

The action of sulfur species and water on organic matter

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The incorporation of inorganic sulfur species into organic matter during early diagenesis stage has been studied and demonstrated by chemical analysis of sedimentary sulfurized organic matter (S-OM) and laboratory experiments. The importance of S-OM as one of the major quantitative and significant sinks of sulfur in sediments and its interaction with the global oxygen and carbon cycles is being recognized in recent years. Sedimentary OM reacts with S species (e.g. HS⁻, S_x⁻², RS⁻) in all stages of OM formation and thermal maturation. Recently, we have shown that elemental S is reactive even under mild temperatures (60-80°C) and aquatic conditions. We have employed detailed chemical analyses and S-isotopic studies to decipher the mechanisms controlling these reactions. A variety of organosulfur compounds as well as oxidized compounds (non-S) such as ketones were formed by the reaction of elemental S and organic model compounds. The sulfurized and oxidized organic compounds seem to form in parallel. There is 5-13‰ isotopic fractionation; between elemental S and H₂S that decreases as a function of temperature. Organosulfur compounds and polysulfides exhibit smaller fractionation relative to elemental S of 0-3‰. We suggest that the action of elemental S on organic matter is two folds: it activates water to produce hydroxyl radical that can oxidize organic compounds, and second, it reacts directly with organic matter to produce organosulfur compounds and H₂S. Similar effect was observed for polysulfides but not for H₂S or SO₂, suggesting that the catenated nature of S-S bonds has a decisive effect, probably through the formation of thyl radical (SH·) from the cleavage of these bonds. This in turn initiates a radical chain reaction that forms secondary radicals such as hydroxyl radicals. This species (OH·) was identified in our simulation experiments and are probably responsible for the ketones formation, demonstrating an important pathway for lowering the activation energy of water splitting and its subsequent reactions with OM. These findings improve our understanding of the intermediate temperature regime during OM thermal maturation that is mostly neglected in previous studies. It also provides new routes for hydrothermal processes such as thermochemical sulfate reduction. More importantly, this study shows the inherent connection of the carbon, hydrogen, oxygen and sulfur in the geosphere under much milder environmental conditions than previously thought.

Iron isotopic fractionation in tropical soils

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Iron is the fourth most abundant element in the continental crust. It is particularly abundant in tropical environment due to the large amounts of poorly mobile oxidized Fe in lateritic soils. A better understanding of Fe biogeochemical cycle remains a major issue, particularly within the tricky problem of environmental change consequences (land use change, climate change, ...). This study focused on iron isotopic compositions of soils from three distinct toposequences in tropical environment: 1/ at the scale of the Nsimi experimental watershed in South Cameroon, 2 and 3/ in the Rio Capim's watershed in the northeast of the Brazilian Amazon, respectively in rainforest and pasture landscape. We worked both on ferralitic soils (i.e., the top of the hills), and on evolved/degraded soils present within the slopes and the bottom of the hills in connection with stream waters.

The objectives of this study were 1) to determine if significant isotopic differences in iron compositions exist between laterites and soils resulting from laterite degradation, 2) to investigate the processes responsible for these differences in isotope compositions, and 3) to evaluate to which extent Fe isotopes can be used as a proxy to understand metal cycling in the environment.

Iron isotope compositions were determined by MC-ICP-MS analysis after a complete microwave mineralization and iron purification.

Samples from evolved/degraded lateritic soils both in forest and pasture show important Fe loss compared to the reference ferralitic soils (i.e., 30 to 90% estimated on the basis of a constant Zr concentration). Our first results on the Fe isotope compositions of these samples reveal that the $\delta^{57}\text{Fe}$ of the evolved/degraded soils ($\delta^{57}\text{Fe} = 0.6 \pm 0.1\%$ for soils at the bottom of the slope in forest and $\delta^{57}\text{Fe} = 0.4 \pm 0.1\%$ for soils under pasture) are isotopically heavier than the continental crust baseline and the reference lateritic soils (i.e; 0.1‰ in $\delta^{57}\text{Fe}_{\text{IRMM-14}}$). These results contrast with previous data published on the Fe isotopic compositions in lateritic soils showing no differences between soils and the continental crust [1]. Hence, our results suggest that chemical weathering and pedogenesis can significantly fractionate iron isotopes under tropical environments. This shows that Fe isotopes can be used as a new geochemical tool to study iron transfer during soil degradation and weathering processes in response to natural and anthropogenic processes.

[1] Poitrasson, F., et al. (2008) *Chemical Geology* **253**, 54-63.