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The influence of organic complexation on Ni isotopic fractionation and Ni recycling in the upper soil layers

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ABSTRACT

The quantification of Ni isotopic fractionation induced by Ni binding to organic acids is a preliminary step to better constrain the mechanisms determining Ni isotopic fingerprint observed in surface soils, waters and plants, as well as the contribution of metal recycling during plant litter degradation. In this study, Ni isotopic fraction induced by reaction with small organic acids, e.g. citric and oxalic acids, and with soil purified humic acids (PHA) was investigated at different Ni-L ratio and pH conditions. The Donnan Membrane Technique was used to separate Ni bound to organic ligands from the free metal. Obtained results highlighted that Ni binding with carboxylic groups produces, in the adopted experimental conditions, a $\Delta^{60}Ni_{bond\text{-}free} < 0.2‰$. This value is not high enough to justify neither metal fractionation previously observed between soil and hyperaccumulators, nor the fractionation between different plant parts, e.g. roots and leaves. In parallel, leaf degradation experiments of two hyperaccumulating plants, where Ni is mainly present as Ni-citrate, were performed to simulate litter decomposition and to highlight the contribution of plants on Ni isotopic composition in surface soils and waters. In the case of the hyperaccumulator *Alyssum murale*, the degradation process did not induce any observable fractionation. On the contrary, during *Rinorea bengalensis* degradation experiment, a fractionation between Ni leached out in the first 10 days and between 10 and 30 days was observed ($\Delta^{60}Ni_{10-30day} = 0.20 \pm 0.05‰$). The observed fractionation evidenced a heterogeneous distribution of Ni within the leaves, and/or distinct chemical bonding to the leaf cells, and finally suggested the influence of the chemical bonding on Ni isotopic signature. Although a precise quantification of plant contribution on Ni isotopic signature in surface soils and waters is still not reached, our results produced important progress to elucidate the role of organic matter in regulating Ni isotopic fingerprint in surface layers.

1. Introduction

Being a biologically active trace metal, Ni is thought to have had a crucial role in the early Earth (Willaims and Frausto da Silva, 2003; Domagal-Goldman et al., 2008) and during the last decade nickel isotopes have attracted increasing interest as a new tool to investigate biogeochemical processes at Earth's surface. The biogeochemical processes controlling Ni isotopic fractionation in surface layers are, however, not yet well understood and require further investigations. In the Earth's crust, Ni is mostly present under the +2 oxidation state (Ni^{2+}) (Fujii et al., 2014) and undergoes redox reactions mainly through anthropogenic processes (Ni metallurgy) (Ratié et al., 2015a). Thus, it is assumed that redox processes cannot be responsible for the different Ni isotopic signatures observed in terrestrial samples as opposed to other metals, such as Fe, Cu and Cr (Wiederhold, 2015). Although the current literature data about Ni isotopic compositions are still quite limited, they highlight an important dispersion of $\delta^{60}Ni$ values among the different studied Earth's surface samples (Ratié et al., 2015a). Indeed, a relatively small Ni variation in isotopic composition of terrestrial samples has been measured, including eruptive rocks (basalts) and continental sediments, with an average $\delta^{60}Ni$ value of +0.15‰ ± 0.24‰ (Cameron et al., 2009). In contrast with those abiotic materials, an isotopic fingerprint between −0.44 ± 0.20‰ and −1.46 ± 0.08‰ was observed for Ni-containing methanogen bacteria in respect to the culture medium, suggesting a high potential of Ni stable isotopes as biomarkers of methanogenesis on the early Earth (Cameron et al., 2009; Cameron et al., 2007; Cameron et al., 2012). Studying for the first time the isotopic composition of dissolved Ni in

