) is calculated empirically as a function of $\delta^{34}S$, $\delta^{18}O_{SO_4}$, and $\delta^{18}O_W$. The same calculation can be done graphically using Figure 3. The results obtained by these two methods agree.

Most tributaries of the Mackenzie River, but also the Peel, Red Artic, and Liard Rivers, essentially show pyrite-derived sulfate. This result is consistent with field observations along the Demster Highway; numerous tributaries of the Peel River, with their red waters, are rich in sulfate and suspended iron oxides. Based on Figure 2, 74%–89% of total dissolved sulfates in the Mackenzie River at the mouth are derived from OWP; our best assessment is 82%. Adding the Peel and Red Artic Rivers, we obtain 85% for the entire Mackenzie basin. This value assumes that no sulfate reduction occurs in soils or rivers (which should lead to heavier $\delta^{34}S$ and $\delta^{18}O_{SO_4}$) and is therefore a lower bound. Our estimate corresponds to an ocean input of pyrite-derived sulfate of 0.13 × 10^{12} mol/yr from the Mackenzie River system. When compared to the global pyrite-derived sulfate input of 0.65 × 10^{12} mol/yr (François and Walker, 1992) or 0.48 × 10^{12} mol/yr (Berner and Berner, 1996), the contribution of the Mackenzie River system appears to be remarkably high, 20%–27%. Although the Mackenzie basin is rich in reduced black shales, this result may indicate that the global estimate of pyrite oxidation on land is significantly underestimated. Clearly, more work should be done to refine the global contribution of OWP.

In the subbasins of the Mackenzie River, the concentration of pyrite-derived sulfate fluctuates between 130 and 1300 μmol/L. As the kinetics of pyrite oxidation are rapid (Williamson and Rimstidt, 1994), we expect that a sustained pyrite oxidation regime can only be maintained if fresh mineral surfaces are continuously exposed to atmospheric oxygen. This view is strongly supported by the observed direct link between sulfide oxidation rates and physical erosion rates (Environment Canada, 1998) in Figure 4. This correlation also holds for concentrations and is therefore not induced by runoff variations. It is an obvious indication that the exposure of fresh surfaces is a key factor controlling the chemical weathering of minerals at the Earth's surface. Mechanical erosion in the Mackenzie basin occurs in the lowlands mainly as landslides along the slopes of the largest valleys. The freeze-thaw cycles, partial melting of the permafrost, incised rivers, and the unconsolidated nature of the bedrock (glacial deposits, shales) are parameters facilitating the massive input of bedrock material to rivers. In the Rockies, glacial erosion is a more efficient mechanism of physical erosion, where a significant amount of solids accumulates as glacial drifts in the flat and swampy part of the valleys. Several studies have now reported evidence of a link between silicate weathering and physical erosion rates at various scales (Gaillardet et al., 1999; Millot et al., 2002). The generation of sulfuric acid by the rapid oxidation of pyrite in fast eroding lithologies could be one of the factors coupling physical and chemical erosion. Fletcher et al. (2006) proposed that spheroidal weathering is controlled by the diffusion of oxygen in the soil layer and the associated oxidation of ferrous minerals. This mechanism allows mechanical fracturing and water penetration into bedrock and can explain how chemical weathering rates increase with erosion rates. The analogy between this mechanism and the oxidation of pyrite generating sulfuric acid shown here is noteworthy.

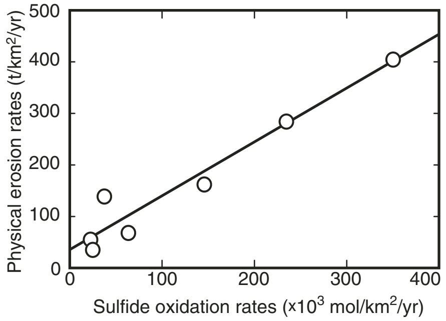

Figure 4. Link between physical erosion rates, calculated from multi-annual river sediment yields (Environment Canada, 1998), and sulfide oxidation rates in some catchments of the Mackenzie basin. This correlation demonstrates that the sustained oxidation of pyrite is favored by continuous exposure of fresh mineral surfaces.

