Mineralogical controls on the Ni and Co recovery from HCl leaching of laterites

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ABSTRACT

The global demand for nickel (Ni) and cobalt (Co) is expected to increase significantly. Laterite deposits are a promising source of these metals. However, current processing methods (e.g., smelting or high-pressure acid leaching, HPAL) are energy-intensive and potentially environmentally hazardous. The ENICON project proposes a novel HCl-based processing route, but the complex mineralogy of laterite ores requires a thorough characterization of both inputs and outputs of the leaching stages. This study reveals the presence of Ni-bearing minerals like asbolane (Mn-hydroxide), nimite (Ni-chlorite), and népouite (Ni-serpentine) in the high-grade samples, with an additional contribution from goethite, chlorite, and serpentine. Cobalt is mainly hosted by asbolane, with smaller amounts in goethite and chromite. HCl leaching effectively dissolves most Ni-Co-bearing minerals, but not chromite and this impedes full Co recovery. In-situ mineral chemistry assists in quantifying the metal deportment in the Ni-Co-bearing minerals. This forensic geometallurgical approach minimizes metal losses by investigating the causes of flowsheet underperformance.

Keywords: Nickel laterites, process mineralogy, critical raw materials, battery metals, forensic geometallurgy

1 Introduction

The global demand for nickel (Ni) and cobalt (Co) is expected to further increase in the near future, mainly due to their use in lithium-ion batteries (Gregoir and Van Acker, 2022; IEA, 2021). Although new battery technologies and recycling may help to buffer this demand, mining and processing of these metals will still be required for global decarbonization efforts. Hence, it is paramount to develop new technologies that decrease greenhouse gas emissions and environmental impacts of the Ni-Co supply chain. The Horizon Europe ENICON project (https://enicon-horizon.eu/) responds to this issue by enhancing the potential of Ni/Co resources within Europe as well as by developing a more sustainable HCl-based processing route for these materials. Nickel and cobalt deposits mainly occur in magmatic sulfide systems and laterites (Horn et al., 2021; Mudd and Jowitt, 2022). Lateritic deposits constitute more than half of the global nickel resources (Butt and Cluzel, 2013; Mudd and Jowitt, 2014) and currently represent the majority of the production (Mudd and Jowitt, 2022; USGS, 2024). However, the exploitation and processing of lateritic ores exhibit the largest environmental footprint in the sector (Bartzas and Komnitsas, 2024, 2015; Jessup and Mudd, 2008; Mudd, 2010). Additionally, the mineralogy of laterites is often complex (Andersen et al., 2009; Elias, 2002; Gleeson et al., 2004; Tupaz et al., 2020; Villanova-de-Benavent et al., 2014) and directly affects the processing efficiency and its energy requirements (Stanković et al., 2022; Watling et al., 2011). Therefore, a thorough characterization of both inputs and outputs of the processing stages is required to understand the mineral features that enhance or impede the efficient extraction of Ni and Co from laterites. This contribution assesses the mineralogical constraints for extracting Ni and Co from laterites in the HCl-leaching route investigated by the ENICON project. The bulk properties and mineralogy of lateritic ores are compared to those from the solid residues after leaching to understand where losses are occurring.

2 Materials and methods

2.1 Samples

Four lateritic deposits, two saprolitic laterites and two limonitic laterites, were investigated (Figure 1). The laterite samples were kindly provided by the industrial partners of ENICON and consisted of run-of-mine (ROM) ores sampled from the stockpiles that feed the partners' processing plants. Ore samples were dried in an oven at 40 °C to remove any moisture before being screened and jaw crushed until a top size below 1 mm was achieved. The crushed material was split in a rifle splitter, with part of the material sent for leaching and part further split into smaller aliquots for characterization. The leaching residues were obtained after leaching the crushed ore samples with 8 mol/L HCl for 3 hours at 95 °C and a solid-to-liquid ratio of 100 and 200 g/L. After filtration of the pregnant leaching solution containing the dissolved metals, the retained solid residues were washed with distilled water to remove any excess acid.

2.2 Bulk characterization

For the quantification of the samples' elemental composition, the ore samples and leaching residues were ground to a powder (< 64 µm) in a ball mill. Geochemical analyses were performed after digesting the samples using lithium metaborate fusion or four acid digestion procedures. Major and minor elements were measured by inductively coupled plasma optical emission spectroscopy (ICP-OES) in a Varian 720ES system at the KU Leuven, Belgium. Trace elements were measured by inductively coupled plasma mass spectroscopy (ICP-MS) in an Agilent 7700x ICP-MS system at the KU Leuven. The bulk particle size distribution of the materials was measured using a Beckman Coulter LS 13 320 laser diffraction particle size analyzer coupled with an Aqueous Liquid Module (ALM) sample feeder at the KU Leuven.

