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UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

Å	Angstrom	min	minute
°C	degree Celsius	µm	micrometer
cm	centimeter	mA	milliampere
h	hour	pct	percent
kV	kilovolt	wt pct	weight percent

CHARACTERIZATION OF LATERITIC NICKEL ORES BY ELECTRON-OPTICAL AND X-RAY TECHNIQUES

By D. Chandra,[1] C. O. Ruud,[2] and R. E. Siemens[3]

ABSTRACT

The mineralogical constitution of a lateritic ore dictates the type of metallurgical process that can be used to extract valuable metals such as nickel and cobalt. To provide needed mineralogical information on the interrelationships of the metals contained in domestic laterites, the Bureau of Mines awarded a grant to Denver Research Institute to study the transition-type, low-grade laterites found in northern California and southern Oregon. For comparison, limonitic-type laterites from New Caledonia and the Philippines were also studied.

X-ray diffraction, electron microscopy, electron beam analysis, and conventional petrography were used to determine the mineralogical associations of nickel and cobalt in the laterites. Results showed that for both laterite types studied most of the nickel and minor amounts of cobalt are associated with the mineral geothite ($FeO(OH)$). Most of the cobalt and minor amounts of nickel are associated with a mixed manganese oxide (wad) mineral.

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INTRODUCTION

NICKEL RESOURCES AND DEMAND

Worldwide nickel occurrences of current commercial value are mainly in the form of either sulfides or laterites (3).[4] The resources from both types of deposits are estimated to total 70 million tons[5] of nickel in 7 billion tons of ore averaging 1 pct Ni (9). Laterites and sulfides differ not only in mineralogical composition and origin, but also in processing economy. At present, world nickel production is primarily (about 60 pct) from the sulfide ores.

The sulfide ores of current commercial value occur mainly in Canada, the U.S.S.R., and Australia. The Sudbury District of Ontario, Canada, has the largest sulfide ore deposit in the world and presently supplies nearly 50 pct of the primary nickel used in the United States. The reserves of the Sudbury deposit presently total more than 300 million tons of ore, containing about 1.5 pct Ni. Lateritic ores are found primarily in New Caledonia, Cuba, the U.S.S.R., the Philippines, Venezuela, the United States, Guatemala, and Australia. Small amounts of laterites are found in Albania, Yugoslavia, Greece, and India.

High-grade sulfide ores are available and readily concentrated. Low-grade lateritic ores cannot be readily beneficiated to produce high-grade concentrates, but must be exploited for the following reasons:

1. The majority of land-based nickel-bearing ores are in the form of laterites. In 1980, laterite sources accounted for only 46 pct of worldwide nickel production, but in future years, about 70 pct of total production is expected to come from laterite sources (1).

2. Worldwide demand for nickel is increasing rapidly, while nickel production is increasing very slowly. In 1982, the primary demand for nickel in the United States alone was 137,500 tons, and U.S. primary production was 3,456 tons. By the year 2000, it is anticipated that U.S. primary annual demand will be 250,000 to 360,000 tons (14). Domestically produced nickel will be sufficient to meet only a small part of this demand unless methods to recover nickel from low-grade domestic resources are developed. In addition to current minable resources, recent exploration has inferred a domestic laterite resource of about 217 million tons (13). Rest-of-world demand is expected to increase at a higher rate than in the United States. To meet the expected future demand, maximum utilization of all feasible nickel-bearing resources will be necessary.

GEOLOGY OF NICKEL-BEARING LATERITES

Nickel-bearing laterites are formed by weathering of serpentinized ultramafic rock (2, 19). The weathering process is quite complex, but it is basically a hydrolysis reaction that results in the depletion of silica and magnesia from silicate minerals and the subsequent concentration of Fe, Al, Ni, Cr, and some other minor constituents.

The lateritic nickel ores can be broadly classified into three main categories, as follows:

1. Nickeliferous limonitic ores which contain about 0.8 to 1.5 pct Ni, $\geq$ 40 pct Fe, about 0.6 Mg, and about 2.3 Si. The nickel-to-cobalt ratio is typically 10:1. Nickeliferous limonitic ores usually occur just below a hematitic cap, with the nickel disseminated in the fine iron minerals (11).

2. Transition ores which contain about 0.7 to 2.0 pct Ni, 20 to 40 pct Fe, 3 to 9 pct Mg, and 3 to 9 pct Si. The nickel-to-cobalt ratio is generally about 50:1

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[4] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

[5] "Tons" indicates short tons throughout this report.

but decreases sharply where there is manganese enrichment. The transition ores occur just below the nickeliferous limonitic ores with nickel disseminated in iron oxide and in some silicate minerals.

