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Laboratory weathering of Ca- and Mg-bearing silicates: Weak effect of CO₂ and organic ligands

S.V. GOLUBEV, O.S. POKROVSKY AND J. SCHOTT

LMTG, UPS-CNRS, 38 Rue des 36-Ponts, 31400, Toulouse France (oleg@lmtg.ups-tlse.fr)

The goal of this study is to rigorously evaluate the effect of dissolved CO₂, carbonate and bicarbonate ions and organic ligands on the dissolution of major basic rock-forming minerals under weathering conditions prevailing in soil environments. For this purpose, dissolution rates of diopside, forsterite, wollastonite and hornblende were measured at 25°C in NaCl solutions as a function of pH (1 to 12), pCO₂ (0 and 1 atm) and activity of HCO₃⁻ and CO₃²⁻ (10⁻⁵ to 0.1 M of total CO₂). Dissolution rates of all four minerals are not affected, within the experimental uncertainty, by 0.034 M of CO₂(aq) at pH~4 or by the presence of bicarbonate (up to 0.1M) and carbonate (up to 0.01 M) ions at pH of 8 and 11-12, respectively. Only for wollastonite a catalytic effect of HCO₃⁻ at 0.01 ≤ [HCO₃⁻] ≤ 0.1 M and pH=7-8 and a weak inhibiting effect of CO₃²⁻ at pH~12 were observed. For the first time, we were able to separate the specific effect of pCO₂ and pH and we demonstrated, in general accord with results of previous studies, that the direct effect of CO₂ on the dissolution rates of Ca- and Mg-containing silicates is very weak.

In the second part of this study, we investigated the effect of various organic ligands on wollastonite dissolution kinetics. Experiments were performed at 25°C, pH of 6 to 11 and for concentration of organic ligands ranging from 10⁻⁵ to 0.1 M. Over thirty five different organic ligands, including those containing carboxylic (acetate, formiate, lactate, tartrate, adipate, oxalate, citrate), aromatic (catechol, hydroxyquinolin), sulphhydryl (thioglycolate) and amine (aspartate, glutamate) groups, chelates (EDTA, EGTA), polysaccharides as analogs of bacteria mucus (sorbitol, glucose, saccharose, mannit, urea, gum xanthan, pectin), chemical analogs of bacterial cell envelopes functional groups (gluconate, glucuronic acid), natural humic and fulvic acids and the exudates of live algae cultures were used to evaluate the values of the kinetic and thermodynamic parameters controlling wollastonite dissolution.

An overall result of this study is that very high concentration of most organic ligands, around 0.01 – 0.1 mol/L, are necessary to appreciably affect the rates. Such concentrations can be met only in the microenvironments adjacent to soils bacteria and plant roots. This strongly suggests that, unlike for dissolution of Al-bearing silicates, the effect of soil organics on basic rocks weathering is quite weak.

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Behaviour of Ni, Cr during weathering of basalts under wet temperate climatic conditions

M. SOUBRAND, H. BRIL AND C. NEEL

HydrASA, UMR 6532 CNRS, Université de Limoges, F.S.T., 123 Avenue Albert Thomas, 87060 Limoges Cedex (marilyne.soubrand@unilim.fr)

In the French Massif Central, soils developed from basaltic parental rocks present too high natural contents in metallic trace elements (MTE) to allow to recycle municipal sewage sludges in agricultural fields. The objectives of this study are: (i) to characterise Cr and Ni -bearing phases in primary assemblages ii) to know the distribution of these elements in authigenic phases and iii) to forecast Cr-Ni behaviour during weathering processes according to the micro-environmental conditions.

Three samples (fresh rock, weathered rock, highly weathered rock) for six alkaline basalts of the French Massif Central were studied. Bulk chemical analyses were performed by ICP-AES for major elements and by ICP-MS for trace elements and alkaline melting of dried samples (CRPG, Nancy). The isovolumetric method and the Ti-constant method were applied to quantify compositional changes due to weathering. XRD was carried out on < 2 µm fraction. MTE distribution was investigated by optical and electronic microscopy (SEM-EDS). Chemical composition of primary and secondary minerals including major and trace elements was determined by EMPA (Fialin *et al.*, 1999). Proportions of each mineral were estimated by counting on thin section.

The studied basalts, alkaline basalts or basanites, are rich in Cr (248 - 455 ppm) and Ni (126 – 237 ppm). The total Cr and Ni concentrations are the same in weathered or unweathered basalts. But Cr and Ni - bearing phases change according to the alteration stage. In unweathered basalts, nickel is preferentially incorporated into olivine (1400 to 3600 ppm) whereas chromium is located in spinels (1 to 45 %) and clinopyroxenes (200 to 3000 ppm). On the contrary to the primary phases, authigenic phases (mixed clays and iron oxyhydroxides occurring as pseudomorphs of primary minerals and/or filling fractures) are highly heterogeneous. They contain lower quantities of MTE than primary phases : 60 to 600 ppm (mean =190) Ni and 40 to 500 ppm Cr (mean = 170). The mineral alteration sequence is similar for all sites : olivine > plagioclase > augite > Fe-Ti and Cr-Fe oxide. Mass balance calculations indicate a depletion of Mg, Ca, Na, Si. The most conservative elements are Al, Fe, Ni and Cr.

These two different methods point out that only a minor part (5 to 20 %) of Ni and Cr is mobilised by pedogenetic processes.

Reference

Fialin, M. et al., (1999) *American Mineralogist* **84**, 70 - 77.