Role of river-suspended material in the global carbon cycle

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ABSTRACT

The reaction of Ca derived from silicate weathering with CO₂ in the world’s oceans to form carbonate minerals is a critical step in long-term climate moderation. Ca is delivered to the oceans primarily via rivers, where it is transported either as dissolved species or within suspended material. The relative importance for climate moderation of riverine dissolved Ca vs. suspended Ca transport stems from the total Ca flux and its climate dependence. Data in the literature suggest that, within uncertainty, global riverine dissolved Ca flux is equal to suspended material Ca flux. To determine how these fluxes depend on temperature and rainfall, a 40 yr field study was performed on 4 catchments in northeastern Iceland: Jökulsá á Fjöllum at Grímsstadir, Jökulsá á Dal at Brú, Jökulsá á Dal at Hjardarhagi, and Jökulsá í Fljótshdal at Höll. Suspended material Ca flux depends more on seasonal and annual temperatures and rainfall variation than does dissolved Ca flux in all four catchments. For example, the average difference between the annual maximum and minimum daily suspended Ca flux for the Jökulsá á Dal at Brú is four orders of magnitude, whereas the difference for dissolved Ca flux is only approximately one order of magnitude. Similarly, the annual dissolved Ca flux for this river varies by a factor of 2.6, whereas its annual suspended Ca flux varies by a factor of 7.1. Because suspended material Ca flux is more dependent on climate, it provides a stronger negative feedback for stabilizing Earth’s temperature through the greenhouse effect.

Keywords: weathering, dissolved flux, suspended flux, climate control, atmospheric CO₂.

INTRODUCTION

Atmospheric circulation models indicate that global climate is closely linked to the atmospheric CO₂ content; increased CO₂ leads to warmer temperatures, increased rainfall, and thus increased riverine discharge (Manabe and Stouffer, 1993). The most important climate-modulating process on a geological time scale is the weathering of Ca-Mg silicates (Walker et al., 1981; Berner, 1990, 2004; Brady and Gislason, 1997; Kump et al., 2000; Berner and Kothavala, 2001; Wallmann, 2001). On land, this proceeds via the chemical and mechanical weathering of silicates and the ensuing riverine transport of divalent metals to the oceans, where they combine with CO₂ to form carbonate minerals. Increased temperature and runoff increases Ca and Mg transport to the ocean via rivers, increasing CO₂ fixation, which results in lower temperature and runoff through the greenhouse effect (Walker et al., 1981; Gislason et al., 1996; Gaillardet et al., 1999a; Stefánsson and Gislason, 2001; Dessert et al., 2003). Of the metals involved in CO₂ fixation by carbonate precipitation, Ca is the most important (Berner and Berner, 1996). Long-term climate moderation by terrestrial weathering can, therefore, be quantified from estimates of the global Ca fluxes to the oceans via rivers. Metals are transported via rivers in two forms: as dissolved species and as suspended material. Although a number of studies have quantified the role of dissolved riverine transport in climate moderation (e.g., Gaillardet et al., 1999a; Dessert et al., 2003), the role of river-suspended material transport has yet to be quantified. This study demonstrates that (1) the quantity of Ca flux to the ocean, stemming from dissolution of river-suspended material in the ocean, is similar to that derived from dissolved riverine transport, and (2) that the suspended material Ca flux is far more dependent on discharge than the dissolved Ca flux. Taken together, the climate-modernating effect of suspended material transport is more important than that of dissolved metal transport.

MATERIAL TRANSPORT

The total mass of Ca transported in dissolved form by rivers to the oceans has been estimated to be 501 Mt/yr (Meybeck, 1979; Berner and Berner, 1996). Of this, 326 Mt/yr originates from carbonate dissolution, 90 Mt/yr originates from Ca-silicate dissolution, and the rest from CaSO₄ minerals, pollution, and sea salts (Berner et al., 1983; Berner and Berner, 1996). Ca originating from pollution, sea-salt cycling, and dissolution of carbonates or sulfates has no net long-term effect on atmospheric CO₂ content. Thus only 90 Mt/yr of Ca transported in dissolved form to the oceans contributes to long-term climate moderation.

