

## **Silicate weathering: Where have we come in the last 50 years?**

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In the context of the Geochemical Society's fiftieth anniversary I shall review how ideas on chemical weathering have evolved and where I think the field is going. The field received a large boost in the 1980s and early 1990s in conjunction with public concern over acid deposition. The objective here was to develop quantitative predictions of how acid neutralization by mineral weathering would respond to different levels of acid deposition from the atmosphere. It led to integrated quantitative models of how various ecosystem processes affect surface water chemistry. There was also extensive laboratory work on mineral dissolution kinetics. We learned a great deal about mineral dissolution mechanisms in laboratory systems but we have been remarkably unsuccessful to date in using laboratory results to model quantitatively weathering processes in the field. In the near future we should see new insights into mineral dissolution mechanisms from atomic-scale imaging and various spectroscopies.

In the past decade, the emphasis has been on role of weathering in the global carbon cycle, particularly as a long-term control on the CO<sub>2</sub> concentration and hence temperature of the atmosphere. This brings in the role of tectonic uplift, physical erosion, and various ecosystem processes, including human intervention, in CO<sub>2</sub> consumption by chemical weathering. New insights are coming from the innovative use of various isotopic systems.

Understanding of the role of chemical weathering in environmental processes cannot come from study of weathering processes in isolation. Weathering rates are strongly affected by ecosystem processes, by physical processes, particularly erosion, and by hydrologic processes. We need an integrative approach in order to understand how our planet functions.

## **Does life leave a topographic signature on Earth?**

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If we only had high-resolution topographic data of the Earth's surface, and all signs of human activity were eliminated, could we tell from morphology alone that there is life on Earth? All landscapes on Earth today have evolved since the emergence of terrestrial life. Biotic processes influence nearly all erosion and transport processes, yet very little quantitative theory or observation about the role of biology exists. Consequently, few landscape evolution models explicitly account for biotic effects, hence the results of modeled linkages among climate, topography and tectonics are of uncertain value.

One approach to this problem is to ask how different would processes and landforms be in the absence of life. This analysis concludes that biotic processes strongly affect erosion and evolution of landscapes, but apparently does not lead to a unique topographic signature, i.e. a landform that could only be due to the presence of life. The removal of all life from present day Earth would cause landscapes to be more rocky and steep. Smooth convex hilltops, however, are possible in an abiotic world. Meandering rivers, while certainly less frequent in the absence of life, would still occur. The absence of vegetation would change the spatial pattern of precipitation, which would, in turn, change the height, width and symmetry of mountain belts. This inference argues that life matters, then, to mountain scale topography, although not in a way that leaves a distinctive morphology. If life had never arisen, the Earth might have similar features to today, but one outcome might have been a loss of all liquid water to space, and, as a consequence, an absence of plate tectonics.

## Plenary Address by the Houtermans Medalist

### What earthworms get up to in soil

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#### Introduction

Earthworms are wonderful and important creatures. Soil contains far more individual bacteria or fungi than earthworms but the biomass of these different organisms, a good indicator of metabolic activity, is very similar with earthworms being present at levels of 10 – 150 g m<sup>-2</sup> of soil. Earthworms can consume a mass of soil up to 30 times their own mass in a single day equating to 50 – 1000 x 10<sup>6</sup> g of soil per ha per year. Earthworm burrows can contribute up to 1 % porosity to soils with total burrow length reaching 100 m m<sup>-3</sup> soil. Clearly earthworms can have a major impact on soil.

#### Earthworms and microflora

We have performed experiments characterising the gut flora of earthworms and also investigating the dependence of earthworms on their gut flora for survival. A further point of considerable significance for biogeochemists is that any microbially mediated soil process should occur more rapidly in the earthworm gut or casts where the bacteria to soil ratio is greater than that in the bulk soil.

#### Earthworms and mineral weathering

There are no documented studies regarding the impact of earthworms on mineral weathering despite the mass of soil which they can consume. We are pursuing laboratory experiments, in which earthworms are fed minerals, and field studies, in which mineral-spiked soil is kept in earthworm-rich and earthworm-free conditions to determine whether earthworms influence the weathering rates of minerals in soil.

#### Earthworms and metals

Earthworm metal uptake depends on metal speciation. This is most readily demonstrated by keeping earthworms in solutions and manipulating the solution chemistry. Rates of metal uptake are rapid initially and then slow down. Essential metals are regulated, non-essential metals accumulate. Metals accumulate in a variety of compartments: with proteins, though this compartment fills relatively quickly and, as metal-rich granules, the presence of which are indicative of long term chronic exposure to metals. Earthworms can adapt, either physiologically or genetically to metal-rich conditions. Earthworms change metal speciation after metal uptake and alter metal speciation in the bulk soil.

## Chemical weathering, land plants, and CO<sub>2</sub> sinks: Role of ecological disturbance

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Chemical weathering transfers atmospheric CO<sub>2</sub> to subsurface waters and thence to hydrologic, pedologic, and lithospheric reservoirs with turnover times varying from 10 to 100,000,000 years. Land plants, by the bioturbation and acidification functions of their root systems, are usually assumed to increase the overall rate of transfer relative to landscapes without such vegetation.

We are attempting to test this hypothesis in experimental mesocosm ecosystems at Hubbard Brook Experimental Forest, NH, USA. These large “sandbox” lysimeters crudely represent primary successions with and without vascular plants. We have monitored outflow rates and Ca+Mg and HCO<sub>3</sub><sup>-</sup> concentrations in two of the sandboxes over a 20-year period. One of the sandboxes grew trees for the first 15 years at which time the trees were carefully harvested, eliminating photosynthetic inputs to the subsurface, without physical disturbance. Another box was kept bare of rooted plants. In the forested sandbox Ca and Mg effluxes were 1600 and 300 molc/ha/yr respectively at the beginning of the experiment, waning to less than one third of these rates by time of harvest. After the harvest, cation concentrations increased dynamically while HCO<sub>3</sub><sup>-</sup> concentrations remained relatively steady. Postharvest cation effluxes increased 5-6 times relative to preharvest rates, but even following 5 years of strict regrowth suppression, the cumulative effluxes had not equaled those of the adjacent bare sandbox. These results underline the importance of physical landscape disturbance (experiment initiation in this case) as a driver of chemical weathering. They also suggest that if rooted plants do in fact increase the chemical-weathering CO<sub>2</sub> sinks, the frequencies and magnitudes of ecological disturbances (harvest in this case) are key factors. The results further suggest that ecological disturbances affect the lithospheric (Ca+Mg) sink differently than the hydrologic (HCO<sub>3</sub><sup>-</sup>) sink.

## Rhizosphere iron-redox cycling: Electron transfer reactions that drive mineral weathering

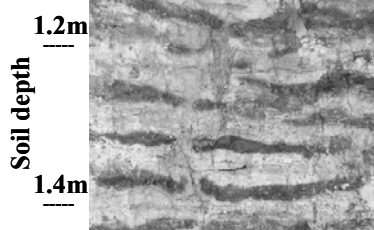
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Roots in wetlands soils are often characterized by orange-colored mottling (iron plaque), a sign that plants supply O<sub>2</sub> to their roots, part of which microbes use to oxidize FeII. In this study we describe a reverse Fe-redox cycle, in which rhizospheres act as conduits of organic reductants that stimulate reductive dissolution Fe (hydr)oxides in the near-root environment. In subsoil rhizospheres where O<sub>2</sub> resupply may be sluggish, FeII is translocated into nearby root-free areas where Fe(II) is oxidatively precipitated. Organic matter in these deep rhizospheres has strikingly modern  $\Delta^{14}\text{C}$  values, and FAME analyses indicate the presence of quinoid moieties, electron shuttles used by microbes to exploit the free energy derived from electron transfers<sup>1-2</sup>. Redox cycling of Fe generates a prominent proton flux, with the proton burden is heaviest away from the near-root environment where Fe is oxidized. Oxidation of Fe adsorbed to the soil cation exchange complex generates co-adsorbed protons which protonate the soil cation exchange complex, and facilitate mineral



dissolution and clay disintegration into colloid-sized particles susceptible to hydrologic transport. The result is clay-enriched rhizospheres with low diffusivity and elevated exchangeable acidity creating favorable conditions for further iron reduction. Such Fe-redox cycling illustrates how rhizospheres significantly interact with the whole soil environment.

