

Dissolution kinetics of Ni-phyllsilicates from the Falcondo Deposit, Dominican Republic

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INTRODUCTION

Ni-phyllsilicates, commonly grouped under the name of “garnierites”, are significant nickel ores found in hydrous silicate-type Ni-laterite deposits worldwide, formed by weathering of ultramafic rocks. Garnierites consist of one or more fine-grained nickel-magnesium phyllsilicates, including serpentine, talc, sepiolite, smectite and chlorite. They often occur as poorly crystalline micron-scale mixtures (e.g. Brindley, 1978).

In the Falcondo Ni-laterite (Dominican Republic), garnierites are found within the saprolite horizon, mainly as fracture-fillings and thin coatings on joints. The Falcondo deposit occurs over the serpentinised Loma Caribe peridotite belt, which is about 4–5 km wide and extends NW for 95 km. The unweathered ultramafic protoliths are clinopyroxene-rich harzburgite, lherzolite, fine-grained black dunite and sheared serpentinite. In general, the major constituents of the host ultramafic rocks are olivine (Fo_{89–92}, 0.35–0.55 wt.%NiO), orthopyroxene (En_{89–92}, NiO 0.1 wt.%) and clinopyroxene (e.g. Lewis et al., 2006).

During laterisation, the primary ferromagnesian silicates, containing small amounts of Ni, are altered to Ni-enriched secondary phases. Mg is solubilised and leached out of the weathering profile, whereas Fe is oxidised and residually concentrated as goethite in the limonite horizon. The Ni released from the silicates is retained in goethite. This Ni may subsequently be leached by percolating acidic solutions to deeper levels in the profile. The Ni is incorporated first in the saprolite Ni-bearing serpentines (Pelletier, 1996). Once the Ni-serpentines are saturated,

the excess Ni precipitates as Ni-Mg-phyllsilicates in fractures near the water table (e.g. Freyssinet et al., 2005). Thus, the Fe in saprolite serpentines is residual, and the Ni is imported from the upper lateritic levels (Trescases, 1973). The precipitation is caused by a sudden change in Eh/pH of the solution. The high stability of the octahedrally coordinated Ni²⁺ ion (Burns, 1970) favours the formation of nickeliferous trioctahedral phyllsilicates (e.g. Trescases, 1975).

In general, the stability of Ni-bearing minerals in lateritic environments is determined by the Eh, pH, and chemical composition of permeating groundwater (e.g. Trescases, 1973). In an Al-free system, such as in the Falcondo profile, the stability of serpentine-, talc- and sepiolite-like garnierites is controlled by the activity of silica (Galí et al., 2012). The precipitation of Ni-phyllsilicates occurs as a succession of mineral phases progressively enriched in Ni and Si, because silica activity increases with time and through the profile. Thus, the first garnierites to precipitate are serpentine-like, followed by talc-like and sepiolite-like (sepiolite-falcondoite) (Galí et al., 2012).

Previous results show that Dominican Ni-phyllsilicates consist of serpentine-, talc- and sepiolite-like phases (e.g. Villanova-de-Benavent et al., 2014). Serpentine- and talc-like garnierites mostly occur as mixtures at the nano-scale (Villanova-de-Benavent et al., 2011). Also, Ni has been found to have a large affinity for the talc-like phases (e.g., Soler et al., 2008; Galí et al., 2012). These Ni-phyllsilicates, which can be recognised optically by different shades of green, were characterized by X-ray powder diffraction (XRD), Scanning Electron Microscopy (SEM), EMP and

Transmission Electron Microscopy (TEM-AEM) (e.g. Villanova-de-Benavent et al., 2011, 2014).

A first study of the dissolution kinetics of a garnierite from Loma de Hierro (Venezuela) was performed by Soler et al. (2008). It was found that garnierite dissolution rate decreases with increasing pH. The dissolution showed to be congruent at pH > 5 and incongruent at pH < 5, indicating different contributions from serpentine and talc to the total dissolution rate (the serpentine component tends to dissolve faster under more strongly acidic conditions).

The overall aim of this work is to extend the study of the kinetics of garnierite dissolution in terms of the structures and compositions of the reacting garnierites. The dissolution kinetics of the selected garnierites has been studied under acidic conditions (pH 3 and 5) by means of non-stirred flow-through experiments.

EXPERIMENTAL SETUP

Four representative samples were selected for this study, which correspond to mixtures of (i) serpentine- and talc-like garnierites, and (ii) sepiolite-like garnierites. They have already been described and analysed in detail by Villanova-de-Benavent et al. (2014).