The total mass of Ca transported to the oceans by rivers was estimated to be 333 Mt/yr (Martin and Meybeck, 1979; Berner and Berner, 1996). The percentage of this mass released in dissolved form to ocean water is difficult to assess in part because of sediment burial. Nevertheless, evidence suggests that much of this Ca is added to the oceans before its deep burial. For example, the concentration of Ca in deep-sea clay is only half of the Ca concentration of the global river suspended material (Martin and Whitfield, 1983). The ultimate fate of Ca after being added to the sedimentary record is the formation of carbonate minerals; in excess of 90% of Ca in sedimentary rocks is situated in carbonate minerals (Ronov and Yaroshevsky, 1969; Garrels and Mackenzie, 1971). Much of this transformation occurs during diagenesis.

The total quantity of Ca originating from silicates transported in suspension to the ocean and eventually released in dissolved form to ocean water can be estimated from the sum of three contributions: (1) the exchange of Ca for Na on clay mineral surfaces in estuaries, (2) diffusive flux from ocean sediments, and (3) the dissolution of Ca-bearing silicate mineral and glass suspended material before its deep burial. Each of these contributions is considered here.

Ion Exchange

The total mass of Ca released to ocean water from Ca-for-Na exchange on clay minerals brought to the ocean as suspended material was estimated to be 37 Mt/yr by Berner and Berner (1996). This estimate was obtained by multiplying the 18 milliequivalent per 100 g cation exchange capacity of average river-suspended material (Holland, 1978) by the 20,000 Mt/yr total global flux of suspended material to the oceans (Milliman and Syvitsky, 1992). The 37 Mt/yr Ca flux to ocean waters from cation exchange in estuaries is more than 40% of that stemming from dissolved riverine transport of Ca originating from silicate dissolution. Although ion exchange reactions do not directly consume carbonate, released Ca combines with bicarbonate in the ocean to precipitate carbonate minerals. In the absence of their transport to the oceans, Ca clays would be left at the weathering site.

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Diffusive Flux

According to Martin and Sayles (1994) the total mass of Ca released to ocean water via diffusion from seafloor sediments is 288 Mt/yr. This flux is more than three times that from dissolved riverine transport of Ca originating from silicates. Nevertheless, the majority of this Ca may originate from the dissolution of carbonate minerals (Berner and Berner, 1996), which would therefore have negligible effects on long-term climate moderation.

Suspended Material Dissolution in the Oceans

The world’s major deltas act like fluidized bed reactors; the seafloor sediments are periodically reworked and mixed with seawater for months after their arrival to the delta, and similar processes occur on smaller scales in most estuarine-shelf systems (Aller, 1998; Aller and Blair, 2004). An important percentage of this suspended material may dissolve during this time. High-relief volcanic and tectonically active islands contribute >45% of river-suspended material carried to the oceans worldwide (Milliman and Syvitski, 1992). Much of this material originates from volcanic islands, such as Iceland, and is rich in basaltic glass. Calculations performed using measured basaltic glass dissolution rates covering the pH and temperature range of ocean waters (Oelkers and Gislason, 2001; Gislason and Oelkers, 2003) and measured gas adsorption surface area (Brumauer-Emmett-Teller; BET) of river-suspended material from Icelandic rivers indicate that ~0.05% of this suspended material dissolves into seawater each day. Moreover, it has been demonstrated that even severely weathered river-suspended basaltic glass readily dissolves when exposed to seawater, releasing Ca and Si (Stefánssdóttir and Gislason, 2005). A significant aspect of dissolution in the oceans is that this process may have a stronger climatic feedback than the dissolution of silicate minerals on land. The dissolution rates of both feldspars and basaltic glass are more temperature dependent in seawater (pH 8) than soil (pH 4–7; Oelkers, 2001; Gislason and Oelkers, 2003).