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## Worm excretion processes and the weathering of Icelandic basalt

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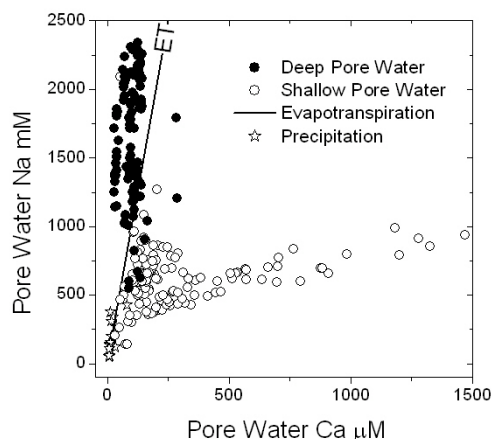
The chemical weathering of rocks is no longer considered to be a purely inorganic process. Microbes can exert a strong control on the weathering rates of silicate minerals. However, the role of macrobiotic sediment ingestion processes and the possible links to chemical weathering are still relatively underestimated. It is important to understand any controls macrobiota might exert on weathering rates since sediment ingestion processes are ubiquitous in the natural environment. Using a series of tightly controlled experiments that simulate marine depositional environments, it is shown that chemical weathering can be enhanced by the ingestion processes of annelid worms. Specimens of the common lugworm, *Arenicola marina*, lived in and consequently ate a mixture of mature, aeolian sand and crushed, unweathered basalt from Iceland. This 'synthetic mud' was determined to be clay mineral free by X-Ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy. The faecal material produced by the worms was also analysed using XRD and FTIR. Faecal casts produced by the worms were regularly sampled along with samples from the control tanks. The mineralogy of the faecal casts were significantly different from the original crushed basalt fed to the worms. The primary plagioclase underwent significant dissolution along with olivine and pyroxene. A variety of secondary neofomed clay minerals (bio-clays) were present in the worm faecal casts, produced by the sediment ingestion and digestive processes. These bio-clays include kaolinite, illite and vermiculite. This enhanced weathering process happens within in a few gut cycles of *A. marina* (approximately 12 hours); a reaction many orders of magnitude faster than inorganic processes. These experiments have revealed a new way to form clay minerals by a macrobiologically-enhanced weathering process that is extremely rapid by geological standards.

## Distinguishing between lithogenic and biogenic processes in soils

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Recently it has been increasingly recognized that many geochemical processes observed in soils result from a combination of chemical weathering and biological cycling. This relationship is particularly important in understanding the distribution of inorganic macronutrients which are products of chemical weathering and are used extensively in the biosphere (Huntington, 2000; Meunier, 1999). Approaches to differentiating between these processes are being investigated in a soil chronosequence (65 to 260 kyrs) developed on silicic sediments contained on paleo-marine terraces near Santa Cruz California. An example of what we term the lithogenic/biogenic fractionation of two common solutes in pore water is shown in the following figure in which deep pore waters are dominated by high Na/Ca ratios reflecting plagioclase dissolution and the shallow pore waters are dominated by preferential cycling of Ca relative to Na in the grassland vegetation. The divergence between these ratios is the fractionation factor; the greater the angle, the greater the difference in chemical behavior. This fractionation is discussed in terms of other major elements, Ge/Si ratios and the isotopes of Ca, Sr and Si.



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## The effect of climate, vegetation, rock age, and human activity on basalt weathering rates in NE-Iceland

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The objective is to quantify the effect of climate, vegetation, soil, rock age, and human activity on the chemical and mechanical weathering rates of basalt and their relative role in the global carbon cycle. This study is based on 3 - 40 years monitoring of 8 catchments in NE-Iceland. This system is ideally suited to determine effects of various parameters on weathering rates as these catchments are 1) pristine, 2) drain a single rock type, and 3) are comprised of rocks that vary in age from 0 - 11 Myr. Moreover, Iceland, as the largest part of the mid-ocean rift system on Earth that is above sea level, is representative of the volcanic and tectonic active islands that contribute over 45% of suspended material to the oceans (Milliman and Syvitski 1992). In addition, the erection of hydropower plants in 2003, provides an unique opportunity to study the effect of dams on weathering processes.

The measured values of suspended and dissolved material concentration are combined with catchment runoff to estimate the daily dissolved and suspended element fluxes in each catchment during the last 4 decades. Seasonal variations for suspended flux are far greater than that of dissolved flux; suspended material flux varies by up to four orders of magnitude, whereas dissolved flux varies by only about one order of magnitude. Chemical and mechanical weathering rates decrease with rock age, but mechanical weathering decreases at a faster rate. Chemical weathering rates increase with increasing primary production and net ecological exchange of vegetation and biota in the catchments.

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## Weathering within soils developed on a chronosequence of glacial moraines in the French Alps

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Samples of recent glacial sediments and 9 soil profiles ranging in age from 360 years to ~300Ky were collected from near Chamonix toward Lyon. The mineralogy of the <2 mm size fraction of each soil as a function of depth was analyzed by quantitative XRD. Soil profiles 17 Kyr and younger were derived almost exclusively from crystalline rocks. Older moraines also contained significant limestone and dolomite.

The 360 yr moraine has a well developed organic horizon, suggesting the high availability of nutrients in the till, but no clear indication of silicate weathering. Within the ~10 Ky till, chlorite (formed by retrograde alteration of biotite) was weathered to smectite in the upper ~20 cm, but there is no major change in plagioclase or other primary silicate concentrations or kaolinite formation. The ~17 Ky till showed plagioclase weathered in the top 15 cm, and an incipient A horizon.

The older tills (>100 Ky, and closer to Lyon) all have well developed A and B horizons, with the B horizon depth increasing with the till age from ~65 to ~150 cm. Weathering of plagioclase and K-feldspar in the soil horizons increases with age, as does the development of an argillic kaolinite horizon. Carbonates in the A and B horizons are severely depleted, but abruptly reach concentrations near that of the unaltered till at the base of the B horizon, the same depth at which silicate weathering appears to cease.

The mineralogy of some <2 µm fractions were also analyzed. Suspended stream sediment and till from modern glaciers has mineral compositions of the <2 µm fraction that are nearly identical to the bulk tills and bedrock. Alteration of the <2 µm fraction of older tills is similar to the <2 mm fraction, with feldspar weathering above the base of the B horizon, but little alteration below. This suggests that the high surface area of the primary silicates in the clay-size fraction of till played a subordinate role in controlling the rate of chemical weathering, and weathering models with a large dependence on mineral surface area may not describe the weathering behavior of this chronosequence. Rather, other factors such as the evolution of solution chemistry may have a major control on weathering rates.

## A diverse ecosystem response to volcanic ash falls

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Marine and terrestrial ecosystems exhibit a diverse response to volcanic ash falls. Through simulation of the mixing of pristine volcanic ash leachate with fresh water and seawater, we found that volcanic aerosols may act as fertilisers in marine environment and show opposite, toxic effects in soils and fresh water systems. The toxic effect in fresh waters is a result of the combination of high aluminium (Al) and fluoride (F) concentrations of the ash leachate. Owing to the mixing of acid ash leachate with fresh water, aluminofluoride complexes ( $\text{AlF}_x^{+3-x}$ ) persist in aqueous systems with low turnover rates and become toxic to both plants and animals. The combination of high Al and F concentrations thus contributes to fluorosis and Al toxicity in terrestrial ecosystems. In contrast, due to the well-buffered and relatively high pH in seawater, the speciation of the ash leachate/seawater mixture shows that complexes of fluoride and aluminium will not be formed in this system. The geochemical modelling of the mixing of ash leachate with seawater shows as pH increases and F concentration decreases with dilution (logarithm of the dilution ratio > 1.0),  $\text{Al}(\text{OH})_x^{+3-x}$  species exceed  $\text{AlF}_x^{+3-x}$  complexes. Hydroxo-aluminum complexes are more important at low levels of dilution than in freshwater systems. Consequently, when ash is falling over the marine environment aluminium will form  $\text{Al}(\text{OH})_x^{+3-x}$  species and aluminium will not persist in large concentrations in the surface water because of low solubility of Al-hydroxides at near neutral pH.

The result by this study supports the volcanic ash fertilization hypothesis as important nutrients were released from the ash material and some oceanic phytoplankton species tolerate extreme concentrations of fluoride [1].

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## Element redistribution during weathering of volcanic rocks in sedentary landscapes

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Volcanic rocks of Plio-Pleistocene age from Hawai'i and Guatemala, in sedentary landscapes, have experienced spheroidal or corestone weathering in which corestones of minimally weathered rock are surrounded by concentric saprolitic shells and saprolite derived from the decomposition of the volcanic rock. These corestone-shell complexes are geochemical dynamic systems. Many major elements and some minor elements (REE) are depleted from the saprolitic portions of these regoliths. The major elements and some of the minor elements are progressively lost from the system as the degree of weathering increases, producing a systematic decrease in concentration from the least weathered part of the system to the most weathered. However, several of the minor elements (e.g. REE) are re-distributed within the regolith, displaying more complex patterns of abundance.

The REE are mobilized to incipiently weathered portions of the corestones, where they incorporated into secondary minerals, resulting in increased concentrations of these elements. The concentration pattern for the REE shows an initial increase during incipient weathering stages, and then a decrease as weathering progresses. As the weathering front moves inward in the corestone, these secondary minerals break down and the weathered rock has similar REE composition to the initial composition of the lava flow. The overall pattern of REE distribution in sedentary regoliths suggests that REE leached from saprolite are transferred within the regolith to secondary minerals formed during incipient weathering. It is not until the most advance stages of regolith formation that these elements are mobilized out of the weathering system.