3. Serpentinous ores contain up to 3 pct Ni, 10 to 20 pct Fe, 9 pct Mg, and 9.4 pct Si. These ores occur just above the bedrock, with the nickel disseminated in the silicate minerals.

NEED FOR ADDITIONAL MINERALOGICAL DATA

At present, selective concentration of nickel from laterites is not economically possible. The total ore is treated during the extraction process, partially because of a lack of knowledge as to where the nickel is distributed in the various minerals present in the ore body. To make it possible to selectively concentrate nickel-bearing minerals and to improve nickel extraction from laterites, the mineral species present must be identified and characterized, and the phase or phases with which nickel is associated must be identified.

PREVIOUS INVESTIGATIONS

The literature describing the association of nickel with the minerals found in laterites is not very clear. On the basis of chemical analysis and mineralogy, Zeissink (19) hypothesized that the nickel is associated with goethite or an unidentified mineral phase intimately mixed with goethite. However, confusion still existed regarding the main mineral components which carry the nickel (15, 19). No substantial unambiguous evidence has appeared on the question, even in the last decade. Conventional research techniques for studies of laterite mineralogy have been bulk X-ray diffractometry, petrography, differential thermal analysis, and standard chemical analysis. However, lateritic ores are, for the most part, so fine that individual minerals cannot be identified by optical microscopy. Furthermore, uncertain mineral compositions and transformation characteristics of the minerals present do not permit straightforward interpretation of bulk chemical or differential thermal analyses.

OBJECTIVES OF THIS STUDY

In the investigation described here, the application of electron microscopy, electron beam microanalysis, selected area electron diffraction, and X-ray analysis were combined with conventional mineralogical methods (4) to yield an ore characterization that is more complete than those previously presented. The objectives were to characterize two domestic transition-type (high-magnesium) laterites and New Caledonian and Philippine limonitic-type ores (less than 1 pct Mg), and define the association of nickel and cobalt with laterite minerals. The study included mineral identification, elemental distribution determination, and particle shape and size analysis.

ACKNOWLEDGMENT

This report is based on work done by the Denver Research Institute, University of Denver, Denver, CO, under a Bureau of Mines grant (G0254028).

CHARACTERIZATION OF LATERITES

An outline of the experiments performed on the laterites is shown in figure 1. X-ray diffraction and chemical analyses were performed on the as-received ores prior to other experiments to provide a general idea of their elemental distributions. The laterites used in this study were domestic transition-type laterites obtained from Eight Dollar Mountain in southern Oregon and Pine Flat in northern California and limonitic-type laterites from New Caledonia and the Philippines.