Taken together, the total Ca flux to the oceans stemming from river-suspended silicates via these three mechanisms is likely similar to the flux stemming from riverine transport of dissolved Ca originating from silicate dissolution on land. As the ocean is saturated with respect to calcite, this Ca flux readily provokes CO₂ consumption via carbonate precipitation. The relative importance of chemical vs. mechanical denudation on climate modulation depends, therefore, on the degree to which each depends on temperature and rainfall.

RESULTS AND DISCUSSION

The effect of climate on both suspended and dissolved Ca transport to the ocean was assessed in this study via the systematic monitoring during the past four decades of four individual catchments in northeastern Iceland: Jökulsá á Fjöllum at Grímsstaðir, Jökulsá á Dal at Brú, Jökulsá á Dal at Hjarðarhagi, and Jökulsá í Fljótsdal at Höll. By focusing on individual catchments, we limited potential ambiguities associated with relief and rock type, which could mask the effects of temperature and rainfall/runoff on transport (Edmond et al., 1995). The catchments chosen for this study are sparsely populated, drain mostly basaltic rocks (Ca-Mg silicates), and experience large variation in runoff. Icelandic catchments were chosen for a number of reasons. First, Iceland is a volcanic island representative of the high-relief, volcanic and tectonically active islands that contribute >45% of suspended material to the oceans (Milliman and Syvitski, 1992). These islands dominate suspended material flux to the oceans due to the combined effect of high relief, high runoff, the presence of rapidly weathering volcanic rocks, and a lack of sedimentary traps. Moreover, the degree of alteration of Icelandic suspended material is representative of those islands that overwhelmingly contribute to the global suspended material flux. Gaillardet et al. (1999b) defined a weathering intensity on a scale from 1 to 25. The weathering intensities for the volcanic islands that have been studied to date are Iceland: 1.1; Azores: 1.8; Reunion: 1.6; and Java: 4. In contrast, the low-relief, inactive continental catchments, which contribute a negligible amount, considering their size, to the suspended material transport (e.g., the Orinoco, Niger, and Amazon rivers), have weathering intensities of 20 or greater. Thus, the weathering intensity of Iceland is far more representative of the terrains that dominate suspended material transport than that of the world’s major rivers, such as the Amazon. In total, mechanical weathering in Iceland delivers ~0.7% of the global suspended flux to the ocean; this percentage is approximately a quarter of that from Africa (Tómasson, 1990; Milliman and Syvitski, 1992).

The four catchments cover 9058 km² of northeastern Iceland. The youngest rocks are within the rift zone. The area-weighted ages of the catchment rocks range from 0.3 Ma to 2.1 Ma, increasing from west to east (Table 1). According to the classification of global rivers by Meybeck et al. (2003), three of the four rivers draining the studied catchments have medium suspended solids concentration; the river draining the youngest rocks has a high suspended solids concentration. The discharge, concentration, and grain-size distribution of the suspended material in these 4 rivers have been monitored for 30–40 yr. The chemical composition and surface area of the suspended material and the concentration of dissolved constituents have been monitored 8–10 times per year for the past 5 yr. The suspended material is basaltic; it is composed of 51–53 wt% SiO₂ and 7–11 wt% CaO. The easternmost and oldest catchment has the highest SiO₂ and lowest CaO content. The suspended-material chemical composition of each catchment is relatively constant; the standard deviation of SiO₂ and CaO concentration in suspended material from each catchment is less than 4% and 8% of the absolute concentration, respectively, and there is no compositional correlation with discharge. The average chemical composition of suspended matter during the past 5 yr was used together with measured suspended material concentration to calculate the total Ca present within suspended material in these rivers over the past 40 yr. The results of this calculation are illustrated in Figure 1A for Jökulsá á Dal at Brú, which drains an intermediate-aged catchment (1.3 Ma). The corresponding dissolved Ca concentration present in this river is shown in Figure 1B. This latter concentration was corrected for Ca originating from rainwater by assuming all dissolved Cl present in the river originated from rainwater and by using the Ca/Cl ratio of Icelandic precipitation (Gislason et al., 1996). The global airborne dust flux of Ca is negligible, so no correction was made to account for this source. The results shown in Figures 1A and 1B are representative of the four studied catchments; suspended material Ca concentration increases with discharge, but dissolved Ca concentration decreases with discharge. The observation that suspended ma-