2.3 Mineral/Particle characterization

Ore and leaching residue samples were mixed with graphite powder and mounted in Epoxy resin before being measured by Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN) at the Camborne School of Mines (CSM), University of Exeter, England. The instrument is a Quanta 650F FEI (Thermo Fisher) field emission gun scanning electron microscope (FEG-SEM) with two energy dispersive X-ray spectroscopy (EDS) detectors (6030 SDD Bruker). Quantitative *in situ* mineral chemistry was obtained by wavelength dispersive X-ray spectroscopy (WDS) in a JEOL JXA8200 electron probe microanalyzer (EPMA) at CSM. Analyses were carried out using a 15 nA electron beam accelerated to 15 keV and a 1 µm spot size. The ZAF matrix correction was applied to translate the raw signal into the composition of unknown samples.
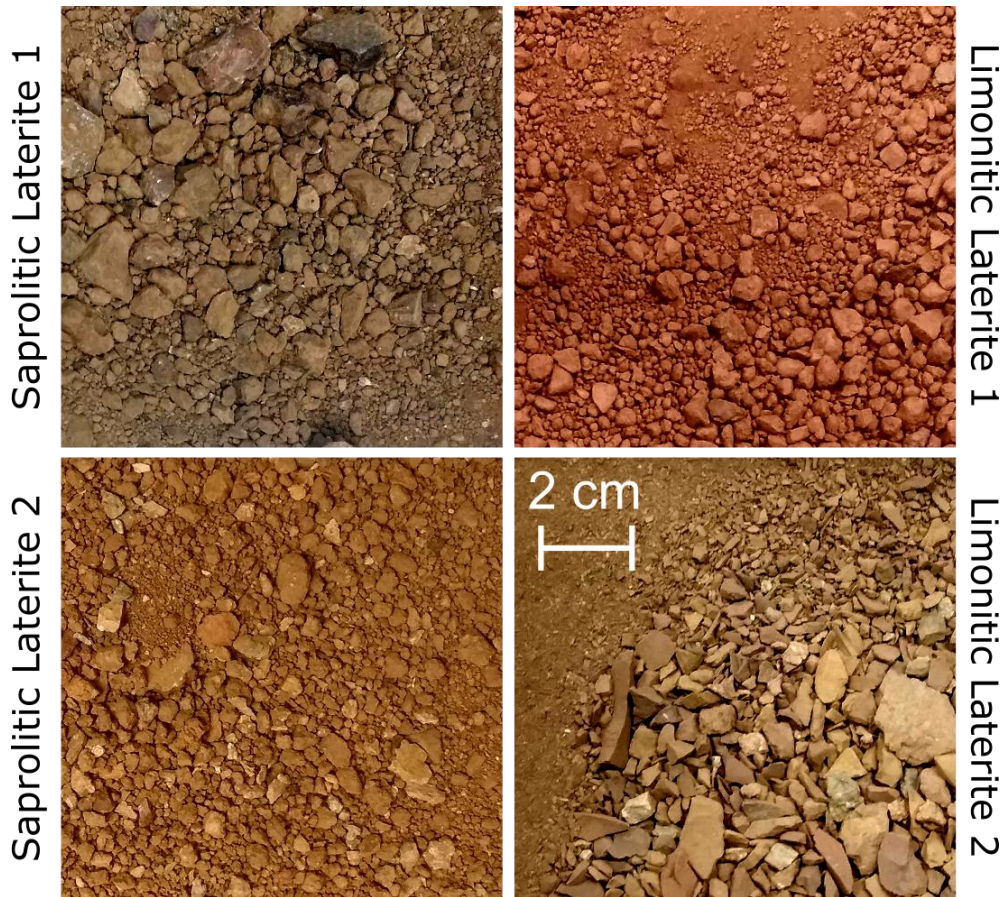
Figure 1: General aspect of the lateritic ores sampled from stockpiles at the mine sites. The same scale (shown on the image at the lower right) applies to all images.

3 Results

3.1 Bulk geochemistry

The laterite ores (saprolitic laterite 1, SL1; limonitic laterite 1, LL1; saprolitic laterite 2, SL2; and limonitic laterite 2, LL2) are mainly rich in SiO_2, Fe_2O_3, Al_2O_3, and MgO, with CaO also important in some cases (Table 1) Bulk nickel content varies from around 1 to 2 mass%, whereas the cobalt content ranges from 250 to 1000 ppm.

