Dissolution rate of fluor-apatite crystals inserted in acid soils of a forested catchment (Vosges Mountains, NE France)

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In the Strengbach catchment (Vosges Mountain, NE France), the Ca and Mg nutrition of spruce and beech stands is very poor. Water and mineral fluxes through beech and spruce stands have been monitored at these sites since 1987. Ca supply is limited because its amount in the granite bedrock (CaO = 0.15–0.30 wt.%), in the bulk soil (CaO = 0.01–0.30 wt.%) and on the cation exchange capacity (CaO = 0.01–0.3 cmol$_c$ kg^{-1}) is very low. Total and exchangeable Ca in the fine earth (< 2mm) of the layer soil (0–120 cm) is respectively about 8.4–9.6 t.ha^{-1} and 130–140 kg ha^{-1}. The rate of calcium release by weathering of soil primary minerals has been computed from detailed quantitative mineralogical data and mineral fluxes monitored at these two sites using steady state soil chemistry model PROFILE (Sverdrup and Warfvinge; 1993). Obtained values were extremely low (0.1–1.2 kg ha^{-1} yr^{-1}) (Fichter *et al.*, 1998a). Ca-bearing minerals in soils are albite and apatite. Although, apatite is the trace mineral in soil, Ca is principally located in this mineral because Ca content in albite is very low (CaO:0.45–0.53 wt.%) (Fichter *et al.*, 1998b). Only few data of fluor-apatite dissolution rate of fluor-apatite were published. In the aim to determinate the dissolution rate of fluor-apatite in these soils, the mineral test technique was used.

Material and methods

Apatite crystal from Durango (Mexico) ($P_{5.93}$ $(Na_{0.09}Ca_{10.27}Ce_{0.03})F_{1.43}OH_{0.19}Cl_{0.13}$) was used because fluor content corresponded to fluor amount in apatite in the Strengbach catchment (F = 1.70). The weight (0.6 < W0 < 4.3 g) and surface (2 < S < 6.8 m^2.g^{-1}) of each crystal were measured. Twelve replicates of single crystals were cautiously introduced in the main horizons of two soil profiles located under spruce (S) and beech (B) stands. Four replicates were sampled after one year and four others after two years. They were washed in distilled water, dried and weighted (Wf). Their surface were observed before the washing using a SEM microscope.

The climate in Strengbach catchment is temperate oceanic mountainous with a main temperature at 6°C and a mean annual rainfall about 1500 mm.

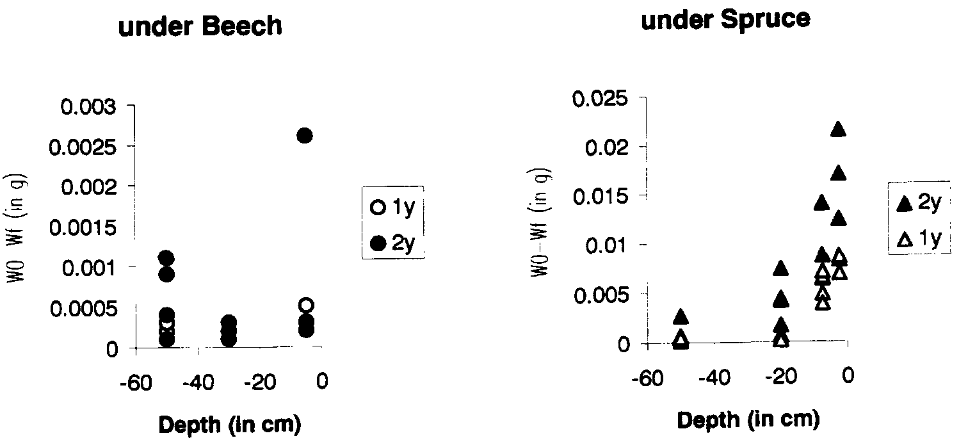

FIG. 1. Weigth losses (W0-Wf) of fluor-apatite crystal during the incubation in two soils under beech and spruce stands (1 or 2 years).

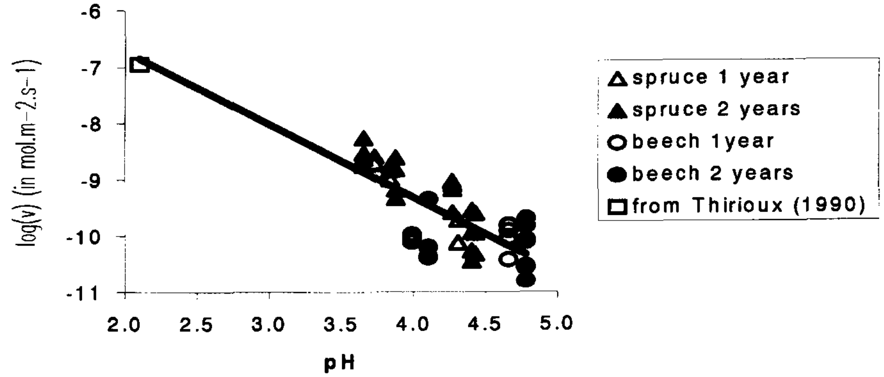

FIG. 2. pH *vs* dissolution rate of fluor-apatite (V) obtained in two soils under spruce and beech stands during incubation of 1 or 2 years and in laboratory experiment (Thirioux, 1990).

Results and discussion

Apatite crystals incubed in soil presented numerous corrosion marks as denticulated margin. The dissolution was the most intense in the upper horizon of the profile under spruce. Apatite deposits were observed on the faces of prism (100) and give evidence of recrystallisation and heterogenous dissolution as already described. These deposits trapped soil minerals (phyllosilicates, iron oxyde) during their precipitation and presented hexagonal dissolution etch pits. The superposition of dissolution-crystallisation figures give evidence of dessication-humectation events. The surface of crystal was more altered below mycelium hyphae observed on the surface of crystals.

Results of weigth losses for the four replicates were very similar except for one crystal incubed two years in the first horizon of soil under beech. The weigth losses of apatite were more pronunced under spruce than under beech and increased with time (Fig. 1). For the second year, the increase was the highest at a depth of −20 cm under spruce. Under spruce, weigth losses of apatite decreased with increasing depth and corresponded to an increase in pH.

Annual dissolution rates of apatite were calculated, weight losses divided by initial geometric surface-area of each crystal. Dissolution rates ranged between 10^{-7} and 10^{-11} mol m^{-2} s^{-1} and were linearly related to pH (Fig. 2). However the dissolution rate of apatite introduced in the upper horizon under beech appeared below the regression law. No decrease of dissolution rate was observed with time. Obtained data were compared to a literature data (Thirioux, 1990). From data of laboratory experiment of Durango's apatite dissolution (Thirioux, 1990) and from personal communication of J.C. Touray about the geometric surface-area of crystal used, the dissolution rate was calculated at the temperature of 40°C. Dissolution rate at 6°C was corrected for temperature using Arrhenius factor given by Sverdrup and Warfvinge (1993). Experimental and field data follow a relationship between dissolution rate and pH:

$$\log(v) = -1.3 \text{ pH } -4.1.$$

The high coefficient (1.3) is probably partly due to the calculation using initial BET surface area. Corrosion marks strongly increased suggesting a increase in surface area but this increase could not be measured.

The calculated dissolution rate was much higher than that used in the initial data bank of PROFILE. So, that calcium release rate by weathering of mineral fine earth calculated with PROFILE might be underestimated. Results must be confirmed on a longer term by next samplings of fluor-apatite crystal introduced in the soil.

References

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