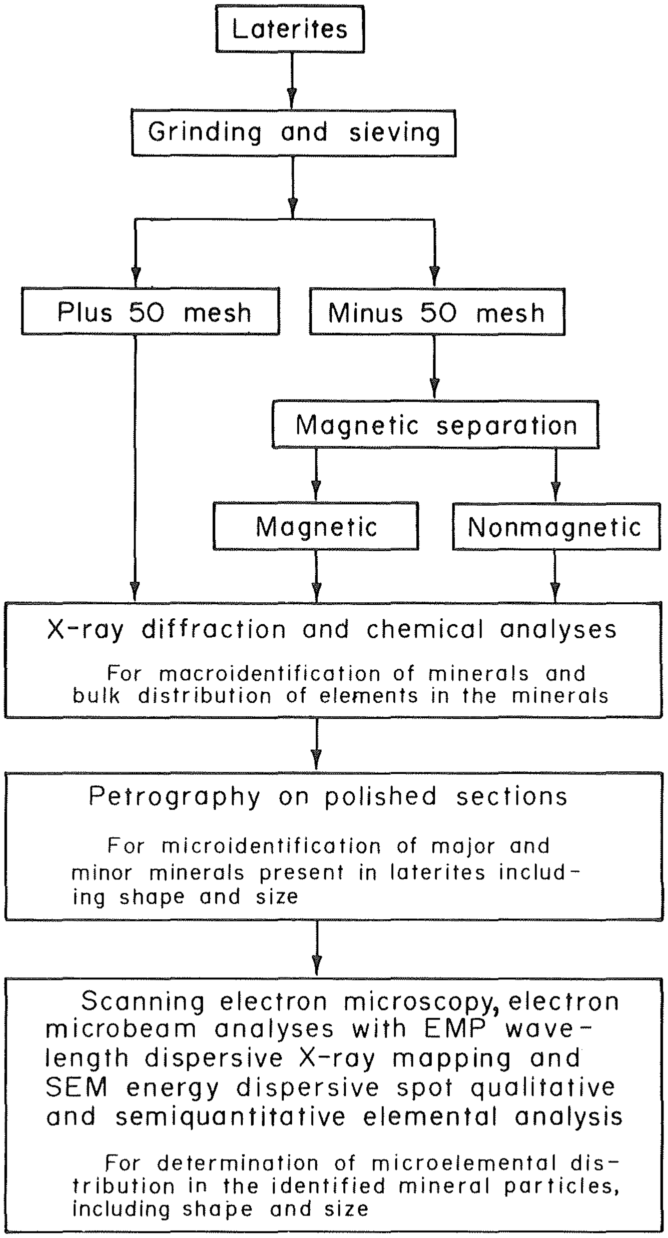

FIGURE 1. - Scheme of experiments for laterite characterization.

SAMPLE PREPARATION

For each of the laterites studied, as-received samples were thoroughly blended in a mixer and from the mix several representative samples were obtained by using the conventional cone and quarter splitting method. These samples were ground in a ball mill with precautions taken to minimize contamination by the balls during grinding. Each sample was ground for 15 min, the optimum time for obtaining a wide range of particle size distribution. The ground samples were then dry sieved on a 50-mesh screen. For each laterite, five samples split from each of the two fractions (plus 50 and minus 50 mesh) were obtained. Elemental analyses of each sample were obtained by wet-chemical techniques.

MAGNETIC SEPARATION

Experiments were conducted to determine the effects of dry and wet magnetic separation on the domestic transition-type laterites. Dry magnetic separation was ineffective; a wet separation method produced the best results (4).

X-RAY, ELECTRON BEAM, AND PETROGRAPHIC STUDIES

The first step in the characterization studies was to examine the laterites using both X-ray powder diffractometer scans and the Debye-Scherrer method (Straumanis film arrangement). A Phillips[6] X-ray diffractometer was used. Copper Kα radiation was used for the diffractometer scans, and chromium Dα radiation was used for the Debye-Scherrer method. Copper radiation was produced with a graphite monochromator at 45 kV and 40 mA; chromium radiation was produced at 30 kV and 25 mA using a vanadium filter.

Copper radiation was preferred over other radiations for the diffractometer because of the high-intensity X-ray peaks obtained at the higher power rating. The background produced by iron fluorescence was removed by the monochromator. Standard compaction methods were used for the diffractometer studies.

Polished sections of very fine particles were prepared using individual particles or clusters of particles. A careful selection of the epoxy was necessary because the sections were to be examined later under an electron microprobe. For microprobe examination, good thermal stability and low X-ray background are required.

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[6] Reference to specific products does not imply endorsement by the Bureau of Mines.

The first step in preparing the polished sections was to place a thin film of silicone grease on a flat tray coated with a fluorocarbon polymer. The tray was then preheated to 50° C, and randomly selected particles were sprinkled on a small area of it (about 1 cm diam). Two glass spacers were placed on either side of the particles. Three or four drops of heated epoxy were poured on the particles, and a frosted, thin-section slide was placed across the two glass spacers. The epoxy adhered to the frosted slide and hardened in about 1 h, encapsulating the particles. The thin sections were polished with 0.25-µm diamond-polishing compound and cleaned ultrasonically.

Petrographic examinations of the minerals in the laterites were performed, and the phases associated with the particles were identified by color, morphology, reflectivity, and surface texture. The characteristic features of the different mineral phases were checked using standard minerals, or synthetic materials in some cases (16-17).

ELECTRON MICROSCOPIC AND ELECTRON MICROPROBE STUDIES

Samples to be examined with the scanning electron microscope (SEM) or electron microprobe were prepared by removing the immersion oil with xylenes and evaporation coating the surface with a thin film of carbon. High-resolution microscopic examination, along with X-ray microanalysis of the very fine particles, was performed with an AMR-900 (Advanced Metals Research Corp.) SEM equipped with a Kevex energy dispersive multichannel analyzer. The SEM used has a resolution of 100A. The X-ray spectrum for each particle was displayed on a cathode-ray tube (CRT) and recorded on an X-Y recorder.

