



Weathering and vegetation controls on nickel isotope fractionation in surface ultramafic environments (Albania)



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ARTICLE INFO

Article history:

Received 19 December 2014

Received in revised form 7 April 2015

Accepted 9 April 2015

Available online 2 May 2015

Editor: G.M. Henderson

Keywords:

nickel biogeochemical cycle

ultramafic environments

nickel isotopes

weathering

vegetation

hyperaccumulating plants

ABSTRACT

The dissolved nickel (Ni) isotopic composition of rivers and oceans presents an apparent paradox. Even though rivers represent a major source of Ni in the oceans, seawater is more enriched in the heavier isotopes than river-water. Additional sources or processes must therefore be invoked to account for the isotopic budget of dissolved Ni in seawater. Weathering of continental rocks is thought to play a major role in determining the magnitude and sign of isotopic fractionation of metals between a rock and the dissolved product. We present a study of Ni isotopes in the rock–soil–plant systems of several ultramafic environments. The results reveal key insights into the magnitude and the control of isotopic fractionation during the weathering of continental ultramafic rocks. This study introduces new constraints on the influence of vegetation during the weathering process, which should be taken into account in interpretations of the variability of Ni isotopes in rivers.

The study area is located in a temperate climate zone within the ophiolitic belt area of Albania. The serpentinized peridotites sampled present a narrow range of heavy Ni isotopic compositions ($\delta^{60}\text{Ni} = 0.25 \pm 0.16\text{‰}$, $2\text{SD } n = 2$). At two locations, horizons within two soil profiles affected by different degrees of weathering all presented light isotopic compositions compared to the parent rock ($\Delta^{60}\text{Ni}_{\text{soil-rock}}$ up to -0.63‰). This suggests that the soil pool takes up the light isotopes, while the heavier isotopes remain in the dissolved phase. By combining elemental and mineralogical analyses with the isotope compositions determined for the soils, the extent of fractionation was found to be controlled by the secondary minerals formed in the soil.

The types of vegetation growing on ultramafic-derived soils are highly adapted and include both Ni-hyperaccumulating species, which can accumulate several percent per weight of Ni, and non-accumulating species. Whole-plant isotopic compositions were found to be isotopically heavier than the soil ($\Delta^{60}\text{Ni}_{\text{whole plant-soil}}$ up to 0.40‰). Fractions of Ni extracted by DTPA (diethylenetriaminepentaacetic acid) presented isotopically heavy compositions compared to the soil ($\Delta^{60}\text{Ni}_{\text{DTPA-soil}}$ up to 0.89‰), supporting the hypothesis that the dissolved Ni fraction controlled by weathering has a heavy isotope signature. The non-hyperaccumulators ($n = 2$) were inclined to take up and translocate light Ni isotopes with a large degree of fractionation ($\Delta^{60}\text{Ni}_{\text{leaves-roots}}$ up to -0.60‰). For Ni-hyperaccumulators ($n = 7$), significant isotopic fractionation was observed in the plants in their early growth stages, while no fractionation occurred during later growth stages, when plants are fully loaded with Ni. This suggests that (i) the high-efficiency translocation process involved in hyperaccumulators does not fractionate Ni isotopes, and (ii) the root uptake process mainly controls the isotopic composition of the plant. In ultramafic contexts, vegetation composed of hyperaccumulators can significantly influence isotopic compositions through its remobilization in the upper soil horizon, thereby influencing the isotopic balance of Ni exported to rivers.

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1. Introduction

Nickel isotope fractionation in geological settings has so far been shown to span a range of 3.5‰ on the $\delta^{60}\text{Ni}_{\text{NIST-986}}$ scale. Various igneous rocks and deep-sea clay sediments present a narrow range of fractionation, from -0.13‰ to 0.34‰ (Cameron et al., 2009; Steele et al., 2011; Gueguen et al., 2013). The isotopically lightest lithologies are magmatic sulfides (-0.20‰ to -1.03‰) (Hofmann et al., 2013; Gueguen et al., 2013), whereas the heaviest are represented by organic-rich marine sediments (0.20‰ to 2.50‰ , Porter et al., 2014) and hydrogenous Fe–Mn crust (0.90‰ to 2.50‰) with an average $\delta^{60}\text{Ni}$ of $1.60 \pm 0.40\text{‰}$ (1SD, $n = 24$) (Gall et al., 2013). The latter are a major sink of Ni in the ocean and have an average isotopic composition that is similar to that of dissolved Ni in the ocean ($\delta^{60}\text{Ni} = 1.44 \pm 0.15\text{‰}$, 2SD, $n = 29$, Cameron and Vance, 2014). This may indicate that adsorption of Ni onto manganese oxides has apparently little effect on Ni isotopes (Gall et al., 2013). However, the major input of Ni to the ocean is the dissolved phase in rivers, which presents a heavy isotopic composition of 0.8‰ (the weighted average of the world's large rivers) relative to silicate rocks and sediments (Cameron and Vance, 2014). This composition is not heavy enough to close the mass balance of Ni in oceans however, and either another heavy source or an additional light sink is required. Nevertheless, the dissolved phase in river water exhibits a large range of fractionation (0.29‰ to 1.34‰). In metal isotope systems such as Si, Fe, Mo and Ge (Bergquist and Boyle, 2006; Opfergelt and Delmelle, 2012; Pokrovsky et al., 2014; Voegelin et al., 2012), weathering of continental bedrocks and soils is the main geochemical process responsible for driving heavy isotopes into the dissolved phase. Evidence for Ni isotopes has been found during the weathering of serpentinized peridotite in a tropical climate, leading to the incorporation of light Ni isotopes in lateritic regolith (Gall et al., 2013; Ratié et al., 2015). However, the influence of weathering conditions on the extent of fractionation still requires testing in order to better constrain the signatures of dissolved and particulate Ni exported to rivers.