## Desert soils and global climate cycles: Vapor lock in the earth's weathering engine

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In most of earth's surficial environments, ecosystems and hydrology interact to fuel the weathering engine. Atmospheric deposition and by-products of biota combine to solubilize minerals, and circulating water carries away both the dissolved materials and the atmospheric deposition, leaving only the least soluble by-products behind. Recent research has emphasized that desert ecosystems operate in a fundamentally different fashion. The interaction of vegetation and hydrology produces upward hydraulic gradients through the vadose zone, isolating soils from groundwater and surface water systems. Soils become quantitative sinks for deposited and dissolved materials, instead of sources. Even nutrients such as nitrate are retained. Instead of promoting weathering, vegetation produces the "vapor lock" of upward hydraulic gradients and thus stalls the weathering engine. This stalled engine is periodically kick-started by global climate cycles. Increased precipitation (and possibly decreased temperature) effect changes in the ecosystem. These ecosystem shifts, in turn, begin to permit downward fluxes through the vadose zone. Solutes and nutrients that have been accumulating in the vadose zone for millennia are flushed into newly-invigorated groundwater and surface water flow systems and are exported. Arid regions do possess a chemical weathering cycle, but both the timescales and the products of the process are fundamentally different than under humid climates.

## The links between climate, tectonics, and denudation from cosmogenic nuclides in river sediment

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Two different schools of thought have dominated the debate over the Earth's long-term climate regulation through silicate weathering and CO<sub>2</sub> drawdown. One has been suggesting a climate-controlled feedback mechanism; the other promoted mountain building as primary requirement. A consensus has not been reached partly because the rates of the contributing processes are not known with sufficient reliability. Previous estimates of weathering fluxes in any given tectonic or climate environment did not allow for conclusive support of either hypothesis.

*In situ*-produced cosmogenic nuclides now provide the means to determine rates of denudation on time scales typical for weathering processes (roughly the residence time of a 0.5-1m soil layer). Measuring <sup>10</sup>Be or <sup>26</sup>Al in sediment from streams allows a convenient spatial integration on a wide range of scales (ranging from a small creek to an entire drainage basin).

A somewhat surprising pattern is now emerging from a global compilation of such denudation rates of non-glaciated areas that allows to identify the sites and processes of high denudation. (1) Neither precipitation nor mean annual temperature appears to correlate in any way with total denudation. (2) Topographic relief alone does not result in high rates of denudation (an extreme example are the high, steep, wet, and hot tropical highlands of Sri Lanka that features some of the lowest rates measured to date). (3) Denudation rates are high in areas of landscape rejuvenation; which is triggered and controlled by tectonic activity (faulting, escarpment formation and retreat, rifting, surface uplift). These areas include, but are not limited to active orogens. (4) Rates of weathering (using cosmogenic nuclides with zirconium-normalised cation loss balances, Riebe et al. EPSL 2004) depend mainly on physical erosion rate and only to a lesser degree on climate. (5) If climate control plays a stronger role it does so through climate cycling (e.g. waxing and waning of periglacial processes).

These new findings allow the possibility that tectonic activity exerts the primary control over weathering and erosion. This leads to base level lowering, readjustment of drainage networks, reduced soil pore water saturation by rearranged subsurface hydrology, therefore increased rates of mineral dissolution and, finally, higher physical erosion.

## Rapid response of erosion to recent climatic changes: New insights from uranium-series

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Previous studies have used the composition of river-borne material to estimate, at the scale of a drainage basin, continental erosion rates (e.g. Martin and Meybeck, 1979; Milliman and Meade, 1983; Gaillardet et al., 1997). All these studies are based on the assumption that erosion operates at steady-state, i.e. that there is a perfect balance between the amount of rock converted into soil and the amount of erosion products exported by the river. To test this hypothesis, major and trace elements have been used (e.g. Gaillardet et al, 1997), but in that case, major assumptions must be made about the composition of the eroded bedrock. Uranium-series can be used to address this question because they are in secular equilibrium after 1Ma. Hence for a bedrock older than 1Ma, its U-series composition is known and no starting composition assumption is required.

In the present study (Dosseto et al., submitted), U-series isotopes have been measured in riverwaters from the Amazon basin. Our results suggest that (1) erosion in the Andes is clearly not in steady-state and destruction of soils is faster than production, (2) erosion is characterized by short timescales (a few ka). Combining these two observations, we propose that the deviation of erosion from steady-state is the result of a recent change in the erosional regime probably linked to climatic changes in the basin. The implication is that erosion can respond rapidly to high frequency external forcings.

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## Mechanical-chemical weathering linkage: Erosion and solute fluxes due to glaciers

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Mechanical and chemical weathering processes are usually so tightly coupled that it is difficult to determine which drives which. Glaciers present a simplified case in which physical erosion processes clearly dominate: sediment fluxes substantially exceed solute fluxes, and the erosional products from a glacier, once the carapace of weathered rock is removed at the beginning of glaciation, consist of fresh rock fragments ranging in size from clay to boulders. It is possible to ask in this system whether increasing erosion rates impacts chemical weathering fluxes. The answer highlights the importance of both physical erosion and climatic factors in driving weathering fluxes.

Erosion rates under glaciers can exceed the highest non-glacial erosion rates (Hallet et al., 1996). About half the sediment produced is finer than fine sand. A small 7 km<sup>2</sup> glacier eroding at 1.5 mm/y can produce nearly 8000 km<sup>2</sup> of mineral surface area. Although this surface area production rate can reasonably predict the silicate weathering flux, low (0°C) temperatures at the glacier bed keep these fluxes low (Anderson, 2005). Even the high water fluxes typically found through glaciers are insufficient to compensate for low temperatures. The subglacial environment is one in which erosion rates appear to drive silicate weathering fluxes, but these fluxes are damped due to the low temperature environment.

The linkage between erosion and chemical weathering becomes extended over time and space when one considers the fate of glacially-derived sediments. Silt-sized glacial loess blankets large areas. Accumulations of as little as 5 cm may double silicate weathering fluxes from the depositional environment. Thus, surface area production by mechanical processes alone is insufficient to enhance silicate weathering fluxes. Appropriate environmental conditions (temperature, water flux) are required as well.

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## Non-steady state erosion of shales in the Mackenzie River basin (Canada): Evidence from boron isotopes

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The Mackenzie River basin (Canada) is mostly made of shales. Both the denudation rates of carbonates and silicates have been previously determined (Millot et al., 2003). It is therefore an ideal place to look at the mechanisms of sedimentary silicates weathering under cold climatic conditions.

We have analyzed boron isotopes in samples of the river waters. Boron has two isotopes (<sup>10</sup>B and <sup>11</sup>B) that are strongly fractionated by adsorption processes on mineral surfaces. Boron isotopes in waters are therefore an appropriate proxy for investigating interactions at the water/mineral interface.

The B isotopic compositions measured in the river waters of the Mackenzie show a large range of variations (from +3.5‰ in the Rocky and Mackenzie Mountains up to +29‰ in the interior plains). Examination of the water chemistry demonstrates that dissolved B is regulated by weathering reactions involving silicates with minor contributions of atmospheric inputs and dissolution of carbonates and evaporites. This conclusion is confirmed by a clear correlation between B isotopes and the total dissolved load originating from the weathering of silicates.

The relative enrichment in <sup>11</sup>B found in river waters of the lowlands compared to the source rocks, is explained by ion exchange reactions of B onto clay minerals in soils and groundwaters system. This implies that dissolved B in rivers is regulated by surface reactions onto B adsorbing surfaces and is therefore affected by both the nature of the weathered minerals and the hydrological setting of the basin (water pathways).

Comparison of B carried by the solid and the dissolved phases in rivers also indicates that the weathering mechanisms responsible for the release of B are clearly out of steady state conditions. Because of the correlation between dissolved B and total solutes, this rises the question of the global impact of groundwaters on geochemical fluxes and of the mechanisms of the cation release during the weathering of sedimentary silicates.

## Modelling the global riverine U fluxes to the oceans

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Mean U isotopic ratio of the ocean has remained roughly constant since about 600 kyrs (Henderson, 2001). This 1.14 value cannot be explained considering the present day value of the U riverine ratio (1.17, Chabaux et al., 2001). However, the mean riverine ratio was calculated on half of the total continental runoff. Is this partial mean value really representative of the mean value? If yes, might this value have changed over a glacial-interglacial cycle?

We build up a numerical model calculating the flux of U transfer to the ocean through weathering. The spatial resolution of the model reaches  $0.5^\circ\text{lat} \times 0.5^\circ\text{long}$ . Lithology is modified from Amiotte-Suchet et al. (2003). Weathering fluxes are estimated from simple parametric laws, calculating the flux of total dissolved solids from mean annual temperature and runoff. Soil  $\text{PCO}_2$  is used to estimate carbonate dissolution rates, and is calculated from a simulation of the CaraiB model. Uranium fluxes are estimated proportional to the TDS flux, weighted by its abundance in the source rock.  $\text{CO}_2$  consumption through weathering is simultaneously computed. The  $^{234}\text{U}/^{238}\text{U}$  ratio of the river is calculated according to a correlation existing between the measured  $^{234}\text{U}/^{238}\text{U}$  and runoff, showing a decrease of this ratio with increasing runoff. The model is first validated over several large watersheds, including the Amazon, the Ganges-Brahmapoutra, the Mississippi, and the Congo rivers. Global runs are then performed, showing that the modelled mean global value is close to the measured partial mean of 1.17.

We explore then possible variations of the modelled ratio at the last glacial maximum. Temperature and runoff fields are taken from LGM simulations of the ECHAM GCM. Extension of ice sheets is assumed to cut off part of the weathering fluxes, producing possible fluctuations in the riverine U isotopic ratio, as well as changes in the regional runoff pattern.