IMPLICATIONS FOR THE CARBON CYCLE AND CLIMATE

Carbonate weathering reactions overwhelm the chemical flux into rivers of the Mackenzie basin (Reeder et al., 1972; Millot et al., 2003). The dominant reactions are:

$$2CaCO_3 + H_2SO_4 \rightarrow 2Ca^{2+} + 2HCO_3^- + SO_4^{2-} \quad (4)$$

and

$$CaCO_3 + CO_2 + H_2O \leftrightarrow Ca^{2+} + 2HCO_3^-. \quad (5)$$

These equations show that dissolved inorganic carbon (DIC) originates either from the atmosphere (Equation 5) or from ancient sedimentary C (Equations 4 and 5). Millot et al. (2003) allocated the different solutes of the Mackenzie rivers to silicate and carbonate + gypsum weathering, but were not able to conclude the origin of DIC. Our study makes it possible to calculate the respective contributions of the two sources of DIC shown in Equations 4 and 5 (see the Data Repository). The result is that 62% of the DIC discharged into the ocean by the Mackenzie River system is from carbonate rock and only 38% derives from the atmosphere through carbonate and silicate weathering. This sedimentary-dominated carbon ocean input has climatic implications because the subsequent carbonate precipitation will release more CO_2 into the atmosphere-ocean system than was consumed on continents during weathering. When the weathering products of Equation 4 precipitate in the oceans (Equation 6), 1 mol of Ca^{2+} and C are removed from the ocean as carbonate and 1 mol of sedimentary C is released as CO_2 in the atmosphere-ocean system:

$$2Ca^{2+} + 2HCO_3^- + SO_4^{2-} \rightarrow Ca^{2+} + SO_4^{2-} + CaCO_3 + CO_2 + H_2O. \quad (6)$$

Ultimately, on typical time scales of the sulfate residence time in ocean (>10^7 yr) (Claypool et al., 1980; Berner and Berner, 1996), the oxidation of organic carbon (CH_2O) associated with sulfate reduction in ocean sediment pore fluids (Equation 7), counterbalances the previous release of sedimentary C.

$$\begin{aligned} &Ca^{2+} + 2CH_2O + SO_4^{2-} \rightarrow \\ &H_2S + 2HCO_3^- + Ca^{2+} \rightarrow \\ &H_2S + CaCO_3 + CO_2 + H_2O. \end{aligned} \qquad (7)$$

However, the long residence time of sulfate permits transient decoupling between sulfide oxidation on continents and sulfate reduction in the ocean, typically on glacial-interglacial time scales. Furthermore, the difference in residence time between ocean inorganic C (~10^5 yr) (Berner and Berner, 1996) and sulfate implies that any changes in river input flux will have no effect on sulfate reduction rate, but will affect carbonate deposition and the related net transfer of ancient sedimentary C to the atmosphere-ocean system. Consequently, the tight coupling between sulfide oxidation and physical erosion (Fig. 4) suggests that periods of high physical erosion (deglaciation, active landslide regime) generate net transfers of sedimentary CO_2 to the atmosphere. Therefore, the weathering of carbonate by sulfuric acid is likely to be responsible for transient releases of sedimentary CO_2 into the atmosphere. This contradicts the conventional view that carbonate weathering has no climatic implication.

ACKNOWLEDGMENTS

We thank P. Louvat, C. Dessert, B. Carter-Stiglitz, E. Tipper, R. Millot, and J. Bouchez for critical comments on the manuscript. Reviews from R. Berner and two anonymous reviewers were greatly appreciated. Calmels benefited from a grant from the French Ministère de l'Education Nationale. This work was supported by the Programme National sur les Sols et l'Erosion from the Institut National des Sciences de l'Univers–Centre National de la Recherche Scientifique. This is Institut de Physique du Globe de Paris (IPGP) contribution 2251.

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Manuscript received 30 May 2007
Revised manuscript received 26 June 2007
Manuscript accepted 27 June 2007

Printed in USA

Sustained sulfide oxidation by physical erosion processes in the Mackenzie River basin: Climatic perspectives