Compared to the ores, the leaching residues are enriched in SiO_2 and CrO_2, with similar concentrations of Co, Zn, and V (Table 2). The Ni concentration in all leaching residues is several orders of magnitude lower than in the ores, whereas Co mostly shows similar ranges between ores and residues (Figure 2). The exception is sample SL2, i.e. the sample with the highest grade, where the Co concentration of the residue is significantly lower than in the ore.

Table 1: Bulk major element composition (oxide mass%) of laterite ores and leaching residues investigated in this study.

Sample	SiO_2	TiO_2	Al_2O_3	Cr_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	LOI	Total (%)
SL1	37.0	0.02	1.0	1.2	22.1	0.3	15.1	8.2	0.02	0.04	0.02	14.6	99.5
LL1	36.1	0.3	6.5	2.2	38.9	0.2	4.8	2.2	0.06	1.1	0.01	4.9	97.3
SL2	36.4	0.06	4.2	1.3	32.0	1.0	5.9	3.4	0.02	0.06	0.02	15.0	99.4
LL2	14.6	0.2	5.5	1.9	53.9	0.5	3.0	4.4	0.04	0.1	0.05	10.8	94.9
Res_SL1	83.0	0.03	0.8	2.1	1.0	0.1	1.2	0.2	0.04	0.05	< 0.01	n.a.	88.3
Res_LL1	79.9	0.2	4.2	4.3	3.2	0.1	1.6	0.1	0.1	0.9	< 0.01	n.a.	94.4
Res_SL2	84.0	0.06	2.2	1.8	1.4	0.02	0.7	0.1	0.02	0.02	< 0.01	n.a.	90.1
Res_LL2	68.7	0.3	6.0	5.9	2.8	0.3	1.9	0.2	0.2	0.3	0.01	n.a.	86.5

LOI = loss on ignition; n.a. = not analyzed

Table 2: Minor and trace element concentrations (ppm) of elements of interest in laterite ores and leaching residues

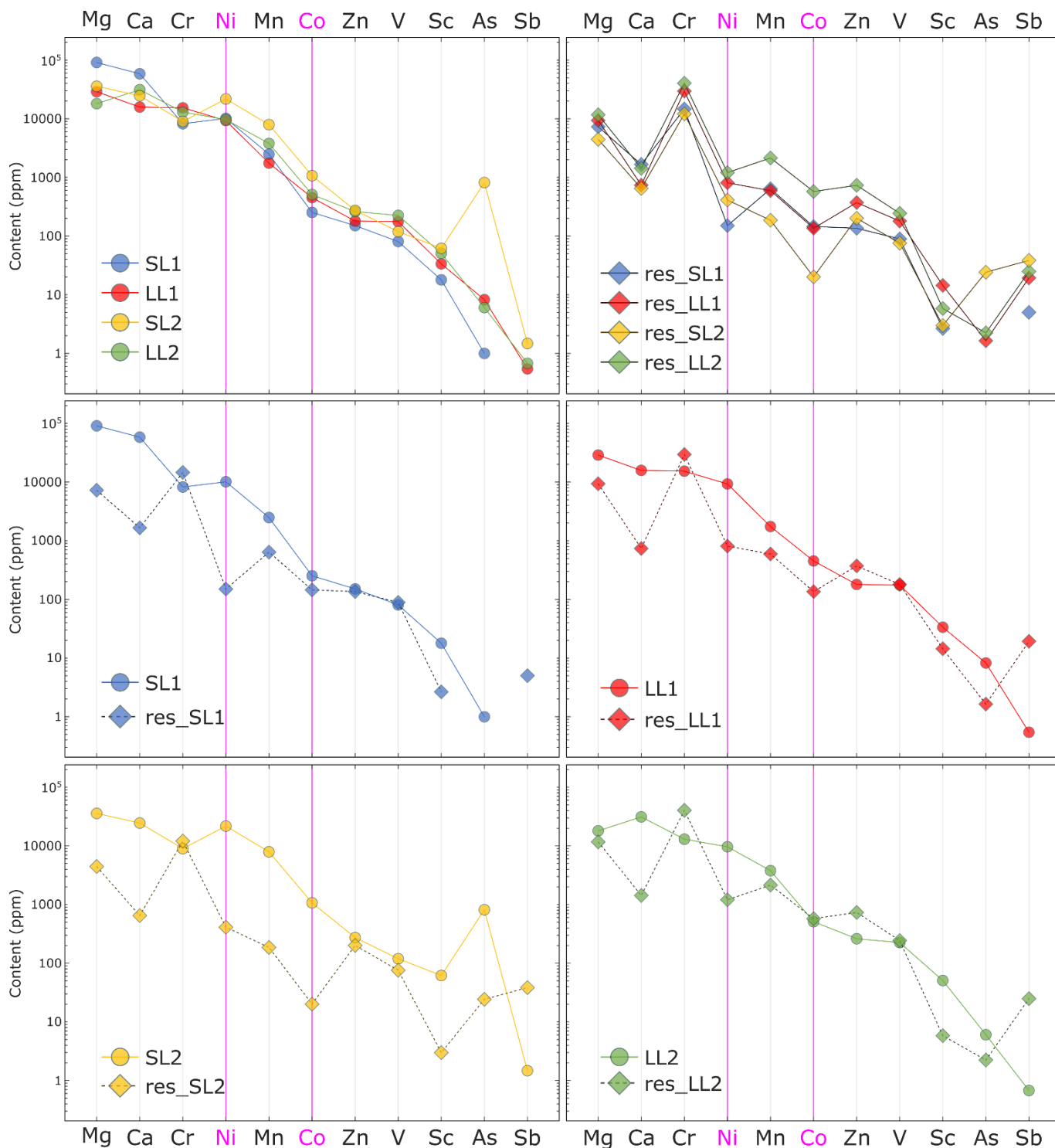| Sample	Ni	Co	S	Zn	V	Cu	Sc	Sr	Y	As	Pb	Sb
SL1	10113	253	< 40	151	81	21	18	13	0.9	1	2	< 0.1
LL1	9290	452	529	180	176	33	34	44	16	8	8	0.5
SL2	21724	1069	273	274	119	47	62	61	11	815	2	1.4
LL2	9646	509	200	262	224	64	51	24	7	6	7	0.7
Res_SL1	150	145	< 2	136	89	5	3	5	0.7	< 0.3	1	5
Res_LL1	809	136	512	372	180	17	14	5	19	2	1	19
Res_SL2	410	20	70	201	76	5	3	5	0.6	23	1	38
Res_LL2	1206	574	37	733	244	18	6	20	6	2	2	25

