

The role of Mn oxides on the geochemical cycle of chromium: A field study in New Caledonia

D. FANDEUR¹, F. JUILLLOT¹, E. FRITSCH¹, L. OLIVI²,
A. COGNIGNI², G. MORIN¹ AND J.P. AMBROSI²

¹Institut de Minéralogie et de Physique des Milieux Condensés (IMPMP), UMR CNRS 7590, Université Pierre et Marie Curie – Université Denis Diderot - IPGP, 75015 Paris, France

²ELETTRA, Sincrotrone Trieste -Area Science Park, 34012 Basovizza, Italy

³Centre Européen de Recherche et d'Enseignement en Géosciences de l'Environnement (CEREGE), UMR CNRS 6635, Université Paul Cézanne – Université de Provence, 13545 Aix en Provence, France

Chromium is naturally released in the environment upon weathering of ultramafic rocks containing Cr³⁺-bearing minerals [chromite FeCr₂O₄, magnetite Fe_{3-x}Cr_xO₄, olivine (Mg,Fe)_{2-x}Cr_xSiO₄ or pyroxene (Ca,Mg,Fe)_{1-x}Cr_xSiO₃]. In surface conditions, chromium occurs under two main redox states (Cr³⁺ and Cr⁶⁺), the former being much less soluble, bioavailable and toxic than the latter (Anderson, 1989). Several laboratory studies have shown that Cr³⁺ ions could be oxidized to Cr⁶⁺ ions by Mn oxides (Fendorf and Zasoski, 1992; Silvester *et al.*, 1995; Weaver and Hochella, 2003), which suggest that the concomitant occurrence of chromium and Mn oxides in soils could be hazardous. Although few field studies already addressed the question of the mobility and bioavailability of chromium in naturally Cr-enriched soils (Neel *et al.*, 2007; Garnier *et al.*, 2006; Becquer *et al.*, 2003), only one (Cooper, 2002) focused on the role of Mn oxides on these geochemical parameters.

The present study, which is supported by the french ANR-ECCO program, aims at increasing our knowledge on the actual role of Mn oxides on the geochemical cycle of chromium in soils developed upon weathering of ultramafic rocks. To reach this goal, soil samples were collected along a 60 m core drilled across a weathering sequence in New-Caledonia. Chemical and mineralogical analyses along this sequence indicate the occurrence of a saprolitic unit (ultramafic rocks more or less altered) at the bottom. This unit is overlaid by a first lateritic unit containing goethite, hematite and chromite and particularly enriched in Mn oxides (asbolan), which is itself overlaid by a second lateritic unit containing no Mn oxides. XANES analysis allowed detection of significant amounts of Cr⁶⁺ (up to 20 wt% of total chromium) in the unit containing Mn oxides whereas no oxidized chromium could be detected in the other units of the drilling core. These results strongly suggest that the reactivity of Cr³⁺ with Mn oxides observed in laboratory experiments is effective in soils and that these Mn oxides actually play a key role on the redox state of chromium, and in turn, on the geochemical cycle of this element in surface environments.

Constraining reaction rates in marine carbonate sediments using reactive transport modeling: Investigating the effects of diagenesis on Sr, Ca, and Mg

M.S. FANTLE¹ AND D.J. DEPAOLO²

¹Pennsylvania State Univ., Geosciences Dept., University Park, PA 16802; (mfantle@geosc.psu.edu)

²University of California, Earth and Planetary Science Dept., Berkeley, CA 94520-4767; (depaolo@eps.berkeley.edu)

Numerical modeling, in conjunction with pore fluid chemical and isotopic measurements, can be used to deduce mineral dissolution and precipitation rates in natural systems. The current study reports calcite recrystallization rates for a marine sedimentary section (ODP Site 807A, Ontong Java Plateau). The rates are constrained by Sr isotopes (⁸⁷Sr/⁸⁶Sr), which are sensitive at multi-million-year time scales, and Ca isotopes ($\delta^{44}\text{Ca}$), which are sensitive at time scales of tens of thousands of years. Recrystallization rates for sediments that are older than 2 Ma are ~0.2 to 2 %/Myr, which are similar to those reported in previous studies for other locations. However, reaction rates deduced for relatively young (≤ 2 Ma) carbonate sediments using Ca isotopes are significantly faster (30 to 40 %/Myr), indicating that the approximate inverse age dependence of recrystallization rate extends to carbonate sediments as young as 0.1 Ma.

Rapid rates of recrystallization in relatively young carbonate sediments have implications for the fidelity of elemental and isotopic proxies of past climate and ocean chemistry. Recrystallization may change the original elemental and/or isotopic composition of carbonate, complicating attempts at paleo-reconstructions. The current study presents model results that describe the effects of diagenesis on the Sr/Ca and Mg/Ca elemental ratios, as well as the Ca isotopic composition, of marine carbonates. Using the reaction rates constrained by Sr and Ca pore fluid geochemistry, we use numerical models to estimate that up to 25 to 30% of the initial Sr and Mg in the solid phase may be lost during diagenesis. This conclusion is different from that inferred from the Sr isotope data only. The pattern of loss is dependent on the sedimentation history, so that loss is not constant throughout the column. If there is no externally imposed advection in the sedimentary column, then Ca isotopes are not significantly modified by diagenesis. Given the upper limit of reaction rates determined at 807A, the $\delta^{44}\text{Ca}$ of the bulk carbonate sediment is altered by no more than +0.15%. The small degree of diagenetic alteration is due to the fact that Ca is a major element in calcite, as opposed to the trace constituents Sr and Mg. Finally, diagenesis is not likely to account for the fluctuations observed in the seawater Ca isotope curve over the Late Cenozoic that is derived from measurements of bulk carbonate sediments.