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GSA Data Repository

Contents

Appendix DR1- Methods for analytical procedure

$BaSO_4$ was precipitated from water sample by addition of $BaCl_2$ after acidification at pH 4. A GV-Isoprime mass spectrometer coupled in He carrier continuous flow mode to an elemental analyser was used for O and S isotopic analyses. For $\delta^{34}S$ the method is adapted from (Giesemann et al., 1994). $BaSO_4$ sample, conditioned in a Sn cup, was droped at the top of a WO_3 reactor at 1100°C with a pulse of oxygen which generates flash combustion of the cup. The SO_2 gas produced is purified over Cu at 800°C for O_2, Mg-perchlorate for water and a short chromatographic column (0.8 m PorapakQ) for CO_2. The method for $\delta^{18}O$ is derived from(J. Koziet, 1997). $BaSO_4$ samples were conditioned in Ag-cup and pyrolysed at 1270°C in a glassy carbon reactor. The presence of nickel catalyst in the reactor favoured the CO production over CO_2. Yields of O_2 measured using major peak height and sugar analyses calibration were repeatedly in the range 93 to 98%, possibly due to a slight CO_2 generation. This however does not affect the reproducibility. Gases produced (CO and N_2) were separated by a short chromatographic column (1.5 m, 5 Å molecular sieve) at 75°C. No blank correction is necessary since we use a sample injector allowing vacuum pre-treatment of the crucible prior injection under He. Results are expressed in the classical δ notation in ‰ relative to CDT (Canyon Diablo Troilite) for $\delta^{34}S$ and V-SMOW (Vienna Standard Mean Ocean Water) for $\delta^{18}O$. Scaling corrections were applied using the barium sulfate reference material NBS-127 ($\delta^{34}S$ 20.3‰ CDT and $\delta^{18}O$ = 9.3‰V-SMOW). Linearity was controlled using CRPG internal standards. The overall reproducibility at 2sigma on internal standard is better than ±0.3‰ for both O- and S- analyses.

The $\delta^{18}O_{SMOW}$ values of water samples were measured by using the classical CO_2 equilibration method of (Epstein and Mayeda, 1953) in the modified VG 602-mass spectrometer. Over all reproducibility is ± 0.1 ‰.

Appendix DR2- Methods for dissolved inorganic carbon (DIC) calculations

A previous study on the Mackenzie Basin (Millot et al., 2003) calculated the ionic contribution of each rock reservoir in the dissolved phase but authors were not able to separate the sedimentary sulfate reservoir from the carbonate reservoir. Based on the results of our study, it is now possible to make this distinction and to calculate the amount of DIC derived from carbonate. For each mole of carbonate weathered by either carbonic or sulfuric acid, one mole of calcium or magnesium and one mole of sedimentary carbon are dissolved. The contribution of sedimentary carbon within the total DIC carried by rivers is calculated as follows:

$[HCO_3^-]_{carb} = [Ca^{2+}+Mg^{2+}]_{carb+gyp} - [SO_4^{2-}]_{gyp}$ (Eq. S1)

$[HCO_3^-]_{Total} = [HCO_3^-]_{carb} + [HCO_3^-]_{atm}$ (Eq. S2)

where

$[SO_4^{2-}]_{gyp} = [Ca^{2+}+Mg^{2+}]_{gyp}$

$[HCO_3^-]_{Total}$: total amount of DIC as HCO_3^- is the main specie of dissolved carbon at the pH of our samples

$[HCO_3^-]_{carb}$: amount of DIC coming from carbonate rock

$[HCO_3^-]_{carb}$: amount of DIC coming from the atmosphere/soil

$[Ca^{2+}+Mg^{2+}]_{carb+gyp}$: amount of calcium plus magnesium derived from carbonate and gypsum (calculated from a previous study (Millot et al., 2003))

$[SO_4^{2-}]_{gyp}$: amount of sulfate derived from gypsum dissolution

$[Ca^{2+}+Mg^{2+}]_{gyp}$: amount of calcium plus magnesium derived from gypsum dissolution.

The difference between $[HCO_3^-]_{Total}$ (Millot et al., 2003) discharged into the ocean by the Mackenzie River at mouth (Mackenzie + Peel + Red Arctic) and $[HCO_3^-]_{carb}$ gives us the contribution of DIC coming from the atmosphere. We calculate for the Mackenzie River system that $[HCO_3^-]_{carb} = 0.38 \times 10^{12}$ mol/yr and $[HCO_3^-]_{Total} = 0.61 \times 10^{12}$ mol/yr. These results indicate that 62% of the DIC river input into the ocean have a sedimentary origin.

