

PHENOMENA IN THERMAL TREATMENT OF LATERITIC NICKEL ORES UP TO 1300°C

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ABSTRACT

Nickel is recovered from laterite ore by pyrometallurgical processes as ferronickel. However, the processing of lateritic nickel ore is quite difficult, since the nickel-bearing minerals are finely disseminated in the ore bodies. An important group of nickel-bearing minerals in laterite ore bodies is the garnierites, which have become an important source for nickel. Garnierite is a general name for hydrous nickel-magnesium silicate minerals such as chlorite, clay and serpentine silicates. The object of the work reported here was to determine the phases that will be formed during thermal treatment of garnierite. Dehydroxylation and recrystallization of three samples, from different localities of nickel-containing minerals, have been studied under Ar-atmosphere from room temperature up to 1300°C by simultaneous Differential Scanning Calorimetry-Thermogravimetry (DSC-TG) method. The X-ray diffraction analyses of initial samples showed that they are mixture of serpentine and chlorite. Also vermiculite (clay) pattern was recognized in some of the samples. After the experiments the samples were examined by X-ray diffraction and scanning electron microscopy (SEM-EDS). The curves of all samples acquired from DSC revealed to have two endothermic peaks at 250°C and 600°C due to release the crystalline water, followed by an exothermic peak at 820°C which can be attributed to the change in crystal structure and consequent formation of a new phase. X-ray diffraction analyses of the samples after experiments showed the formation of olivine and enstatite phases. Nickel ions play similar roles than magnesium ions in nickel bearing hydrosilicates. According to the MgO-NiO-SiO₂ ternary diagram Ni replaces Mg in enstatite, metasilicate phase only to a small extent, corresponding to 7 mole percent NiO, whereas Ni can replace Mg in all proportions in forsterite phase which is olivine group orthosilicate.

1 INTRODUCTION

The reserves of nickel ore in the world are estimated to be at least 24000 million tons of which laterites represent 73%. Approximately 40% of these ores would be suitable for smelting. The majority of metallic nickel nowadays is recovered from sulphide ores and only about 40% nickel production takes place from the nickeliferous laterite ores [1]. Although, the production cost limits the utilization of laterite ores, the world primary nickel production from such ores seems to be increasing.

An important group of nickel-bearing minerals in laterite ore bodies is the garnierites, which is a general name for all hydrous nickel-magnesium silicate minerals such as chlorite, clay and serpentine silicates. Garnierites are related to the fine-grained nature, their poor crystalline order, and especially occurrence as intimate mixtures of two or more components. Apparently, these components of garnierite usually occur as lizardite, antigorite, chrysotile and with high percentage

of nickel as nepouite in serpentine while, vermiculite and talc occur as clay whereas clinochlore in chloride group [2].

In the case of sulphide ores nickel content can be successfully concentrated by means of traditional mineral processing methods such as milling and flotation. Laterite ores are amenable to minor upgrading only by screening. In spite of many attempts to develop techniques, which can render lateritic ores amenable to concentration prior to smelting, desirable technique has not yet been innovated. The reason why the processing is quite difficult is that the fine-grained nickel bearing minerals are finely disseminated and spread throughout the silicate and oxide ores.

Though various investigations for utilization of laterite ore in ferronickel and stainless steel smelting processes have been carried out, there are still a lot of issues that need to be studied. Better knowledge of nickel-bearing minerals in lateritic ores and their behaviour at high temperatures is important for developing the prereduction process [3,4]. In this study the mineralogy and morphology of three different laterite ores as well as their behaviour during heating have been investigated.

2 MATERIALS AND EXPERIMENTAL

Three different nickel laterite ores supplied from Brazil (Mirabela-deposit) and Colombia (Colombia-1 and Colombia-2) were investigated in this study. The phase analyses and typical chemical compositions of these ores are shown in Tables 1 and 2 respectively.

Table 1: Phases and minerals formula

Phases	Mirabela	Colombia-1	Colombia-2
Clinochrysotile, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$		x	x
Antigorite, $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$		x	
Lizardite, $(\text{Mg},\text{Al})_3(\text{Si},\text{Al})_2\text{O}_5(\text{OH})_4$		x	x
Clinochlore, $(\text{Mg},\text{Al})_6(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_8$		x	x
Quartz, SiO_2	x	x	x
Enstatite, MgSiO_3		x	
Vermiculite, $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$	x		
Nepouite, $(\text{Ni},\text{Mg})_3\text{Si}_2\text{O}_5(\text{OH})_4$	x	x	
Iron silicate, Fe_2SiO_4	x		
Grimaldite, $\text{Cr}^{3+}\text{O}(\text{OH})$	x		
Muscovite, $\text{KAl}_3\text{Si}_3\text{O}_{10}(\text{OH})_2$	x		
Hematite, Fe_2O_3	x		
Goethite, FeOOH		x	x
Forsterite ferroan, $(\text{Mg}_{0.6}\text{Fe}_{0.4})_2\text{SiO}_4$			x