Figure 2: Semi-log line plots showing the concentration of some relevant elements in ENICON laterite ore samples and respective leaching residues. Missing symbols represent elements below the detection limit.

3.2 Particle size distribution (PSD)

The laterite ore samples (feed to leaching, after crushing) present P80 between 200 and 300 µm, and P10 between 0.5 and 1 µm (Figure 3). The sample SL2 shows smaller particle sizes than the other laterites, especially in the coarser range (P80 at 40 µm). The leaching residues are more uniform in size distribution, with P80 between 20 and 40 µm, and P10 between 1 and 3 µm.
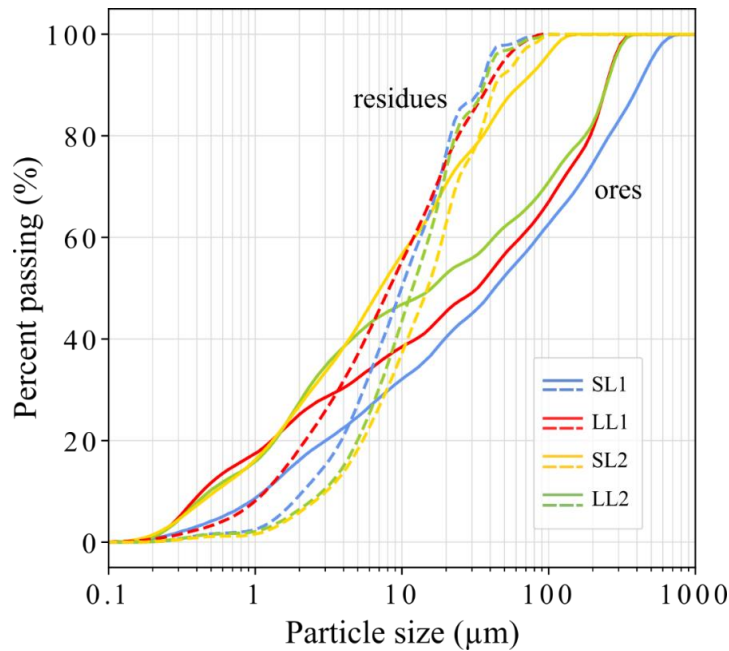

Figure 3: Particle size distribution (PSD) of laterite ores (solid lines) and leaching residues (dashed lines).