### TABLE 1. DISCHARGE DEPENDENCE OF SUSPENDED AND DISSOLVED CA FLUXES OF THE RIVERS IN NORTHEASTERN ICELAND

<table>
<thead>
<tr>
<th>River</th>
<th>*Age (Ma)</th>
<th>Suspended Ca flux (mol/s)</th>
<th>Dissolved Ca flux (mol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jökulsá á Fjöllum at Grímsstaðir</td>
<td>0.299</td>
<td>0.0000001X^2.94</td>
<td>0.3027X^2.497</td>
</tr>
<tr>
<td>Jökulsá á Dal at Brú</td>
<td>1.32</td>
<td>0.00361X^2.651</td>
<td>0.3837X^2.641</td>
</tr>
<tr>
<td>Jökulsá á Dal at Hjarðarhagi</td>
<td>1.71</td>
<td>0.00008X^2.682</td>
<td>0.6026X^2.320</td>
</tr>
<tr>
<td>Jökulsá í Fljótsdal at Höll</td>
<td>2.14</td>
<td>0.0087X^2.949</td>
<td>0.4826X^2.514</td>
</tr>
</tbody>
</table>

*Area weighted average age of the catchment rocks.

†X represents discharge (m³/s).

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Figure 1. Suspended material and dissolved Ca concentrations and fluxes in river Jökulsá á Dal at Brú, northeastern Iceland. A: Suspended material Ca concentration vs. discharge. B: Dissolved Ca concentration vs. discharge. C: Suspended material Ca flux vs. discharge. D: Dissolved Ca flux vs. discharge. Note that for this catchment, discharge of 100 m³/s is equivalent to runoff of 600 mm/yr.

The flux data given in Table 1 were used together with the continuous discharge records to estimate the total dissolved and suspended Ca fluxes for each day during the past 30–40 yr for each catchment (see Data Repository1). A representative evolution of the suspended and dissolved Ca flux of the Jökulsá á Dal at Brú during 1976 is presented in Figure 2A. Suspended material Ca flux depends far more on seasonal variations than dissolved Ca flux. In the summer, discharge is high and suspended Ca flux is much greater than the dissolved Ca flux. In the winter, discharge is low and the suspended Ca flux is less than the dissolved flux. The evolution of the dissolved and suspended Ca flux of this river from 1971 to 2003 is presented in Figures 2B and 2C. The scales of Figures 2B and 2C are identical, facilitating the comparison of these fluxes. Both suspended and dissolved Ca fluxes exhibit seasonal variations, with a summer maximum and a winter minimum. The amplitudes of these seasonal variations, however, are far greater for suspended Ca flux; the average difference between the annual maximum and minimum daily suspended Ca flux is four orders of magnitude, whereas this difference for dissolved Ca flux is only approximately one order of magnitude. Annual variations are also evident. Over the past 30 yr, the annual runoff varied by a factor of 3 from 1136 mm/yr to 3410 mm/yr, and annual dissolved Ca flux varied by only a factor of 2.6, but the annual suspended Ca flux varied by a factor of 7.1. Thus, the annual suspended Ca flux was 2.6 times more dependent on annual discharge/runoff than the dissolved flux. Similar results...
were found for all of the studied catchments. Although some differences were observed among the individual catchments, as seen in Table 1, suspended Ca fluxes were more dependent (more than an order of magnitude) on discharge/runoff than their corresponding dissolved Ca flux in each of the studied catchments.

IMPLICATIONS

The results presented in this study show that suspended Ca flux to the ocean is far more dependent on discharge than is dissolved Ca flux. As river discharge is a direct function of temperature and rainfall, this result demonstrates that suspended material transport provides a stronger negative feedback for the stabilization of Earth’s temperature through the greenhouse effect. Models of past atmospheric CO₂, taking account of mantle degassing, weathering, sedimentation, diagenesis, and metamorphism, need to include this additional feedback to accurately predict global climate evolution.

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52

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