The SEM was also used, in an X-ray line-scan mode to examine the distribution of elements in individual particles and clusters of particles. One or more X-ray line scans could be superimposed on a scanning electron micrograph of the particle or particles (using the y-axis modulation on the CRT) to facilitate interpretation. The X-ray line scans were recorded on one or two micrographs, depending on the number of elements present in the particles. The locations of all the elemental X-ray line scans across the particle(s) were shown in a micrograph using secondary electron-line scans. A background line scan of the continuous radiation was made for all particles as a reference X-ray scan. The lower detection limit of the X-ray energy dispersive unit was dependent upon the matrix of the element in question and the beam current. The analyses obtained were semiquantitative.

The microbeam analyses were performed with a Norelco AMR-3 electron microprobe (EMP) equipped with a wavelength dispersive vacuum spectrometer. The spectrometer was used to obtain raw data for quantitative elemental analyses. Semiquantitative elemental spot analyses were performed on selected particles. The data were refined using a modified Colby method (8) that corrected for X-ray fluorescence, X-ray absorption, and atomic number effects.

RESULTS AND DISCUSSION

PHYSICAL AND CHEMICAL CHARACTERIZATION

The domestic transition-type and imported limonitic laterites characterized in this study represent two of the three major lateritic nickel ore categories. All of the laterites examined were typical yellowish brown in color. The chemical analyses reported in table 1 show that in general, the laterites were high in iron (30 to 47 wt pct) and low in nickel (0.8 to 1.2 wt pct), cobalt (0.08 to 0.23 wt pct), and chromium (1.3 to 3.1 wt pct). The magnesium and silicon concentrations were considerably higher in the transition materials than in the limonitic materials. The higher levels of these elements, along with higher aluminum levels, pose a serious problem in the processing of transition-type

TABLE 1. - Chemical analyses of the lateritic ores studied, weight percent

Laterites	Metals								
	Ni	Co	Fe	Al	Mg	Si	Cr	Ca	Cu
Transition type:									
Eight Dollar Mountain (OR).	1.20	0.08	30.60	5.03	3.93	11.22	1.32	0.14	ND
Pine Flat (CA)............	.82	.23	32.80	2.38	4.26	8.74	2.19	.29	0.05
Limonitic type:									
New Caledonia.............	1.00	.10	45.00	3.50	.70	4.10	3.10	.18	.01
Philippines...............	1.15	.13	47.40	1.43	.75	2.56	2.16	ND	ND

ND Not determined.

laterites (5); undesirable refractory complex silicates form during reduction roasting (7). Thus, the quality of a lateritic ore is governed not only by the nickel content but also by its Mg, Si, and Al contents.

MINERAL IDENTIFICATION

The association of nickel with the minerals present in laterites was determined with the combined use of SEM, EMP, X-ray diffraction, and petrographic techniques. The minerals that constitute the laterites (table 2) were determined by X-ray diffraction analysis. The results shown in table 2 were not determined by simple bulk X-ray diffraction analysis, but by special techniques described in the experimental section of reference 6. Bulk analysis revealed the presence of only the major minerals, goethite and quartz.

Other methods were used to identify small amounts of silicates such as serpentine, and oxides such as chromite, and other minerals. Serpentines were generally coarse grained and were identified by examining the plus 50-mesh fractions. (These fractions, however, had to be reground for the X-ray diffraction analyses.) Although the chromite particles were only weakly ferromagnetic, they were generally attached to magnetite particles. The chromite particles were identified by examining the magnetically

TABLE 2. - X-ray diffraction analyses of lateritic ores studied

Mineral	Formula[1]	Intensity[2] of X-ray diffraction peak				Structure[3]
		Eight Dollar Mountain ore	Pine Flat ore	New Caledonian ore	Philippine ore	
Goethite..............	α-FeO(OH)........	High....	High..	High....	High...	Orth.
Hematite..............	α-Fe_2O_3..........	Low.....	Low...	Low.....	Medium.	Rhomb.
Quartz................	α-SiO_2..........	High....	Medium	ND......	Low....	Hex.
Magnetite.............	Fe_3O_4............	Low.....	Trace.	Trace...	Trace..	FCC
Chromite..............	$FeO(Cr \cdot Al)_2O_3$....	Trace...	Trace.	Trace...	Trace..	FCC
Maghemite.............	γ-Fe_2O_3..........	ND......	ND....	ND......	Low....	FCC
Serpentine (Antigorite)	$Mg_3Si_2O_5(OH)_4$....	ND......	Low...	ND......	Trace..	Moncl.
Chlorite..............	$(Mg_{2.6}Fe_{2.2}Al_{1.2})Si_{2.8}Al_{1.2}O_{10}(OH)_8$.	Low.....	ND....	ND......	ND.....	Monocl.
Tremolite.............	$Ca_2Mg_5Si_8O_{22}(OH)_2$	Trace...	ND....	ND......	ND.....	Monocl.
Talc..................	$Mg_3Si_4O_{10}(OH)_2$...	ND......	ND....	Low.....	ND.....	Monocl.