3.3 Mineralogy

Scanning electron microscope (SEM)-based automated mineralogy (QEMSCAN) reveals the Ni-bearing minerals asbolane (Mn-hydroxide), nimite (Ni-chlorite), and népouite (Ni-serpentine) in the samples (Figure 4), especially in SL2 (the sample with the highest Ni and Co concentration). Although other samples do not show substantial concentrations of these phases, they contain considerable amounts of Mg-Fe silicates (serpentine group minerals), chlorite, and iron oxides (goethite and or hematite), which contain minor amounts of Ni or Co (see below). The leaching residues are largely composed of quartz, chromite, with other silicates occurring in variable but often minor proportions.
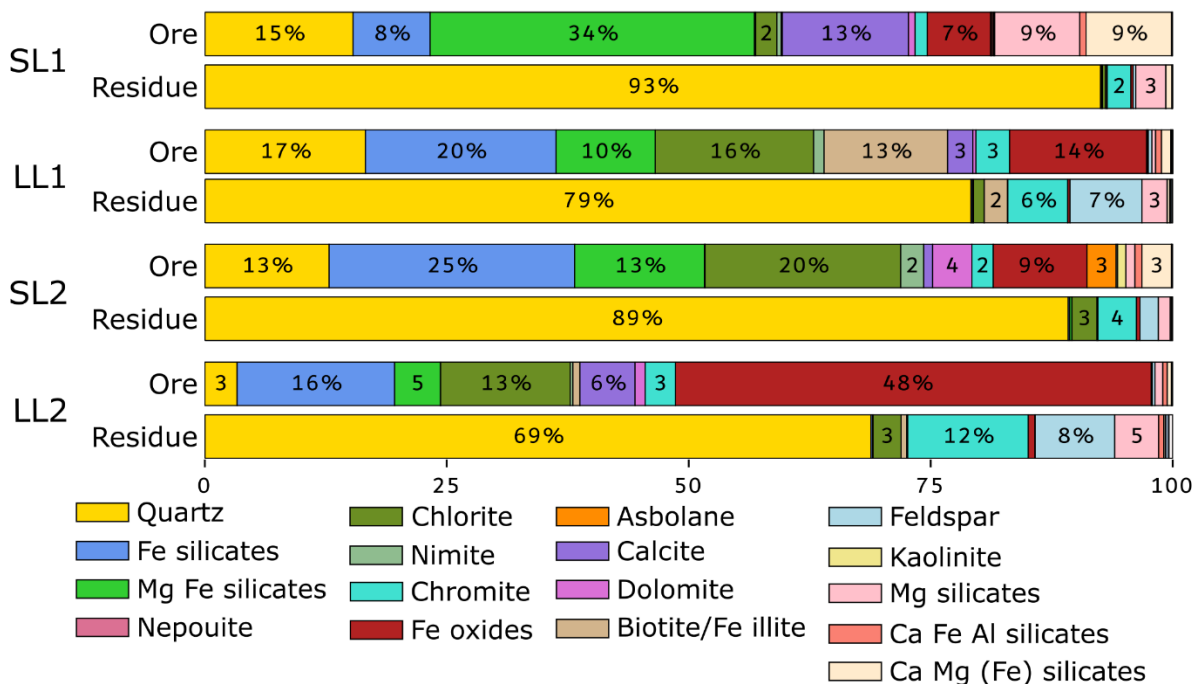

Figure 4: Modal mineralogy of laterite ores and leaching residues obtained by SEM-based automated mineralogy.