## Dissolved and adsorbed rare earth element (REE) transport by rivers in the Canadian Cordillera: Influence of weathering and erosion

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Labile REE (equals the sum of dissolved REE plus REE adsorbed to suspended particulate matter) were measured in three large river systems draining the western Canadian Cordillera into the Pacific Ocean (Fraser, Skeena and Nass). The results are used to interpret chemical and physical weathering processes within these watersheds.

Labile REE patterns are found to vary widely across the Cordillera, and reflect basin lithology, with chondrite normalised La/Yb ranging from 2.4 to 13.2. The labile REE composition of the Fraser River near the mouth represents a mixture of inputs from individual tributaries, indicative of the conservative nature of the labile REE. Furthermore, there is sufficient variability in labile REE patterns between watersheds to support the development of labile REE as a chemical weathering or hydrological tracer.

Kd (adsorbed / dissolved) values in June (high water stage, average  $\approx 1000$ ) are approximately 50 times lower than in October (low water stage, average  $\approx 50000$ ). This indicates a change in the composition of the suspended particulate matter, suggesting a shift in particulate source from recently eroded rock flour (alpine source) in June, to alluvial soils (valley source) in October, which have developed over the Holocene and have greater proportion of clay minerals and therefore higher adsorptive capacity.

The observed seasonal shift in particulate source and composition suggests that silicate weathering (and  $\text{CO}_2$  drawdown) is occurring in the valley regions of these watersheds (relatively low physical erosion rates), not the alpine regions (high physical erosion rates). This means that silicate weathering in the Canadian Cordillera is not directly coupled to physical erosion.

Furthermore, approximately 80% of the annual particulate burden of these rivers is discharged during the high water stage. The REE distribution (adsorbed / dissolved) indicates this material is dominated by freshly eroded material being shed off the alpine regions of the catchments. This suggests that the sediment budget of these rivers is controlled by current uplift and erosion rather than re-working Pleistocene glacial sediments; in turn, this suggests that the erosional regime in the Canadian Cordillera may be approaching steady state.

## Basalt weathering laws and the impact of basalt weathering on the global carbon cycle

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Continental chemical weathering is a key process of the Earth global geochemical cycles. Of particular interest is the CO<sub>2</sub> cycle, since atmospheric CO<sub>2</sub> is a greenhouse gas directly impacting on the climate. Over geological time scales, this cycle is driven by two processes : the CO<sub>2</sub> degassing through volcanism and metamorphism, and the consumption through chemical weathering of silicate rocks and the storage of organic carbon in oceanic sediments.

Investigating the geochemistry of river waters draining several basaltic provinces, we emphasized the very important contribution of basalts to the global flux derived from continental silicate weathering. We demonstrated that the chemical weathering rate of volcanic rocks is 5-10 times higher than the chemical weathering of granite and gneiss. Moreover, we proposed a parametric law quantifying the atmospheric CO<sub>2</sub> flux consumed by basalt weathering, as a function of continental runoff and temperature. Coupled with geological and geomorphic data, this allows us estimating the atmospheric CO<sub>2</sub> consumption flux related to basalts to represent 30% of the global flux derived from continental silicate weathering [1].

Since first-order effects that influence basaltic weathering on the global scale are relatively well constrained [1], we are now interested in studying basalt weathering in natural environment at a smaller scale in order to better understand the processes governing chemical weathering of basalts. We particularly emphasize the relationship between the chemical composition of various weathering products transported by the rivers (dissolved and solid loads), the chemical composition of the basaltic rocks, and the climatic parameters (temperature and runoff). It is noteworthy that the chemical signatures of rivers draining basalts differ from those of rivers draining other silicate rocks. Finally, we will show how the introduction of new weathering laws, based on the studies of river waters, leads to the implementation of new models of past atmospheric CO<sub>2</sub> [2].

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## The Mackenzie River Basin: Limited atmospheric CO<sub>2</sub> consumption by rock weathering

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Chemical weathering of rocks is considered as the main sink of atmospheric CO<sub>2</sub> at geological time scale. CO<sub>2</sub> consumption by rock weathering is classically estimated after mass budgets based on major ions chemistry in river waters. These calculations usually do not take into account water acidification by oxidative weathering of reduced material containing sulfur, such as pyrite. During oxidative weathering of sulfide, both sulfate and protons are added in solution. These protons will react with rock minerals and dissolve them in the same way that protons coming from CO<sub>2</sub> dissolution. In order to quantify this supply of protons and to refine the real CO<sub>2</sub> consumption by rock weathering, we need to constrain the origin of dissolved sulfate.

We present results on the Mackenzie River Basin, one of the largest river system, which shows high dissolved sulfate concentration and which is well known to contain both gypsum and sulfide mainly in reduced black shales. To identify sulfate sources, S and O isotopic measurements of sulfate molecules have been performed. δ<sup>34</sup>S values range from 9.87‰ to -18.47‰ but do not allow to decipher between gypsum or sulfide oxidation origin, mainly for positive data. The δ<sup>18</sup>O compositions of sulfate coupled to δ<sup>34</sup>S are consistent with a major contribution of sulfide oxidation all over the basin, except for a few samples which tend to gypsum composition. Assuming that protons originating in pyrite oxidation react preferentially with carbonate rocks, we can calculate the net fluxes of CO<sub>2</sub> during chemical weathering. Atmospheric CO<sub>2</sub> fluxes are obtained after calculation of the assessment of carbonate weathering by sulphuric acid and silicate weathering by carbonic acid. Results suggest that there is a very limited atmospheric CO<sub>2</sub> consumption by chemical weathering in the Mackenzie Basin.

## Links between climate, paleogeography and silicate rock weathering: A Cretaceous vs present day comparative study with the GEOCLIM model

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Global models (0D spatial resolution) calculating atmospheric CO<sub>2</sub> and global climate at the geological timescales assume simple linear runoff and exponential temperature dependence of silicate weathering, predicting increasing CO<sub>2</sub> consumption when global climate is getting warmer and wetter. Transposed to the present day world, such laws suggest that CO<sub>2</sub> consumption through silicate weathering is maximum in the equatorial band. These laws heavily impact on predicted partial CO<sub>2</sub> pressure in the past and hence on reconstructed global climate, and might be partially wrong: (a) weathering rates are limited by the development of thick soils, under high temperatures and large runoff (typically equatorial climate) and sustained chemical weathering requires active physical erosion, (b) the simple assumption of increasing runoff with increasing temperature, although valid at global scale, is heavily dependent on the paleogeographic distribution.

Here we propose the definition of new global weathering laws for silicate lithologies accounting for the effect of soils, based on a compilation for large world rivers. A set of weathering laws where CO<sub>2</sub> consumption is made proportional to runoff is calculated for the 5 major biogeographic zones of the Köppen classification, accounting explicitly for the effect of thick soils in equatorial environments. A new world weathering map is produced with a resolution of 0.5° lat × 0.5° long, showing that equatorial environments are not the main CO<sub>2</sub> consumers through weathering, and is compared to previous study. These laws are then exported into the GEOCLIM model (coupling the global biogeochemical model COMBINE to the FOAM GCM) allowing the calculation of the CO<sub>2</sub> partial pressure during the Cretaceous climate optimum (Cenomanian). A study of the sensitivity of the Cretaceous climate system to changes in solid Earth degassing rates is finally proposed.

## Reactive transport modeling of reaction fronts

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Reaction fronts define the rates and mechanisms of chemical weathering for a given system with implications for nutrient cycling, long-term regulation of atmospheric CO<sub>2</sub>, and in a steady-state system, the rate of formation of soil. The three-million-year old Merced chronosequence has been an ideal field location for successful calculations of field weathering rates. Mineralogical and chemical data from Merced indicate the development of reaction fronts defined by a loss of minerals in the upper part of the older soils. The reaction front extends over at least 3 to 4 m. The meter-scale thickness of the reaction front in this granitic alluvial material contrasts with thinner reaction fronts in other weathering systems, especially those developing on bedrock. For example, reaction fronts on weathering basalt clasts in river terraces in Costa Rica are less than a millimeter in thickness while such fronts on weathering granite in Rio Icacos, Puerto Rico are centimeters in thickness. The steeper Merced weathering gradient implies that weathering is proceeding slower in the unconsolidated alluvium than in the other two systems. In part, the lower and more episodic rainfall at Merced cases pore waters to approach equilibrium more quickly, reducing dissolution rates in the alluvium relative to the the tropical samples. This approach to equilibrium is modeled with the reactive transport code FLOTRAN using a single continuum formulation that ignores the presence of fast pathways in the weathering profile. As expected, model-calculated weathering that uses laboratory dissolution rates occurs more rapidly than weathering in the field. Better correlation between model and field results was sought by changing chemical affinity parameters or reactive surface area parameters. Preliminary results from a simplified mineralogical system have shown that the evolution of the chemical weathering in the Merced chronosequence can be modeled with FLOTRAN, elucidating controls on the thickness and the rate of advance of the reaction front. Future simulations will consider a dual continuum formulation to account for fast pathways.