ND Not detected.

[1] As listed by JCPDS International Centre for Diffraction Data.

[2] "High" indicates >80 pct; "medium," 45 to 55 pct; "low," <40 pct; "trace," <50 pct.

[3] Orth. Orthorhombic, Rhomb. Rhombohedral, Hex. Hexagonal, FCC Face-centered cubic, Monocl. Monoclinic.

separated concentrates. Talc and chlorites were identified following selective dissolution of iron oxides.

The SEM, EMP and X-ray diffraction results were complemented by examinations of polished sections under an optical microscope. Goethite appeared in clusters of a fine cryptocrystalline nature and had a characteristic yellow color under polarized light (16-17). Chromites were generally coarse grained and appeared dark gray in color.

INTERRELATIONSHIPS OF METALS AND MINERALS IN LATERITES

An example of a large-grained chromite particle surrounded by clusters of goethite particles is shown in figure 2*A*. Particles *1*, *2*, and *3* were optically identified as goethite, and particle *4*, which totally surrounds particle *3*, was identified as chromite. These particles were identified by observation of their characteristic optical properties under reflected-light microscopy. Panels *B* through *E* in figure 2 show the elemental distribution in the minerals as determined by EMP X-ray mapping. As expected, the nickel was present in the goethite, but not in the chromite. An elemental spot analysis performed on particle *1* showed that it contained 55.8 wt pct Fe, 2.0 wt pct Ni, 1.1 wt pct Cr, 1.6 wt pct Al, and 39.5 wt pct O.[7] Particle *3* contained slightly higher chromium and aluminum concentrations. This was attributed to its slight overlap with the chromite particle. Analyses were not performed on particle *3* because of uncertainty concerning absorption corrections. Chromium can also be expected to be present in solid solution with goethite because of similar ionic radii of Cr(III) (0.68 Å) and Fe(III) (0.64 Å) (10, 12). In the iron scan, figure 2*D*, the particle in the upper right part of the panel is the one that is only partially shown at the top right of figure 2*A*. This was an iron oxide particle which was more visible in the scan because the X-ray mapping image was rotated approximatley 15° with respect to the optical micrograph.

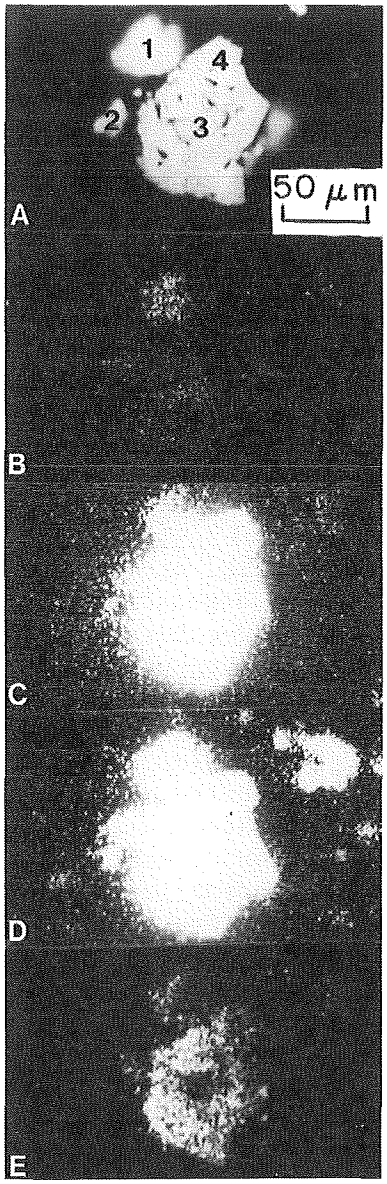

FIGURE 2. - Chromite and goethite particles. *A*, Optical micrograph. (Particles *1*, *2*, and *3* are goethite, and particle *4* is chromite.) EMP X-ray wavelength dispersive scans: *B*, Ni-Kα; *C*, Cr-Kα; *D*, Fe-Kα; and *E*, Al-Kα.

From a comparison of panels *A* and *E* in figure 2, it can be seen that some aluminum substituted for Cr(III) in chromite (particle *4*), and some aluminum was found in the goethite structure (particle *1*).