3.4 Mineral chemistry

Nickel and cobalt occur in variable concentrations in several minerals in the laterite ores (Figure 5). Solid solutions are a common feature in those samples and minerals are combined into a single group to facilitate comparisons. Only in the cases where a separated compositional group is observed, as in the case of nimite (Ni-chlorite) and népouite (Ni-serpentine), those are distinguished from the main group of chlorite and serpentine, respectively. High-grade Ni and Co phases (> 10% NiO or 5% CoO) are observed only in the SL2 sample, represented by asbolane, nimite, and népouite, as indicated by QEMSCAN. Cobalt is mainly hosted by asbolane, with some contributions from chromite and goethite.
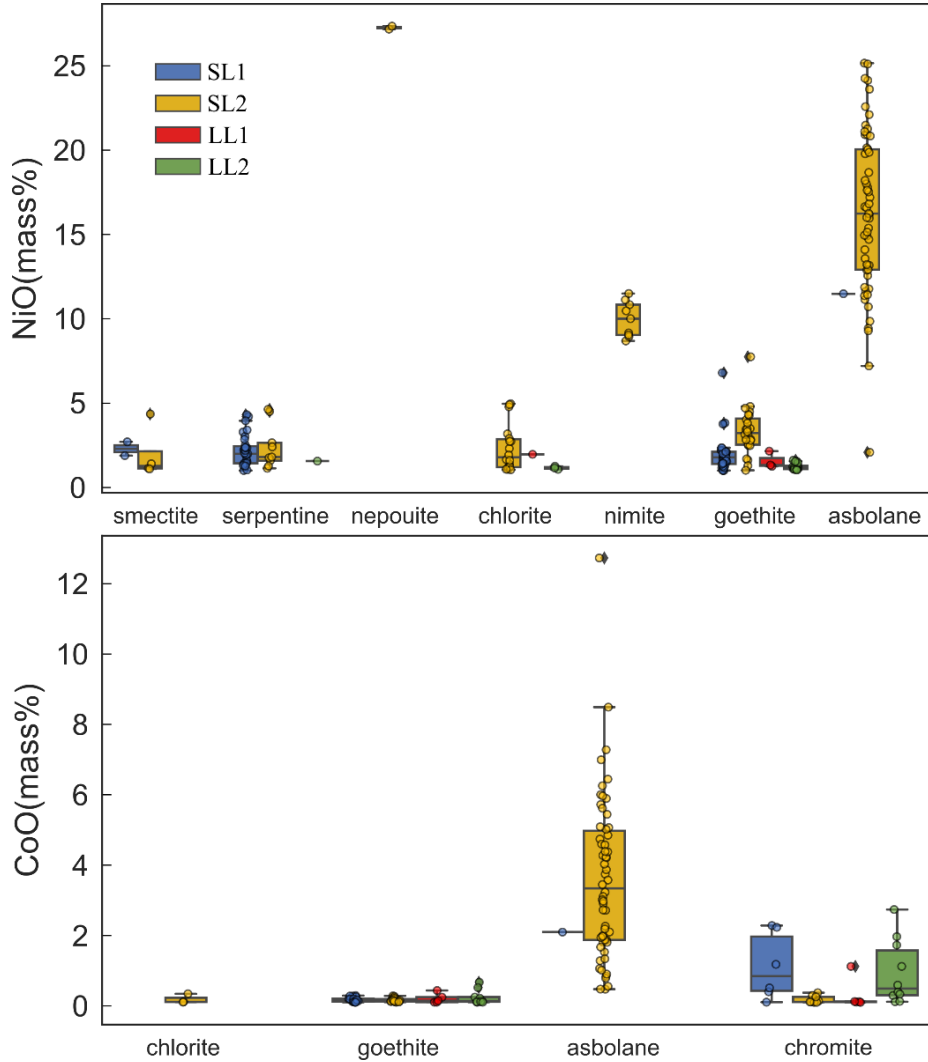

Figure 5: CoO and NiO concentration (mass%) in the ENICON laterite ores. For samples and minerals not shown, the concentration was below the detection limit (around) and, therefore, is not reported.

4 Implications and Conclusions

The HCl leaching route developed in the ENICON project for processing laterite deposits is effective in extracting nickel from the ores. However, for cobalt, the picture is slightly more complicated. Both bulk geochemical and mineralogical data suggest that nickel-bearing ore minerals (Mg-Fe phyllosilicates, mainly serpentine and chlorite, and oxide-hydroxides, mainly asbolane and goethite) are fully dissolved during the HCl leaching stage. Therefore, nickel is quantitatively extracted from the mineral structures and reports to the leachate solution. Contrarily for Co-containing minerals, oxide-hydroxides (asbolane and goethite) effectively dissolve during leaching, but chromite is not attacked by HCl at the experimental conditions. Chromite contains up to 2.5% CoO (median at about 0.5%), thus retaining some of the cobalt in the solid residue. This interpretation correlates with the predominance of SiO_2 and Cr_2O_3 in the measured composition of the leaching residues and the occurrence of large amounts of quartz and chromite in these samples. Accordingly, all the elements hosted by chromite (Cr, Zn, V, and Co) report to the leaching residue and do not allow for quantitative cobalt recovery. To effectively extract both nickel and cobalt from laterite ores, the leaching of chromite in harsher conditions is required.

5 Acknowledgments

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