Weathering processes in the granitic Strengbach catchment (North-Eastern France): Laboratory experiments under acidic conditions and field assessment using Sr isotopes

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In industrial areas, ecosystems are constantly under the influence of acid atmospheric inputs. In soil, saprolite and bedrock, weathering and cation exchange are the main neutralising processes. These processes were investigated in a small granitic spruce forested catchment (Vosges mountains, N-E France) receiving subsequent inputs of protons. In this study, we try first to simulate in the laboratory the effects of natural acid solutions on the whole bedrock dissolution. The aim is to determine which minerals are mainly weathered and estimate their weathering rates. In the field, strontium is used as a tracer of weathering in this granitic catchment to assess the respective contribution of atmospheric inputs and mineral weathering to surface water chemistry.

Strong mineralogical investigations indicated that K-feldspar and albite were the dominant minerals (about 50%). Biotite content was low, only traces of apatite were detected and no calcite was found in spite of a major hydrothermal event affecting part of the granite.

Different kinds of solutions have been used in batch experiments to simulate acid natural water interaction with the granite: soil solution from 60 cm depth (pH = 4.4), spring water (pH = 4.8), H_2SO_4 solution (pH = 3.5) and distilled water. Two samples of granite (affected or unaffected by hydrothermal events) were crushed and washed with a HNO_3 solution (1M). Experimental solutions were regularly analysed for between 1 to 81 days for the major elements, strontium content and strontium isotopes.

In summary, the experimental results show an increase with time in H_4SiO_4, K and Na concentrations in the solution, mainly after 40 days of water-rock interaction. This increase can be essentially interpreted as feldspar weathering. The most rapid increase has been found in the case of soil solution compared to spring water, particularly concerning silica. Smectite was been detected after 20 days of interaction and simultaneously Ca, Mg and Sr decreased in the solution, whereas Na, K and Si continued to increase. Meanwhile pH increased steadily up to 5.5. During the first stage of interaction, the isotopic Sr ratio is mainly controlled by plagioclase weathering (albite: $^{87}Sr/^{86}Sr = 0.742$) whereas after 15 days, it increases significantly due to the influence of biotite weathering ($^{87}Sr/^{86}Sr = 5.4$), as confirmed by the formation of smectite. However, because of the low content of biotite in the granite, the isotopic ratio of the solution does not reach this strontium ratio as it is finally mainly controlled by the albite weathering ($^{87}Sr/^{86}Sr = 0.75$ after 81 days of experiment). As indicated by STEM observations, the mineral surfaces present substantial signs of weathering particularly for plagioclase and biotite whereas muscovite did not change. Because of its importance in this catchment, experimental rate of albite weathering with soil solution and spring water was estimated. The results are respectively, for the two types of solutions: $3.2\ 10^{-18}$ mol.cm^{-2}.s^{-1} and $2.2\ 10^{-18}$ mol.cm^{-2}.s^{-1} according to BET measurements and $3.2\ 10^{-16}$ mol.cm^{-2}.s^{-1} and $2.2\ 10^{-16}$ mol.cm^{-2}.s^{-1} with geometric surface estimations. These values are in agreement with those of the literature (White *et al.*, 1996; Mast *et al.*, 1987). The dissolution rate of albite is 1.5 times quicker in soil water than in spring water.

These experiments allow us to determine the weathering processes and to distinguish the minerals involved in buffering the proton input in the Strengbach catchment.

In the second part of our work, we determined the behaviour of the strontium within the catchment using surface water isotopic characteristics . $\Delta^{87}Sr$ was determined following Graustein's method (1989) and the proportions of atmospheric (A) and weath-

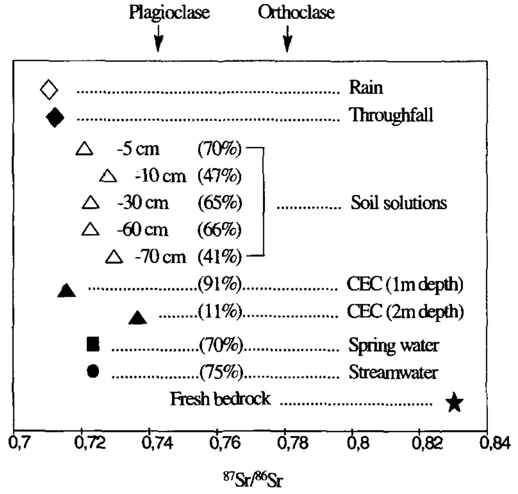

FIG. 1. Proportion of throughfall inputs in the soil solution, in the fine fraction exchange complex (CEC), in the spring and stream waters.

ering (B) end-members were estimated after Miller *et al.* (1993). The isotopic signature of 'A' was that of throughfall in order to take into account the crucial importance of dry deposits. In similar studies, laboratory experiments have been commonly used to determine 'B', with leachate of crushed bedrock with strong acid. However, this method overestimates this end-member because of the influence of hydrological conditions, temperature and mineral surface area in water-mineral interaction. Thus, in this study, we decided to use an original approach. The 'weathering end-member, was assessed by simulating the dissolution of the saprolite minerals by acid solutions using strontium in the water-rock interaction kinetic model KINDIS (Madé *et al.*, 1994). The model argues that the Sr isotopic ratio of the actual weathering end-member reaches the albite Sr ratio (0.742029 ± 5).

According to the first results, 3/4 of dissolved Sr in streamwater would originate from atmospheric input. The isotopic ratio $^{87}Sr/^{86}Sr$ of the exchangeable Sr in the fine fraction, measured at 1 and 2 m depth, is respectively 0.714993 ± 7 and 0.735765 ± 16. This means that in this catchment, except in the deep saprolite where weathering processes could supply for Sr (and in the same way for Ca), the amount of exchangeable Sr seems to be essentially controlled by atmospheric input as shown in Fig. 1. Hence, according to mineralogical investigations and strontium isotope indications, the important Ca losses detected in catchment hydrochemical budgets (Probst *et al.*, 1995), as a result of the neutralisation of substantial proton inputs, do not mainly originate from weathering processes.

These results indicate that on the long term, in such sensitive areas, the availability of forest nutrients which seems mainly atmospheric dependent, might be strongly limited and surface waters consequently acidified.

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