The ores examined in this study include nickel hydrous magnesium silicates, which are typically green minerals due to their NiO content. Minerals of this group contain Mg and Si as major cations, with little Fe, Al and Ni. According to Table 1 the formula of minerals have the following significance: the compositions with respect to (Mg+Ni)/Si ratio 3/2 corresponds to serpentine with general formula $(\text{Mg},\text{Fe})_3\text{Si}_2\text{O}_5(\text{OH})_4$ (antigorite, lizardite, clinochrysotile and nepouite) and chlorite $(\text{Mg},\text{Fe},\text{Al})_6(\text{Si},\text{Al})_4\text{O}_{10}(\text{OH})_8$ (clinochlore) groups, while 3/4 ratio corresponds to clay $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ (talc, vermiculite) [5].

The formation of serpentine group of minerals involves the hydration of anhydrous (olivine and pyroxene) or less-hydrated Mg-rich silicates and carbonates by the hydration of forsterite to serpentine and brucite $(\text{Mg}(\text{OH})_2)$ [6,7,8,9], hence several types of serpentine minerals are found in the nature. Serpentine minerals are a common member of the phyllosilicates, their structure is composed of layers of silicate tetrahedrons and brucite octahedrons, and also water is linked between layers. The serpentine minerals are related to the chlorites and kaolinite minerals; their chemical composition is much more variable than that of other minerals and they pose many problems in nickel reduction and smelting processes [2,4].

Chemical analyses of materials (Table 2) show that they are complex with different components and with major oxides such as silica, magnesia and iron oxide. Moisture content of the samples is quite high which is typical for laterite ores. Moisture is water trapped between layers but mainly as chemical bonded water (hydroxyl groups), which should be evaporated during heat treating. The moisture content of the ores has been measured by heating the ore up to 1000°C.

Table 2: Chemical analyses of laterites

Component	Mirabela	Colombia-1	Colombia-2
Ni	2.6	0.76	2.3
Fe _{total}	12.5	7.4	12.4
Fe ²⁺	0.73	1.0	2.5
SiO ₂	49.6	44.9	44.9
Al ₂ O ₃	1.4	0.77	1.7
MgO	17.2	26.6	14.7
CaO	0.03	0.55	0.36
Cr ₂ O ₃	1.8	0.20	0.70
Mn	0.14		
Co	0.05	0.02	0.04
Cu	<0.01		
S	0.04	0.23	0.46
C	0.13		
moisture	10.7	13.4	9.4
SiO ₂ /MgO	2.88	1.69	3.05

Experiments were carried out by using Simultaneous Thermal Analyzer (Netzsch STA 449C Jupiter) which allows measurement of mass changes and thermal effects of the sample at the same time.

In a typical experiment a laterite sample, about 50 mg, was charged into alumina crucible and heated under Ar-atmosphere (purity 99.9990%) from room temperature to 1300°C by using constant heating rate 10°C/min. After heating, the sample was cooled down to room temperature in argon atmosphere in order to prevent from rehydration and oxidation. The cooled sample was then examined by X-ray diffraction and Scanning Electron Microscopy (SEM-EDS) for determination of phase, mineralogical and morphological transformations.

3 RESULTS AND DISCUSSION

3.1 Differential Scanning Calorimeter and Thermogravimetric Analyses (DSC-TGA)

Figure 1 shows DSC curves for the three different nickel laterite ores heated under Ar-atmosphere from room temperature to 1300°C.

According to the DSC curves in Figure 1 all samples have three endothermic peaks followed by an exothermic peak. As can be seen the positions of the peaks are close to each other but peak sizes vary considerably between the samples. The sizes of the endothermic peaks depend on the amount of free and crystalline water as well as particle size and morphology of the samples.

