

WHAT THE GEOCHEMISTRY OF LARGE RIVERS TELLS US ABOUT CHEMICAL WEATHERING RATES AND LONG-TERM CO₂ CONSUMPTION RATES

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One of the links between the atmosphere, hydrosphere and ocean reservoirs is chemical weathering. The interaction between the rocks exposed at the surface of the Earth and is responsible not only from one of the major mass transfer on Earth, but also from the consumption of CO₂ from the atmosphere because the acidity which is needed to weather the rocks is mainly provided by the dissolution of CO₂ dissolved in rain and soil waters. The result of the neutralization of atmospheric CO₂ by rock weathering is the production of cations and HCO₃⁻ ions. These anions are precipitated into the ocean as calcium and magnesium carbonates therefore allowing C to be stored as limestones for a long period of time.

The sequestration of C by chemical weathering and associated precipitation of secondary minerals in the ocean must have played a key role in the evolution of the early atmosphere and is probably still one of the processes regulating the amount of CO₂ in the atmosphere. More precisely, the chemical weathering of carbonates is compensated by the precipitation of calcite in the ocean and only the weathering of silicates and associated oceanic precipitation of calcite leads to a net sequestration of atmospheric carbon. The secular history of global silicate weathering is therefore not independent from the evolutions of climate, ocean composition and sedimentary rock composition.

In order to constrain the present day fluxes and control of chemical weathering, our team focused on the largest rivers of the world. It is remarkable that the 50 largest rivers cover half of the Earth's exorheic surface. Big rivers should therefore lead to averaged laws of chemical weathering. Many studies have focused on the chemical investigation of small rivers draining one single type of rock. Such rivers are necessarily first order streams (according to Horton classification) and do not allow to deduce an integrated view of chemical weathering in the whole catchment. In particular, physically eroded materials in the headwaters are transported downstream and deposited in the floodplains where there are being chemically weathered. We thus have to consider large basins as a whole, rather than as the simple addition of small drainage units.

We sampled a number of large river systems and in each case, we made an effort to sample the different phases transported by the rivers: dissolved, suspended (separated from the dissolved phase by frontal or tangential flow filtration) and sands. These phases are analyzed for major and trace elements as well as for isotopic ratios (Sr, Nd, and Pb).

Solutes from large rivers and weathering fluxes

The chemical composition of the dissolved phase of the largest rivers is now well documented, at least for the major soluble elements (Na, Ca, K, Mg, SiO₂, Cl, SO₄ and HCO₃⁻). We compiled the chemical composition of the 60th largest rivers, mainly based onto work of Meybeck and Ragu (1999). In order to deduce silicate weathering rates from the composition of rivers, a first step is needed to correct the dissolved load from the effect of

lithology. It is indeed well known that the different types of rocks do not weather at the same rates, carbonates being generally more soluble than granites or gneisses. Using Sr isotopic ratios and elemental ratios for major elements, we have shown that the abundances of river solutes can be explained very simply, at a first order, by the mixing of three major types of waters: waters draining silicates, waters draining carbonates and waters draining evaporites. To characterize the signature of each endmember, we used the chemical composition of rivers draining one type of lithology that have been published by different authors. One particularly powerful tracer of silicate versus carbonate dissolution is the Ca/Na ratio. We favored a silicate endmember characterized by Ca/Na ratios close to 0.3-0.4, in agreement with the data on small silicate streams of Negrel et al. (1993) and Edmond et al. (1995). The recent investigations of White and Blum (1999) demonstrating that the presence of calcite in granitic rocks enhances the Ca/Na ratio of the waters they are in contact with, are also consistent with this choice. The dependence of the Ca/Na ratio with climate has not been taken into consideration so far, but should be addressed in future works.

A mass budget model can be written using the different constraints of Ca/Na, Mg/Na... and ⁸⁷Sr/⁸⁶Sr ratios. Our model is thus constituted of a series of equations and has been solved using an inverse procedure, which consists of calculating the mixing parameters that best fit all the equations of the model. The inversion procedure makes it possible to calculate for each soluble element the proportions, which is derived from the weathering of each lithology. In particular, for HCO₃⁻, we can deduce the concentration in the river due to the weathering of silicates only and hence CO₂ consumption by silicate weathering.

The result of the mixing model is that the present-day weathering rate of Na, K, Ca and Mg-aluminosilicates on the continents is 550.10⁶ t/yr, or 26 % of the total flux of dissolved material transported by rivers to the oceans. The atmospheric CO₂ consumption resulting from silicate weathering on the continents is found to be 0.104 GtC/yr. We show that recent estimates of weathering rates of rivers draining oceanic islands and volcanic arcs lead to a flux of consumed CO₂ by the weathering of young volcanics of 0.036 GtC/yr, i.e. more than 30 % of the continental CO₂ consumption. Considering that only the weathering of Ca and Mg silicates is important for the global C cycle and climate regulation, we estimate a flux of consumed CO₂ of 0.058 GtC/yr. This flux is lower than that classically admitted (Berner et al., 1983; Godderis and Francois, 1995).

As the total basin area of large rivers is never entirely underlain by silicate crustal rocks, the calculation of silicate weathering rates per unit area for the largest rivers is not easy. An attempt has been made to correct from this surface area effect and the control by several potentially controlling parameters has been explored.