A small amount of aluminum set free by the weathering of serpentine has been

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[7] Oxygen content determined by difference.

reported to incorporate into the lattice of goethite, and up to 12 wt pct AlO(OH) has been reported in laterites (19). It seems reasonable to assume that Al(III) can be incorported in goethite (Fe(III)), because of their similar ionic radii (18). The mechanism for the concentration of nickel in the goethite is still unclear; however, considering the charges and ionic radii of Ni(II) (0.78 Å) and Fe(III) (0.67 Å), a diadochic substitution is unlikely in goethite. Zeissink (19) suggested that Al(III) substitution in the structure of goethite creates defects which may permit the incorporation of nickel.

There are several other theories proposed for the incorporation of nickel in the structure of goethite. Esguerra and Santos-Ynigo (10) suggested that divalent nickel tends to form insoluble hydroxides. Raymond (12) reported that natural nickel hydroxide ($4Ni(OH)_2 \cdot NiOOH$) was found in bauxites and serpentines, and that a hydrated nickel aluminate., $Ni_5(Al_4O)(OH)_{18} \cdot 6H_2O$, was found in the New Caledonian parent rock (peridotite). Distortion of the structure or substitution of nickel for iron in goethite is possible.

If it is assumed that Ni, Cr, and Al are all present in the goethite structure, then the sum of the Fe, Ni, Al, and Cr concentration of particle *1* in figure 2 should nearly equal the iron content of goethite. The EMP analysis of particle *1* showed that the combined Fe, Ni, Al, and Cr content was 60.4 wt pct, which in fact is close to the iron content of goethite (62.8 wt pct). In a similar manner, the spot analyses of particle *2* can be explained; however, the relative increase in chromium and aluminum in particle *2* occurred because the electron beam overlapped the adjacent chromite particle.

The goethite particles, particularly the ones in high silicon transition-type laterites, were sometimes either coated with silicate minerals or had silicon inclusions. An EMP elemental analysis of a silicon bearing goethite particle showed that it contained 54.8 wt pct Fe, 1.1 wt pct Ni, 0.4 wt pct Cr, 2.8 wt pct Si, 1 wt pct Al, and 39.9 wt pct O.[8] It is possible that silica is present as fine cryptocrystalline grains intergrown into the goethite. A cluster of particles found in the Pine Flat laterite is shown in the scanning electron micrograph in figure 3 (top). The particles (or clusters of cryptocrystalline particles) *1*, *2*, *3*, and *4* were optically identified as magnetite, chromite, cryptocrystalline goethite, and hematite, respectively. The bulk X-ray diffraction analysis (table 2) confirmed the presence of these phases. An X-ray energy dispersive elemental spot analysis was performed on each particle (figure 3, bottom), and the results support the optical mineral identification.

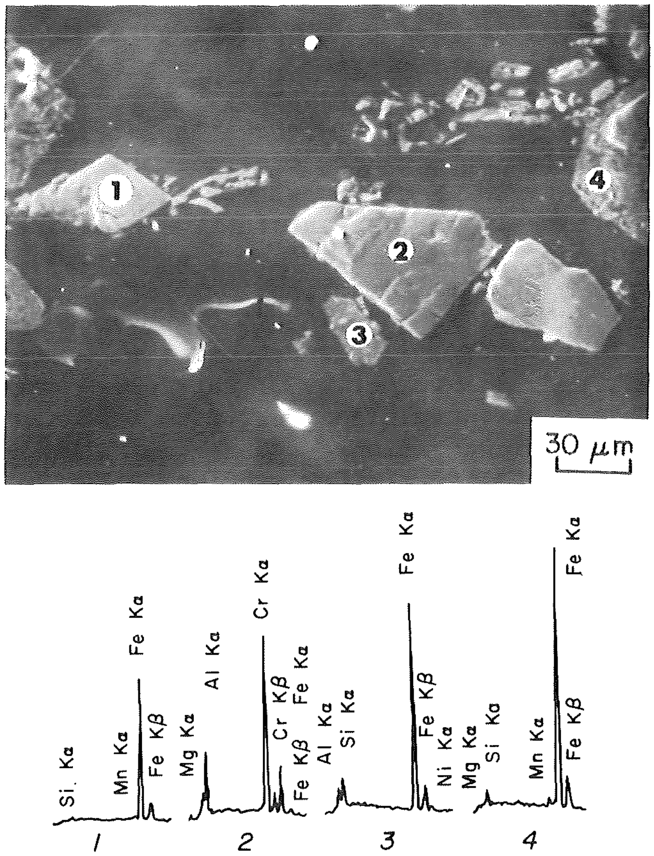

FIGURE 3. - Scanning electron micrograph (top) and X-ray energy dispersive analyses (bottom) of optically identified particles found in a typical laterite. *1*, magnetite; *2*, chromite; *3*, cryptocrystalline goethite; *4*, hematite.