The low-temperature endothermic peaks around 100°C and 250°C are caused by the removal of free water and by dissociation of goethite, respectively. The high-temperature endothermic peak at temperature range 550-650°C is attributed to the loss of crystalline water by so called dehydroxylation reactions. A gentle bowing endothermic peak around 700°C is due to multistage dehydroxylation [10] or presence of another mineral component such as chlorite minerals [6]. At the temperature interval 650-800°C it is supposed that the minerals have decomposed and are free from silica matrix. According to literature [11,12,13], serpentine materials that yield small exothermic peaks seem to contain forsterite in the temperature interval between the endothermic and exothermic reactions, while those that yield large exothermic peaks are amorphous. The dehydroxylation peak is followed by an exothermic peak at about 800°C (see Figure 1), which is apparently associated with crystallization of new phase.

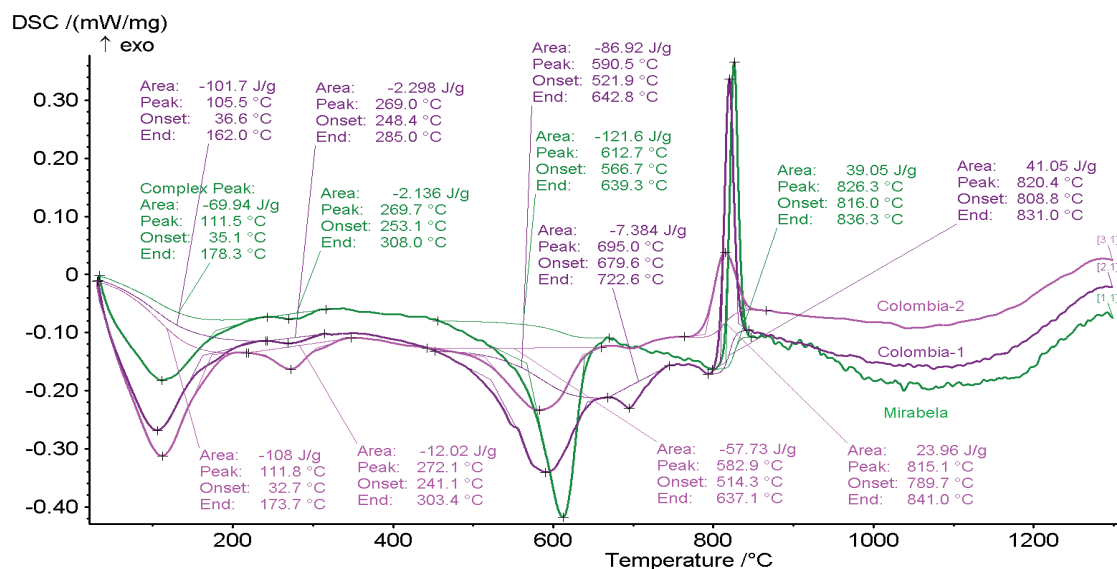


Figure 1: DSC curves for Mirabela, Colombia-1 and Colombia-2 when heating up to 1300°C

Crystallization of new phases (forsterite and enstatite) has been discussed in detail by many investigators and little can be added to this account. Dehydroxylation of a mineral such as serpentine may proceed by migration of H^+ ions to a reaction site where water is formed and liberated, with a converse migration of cations, Mg^{2+} and Si^{4+} to maintain electrical neutrality.

Ball and Taylor [14] have given a detailed description of the heterogeneous processes by which the dehydroxylation and recrystallization of serpentine may take place as follows:

1. *Dehydration*; Protons migrate to reaction zones, Mg and Si ions counter-migrate,
2. The oxygen arrangement remains more or less unchanged, the Mg:Si ratio remains at 3:2, and the product is partly disordered material.
3. *Cation reorganization*; Partial separation into Mg-rich and Si-rich regions commences.
4. *Forsterite crystallization*; An ordering of cations and a change in oxygen ion packing result in formation of forsterite.
5. *Enstatite formation*; the Si-rich regions change to enstatite, but this stage occurs less readily than the others and the process is easily halted at the end of stage 3.

They also considered the formation of forsterite to take place firstly at high temperature followed by formation of enstatite.

Figure 2 shows the corresponding weight-loss curves. The shape of the weight-loss curves depends on the dehydration energy of compounds. Also iron atoms induce a distinct change in thermal behaviour and in shape of TG curve of silicates because a) the $Fe^{3+} - OH^-$ bond is weaker than the $Al^{3+} - OH^-$ or $Mg^{2+} - OH^-$, b) the size of iron ions is larger than Al or Mg ions and therefore they do not fit into the structure as well, c) ferrous (Fe^{2+}) ions are subject to oxidation [15]. According to Figure 2 water is lost slowly over the range 250-550°C followed by rapid loss of crystalline water in the temperature range 550-700°C. This kind of behaviour is typical for serpentine-vermiculite mixtures (Mirabela) and for serpentine-Chlorite mixtures (Colombia-1 and Colombia-2). When comparing the final weight-loss of the samples and their initial moisture content (Table 1) it can be concluded that in Colombia-1 and in Mirabela there is still some crystalline water left in the structure whereas in Colombia-2 all the water had been volatilized. This was also confirmed by XRD-analyses of the samples after the experiments.