## Quantitative model of spheroidal weathering: Coupling of transport, reaction, and fracture in the transformation of rock to soil

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In spheroidal weathering, successive rindlets of weakly weathered but sound rock separate from corestone along discrete fractures. We postulate that rindlet bounding fractures result from dilatation-induced stress associated with initial weathering. In the Rio Blanco Granite within the Rio Icacos watershed (Puerto Rico), sequences of 2 - 4 cm rindlets ~ 0.4 m in thickness separate unweathered corestone from saprolite. Sequences extend downward along joints and faults that serve as conduits for reactive fluid. Rindlet-bounding fractures and those cutting through them give reactive fluid rapid access to fresh rock, thus greatly increasing the rate of weathering relative to that by intergranular diffusive transport alone. We use first-order assumptions to build a conceptual and quantitative model of spheroidal weathering incorporating chemical transport, reaction kinetics, and macroscopic fracture. The model is calibrated by using field observations from the Rio Icacos watershed, El Yunque National Forest, Puerto Rico. We postulate that initial corestone weathering is dominated by the reaction of biotite to hydrobiotite + Fe-oxide. The criterion adopted for fracture is that the elastic strain energy in an incipient rindlet equal the fracture surface energy. Dilatation is not uniform and the elastic strain energy is integrated inward from the last-formed crack to the current position of a nucleation barrier for the Fe-oxide. Approximation of a stationary diffusion profile is used to obtain the rindlet thickness and the time between fracture events. Using plausible tuned parameter values, the predicted rindlet thickness is ~ 2 cm and the interval between fracture events is ~ 200a the value latter consistent with an observed weathering rate in the watershed of  $\approx 1\text{cm}/100\text{ a}$ . Crack spacing and the time between cracking events are uniform, implying steady state weathering; in a no-fracture model, the reaction front moves inward at a rate  $\propto 1/\sqrt{t}$ .

## Weathering and uptake of silicon in the Santa Cruz terraces: new evidence from silicon isotopes.

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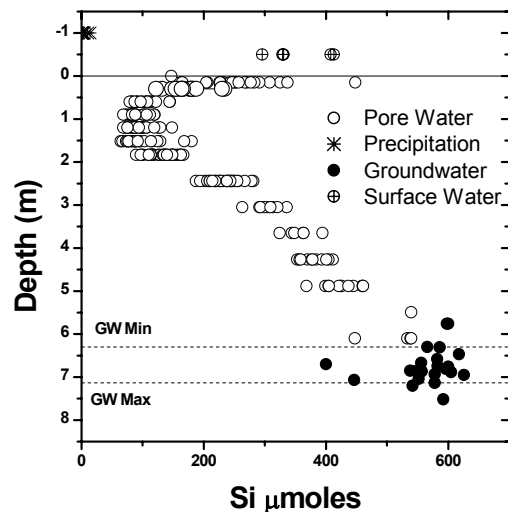
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The Santa Cruz terraces along the Central Coast of California, USA, provide an excellent environment in which to examine the weathering cycle of silicon. The rainfall at Santa Cruz is limited to a few months in the winter during which plant growth is rapid. For the remainder of the year many plants are almost dormant. Since plants take up silicon from porewaters and groundwaters for the production of phytoliths, there is a seasonal variation in Si concentration of these waters.

A profile of Si concentration in groundwaters and soil porewaters show a rapid reduction in Si concentration with depth through the porewater profile followed by a steady increase with depth to groundwater. This pattern can be explained by the uptake of Si by the plants and concentration of the Si through tight cycling at shallow depths, while soil and rock weathering progressively dominates release of Si to waters at depth.

Data so far indicate that deep groundwaters have the heaviest Si isotope ratio with a  $\delta^{30}\text{Si}$  of +5.8 per mil.  $\delta^{30}\text{Si}$  values of the porewaters are lighter and more variable (1.7 to 2.4 per mil). Before the onset of the wet season the soil pore waters have the lightest  $\delta^{30}\text{Si}$  values, indicating that during plant decomposition loss of Si due to phytolith dissolution results in the addition of light Si to the porewaters. Subsequently, at the peak of the growing season, the soil pore waters have greater  $\delta^{30}\text{Si}$  suggesting that the phytoliths take up light Si from the porewaters, thus completing the cycle.



## The susceptibility of peraluminous two-mica granites to weathering: Implications in the stone decay of built heritage (Oporto, NW Portugal)

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In Nature all rock types tend to get weathered in contact with climate agents. This natural tendency is enhanced when the rock is applied in built heritage. The present study aims to show that both primary geochemical characteristics and the late to post-magmatic alteration processes observed in two-mica peraluminous granites are intrinsic factors that directly induce the susceptibility to weathering and deterioration. The selected granite constitutes the bedrock of Oporto city and the stone every monument of its historical centre is built of. It is classified as a medium to coarse-grained leucogranite, syntectonic in relation with the third Hercynian deformation phase. A U-Pb geochronological study on zircon and monazite yielded the minimum emplacement age of  $318 \pm 2$  Ma. The high A/KCN molar ratio, between 1.3 and 1.5, reveals a strong peraluminous character due to primary muscovite. The granite occurs always affected by late to post-magmatic alteration processes. The K-feldspar is intensely kaolinized. The stones used in buildings had various weathering degrees and, consequently, different susceptibilities to decay. Granular disintegration, plates, flakes, black crusts, thin black layers and biological colonization are the main deterioration types. The identification of the soluble salts responsible for the stone decay, namely gypsum, halite, niter and glauberite, was performed by SEM analyses and X-ray diffraction. The main source of salts is rainwater, affected by the proximity with the Atlantic Ocean.

## A possible CO<sub>2</sub> sink through submarine weathering of detrital silicate minerals

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The role of submarine silicate weathering reactions in the long term carbon cycle is thought to be negligible. We describe two low-temperature diagenetic environments dominated by the alteration of detrital silicate minerals which suggest that, contrary to previous assumptions, CO<sub>2</sub> consumption could be widespread in organic matter-rich continental margins.

Fluids expelled from the Odessa mud volcano in the Black Sea originate from shallow (100–400 m deep) sediments which are poor in volcanic materials but rich in anorthite. These fluids are depleted in Na<sup>+</sup>, K<sup>+</sup>, Li<sup>+</sup>, B, and <sup>18</sup>O and enriched in Ca<sup>2+</sup> and Sr<sup>2+</sup>, indicating that anorthite is dissolving and authigenic clays are forming (Aloisi et al., 2004). Similarly, pore waters in biotite- and feldspar-rich sediments of the Sakhalin Slope (Sea of Okhotsk) are particularly rich in the products of silicate weathering (Mg<sup>2+</sup> and alkalinity). Moreover, they have low <sup>87</sup>Sr/<sup>86</sup>Sr ratios, confirming that the <sup>87</sup>Sr-poor detrital silicates transported by the Amur river from the Central Asian Orogenic Belt to the Sakhalin Slope are dissolving.

A simple chemical model shows that the pH of Black Sea pore waters is up to 1.5 pH units lower than in most deep marine sediments and that PCO<sub>2</sub> levels are up to several hundred times higher than in the atmosphere. These conditions favor the weathering of silicate minerals in subaerial soil environments. In marine sediments, these conditions arise via CO<sub>2</sub> production through bacterial methanogenesis. As a result, silicate mineral weathering, which is thought to be a sluggish process in most marine environments, is likely to proceed rapidly in organic matter-rich continental margins fed with fresh detrital silicates.

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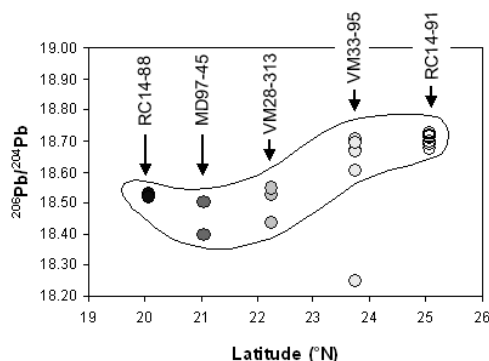
## Erosion on Taiwan: Trace element and (Sr, Pb, Zn) isotopic constraints on marine sediment provenance

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The very high rate of erosion on Taiwan makes this orogen an important source of sediments. A comparison between trace element concentrations and isotopic compositions (Sr, Pb, Zn) of the detritic part of the marine sediments and the results obtained on samples from Taiwan should allow identifying the sedimentary contribution of Taiwan orogen versus the sedimentary contributions by oceanic currents and atmospheric dust.

Five marine cores offshore Taiwan have been analysed. Continental samples (andesites, sedimentary material and Taitung River suspended load) of Taiwan have also been analysed to give best estimate of Taiwan end-member. Sr and Pb isotopic results on the marine cores are very spread out for the silicate fraction:



The core located in the Okinawa basin shows the more radiogenic Sr and Pb compositions, which can be modelled by mixture between Taiwan rock and Yellow Sea sediment contributions. In contrast, core samples close to Luzon arc present typical volcanic isotopic signatures. Zn isotopic compositions of the detritic part of marine sediment present clustered values similar to the literature data measured on sedimentary material, except for the Manila trench core, which presents the highest values, close to those obtained on Taiwan rocks. These results comfort the Sr and Pb isotopic data.

Mixing lines between the different potential end-members evidence that the marine core samples represent mixture between volcanic arc, Taiwan sedimentary material and Yellow sea Sediment (i.e. Yellow river and China Loess).

