Study of Ni exchangeable pool speciation in ultramafic and mining environments with isotopic exchange kinetic data and models

I. Zelano [a, b], Y. Sivry [a, *], C. Quantin [c], A. Gélabert [a], M. Tharaud [a], S. Nowak [d], J. Garnier [e], M. Malandrino [b], M.F. Benedetti [a]

[a] Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Univ. Paris Diderot, UMR 7154 CNRS, F-75005 Paris, France
[b] Univeristà degli Studi di Torino, Via Pietro Giuria 5, 10125 Torino, Italy
[c] UMR8148 GEOPS, Univ. Paris Sud-CNRS-Université Paris Saclay, Rue du Belvédère, Bât. 504, 91405 Orsay Cedex, France
[d] Univ. Paris Diderot, Sorbonne Paris Cité, ITODYS, UMR 7086 CNRS, F-75205 Paris, France
[e] Universidade de Brasilia, IG/GMP-ICC Centro, 70919-970 Brasilia-DF, Brazil

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ABSTRACT

Soils and ore samples influenced by mining and metallurgical activity were collected in ultramafic soils (UM) complexes of Barro Alto and Niquelândia, in order to determine the contribution of each Ni bearing phases to the total exchangeable pool of Ni, and to point out if this pool was affected by anthropic activities. For this purpose, the IEK-model previously developed by the group (Zelano et al., submitted) was applied, on the basis of IEK experiments performed on pure typical Ni scavengers (serpentines, chlorite, smectite and iron oxydes) from ultramafic systems. For each typical scavenger, this model describes the percentage of Ni associated to exchangeable pool(s) as well as their corresponding kinetic constant(s) of exchange. The mineralogical composition of soil and ore samples and Ni solid speciation were first determined, and the IEK-model was applied on these bases. In almost all samples, an important contribution of serpentine to Ni exchangeable pool was highlighted, ranging between 10% and 45%. The important amount of organic matter (OM) in one of the studied soil samples, allowed to extrapolate generic OM E_{Ni} and k parameters, which were introduced in the IEK-model to improve its predictive capability. Obtained results provided evidences of how even a small content (3 wt%) of organic carbon (OC), can represent an important contribution of OM to the total E_{Ni} pool (60%). In the investigated ore samples, up to the 60% of E_{Ni} was attribute to smectite, responsible for fast E_{Ni} pool kinetic evolution. In addition, the model highlighted the role of the Fine Black Ash (FBA), by-products of the pyrometallurgical activity, detected into a soil sample, that is responsible for the 15% of E_{Ni}. This approach allowed to determine, for the first time, the relative contribution of each Ni bearing phase to the total exchangeable pool, in terms of concentration and kinetics.

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1. Introduction

Ultramafic (UM) rocks and serpentines of ophiolite represents only the 1% of emerging rocks (Oze et al., 2007), but attract enormous economic interests because of their richness in heavy metals. They indeed, exhibit a high metal content such as Mn, Ni, Cr or Co, usually at harmful concentrations for the environmental systems (Becquer et al., 2010; Bonifacio et al., 1997; Garnier et al., 2009; Whittaker, 1954a, 1954b). Several studies focused on the determination of the mineralogical composition of UM soils and on the metal content of Ni bearing phases (Becquer et al., 2006; Garnier et al., 2006), as lateritic formations developed on ultramafic rocks hold more than 70% of world Ni stocks (Brand et al., 1998). In UM rocks, the mineral phases to which Ni is associated are mainly olivine (in particular forsterite), spinel, amphiboles, serpentines and pentlandite (Kierczak et al., 2007; Quantin et al., 2008). Weathering of these rocks leads to the release of Ni with subsequent sequestration in secondary minerals, such as clay minerals (as serpentine, talc, chlorite and smectite), Fe oxy(hydr) oxides and, to a lesser extent, Mn oxides (Dublet et al., 2012; Fan and Gerson, 2015; Fandeur et al., 2009; Manceau et al., 2000; Quantin et al., 2008).

* Corresponding author.
E-mail address: sivry@ipgp.fr (Y. Sivry).

The Ni richness of natural areas has always induced an associated important mining activity and a consequently large production of Ni-rich wastes (Raous et al., 2013), as in the case of Barro Alto and Niquelândia complexes, Goias State, Brazil. These intrusive mafic–ultramafic complexes, represent one of the biggest Ni deposit in the world (Ferreira-Filho et al., 1994), with Ni stocks estimated to be higher than 100 million tons. Ni concentration can be up to 1.25 mg kg^{-1} in rocks, and can vary between 3000 and 74,000 mg kg^{-1} in soils (Garnier et al., 2009). The pyrometallurgical activity developed in situ produces wastes, slags and ashes, with a Ni content ranging between 1000 and 32,000 mg kg^{-1} (Ratié et al., 2016). These wastes are usually stored in settling pounds, directly in contact with soils and subjected to rain water and wind activity. The most serious environmental problems associated with solid mine wastes are their tendency to react with air and water (Jamieson, 2011). The fundamental processes that control toxic element release or sequestration and/or their dispersion in the environment, depend on the interaction between mobile metal ions concentration and mineral surfaces (Alloway, 1995), rather than on the total metal concentration. Hence, detecting the mineral phases controlling the dynamic pools of metal is a great environmental challenge. To understand and control the fate of metals in soils, and to point out the potential consequences of mining activity on natural metal cycles, it is therefore particularly important to determine the link between the mobility of metals and their solid dynamic speciation.