Runoff acts positively on silicate weathering, but our results do not allow to deduce a general relation between runoff and weathering rates. We suggest that the classical log-log correlations

of weathering rates with runoff must be considered with care and do not contain any pertinent information when the slope is not significantly different from 1. Weathering rates show a reasonable correlation with average temperature only if we discard some rivers having abnormally low chemical weathering rates in spite of optimum climatic conditions. Finally, a positive correlation is observed between chemical weathering rates of silicates and physical weathering rates (Fig. 1), calculated using suspended sediment loads. This correlation supports the idea that the physical removal of soils sustains chemical weathering by continuously

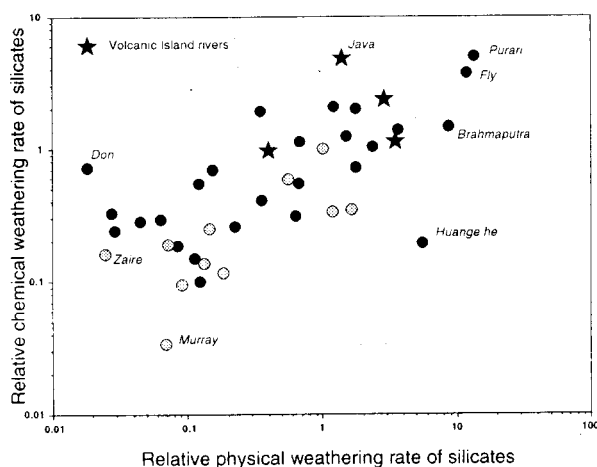


Figure 1: Relation between chemical and mechanical fluxes of silicate erosion, deduced from the largest rivers.

refreshing mineral surfaces and by precluding the development of thick soils. For the global C cycle, this gives importance to regions where rocks and soils are mechanically fragile.

Suspended sediments and weathering intensity

Unlike solute chemical composition, the chemical composition of large river suspended sediments is poorly documented. However, river suspended phase constitute the residue of silicate chemical weathering and should lead to pertinent informations about chemical weathering.

By comparing the chemical composition of the suspended phase of the largest rivers, we showed that these material is depleted for a number of elements by comparison to the composition of Taylor and MacLennan (1985) upper continental crust. These elements are the most soluble elements and it is possible to define for each soluble element a weathering intensity, by simply measuring the amplitude of the depletion. What is more interesting is that these elemental depletions are variable from one basin to another, reflecting the worldwide variability of weathering intensity. Only the warmest climates on Earth are able to produce highly depleted (mature) sediments. A remarkable inverse correlation exists between the intensity of weathering and mechanical denudation rates for the largest basins. The most productive river systems are those that produced the less weathered sediments.

Assuming a steady state of erosion as a working hypothesis, we made an attempt to solve a mass budget model between the upper crust which is submitted to weathering and the dissolved + suspended products of silicate erosion transported by the river. To

solve this mass budget, we need the amount of suspended material which is produced per unit of time, and the composition of the source rocks. In a first time, we supposed that measured river sediments yields (e. g. Milliman and Syvitski, 1992) are good first order estimates of mechanical denudation within the basins. Note that in a number of large basins, the deposition of sediments implies that the measured sediment yields are minimal estimates of mechanical denudation. Using these rates, we deduced from each basin the composition of the continental crust submitted to weathering that satisfies the mass budget model. The result of this calculation clearly indicates that the rocks submitted to weathering in the largest basins do not have a typical grano-diorite composition (of Taylor and MacLennan type) and must be depleted for the most soluble elements. This is possible by admitting that part of source rocks are sedimentary rocks, i.e. ancient river sediments that have been deposited in the sea and then uplifted. We calculate that the participation of « first cycle » rocks to present day weathering is low, and never exceeds 50 % of the mass of the exposed upper crust. We therefore demonstrate the importance of sedimentary recycling, not only for the composition of the upper crust but also for global weathering, because recycled rocks are less « fertile » (in terms of furnishing cations and alkalinity to the rivers) than granites.

The important consequence of this result is the following. Part of the variability of the weathering indexes defined above comes from the contribution of recycled sediments to the source rocks. Once corrected from sedimentary recycling, these indexes of present day weathering are reduced and do not fluctuate very much from one basin to another. In addition, as stated above, an inverse correlation exists between weathering intensity and river sediments yields. For each basin, the chemical flux of weathering (and CO_2 consumption) can be calculated using suspended sediment chemistry by simply multiplying the intensity of weathering (the depletion for each soluble element) with the sediment yield (for ex. in t/yr). Sediments yields fluctuates over 4 order of magnitude, being the highest in mountainous areas, whereas weathering intensities, once corrected from sedimentary recycling fluctuate at best over one order of magnitude. As a consequence, the variations of the chemical fluxes of weathering will be imposed by the amount of physical denudation rather than by the weathering intensity.

This conclusion, based on the chemical investigation of large river suspended sediment is in remarkable agreement with the correlation between chemical and mechanical weathering rates deduced from the study of the dissolved load (Fig. 1). Both results tend to show that the massive production of sediments is more important in terms of CO_2 consumption than their chemical maturity. Chemical maturity depends on climate, whereas sediment yields do not seem to depend strongly of climate, but rather on tectonics. Our results give strong support to the Chamberlain and Raymo hypothesis.

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