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[8] Oxygen content determined by difference.

With electron and optical microscopic techniques (4, 7) it was established that there are no discrete nickel oxides in nickeliferous laterites; the majority of the nickel was found to be associated with the mineral goethite. The X-ray energy dispersive spectra of goethite particles show that small amounts of Ni, Al, and Si are present as impurities. A typical elemental electron microprobe analysis of goethite minerals showed that they contained 56.3 wt pct Fe, 0.9 wt pct Ni, 2.0 wt pct Al, 2.8 wt pct Si, and 38.0 wt pct O.[9] The iron content was much lower than the theoretical value of 62.8 wt pct. However, the combined weight fraction of Fe, Ni, Al, and Si was 62 wt pct, which is close to the theoretical iron content of goethite.

Although the majority of the nickel was associated with goethite, a small amount was dispersed in wad minerals. The manganese content in the laterites studied was quite low (less than 0.85 wt pct); hence, only minor amounts of manganese minerals are expected to be found in both limonitic and transition laterites.

The composition of these manganese minerals varies widely, and generally they are rimmed with goethite. In general, the combined nickel and cobalt content of manganese minerals ranges between 10 and 15 wt pct. These values are much higher than the nickel and cobalt contents of the iron minerals (approximately 1 wt pct each). Several manganese-rich particles were analyzed, and a typical example of the association of manganese and an iron-rich mineral is shown in figure 4. This figure shows wavelength dispersive X-ray mapping of Fe, Ni, Cr, Al, Co, Mn, and S on a manganese wad mineral (*1* in panel *A*) rimmed by goethite particle (*2* in panel *A*). (The wad mineral and goethite particle were previously identified by optical microscopy.) Figure 4 shows the presence of Ni, Co, S, Al, and Fe in the manganese mineral and primarily Ni, Al, Co, and Cr in the iron oxide mineral.

Table 3 shows the results of EMP elemental spot analyses performed on the same manganese mineral and goethite particle as are shown in figure 4. Table 4

TABLE 3. - EMP spot analyses on manganese wad mineral[1] and surrounding goethite particle,[2] weight percent

Element	Manganese wad[1]	Goethite[2]
Aluminum...........	3.5	1.2
Chromium...........	NA	1.7
Cobalt.............	8.7	.7
Iron...............	.1	54.5
Manganese..........	24.8	.3
Nickel.............	11.8	2.4
Oxygen[3]............	51.0	39.2
Sulfur.............	.1	ND

NA Not analyzed. ND Not detected.

[1] *1* in figure 4 (panel *A*).

[2] *2* in figure 4 (panel *A*).

[3] By difference.

TABLE 4. - EMP quantitative analyses of seven manganese-rich particles, weight-percent

Element	Particle						
	1	2	3	4	5	6	7
Aluminum..........	16.8	13.6	7.5	8.1	5.0	5.6	4.7
Chromium..........	.1	.1	NA	NA	NA	NA	NA
Cobalt............	6.5	5.8	5.9	6.4	8.0	9.1	8.4
Iron..............	21.1	20.6	13.5	14.7	6.9	7.0	6.4
Manganese.........	15.6	14.1	24.9	26.7	22.7	24.2	18.5
Nickel............	15.6	13.6	10.9	11.5	12.2	13.7	13.0
Oxygen[1]...........	24.2	32.2	37.2	33.2	45.1	40.3	48.9
Sulfur............	.1	ND	.1	.1	.1	.1	.1

NA Not analyzed. ND Not detected.

[1] By difference.

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[9] Oxygen content determined by difference.