## Chemical and physical weathering in the Kabini River Basin, South India

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### Introduction

The Kabini river basin (7000 km<sup>2</sup>, 900 masl, Southern Karnataka, India) lies on the Deccan passive margin plateau. The west-facing scarp of the plateau (Western Ghats) slows down the Southwest monsoon flux, inducing a steep decline on 50 km of mean annual precipitations (P) from west (P = 7 m) to east (P = 0.5 m) in the Kabini basin. Different regoliths (depth, types of soil) developed on the silicate basement of the Dharwar craton are organized along this climosequence (Gunnell and Bourgeon, 1997). The aim of our study is to investigate the relative influence of regolith depth, tectonic, climate and hydrology on both silicate chemical and physical weathering. The human activity impact is also taken into account.

### Methodology and results

On a local scale, an integrated ecosystem approach is developed on two small paired watersheds (Moole Hole, forested, 4.3 km<sup>2</sup>; Maddur, cultivated, 6.3 km<sup>2</sup>) both located in the transition climatic zone (P = 1 m). Digital Elevation Model and thematic maps for soil, geology and land use were implemented. Mineralogy and geochemistry of the protolith/regolith have been investigated. The atmospheric deposit, groundwater and stream chemistry has been monitored. On a regional scale, four sub-basins (100-1000 km<sup>2</sup>) representative of the humid, semi-arid and transition climatic zones have been monitored in order to assess the spatial variability of the weathering fluxes in the climosequence. Preliminary results will be presented on the weathering fluxes and the hydrogeochemical processes. Comparisons will be carried out with other watersheds from the tropics (Oliva et al., 2003; Braun et al., 2005; White et al., 1998).

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## Strontium isotopes highlight change in Ca sources in forest ecosystems

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Many studies made in Europe and North America have shown an increasing depletion of exchangeable base cations that may cause tree nutritional deficiencies in sensitive soils. The two main sources of Ca in forest ecosystems are mineral weathering release and atmospheric inputs. We use the <sup>87</sup>Sr/<sup>86</sup>Sr ratio (Sr is used as a proxy for Ca) to determine the relative Ca contributions of soil mineral weathering and atmospheric deposition to vegetation in two forest ecosystems growing on Devonian shales in High Belgium. Contributions were calculated using a mixing equation based on the Sr isotopic ratio of bulk precipitation (atmospheric end-member), of 0.1 M HCl-extractable soil fraction (weathering end-member) and of beech wood (mixing compartment) [1]. A second estimation of the weathering end-member using the Sr isotopic composition and the Cl/Ca ratio of stream waters [2] was undertaken. The radial variation of the <sup>87</sup>Sr/<sup>86</sup>Sr ratio in beech and oak tree-rings was used to monitor possible changes of the contributions of the two Ca sources over time. Our results emphasize the importance of the atmospheric Ca-contribution for tree nutrition, but principally show a steep radial decrease of the <sup>87</sup>Sr/<sup>86</sup>Sr ratio since ~1870. This suggests that the atmospheric contribution increases at the expense of the mineral weathering recharge. The studied ecosystems are thought to be sensitive to chemical changes in the environment (atmospheric acid deposition) which are known to increase the loss of soil exchangeable base cations.

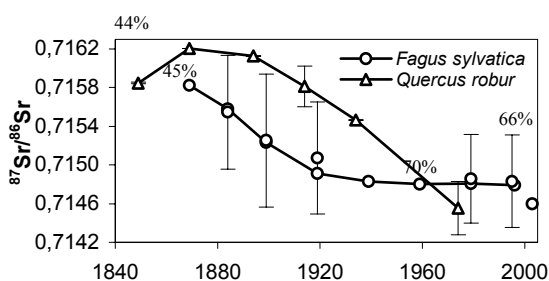


Fig. 1. Sr isotope signal records in tree-rings of European beech and pedunculate oak in a forest stand of High Belgium. Numerals are the estimation of Ca percentage derived from atmospheric source.

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## Basalt and granite dissolution rates in the presence of citrate

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Bacteria, fungi, lichen and plants all produce organic acids, which can strongly affect weathering by increasing the solubility and mobility of elements. Leaching by organic acids may produce trace element signatures which could record the presence of life.

To determine the effect of organic acid on rock dissolution, powdered Columbia River basalt, and Half-Dome granite Tuolumne River Series sampled in Yosemite National Park were dissolved in the presence of 0.01 M citrate and deionized water in long-term column dissolution experiments. In previous experiments, citrate significantly enhanced element mobilization from basalt. The pH of the input solutions was adjusted to 6, and sodium azide or lithium azide was added to prevent microbial growth. Two empty columns were also eluted with identical inlet solutions (with and without citrate) as controls.

Preliminary results indicate that the elements Ca, Mg, Si, Fe, Al, Sr, Y, Zr, La, Ce, W, Th, P, Sc, Ti, V, Cr, Mn, Co, Ni, and Zn may be leached from the basalt to a greater extent in the presence of the citrate as compared to the ligand-free solution. Na, Mg, Ca, Al, P, Ti, Mn, Fe, Y, La, Ce, Th and Si may be leached from the granite to a greater extent in the presence of the citrate as compared to the ligand-free solution. Further work is needed to quantify and better understand this effect, but these results indicate that organic acids may significantly affect the weathering rates of granite and basalt in natural environments, and the trace element signatures of these rocks after weathering.

## Theoretical and observational links between erosion and chemical weathering

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Quantifying the magnitude and nature of chemical weathering is fundamental to understanding CO<sub>2</sub> drawdown and the marine budget of elements of paleo-oceanographic significance. The relationship between chemical weathering and erosion is unclear because chemical weathering, such as occurs during soil formation on stable hillslopes, is a quasi-continuous process but erosion can be episodic, especially rapidly uplifting regions where mass wasting is common. We quantify here the link between chemical weathering associated with soil formation and that associated with mass wasting (dissolution of suspended load and river bedload).

This work is motivated by a recent trip to the southern Sierra Madre in Chiapas, Mexico, a tropical region characterized by rapidly uplifting mountains. Here, landform evolution is controlled largely by landslides, most of which remove the entire soil mantle and expose granitic bedrock (saprolite). Such landform evolution is controlled by a cyclic process in which a soil mantle gradually forms on a hillslope, and when it reaches a critical thickness such that the basal shear stress exceeds the Coulomb-failure criterion, mass wasting occurs.

For a given landform, the growth of soil mantle thickness  $H$  can be expressed as  $H(t) = (1/a) \ln[(1/b) \{e^{(abt)} (E_0 + be^{(aH_0)} - E_0)\}]$  where  $1/a$  is the characteristic lengthscale of an exponentially decaying soil production function,  $E_0$  is the maximum soil production rate,  $H_0$  is the initial soil thickness, and  $b = k (d^2y/dx^2)$ , where  $k$  is the soil diffusivity and  $d^2y/dx^2$  is the curvature of the hill. Averaged over 10+ kyrs, the periodicity (0.5-10 kyr for steep slopes) of mass wasting is controlled by soil formation rate. These results can be extended using empirical dissolution rates to predict the ratio of suspended to dissolved load in rivers. This ratio, however, is much higher than observed in rivers, the discrepancy worsening with increasing topographic relief. This implies that enhanced physical erosion does not simply equate with enhanced chemical weathering. Furthermore, a regolith-based approach overlooks another river component that must be overwhelmingly dominated by dissolved load. Only groundwater weathering satisfies this requirement. If the entire source-to-sink path is of interest, groundwater weathering is thus an essential, but poorly quantified, factor in controlling the chemistries of rivers.

## Geochemistry of amphibolite weathering in different climatic setup of Kaveri catchment of southern India and its implications

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Amphibolite rocks occurring within the Archean Peninsular gneisses in the Kaveri catchment area of southern India have been studied to understand their weathering geochemistry under different climatic conditions. Samples of rocks, saprock and saprolites were collected from semi-arid (annual rainfall: 70-80 cms) and humid (annual rainfall: 300-400 cms) regions in the study area. It has been observed that although all samples exhibit different degrees of physical weathering, not much chemical weathering has taken place in the semi-arid climatic setup. Smectite and chlorite are the major secondary minerals in the weathered products of amphibolites in the semi-arid climatic setup; under the humid conditions, secondary minerals are kaolinite, goethite and gibbsite. The Chemical Index of Alteration (CIA) (Nesbitt and Young, 1984) increases progressively from fresh rock to the most weathered samples (CIA from ~ 32 to a maximum of 87) under semi-arid conditions. In the humid climatic setup, however, the CIA reaches the value of 100 indicating a total loss of mobile major elements.

Behaviour of many trace elements does not show too much dependency to the prevailing climate during weathering. Only the REE and yttrium show dependency on the climate. Under the humid condition, REE are mobilized and fractionated resulting in the removal of HREE and enrichment of Ce; residual saprolites have REE patterns that are similar to those of suspended sediments from many large rivers of the world (Sholkovitz, 1988) and those are complimentary to that of sea-water. The usefulness of REE geochemistry in understanding sedimentary processes needs to be studied in detail.