Despite their relatively rare occurrence at the Earth's surface, ultramafic geological units may locally represent large reservoirs of Ni exported to rivers and oceans (Guillot and Hattori, 2013). Ultramafic soils (also known as serpentine soils), derived from the weathering of ultramafic rocks, are highly enriched in toxic metals such as Ni, Cr and Co, as well as in certain major elements (e.g. Mg and Fe), but are depleted in other essential nutrients such as Ca, P and K (Proctor, 1971). In serpentine soils, typical Ni concentrations are in the g kg^{-1} range, giving it the status of a major element rather than its more usual trace metal status (Butt and Cluzel, 2013). In cold and temperate climates, incomplete weathering of the parent rock (e.g., Harzburgite, Lizardite) leads to the accumulation of secondary minerals with a high exchange capacity for Ni (Massoura et al., 2006). These minerals include amorphous Fe-oxides and high-charge smectites and bear the bioavailable pool of toxic metals (e.g. Ni).

Mineralogy and elemental distribution in the weathered horizons are a function of parent rock, climate, and weathering conditions. The type of soil derived, its location in the toposequence, and the Ni content of weathered serpentine clays and Fe-oxides, can all govern the availability of Ni in the different soil horizons (Lee et al., 2003). For instance, the Ni contents of primary minerals (e.g., chlorite, antigorite) are relatively low compared to secondary minerals such as goethite or smectite (Bani et al., 2014). Ni enrichment in the weathered products mainly results from adsorption and Mg–Fe substitution processes (Butt and Cluzel, 2013). The sorption mechanism onto soil or mineral particles has been studied for several isotope systems (Si, Fe, Zn, Cu, Mo, Cd) and has been shown to lead to contrasting fractionation

in terms of sign and magnitude (Balistrieri et al., 2008; Delstanche et al., 2009; Goldberg et al., 2009; Mikutta et al., 2009; Wasylenki et al., 2014). In the case of Ni, Wasylenki et al. (2015) recently performed experimental adsorption and co-precipitation of dissolved Ni onto Fe-oxyhydroxides and they identified an equilibrium isotope effect leading to the preferential adsorption of light Ni isotopes onto the solid phase with a separation factor ($\Delta^{60}\text{Ni}_{\text{dissolved-sorbed}}$) of $0.35 \pm 0.10\text{‰}$ (1SD).

In the upper horizons of the soil, weathering is affected by biotic processes such as fungi- and bacteria-mediated mineral dissolution, reactions with decomposed organic matter, and root uptake and exudation. Although, methanogen bacteria (Cameron et al., 2009) and certain plants (Deng et al., 2014) have been found to incorporate light Ni isotopes on their own, limited data is available regarding Ni isotope during biological transformations. Moreover, the chemical characteristics of ultramafic soil are mostly responsible for the singular biodiversity of ultramafic environments, in which several plants have evolved towards adapted homeostasis. Like all plant micronutrients, low concentrations of Ni are essential for most plants, but the Ni becomes toxic at high concentrations (Brown et al., 1987). Plants growing on serpentine soils are therefore hypertolerant to Ni and have developed two strategies to prevent the adverse effects of the metal in plant cells (Verbruggen et al., 2009). Hyperaccumulating species do not retain metal in their roots and translocate large amounts of Ni to their aerial organs, where it accumulates in leaves without any poisoning effect (several g kg^{-1} of Ni in leaves, dry-weight). The non-hyperaccumulating species can retain and detoxify the metal in their root tissues and prevent significant root-shoot translocation. Hyperaccumulating plant species growing on ultramafic soils can concentrate up to several per cent Ni per unit of biomass (Van der Ent et al., 2013). Cultivation of these species is therefore regarded as an alternative technique for mining (known as phytomining) or soil remediation (phytoremediation) (Chaney et al., 2007). Over the course of a year, the hyperaccumulating species extract Ni from serpentine soils and redistribute decaying organic residues to the litter, which contains a significant amount of metal that can be easily mobilized for further plant uptake or leaching (Zhang et al., 2005). An experimental investigation of Ni isotopes in a series of higher plants ranging from non-tolerant to hyperaccumulator has indicated that in hydroponics, root uptake favors light Ni isotopes from the solution pool (Deng et al., 2014). Conceptually, plant uptake would leave behind the heavier isotopes and, if the decaying plant material does not return the light isotopes to the porewater, vegetation could contribute to enrichment of the soil solution Ni-pool. The Ni isotope signature of weathered products of ultramafic rocks and soils may therefore be influenced by vegetation. However, the extent of Ni isotope fractionation due to plant uptake and accumulation has yet to be isolated and quantified in in-situ plant–soil systems.

This article aims to document and interpret Ni isotope compositions throughout the rock–soil–plant system of an ultramafic environment in south-eastern Europe, where the climate is temperate. Four locations, which differ in elevation and topography, were sampled in the ophiolitic belt of Albania. Ni isotopes were investigated in parent rocks and in the horizons of two different soil profiles. In order to identify the influence of weathering on isotopes, the mineralogy and elemental compositions of the soils were also measured. Subterranean and aerial organs of nickel-hyperaccumulators and non-hyperaccumulator plants were sampled in order to test the sensitivity of Ni isotopes to the accumulation process. The Ni isotopic composition of the corresponding rhizospheric soil, DTPA-extractable fractions, and litter, were determined in order to decipher the influence of vegetation on Ni isotopes in soils. Unraveling Ni isotope fractionation processes in ultramafic massifs, which are significant contributors to the conti-

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