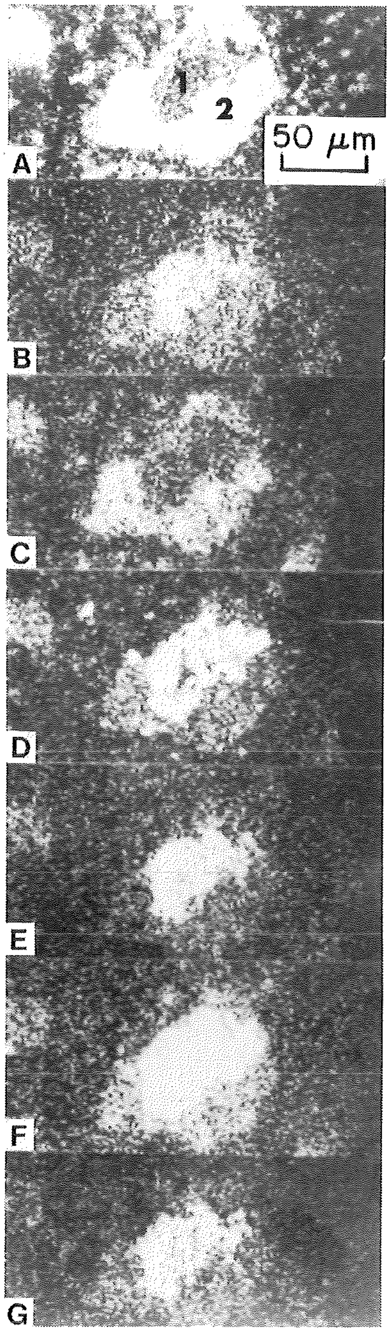

FIGURE 4. - X-ray wavelength dispersive maps on a manganese wad mineral rimmed by a goethite particle. *A*, Fe-Kα (*1*, manganese wad; *2*, goethite); *B*, Ni-Kα; *C*, Cr-Kα; *D*, Al-Kα; *E*, Co-Kα; *F*, Mn-Kα; *G*, S-Kα.

shows the results of EMP quantitative analyses on seven manganese-rich particles. The data in these two tables show that higher nickel contents (up to 16 wt pct) were found in manganese particles and lower nickel contents (up to 2.5 wt pct) were found in the surrounding goethite particles. It was also observed that fine goethite particles coated onto manganese-rich particles have relatively higher nickel concentrations (usually higher than 2 wt pct) than particles coated onto silica or other silicate minerals (usually up to 1.5 wt pct). This may have been because of a possible migration of impurities such as nickel from the manganese-rich to the iron-rich particles. The manganese particles generally did not contain any chromium. A small amount of sulfur (up to 0.1 wt pct) was usually present in the manganese-rich particles.

Identification of the manganese minerals by X-ray diffraction methods was not possible because of their low concentration in the ore and also because individual manganese particles could not be separated from other iron-rich minerals. The lines obtained from Debye-Scherrer patterns from a mixture of manganese and iron minerals always showed lines that matched goethite, along with a few unidentified lines.

Turner (16) suggested the possible presence of manganese compounds such as birnessite $(Na_4Mn_{14}O_{27}\cdot 9H_2O)$ and lithiophorite $[(LiAl)MnO_2(OH)_2]$ in laterites. The presense of the latter compound seems to be the most probable because of the presence of aluminum in all the manganese particles (table 4); however, lithium could not be detected by available instrumentation.

The distribution of cobalt in the lateritic ores was mainly in the manganese-rich wad along with nickel, as discussed above. The manganese-rich particles contained cobalt ranging from about 6 to 9 pct. From table 4 it can be concluded that the contents of cobalt and iron are generally inversely related. Where cobalt was relatively high, iron was relatively low.

In this study of the domestic transition-type laterites, cobalt was mainly found to be associated with wad. Goethite generally does not contain any cobalt unless manganese is also present. In the limonitic laterites, cobalt concentrations of up to 0.7 wt pct were found in the goethite. Low amounts of manganese were also observed in some cases in the goethite particles. (See figure 4 and table 3.) Several other particles examined in the limonitic laterites show the presence of cobalt in goethite. The cobalt and manganese probably substituted for iron into the structure of goethite because of the structural defects created by aluminum (4).

SUMMARY AND CONCLUSIONS

Application of a combination of physical and chemical analytical methods has revealed the nature of four laterites and the distribution of nickel and cobalt in the minerals. Two low-grade domestic transition-type laterites and limonitic-type materials from New Caledonia and the Philippines were studied.

It was established that nickel is mainly associated with the mineral goethite in both the limonitic and transition laterites. Minor amounts of nickel were found to be associated with manganese wad minerals, although the concentrations of nickel were high (11 to 16 pct). Cobalt was mainly associated with the wad minerals in both laterite types; it was also found to be incorporated in the lattice of goethite in the limonitic laterites.

Goethite in cryptocrystalline form is the major mineral present in lateritic nickel ores; and Ni, Al, and Cr or Si are incorporated in its structure. Small amounts of hematite, both fine- and coarse-grained varieties, and traces of magnetite and chromite are also present in the laterites. A variety of non-nickel bearing silicate minerals are found in the laterites in addition to the iron oxide minerals; for example, the Eight Dollar Mountain transition laterite contained quartz, chlorite, and tremolite, while the Pine Flat and Philippine laterites contained quartz and antigorite serpentine.

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