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## Weathering replacement of limestone by clay+iron oxide at Bloomington, Indiana

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At a unique outcrop uncovered in the excavation for a new building on campus we find that the (vertical) contact between Paleozoic limestone and *terra rossa* consists of a set of metasomatic zones:

A) Fresh, stylonitic Salem Limestone consisting of crinoid and bryozoan fragments, 0.5 to 1 mm across each, well cemented by clear calcite. B) A 1-2-mm-thick band of bleached calcite. C) A one-mm-thick black line of manganese oxides(?). D) A zone 6 cm thick where crinoid fragments can be found in all stages of pseudomorphic replacement by orange clay. And E) The massive clay zone; its peds are bounded by a box work of coarse-crystalline authigenic clay. The zones make up a moving front (Merino et al, 1993).

The orange clay is an aggregate of clay crystals with fairly high birefringence. As the crinoid fragments are pressure-dissolved by the growing clay, they develop a striking outline consisting of identical sharp teeth. The observed replacement warrants adjusting the limestone-to-clay mineral reaction *on volume* (Merino & Dewers, 1998), as  $3\text{CaCO}_3(\text{calc}) + 2\text{Al}^{3+} + 2\text{SiO}_2 = \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4(\text{kaol}) + 3\text{Ca}^{2+} + 3\text{HCO}_3^- + 3\text{H}^+$ , where the factor of 3 in front of the calcite formula ensures that the reaction preserves solid volume, as is characteristic of replacement. (Pending accurate identification of the clay and its chemistry we use kaolinite in the reaction above.) In turn the coefficients of the mineral replacement enter into continuity equations as multipliers of the appropriate reaction rates, opening the way for a dynamic modeling of the formation of the *terra rossa* (Wang et al, 1995). The dissolved  $\text{Al}^{3+}$  and  $\text{SiO}_{2(\text{aq})}$  needed to make clay at the moving front probably come from dissolution of dust and loess at the surface, several feet overhead. The  $\text{H}^+$  released by the replacement may dissolve some additional calcite, which would account for the dissolution pits represented by the teeth at the calcite surface.

*Terra rossa* is similar to other laterites (it forms by replacement of parent rock) but presents unique features – the pressure-solution-driven replacement brings about chemical dissolution of calcite at the replacement front.

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## Hydrologic and kinetic modeling of plagioclase weathering rates in the Rio Vouga Basin (Portugal)

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Chemical weathering rates of plagioclase  $W_{i,Pl}$  ( $\text{mol m}^{-2} \text{y}^{-1}$ ) were derived from export rates of major solutes in springs in granites and metasediments in the basin. [1]

$$W_{i,Pl} = (d[\text{PI}]/dt)(V_d/A_{Pl})$$

$(d[\text{PI}]/dt)$  = acquisition of [PI] per unit travel time,  $V_d$  = volume of water with concentration [PI] discharged,  $A_{Pl}$  = surface area of Pl reacting with aquifer water.

The hydrologic travel times of [PI] were calculated by a finite difference method, the  $A_{Pl}$ 's by an earlier described method [2] The  $V_d$ 's were derived from base-flows. [3]

The  $W_{i,Pl}$ 's depend on pH and pollutant concentrations. At pH 5,  $n_H (= \log W_{i,Pl}/dpH) = 0.46 \pm 0.12$ , at pH 6.5  $n_H = 0.12 \pm 0.04$ . An increase of pollutants drops down the  $W_{i,Pl}$  values. These features are in keeping with predictions of kinetic modeling, in which dissolution rates depend on  $\{\text{H}^+\}$ ,  $\{\text{inhibitors}\}$  and affinity ( $f(\Delta G_r)$ ). [4]

Burch et al. [5] described albite dissolution rates kinetically at pH 8.8 and 80°C, considering the forward and backward reactions. We converted their model parameters to  $T$  (15°C) and pH (5 and 6.5) and obtained a couple of model curves in the  $W_{i,Pl}$  vs.  $\Delta G_r$  that fit our data reasonably well. Since the effect of inhibitors was neglected, we fitted our data by a model [6] that specifically takes into account sorption of the network-modifying  $\text{Na}^+$  and  $\text{Ca}^{2+}$ . We could fit our data by introducing a high sorption constant ( $K_{Ca} = 10^{6.4} \text{ L mol}^{-1}$ ) for  $\text{Ca}^{2+}$ .

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## Century-resolved 1 Myr history of paleogeographic changes in Lake Khubsugul (Mongolia), reconstructed from geochemical markers in lake bottom sediments

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Some basic and trace elements were measured in bottom sediments from Lake Khubsugul (Mongolia). The goal of the investigation is to reconstruct paleovariations of geological and geochemical processes in lake/catchment basin during Holocene and Pleistocene and to estimate paleoclimatic parameters of the region. The method for analysis of the sediments was X-ray fluorescence using synchrotron radiation (SR-XRF). Wet and non-destructed fragments of the core were measured in scanning mode; continuous records obtained cover 45 meters of the core (900 kyrs) with 1 mm resolution (ca. 20 years). From the initial XRF data the concentrations of 20 chemical elements from range K-Mo were determined employing modified fundamental parameters procedure.

Results obtained prove that the records of some biogenic and abiogenic elements trace the main patterns of planetary climate changes. In particular, spectral analysis of the records reveals basic orbitally-modulated cycles (100, 41, 23 и 19 kyrs). Abrupt and significant oscillations are also found at the millennial timescale. The geochemical records are the evidences of "switching" geochemical sources of terrigenous supply to the lake and of changing biogeochemical processes within the lake. The major mechanism for these changes we see in significant lake-level variations during Pleistocene due to regional moistening changes (also marked in autigenic minerals formed). The geochemical records allow quantitative estimations of the precipitation/evaporation balance in the lake.

### Acknowledgements

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## Record of the weathering timescale in Himalayan rivers

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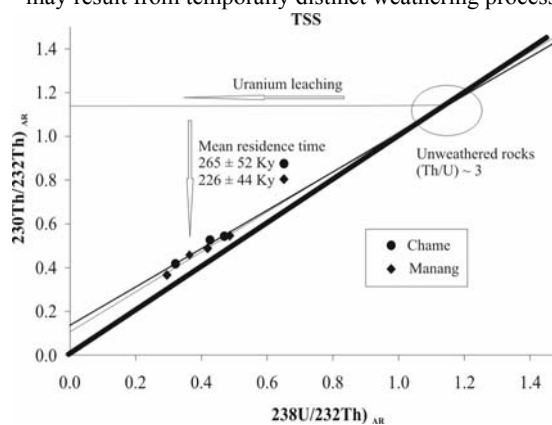
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The timescale of weathering in one of the main Nepalese river catchment is investigated by using U-series. The <sup>230</sup>Th/<sup>238</sup>U and <sup>234</sup>U/<sup>238</sup>U activity ratios were measured in the dissolved and particulate load as well different size fractions of the bedload in the Marsyandi main stream and major tributaries.

In the highest part of the Marsyandi catchment the mean residence time of the weathering products inferred from <sup>238</sup>U/<sup>232</sup>Th and <sup>230</sup>Th/<sup>232</sup>Th activity ratios of different bedload size fractions average 226 to 265 Kyr (fig. 1). These relatively long residence times imply that part of the weathering took place at depth by groundwater circulation.

Dissolved loads however sample a much shorter and recent process (100 years) probably directly linked with surface weathering. Our results show that each component of the river system; dissolved load, suspended load and bedload may result from temporally distinct weathering processes.



## Weathering process on tropical volcanics islands (Guadeloupe, Martinique and Réunion) by using U-series

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The volcanic islands of Guadeloupe, Martinique and Réunion, are particularly interesting for the study of landscape erosion. Their lithology is andesitic (Martinique, Guadeloupe) to basaltic (Réunion). They are located in a tropical climate with high temperatures (24°C to 28°C), high precipitation, sharp relief and very dense vegetation. These characteristics favour high weathering rates with significant variations, over a short distance, from one basin to another.

We have taken samples from main streams of Guadeloupe, Martinique and Réunion (dissolved phase, particles and sand) as well as some thermal springs. U, Th, Ra isotopes have been analysed by MC-ICP-MS and TIMS in order to calculate the rates and timescales of erosion.

The isotopic characteristic of the sand shows that part of the erosion process occurs not only by leaching soils but also directly inside the river bed (by impacts of blocs).

Although Martinique, Guadeloupe and Réunion are very similar in many respects, the process of erosion varies in each island : Martinique and Guadeloupe have very thick soils (~100 m) compared to around 1m in Réunion. Average chemical erosion rates for Guadeloupe and Martinique (122t/km<sup>2</sup>/yr) and associated atmospheric CO<sub>2</sub> consumption rates (1.35 10<sup>6</sup>mol/km<sup>2</sup>/yr) are out of the temperature correlation defined by Dessert *et al.* (2001), which includes Réunion 63-170t/km<sup>2</sup>/yr and 1.3-4.4 10<sup>6</sup> mol/km<sup>2</sup>/yr, Louvat et Allegre, (1998).

Physical erosion is very discontinuous and producing by pulse. During dry season in Guadeloupe and Martinique we have obtain, by U-Th balance, very low values (max 4 10<sup>2</sup> t/km<sup>2</sup>/yr) . In Réunion, mean value had been calculated (max 9 10<sup>3</sup> t/km<sup>2</sup>/yr) by geochemical trace and major elements balance by Louvat et Allegre (1998). Geomorphologist's estimation for a river in rising during flood season is 8 10<sup>5</sup> t/km<sup>2</sup>/yr (Fevre *et al.*, 2004). Those values are modulated by the quantity of infiltrated water (which can be 80% of precipitation). We will compare those values to U-series results, discuss the steady-state hypothesis and the different timescales involved by each estimation.

