Ni ENRICHMENT AND STABILITY OF Al-FREE GARNIERITE SOLID-SOLUTIONS:
A THERMODYNAMIC APPROACH

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Abstract—Garnierites represent significant Ni ore minerals in the many Ni-laterite deposits worldwide. The occurrence of a variety of garnierite minerals with variable Ni content poses questions about the conditions of their formation. From an aqueous-solution equilibrium thermodynamic point of view, the present study examines the conditions that favor the precipitation of a particular garnierite phase and the mechanism of Ni-enrichment, and gives an explanation to the temporal and spatial succession of different garnierite minerals in Ni-laterite deposits. The chemical and structural characterization of garnierite minerals from many nickel laterite deposits around the world show that this group of minerals is formed essentially by an intimate intermixing of three Mg-Ni phyllosilicate solid solutions: serpentine-népouite, kerolite-pimelite, and sepiolite-falcondoite, without or with very small amounts of Al in their composition. The present study deals with garnierites which are essentially Al-free. The published experimental dissolution constants for Mg end-members of the above solid solutions and the calculated constants for pure Ni end-members were used to calculate Lippmann diagrams for the three solid solutions, on the assumption that they are ideal. With the help of these diagrams, congruent dissolution of Ni-poor primary minerals, followed by equilibrium precipitation of Ni-rich secondary phyllosilicates, is proposed as an efficient mechanism for Ni supergene enrichment in the laterite profile. The stability fields of the solid solutions were constructed using [log \(a_{SiO_2}(aq)\), log \(\left(\frac{a_{Mg^2+} + a_{Ni^2+}}{a_{Al^3+}}\right)^{\frac{1}{2}}\)] (predominance) diagrams. These, combined with Lippmann diagrams, give an almost complete chemical characterization of the solution and the precipitating phase(s) in equilibrium. The temporal and spatial succession of hydrous Mg-Ni phyllosilicates encountered in Ni-laterite deposits is explained by the small mobility of silica and the increase in its activity.

Key Words—Garnierites, Kerolite-Pimelite, Ni-laterite, Sepiolite-Falcondoite, Serpentine-Népouite, Stability.

INTRODUCTION

Nickel laterites are regolith materials derived from ultramafic rocks (Trescases, 1975; Golightly, 1981; Brand et al., 1998). Weathering of the rocks results in enriched horizons, so that minor elements such as Ni, Co, and Mn contained in the unaltered parent rock become enriched in the laterite profiles (Brand et al., 1998; Freyssinet et al., 2005; Golightly, 2010). An iron cap (ferricrete or duricrust) is often found at the top of the weathering profile and the cap grades downward through a transitional zone of limonite to a saprolite zone transitional into bed rock. Saprolite is a zone of rapid change and of maximum supergene enrichment of nickel. The protoloth or bedrock is mainly dunite, harzburgite, or lherzolite and their serpentinized equivalents.

Following Golightly (1981), Ni laterites are developed from: (1) unserpentinized peridotite (e.g. Poro, New Caledonia; Soroako West, Indonesia); (2) partially serpentinized peridotite (e.g. Falcondo Mine, Dominican Republic); or (3) totally serpentinized parent rock (e.g. Bonsora, Soroako East, Indonesia). As an example, selected analyses for the most important primary Ni-carrying minerals at Falconde (Table 1) indicate that these minerals are mainly olivine and ‘oceanic’ serpentine. The fate of Ni can be tracked through the different values of the atomic ratio of Fe/Ni in these minerals. Initially, in olivine, Fe/Ni \(\approx\) 19. In oceanic serpentines this value is slightly smaller, indicating that some of the Fe is relocated in other phases like maghemite, which is readily hydrated to goethite. Goethite is able to incorporate or attach Ni (Manceau et al., 2003). The nickel contained in the limonite horizon and in primary serpentines is transferred to percolating meteoric solutions, and moves downward through the profile, being concentrated with Si and Mg within the underlying saprolite horizon to form secondary Ni-enriched phyllosilicates.

In many Ni lateritic deposits of the hydrous silicate type, the lower saprolite is the ore horizon, and the ore minerals are mainly nickelooan varieties of serpentine,