Indeed, solid speciation techniques such as Scanning/Transmission electronic microscopy-EDXS or X-Ray Absorption Spectroscopy, have often been used to identify the principal mineral phases to which metals are associated (Dublet, 2013; Manceau et al., 2000). Nevertheless, the only investigation of metal solid speciation in a complex matrix such as natural soil and/or ore samples, is uncertain and does not allow to discriminate between mobile and non-mobile metal ion. Isotopic Dilution technique (ID) is considered as one of the most attractive method to measure labile metals in soil, as it represents the fraction of metals in dynamic equilibrium with metal species in the solution phases within a certain time-frame (Degryse et al., 2009; Domingos et al., 2014). Performing Isotopic Exchange Kinetic (IEK) experiments, allows to quantify the exchangeable pool (i.e. dynamic speciation, representative of the available pool) of a metal and to follow its dynamic evolution as a function of time. In a previous work of the group (Zelano et al., submitted) an IEK-model was developed on the base of IEK experiments performed on pure typical Ni scavengers in UM soils such as serpentines, chlorite, smectite, goethite and hematite and allowed to quantify, for each of the investigated phases, the number of Ni exchangeable pools (e.g. the different surface reaction mechanisms), the percentage of Ni associated with each pool and their corresponding kinetic exchange constant.

The aim of the present study is to challenge this model with soil and ore samples collected in the UM complexes of Barro Alto and Niquelândia, representative of systems influenced by mining and metallurgical activity, in order to determine the contribution of each Ni bearing phase to the total exchangeable pool of Ni, and to point out if this pool is affected by anthropic activities. To reach our goal, sample mineralogical composition and Ni solid speciation were determined by X-ray diffraction (XRD) technique and Scanning/Transmission Electron Microscope (SEM/TEM), and, on these bases, IEK-model was applied. This approach allowed to determine for the first time, the relative contribution of each Ni bearing phase to the total exchangeable pool, in other words the speciation of exchangeable Ni.

2. Materials and methods

2.1. Field settings and sampling

Together with Barro Alto, Niquelândia and Canabrava ultramafic complexes form a 350 km long discontinuous belt oriented SSW-NNE (Ferreira-Filho et al., 1994), that is one of the most prominent features of the geology of Neoproterozoic Brasilia Belt (Ferreira et al., 2010). In Fig. 1, the map of the area is reported. Niquelândia extends on an area of 40 km long and 20 km large in direction NE of Niquelândia city, while Barro Alto, at SW of Niquelândia, extending between about 100 km long and 20 km large (Dalvi et al., 2004; Pimentel et al., 2006). Because of this richness in metals, these areas are extremely exploited by mining companies.

Solid samples were collected during fieldwork in November 2011, both in the complex of Barro Alto and Niquelândia. The sampling points were chosen in order to assess the potential impact of Ni mining and metallurgy on Ni dynamic speciation. Two ore (S1 and L2) and one soil (BA0-10) samples were collected in Barro Alto, corresponding to the ones already described by Ratie et al. (2015): S1 and L2 are saprolitic and lateritic ores, respectively, characterized by a yellow–green color the first, and by dark red color the second. The soil sample, BA0-10, correspond to a UM soil horizon of brown color, collected between 0 and 10 cm depth. In Niquelândia, one soil representative of pristine ultramafic soils was collected between 2 and 10 cm depth (NIQS7), and one ultramafic soil (NIQS2) was collected close to the settling pond storage basin of fly black ashes (FBA), between 2 and 10 cm depth, both of them showing a dark brown color. FBA are secondary products of pyrometallurgical activity, which still contain up to 1.2 at% of Ni (Zelano et al., 2013). Currently, at both smelting sites FBA from the calcination furnaces is collected and recycled in the smelting process (mixed with the ore), because it contains high levels of Ni. In spite of a preliminary compaction of the settling pond bottom where FBA are stored, the latter can be directly in contact with the surrounding environment. Thus, they can represent an important input of anthropic Ni as a new Ni bearing phase, which has been proved to modify its availability (Zelano et al., 2013). Therefore, an aliquot of FBA was collected within the dumps.

Soil and ore sample were sifted at 0.45 cm and first air dried and then dried at low temperature (45 °C) in an oven for 48 h. Experiments were performed in triplicate.

2.2. Chemical and mineralogical composition

2.2.1. Total content

Total Ni content of soil samples were determined by X-ray fluorescence (XRF) using Panalytical X fluorescence spectrometer equipped with Energy Dispersive Minipal 4 (Rh X-Ray tube-30 kV-9W) at a resolution of 150 eV (Mn Kα). Pellets of soil samples were prepared in triplicate by mixing soil and resin in 5:1 weight ratio. Reported results are an average of the three measurements. The content of total organic carbon (TOC) was determined according to ISO 10694 standard using CHNS Automatic Elemental Analyzer (Thermo Flash 2000).

2.2.2. Mineralogical composition and Ni bearing phases

The mineralogical composition of the samples was determined by X-ray diffraction (XRD) analysis on a PANalytical X'Pert PRO diffractometer with Co Ka (at 40 kV 40 mA) for Fe-rich samples and a PANalytical Empyrean with Cu Ka radiation (at 45 kV 40 mA) for the others, at the X-Ray diffraction Platform of Paris Diderot University. XRD patterns were obtained by scanning powders from 3 to