The four samples were characterised by powder XRD and EMP before the experiment. The samples were ground and sieved to obtain particle sizes between 53 and 106 µm (Figure 1). In the experiments, a known mass of ground garnierite was placed in a reaction cell. Solution was circulated at an average rate of 0.04 mL/min (details in Cama and Acero, 2005).

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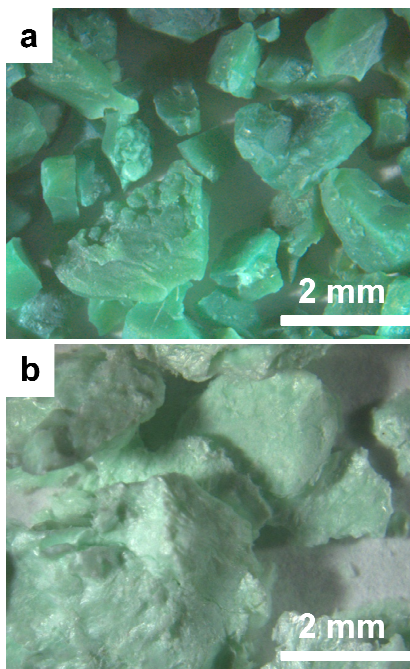


fig. 1. Samples used in the experiments, (a) mixed Ni-talc-serpentine and (b) Ni-rich sepiolite.

Input solutions were prepared with Millipore MQ water ($18 \mu\text{mhos}\cdot\text{cm}^{-1}$) and reagent grade HCl (Merck). The pH of the output solution was measured with a ThermoScientific Orion® combined glass electrode at room temperature ($\sim 25^\circ\text{C}$). Concentrations of Si, Ni, Mg, Fe and Al were measured by Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), using a Thermo Jarrel-Ash spectrometer equipped with a CID detector.

RESULTS AND DISCUSSION

Two samples are mixtures of serpentine- and talc-like garnierites with different talc fractions and Ni contents. The other two are sepiolite-like garnierites also with different Ni contents.

The mixed garnierites have the average structural formulae of $(\text{Ni}_{2.41}\text{Mg}_{0.56})\text{Si}_{2.71}\text{O}_{3.54}(\text{OH})_{3.27}\cdot 0.36\text{H}_2\text{O}$ and $(\text{Ni}_{1.83}\text{Mg}_{1.17})\text{Si}_{3.54}\text{O}_{6.43}(\text{OH})_{2.45}\cdot 0.78\text{H}_2\text{O}$, and a X_{talc} of 0.36 and 0.78, respectively. The compositions of Ni-sepiolites are $(\text{Mg}_{3.41}\text{Ni}_{0.25}\text{Fe}_{0.05})(\text{Si}_{6.10}\text{Al}_{0.01})\text{O}_{15}(\text{OH})_2\cdot 6(\text{H}_2\text{O})$, and $(\text{Mg}_{2.38}\text{Ni}_{1.35})(\text{Si}_{6.12}\text{Al}_{0.01})\text{O}_{15}(\text{OH})_2\cdot 6(\text{H}_2\text{O})$.

The steady-state dissolution rates, normalized to the final reactive surface area, are higher at $\text{pH} \approx 3$ (between 10^{-12} and $10^{-13} \text{ mol m}^{-2} \text{ s}^{-1}$) than at $\text{pH} \approx 5$

(between 10^{-13} and $10^{-14} \text{ mol m}^{-2} \text{ s}^{-1}$).

The garnierite with $X_{\text{talc}} = 0.36$ (2.41 apfu Ni) shows slightly lower dissolution rate than the one with $X_{\text{talc}} = 0.78$ (1.83 apfu Ni) at $\text{pH} \approx 5$. However, at $\text{pH} \approx 3$ the dissolution rate based on Ni release is higher for the garnierite with $X_{\text{talc}} = 0.36$.

At $\text{pH} \approx 5$, the Ni-bearing sepiolite (0.25 apfu Ni) shows higher dissolution rate than the Ni-rich sepiolite (1.35 apfu Ni). At $\text{pH} \approx 3$, the release of Ni is larger than that of Mg and Si in the sepiolite with higher Ni content.

CONCLUDING REMARKS

The preliminary results show that the dissolution rates of the garnierites from the Falcondo deposit decrease with increasing pH. This behaviour is similar to that obtained in garnierites from Loma de Hierro (Venezuela; Soler et al., 2008).

It is currently expected to complement these results with data from experiments performed on garnierites with a wider range of talc fractions and Ni contents. All together, they will provide a more complete overview of the dissolution kinetics of garnierite in lateritic environments.

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