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## Influence of overstory vegetation on long-term chemical weathering rates

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The influence of overstory vegetation on long-term base cation depletion rates in soil is significant in the context of global climate cycles, soil health and forest management, and neutralization of acid deposition. Because other variables that influence chemical weathering in natural systems are often not controlled (i.e. parent material composition, elevation, land-use history), studies that isolate overstory effects on chemical weathering are limited, particularly on timescales that would be evident in the pedogenic record. In this study, we examine the influence of northern hardwood, red pine, white pine, and Norway spruce forests on base cation depletion and long-term chemical weathering in underlying soils. We utilize a unique field site, Marsh-Billings-Rockefeller National Historical Park, to isolate vegetative effects from other soil forming factors on 100 yr timescales. We find that conifer species deplete the upper horizons of the soil to a greater extent than northern hardwood forests, but at greater depths, northern hardwood soils are more depleted. Bulk long-term weathering rates are significantly higher under northern hardwood forests (39.5±2.8 meq\*m<sup>-2</sup>\*yr<sup>-1</sup>) than any of the conifer species (32±3.3 meq\*m<sup>-2</sup>\*yr<sup>-1</sup>). Furthermore, depletion profiles suggest that the species examined differ fundamentally in the mechanisms by and depths at which they most aggressively deplete the soil. In the upper soil horizons, strong weathering agents released from forest floor decomposition and fine root exudation (carbonic acid, low molecular weight organic acids, chelating ligands) in conifer stands, particularly Norway spruce, are more aggressively weathering the soil than under the deciduous trees. At greater depths, the high annual nutrient demand of northern hardwoods results in a more depleted soil than that under conifer stands. As whole, but particularly at depth, northern hardwood soils are more depleted in mineral sources of macronutrients than soils under conifer species when other soil forming factors are constant, which has important implications for forest management and global change, particularly in the Northern Forest..

## U-series ages of the latest silicification event in regolith of the Yilgarn Craton, Western Australia

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There are several geologically distinct silicification events that are regionally recognized in the regolith of the Yilgarn Craton, Western Australia. The latest event that affected large areas in the northern part of the craton is the silicification of river valley calcretes.

$^{230}\text{Th}$ - $^{234}\text{U}$ - $^{238}\text{U}$  ages from two samples of on opaline silica veins which cross cut the calcrete matrix have been investigated by Sensitive High Resolution Ion Microprobe (SHRIMP).

The first sample from Yalgoo comprises a network of 1 – 5 mm opal vein. A 3 mm thick vein was analysed from the centre to the edges and records discontinuous age range that defines at least 3 periods of deposition. Analyses from the centre of the vein yield a weighted average age of  $129 \pm 23$  kyr, close to the contact a weighted average age of  $90.4 \pm 8.9$  kyr and analyses from the most outer parts of the vein gave a weighted average age of  $62 \pm 13$  kyr.

A similar pattern of ages is seen in the Nangarrong Spring sample. The oldest opal in this sample records a weighted average age of  $91.0 \pm 9.1$  kyr. A separate system of veins yields younger ages with a weighted average age of  $65.6 \pm 6.7$  kyr and  $43.7 \pm 6.7$  kyr from the vein centre to the vein-wall contact of the 3 mm vein, respectively.

Ages decrease systematically from the centers of the veins to the contacts in both samples showing that they developed by antitaxial growth. The vein, originally a fissure, became filled with crystalline material from a silica solution at the same time as it is progressively opened forming the vein.

These two samples show 4 periods of rapid deposition over a ~85 kyr period and in between these periods there was no or very little deposition of opal. Three main factors can influence opal deposition from the ground water; silica dissolution-precipitation kinetics, groundwater evaporation rate and the supply of silica. The variation in the observed opal growth may be correlated to regional palaeoclimatic changes, specifically fluctuations in rainfall and temperature.

## Sediment tracing in the Ganga River System

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A detail study of the chemical and isotopic (Sr & Nd isotopes) composition of sediments of the Ganga River System has been initiated to trace their sources and determine the spatial variability in the erosion rates in its various sub-basins.

Sediments have been collected from the Ganga at its origin, Bhagirathi, in the Higher Himalaya to the Farakka dam in the plains, near Indo-Bengladesh boundary and from almost all its tributaries in the Himalaya and plains (Fig.1). Silicate fraction of the sediments were analysed for their Sr concentration and  $^{87}\text{Sr}/^{86}\text{Sr}$ .  $^{87}\text{Sr}/^{86}\text{Sr}$  vary from 0.74739 to 0.84279 with Sr in the range of 37 to  $119 \mu\text{g g}^{-1}$ . The sediments of the Bhagirathi at the source itself has  $^{87}\text{Sr}/^{86}\text{Sr}$ , 0.78785 even though they are derived from the Higher Himalaya. The ratios remain nearly invariant downstream. The  $^{87}\text{Sr}/^{86}\text{Sr}$  of the Ganga at Rishikesh (foothills of the Himalaya) is ~0.78652, which is nearly the same as that of the Bhagirathi indicating the later's dominant role in the sediment budget of the Ganga at the foothills of the Himalaya. In the Gangetic plain the Ganga receives six major tributaries (Gomti, Yamuna, Ghaghara, Son, Gandak and Kosi) of which the Gandak and Kosi have been analysed. The downstream

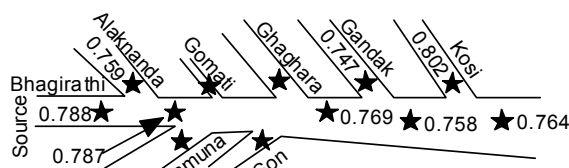


Fig. 1: Variation in  $^{87}\text{Sr}/^{86}\text{Sr}$  of sediments of the Ganga and its tributaries from source to the mouth

variation in  $^{87}\text{Sr}/^{86}\text{Sr}$  of the Ganga shows that it decreases from 0.78652 at the foothills to 0.75772 at Barauni which marginally increases to 0.76354 at Rajmahal (just before Farakka dam) due to the confluence of the Kosi with  $^{87}\text{Sr}/^{86}\text{Sr}$  0.80183.

Preliminary results of material balance calculation using Sr and  $^{87}\text{Sr}/^{86}\text{Sr}$  of the sediments show that the Gandak is the dominant supplier of sediments to the Ganga at its outflow. Surprisingly, the contribution of Kosi to the sedimentary budget of the Ganga seems low compared to its water discharge, possibly due to its large fan in the plain.

## Geochemistry and origin of ferruginous nodules from the weathered gneissic rocks of presently subarid southern India Mysore plateau

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Fe nodules developed within the weathered gneisses of presently semiarid regions of Mysore plateau of southern India has been studied for their geochemistry including chemical speciation. It has been found that the nodules originated by the replacement of kaolinite by goethite or by its precursor minerals. This implies that the study area must have gone through a humid phase prior to the present aridity. The changing local geodynamic situations and the proximity of the study area, having Fe nodules, to the humid regions of Western Ghats (<100Km) suggest that evolving landscapes of this region could have affected the climate locally. The trace elements distribution in the nodules was mainly controlled by manganese phases in the nodules, whereas during weathering they were associated with amorphous Fe and Mn phases, occurring as coatings on resistant minerals. The rare earth elements (REE) geochemistry of the weathering profiles and nodules developing on the gneisses suggest that REE were mobilized from weathering system and reprecipitated with the minerals of the nodules. We suggest that the positive Ce anomaly with the nodules is due to the decoupling and concentration of Ce with the nodules in favorable oxidizing condition. The geochemistry of the soil nodules in this study shows enrichment of trace elements similar to sea nodules but to a lesser extent. Although these nodules may not be economically that important but has great implication to the nutrient transfer from the catchment to the floodplains of Kaveri as discrete nodule phases. In the anaerobic environments of the flood plains they could become a source of the nutrients through microbial mediation.

## Geochemical landscapes of Alaska

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Geochemical patterns are presented for 23 elements, ash yield, and pH in soils and other unconsolidated surficial materials from 265 collection locations throughout Alaska. Originally published in 1988 these ultra-low density data (approximately one sample per 6,000 km<sup>2</sup>) are now interpreted based on landscape geochemical principles (such as the role of regional soils groups, climate, and vegetation) that influence observed areal patterns. A 5-division ecoregion classification system is used to evaluate feldspar chemical weathering processes and to examine relations among climate (mean annual temperature and precipitation) and soil properties (chemistry, pH, and organic matter). Principal components analysis of these climatic and soil properties resulted in 5 factors that explain 77 percent of the total variance in the data.

Factor	Eigen-value	Percent of Total variance explained	Cumulative percent
1	5.37	34	34
2	2.08	13	47
3	1.97	12	59
4	1.76	11	70
5	1.04	7	77

The factors were identified as (1) clay or reactive oxides, (2) physiographic or latitude, (3) soil organic matter, (4) carbonate and soil ion exchange, and (5) soil potassium feldspar. These data should prove useful in assessing geochemical baselines and interpreting geochemical landscapes to identify broad regional patterns.