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ocean and river waters, Cameron and Vance (2014) pointed out a nickel isotopic mass balance incoherence. On one hand, they reported an average δ^{60}Ni value of 1.44‰ ± 0.15‰ in a homogeneous set of seawater, consistent with the range of the δ^{60}Ni values measured for organic-rich marine sediments (0.2‰ to 2.5‰) (Porter et al., 2014) and for the ferromanganese crust (0.9‰ to 2.5‰, with an average of δ^{60}Ni = 1.6 ± 0.8‰) (Gall et al., 2013), both representing the principal output of Ni from the oceans (Gall et al., 2013). On the other hand, dissolved Ni in river waters, supposed to be a considerable Ni ocean input, presented highly variable isotopic compositions, with δ^{60}Ni ranging between 0.29‰ and 1.34‰. Thus the δ^{60}Ni values measured for continental waters are not high enough to explain δ^{60}Ni values in seawater, even though they are up to 1‰ heavier than the reported values for continental silicate rocks (Cameron and Vance, 2014), suggesting a major influence of weathering processes on Ni isotopic fractionation. Few results have been reported about Ni isotope fractionation due to weathering (Gall et al., 2013; Ratié et al., 2015b). For instance, Ratié et al. (2015b) investigated the effects of weathering on lateritic profile of ultramafic sites, showing that formation of Ni-bearing clays and Fe-oxides induced a depletion of Ni heavy isotopes in the solid phases as well as their export in the dissolved phase, $\Delta^{60}Ni_{soil\text{-}bedrock}$ up to −0.47‰. These results are consistent with the δ^{60}Ni values measured in the exchangeable pool of an ultramafic soil, the labile pool, which were higher than those of the corresponding bulk sample (average $\Delta^{60}Ni_{exch\text{-}tot}$ = 0.29‰ (Ratié et al., 2015b)). Those data were also in good agreement with Ni sorption/precipitation experiments onto ferrihydrite, where a preferential adsorption of light isotopes onto the solid phase was observed, $\Delta^{60/58}Ni_{dissolved\text{-}sorbed}$ = + 0.35 ± 0.10‰ (Wasylenki et al., 2015; Wang and Wasylenki, 2017).

Up to now, no data is available concerning Ni isotopic fractionation after complexation with soil organic matter. Nevertheless, metals present a high affinity for humic substances, which are a dominant phase influencing metal bioavailability. Moreover, even though it is widely assumed that biogeochemical cycle of metals is influenced by biotic processes, only few data have been published on the role of living organisms on Ni isotopic fractionation (Deng et al., 2014; Estrade et al., 2015). A fundamental example is hyperaccumulators, that are plants characterized by a unique capability to accumulate extremely high concentration of metals in their biomass (Van der Ent and Mulligan, 2015). Most of those plants are nickel hyperaccumulators, with a nominal threshold concentration fixed at 1000 μg g^{-1} foliar Ni (Reeves, 2003). Replenishment of available Ni pools in soils through the biogeochemical recycling represents, therefore, a considerable contribution to Ni global cycle. This contribution is even more important in the context of ultramafic areas, which are among the most important Ni continental reservoirs, and where hyperaccumulators mainly grow. Hyperaccumulators found in ultramafic complexes of Mediterranean Region are mainly in the genus of *Alyssum* (Brassicaceae), while several different families are present in tropical ultramafic outcrops, e.g. *Rinorea bengalensis* (Violacee), *Phyllantus securinegioides* (Phyllanthaceae), etc. (Van der Ent and Mulligan, 2015). Despite the increasing attention dedicated to hyperaccumulating plants, suitable for soil remediation and agromining activity (Van der Ent et al., 2015), the ecological reasons for nickel hyperaccumulation are still not well understood (Van der Ent and Mulligan, 2015). The role of those plants in nickel cycle is, however, crucial as they represent, together with the precipitation of secondary minerals, the major sink for metals. Moreover, the potential contribution of vegetation on Ni isotopic composition in the upper soil horizon and its influence on Ni exportation towards aqueous compartments has been advanced (Estrade et al., 2015). However, the discrimination of stable isotopes of Ni within plants through accumulation processes has just been unraveled with a preliminary study so far (Deng et al., 2014; Estrade et al., 2015). Similarly, it is recognized that plant litter degradation is one of the main source of dissolved major and trace elements in rivers (Fraysse et al., 2010; Pokrovsky et al., 2005), but no data has been published concerning the study of Ni isotopic fractionation potentially occurring during litter degradation process. A complete investigation of Ni cycle, including plant uptake and plant recycling, deserves, therefore, a greater attention. Deng et al. (2014) performed experiments on plants grown in hydroponic conditions and showed a preferential uptake of light Ni isotopes by plants. In another study, plants naturally grown on ultramafic systems were investigated reporting a whole-plant isotopic composition heavier than the soil, with $\Delta^{60}Ni_{whole\ plant\text{-}soil}$ up to 0.40‰, but lighter than the bioavailable pool, $\Delta^{60}Ni_{DTPA\text{-}rhizosoil}$ up to 0.89‰ (Estrade et al., 2015). This supports the hypothesis that the bioavailable Ni in soil presents a heavy isotopic signature compare to the total soil, and that plants probably take up the lighter fraction of isotopes from this heavy pool.