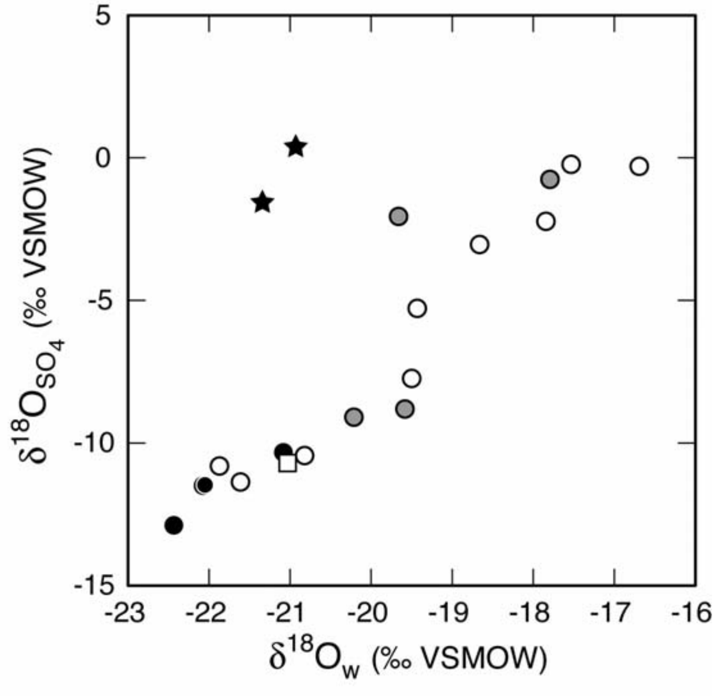

Figure DR1: Relationship between $\delta^{18}O_{SO4}$ and $\delta^{18}O_W$ is consistent with sulfate mainly coming from OWP. This correlation indicates that the oxygen isotopic composition of dissolved sulfate is influenced by the $\delta^{18}O$ of water molecules. As isotopic exchange between water and sulfate is a very slow process at low temperature and circum-neutral pH (Lloyd, 1968), such a relationship can only be explained by oxidative weathering of pyrite. $\delta^{18}O_{SO4}$ resulting from sedimentary sulfate dissolution is not dependent on $\delta^{18}O_W$ and preserves a constant value around 13‰. Different oxidation pathways (see main text for details) may explain the larger $\delta^{18}O$ variation in sulfate than in water. The two stars, where a contribution of gypsum dissolution was already suggested in the Figure 2, are out of the correlation. Contrary to Figure 2, the sample from the Western Cordillera enters the same trend.

	River name	Discharge	Runoff	TSS	SO_4^{2-}	$\delta^{34}S$	$\delta^{18}O_{SO4}$	$\delta^{18}O_W$
	@location	km^3/yr	mm/yr	mg/l	µmol/l	‰	‰	‰
Main Tributaries	1- Peel	21.65	307	932	761	-1.02	-10.8	-21.89
	2- Mackenzie @Tsiigehtchic	283.70	169	415	452	4.79	-5.2	-19.45
	3- Red Arctic	5.02	270	1505	1334	3.42	-11.3	-21.63
	4- Peace @PeaceRiver	57.75	310		142	1.81	-7.7	-19.52
	5- Mackenzie @FortSimpson	137.90	139		254	4.14	-0.2	-17.55
	6- Liard @FortSimpson	77.32	281	584	503	-1.05	-10.4	-20.84
	7- Peace @PeacePoint	67.01	219	643	203	0.83	-3.0	-18.68
	8- Slave	100.98	164	348	160	0.41	-2.2	-17.86
	9- Athabasca @FortMcMurray	20.26	155	240	209	3.51	-0.3	-16.71
Rockies	10- Stewart	13.10	374		794	4.42	-11.4	-22.09
	11- Liard @LiardRiver	11.71	351		322	9.87	-10.3	-21.10
	12- Athabasca @Hinton	5.46	558		314	8.26	-1.5	-21.36
	13- Rocky	0.47	412		735	6.42	0.4	-20.95
	14- Toad	1.37	533		647	9.07	-11.4	-22.07
	15- Racing	2.30	1211		408	2.06	-12.8	-22.45
Plains	16- Hay@mouth	3.60	77		483	-12.84	-0.7	-17.81
	17- Mc Leod	2.11	232		220	-3.25	-9.0	-20.23
	18- Doig	0.35	95		422	-18.47	-2.0	-19.68
	19- Halfway	1.12	296		329	-3.91	-8.8	-19.60
Western Cordillera	20- Stikine	23.83	811		92	-5.49	-10.7	-21.05

Table DR1: Chemical, isotopic and hydrological data for all river samples. Sulfate concentrations are from (Millot et al., 2003), total suspended sediment concentrations (TSS) and discharges are calculated after available river data (Environment Canada, 1998). Isotopic analyses are reported in the standard delta notation in ‰ relative to VSMOW for O and CDT for S.

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