A considerable number of processes are known to involve Ni binding to organic molecules, such as mobilization and uptake of nutrients by plants and microorganisms, detoxification processes by plants, microbial proliferation and dissolution of soil minerals (Marschner and Marschner, 2012; Jones, 1998). Among all the organic ligands produced by biological entities and slow degradation of biological material in soils, waters and sediments, the principal group consists of molecules bearing carboxylate functional groups. Those organic ligands commonly occur as low-molecular-weight molecules, such as acetate, malate, citrate, oxalate, and as macromolecules, such as humic substances (Strathmann and Myneni, 2004; Thurman, 1985). The isotopic composition of Ni in plants can be, then, strongly correlated to the potential isotopic fractionation induced by complexation with organic ligands involved in uptake mechanisms by root cells (Deng et al., 2014), in translocation and storage mechanisms in aerial parts of the plant, as well as by complexation with organic ligands present in soil solutions. The quantification of potential Ni isotopic fractionation when reacting with organic ligands is, therefore, necessary to elucidate the role of organic matter in the biogeochemical cycle of Ni.

In the present study, we aimed to determine the extent of Ni isotopic fractionation due to interaction with Purified Humic Acid (PHA), used as a proxy surrogate for reactive soil organic matter, and with oxalic and citric acids, both being representative of low-molecular weight organic molecules, involved in Ni plant uptake and storage processes (Jones, 1998). To this purpose, the Donnan Membrane Technique (DMT) (Temminghoff et al., 2000) was used to separate free Ni (Ni^{2+}) from the Ni bound to organic ligands (Ni-L) after complexation reaction. The DMT system consists of a donor and an acceptor solution divided by a negatively charged membrane, only permeable to free metal. The DMT has often been used to study metal interaction with organic and inorganic ligands, both in laboratory and field applications (Kalis et al., 2006). However, the combination of this technique and the investigation of metal isotopic fractionation as a consequence of metal-ligand interaction has only been applied to Zn (Jouvin et al., 2009) and Cu (Ryan et al., 2014) so far. In this work, the combined effects of pH and degree of complexation between Ni and organic ligands on metal isotopic fractionation were investigated. This approach allows unravelling the influence of Ni interaction with organic molecules on Ni isotopic composition, which is still missing for a correct interpretation of Ni biogeochemical cycling. Moreover, in a second part of the work, the role of vegetation recycling in the upper soil layers was studied simulating, in controlled conditions, leaf degradation of two hyperaccumulators: *Alyssum murale*, a small shrub from temperate area, and a tropical young tree of *Rinorea bengalensis*, potentially growing up to 25 m high. This experiment aims to furnish new information necessary to introduce biological processes contribution in Ni isotopic cycle. Up to now, indeed, nothing is known, qualitatively and quantitatively, about how plant accumulation and release processes can modify Ni isotopic signature. To this purpose, Ni concentration and isotopic signature in leached solutions were monitored as a function of time, and results were interpreted on the basis of Ni speciation in plant leaves previously reported in literature, and on isotopic signature of Ni^{2+} and Ni-L, determined with DMT system.