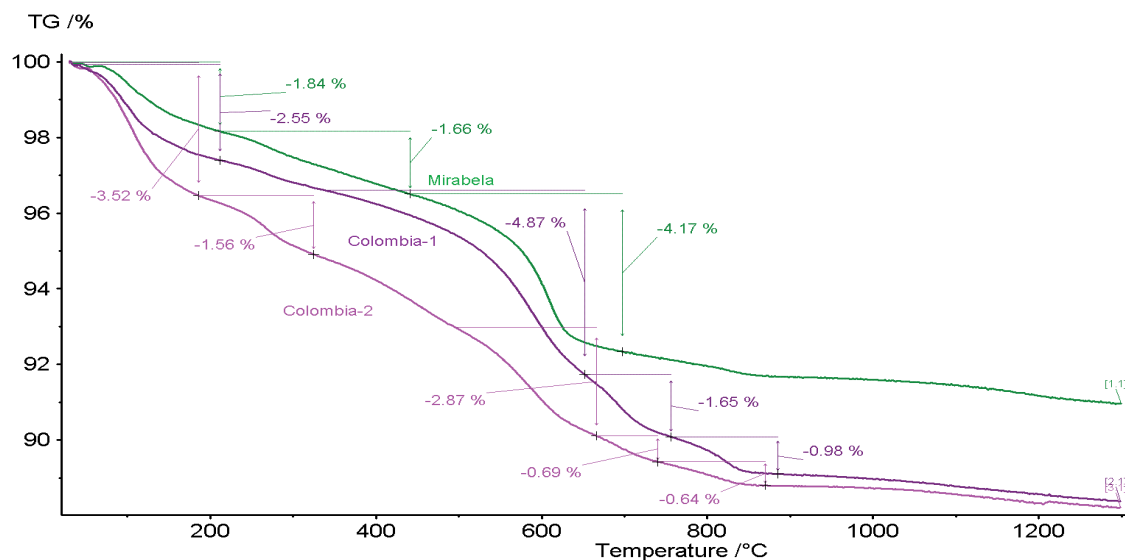


Figure 2: TG curves for Mirabela, Colombia-1 and Colombia-2 when heating up to 1300°C

3.2 Microstructural Changes

Electron micrographs of materials have been recorded to show the morphological character of minerals. Figures 3-8 underneath represent the electron micrographs of examined samples before and after the heat treatment.

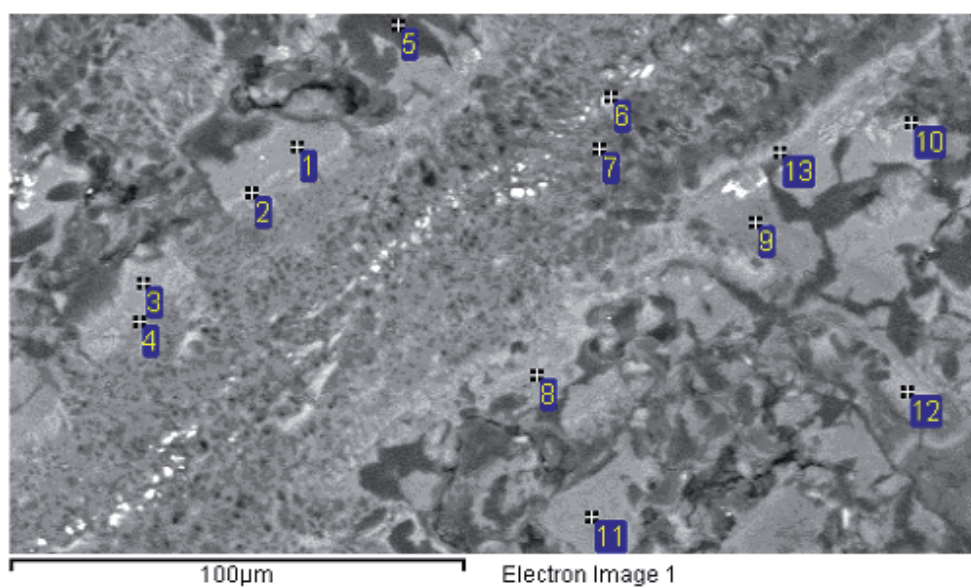
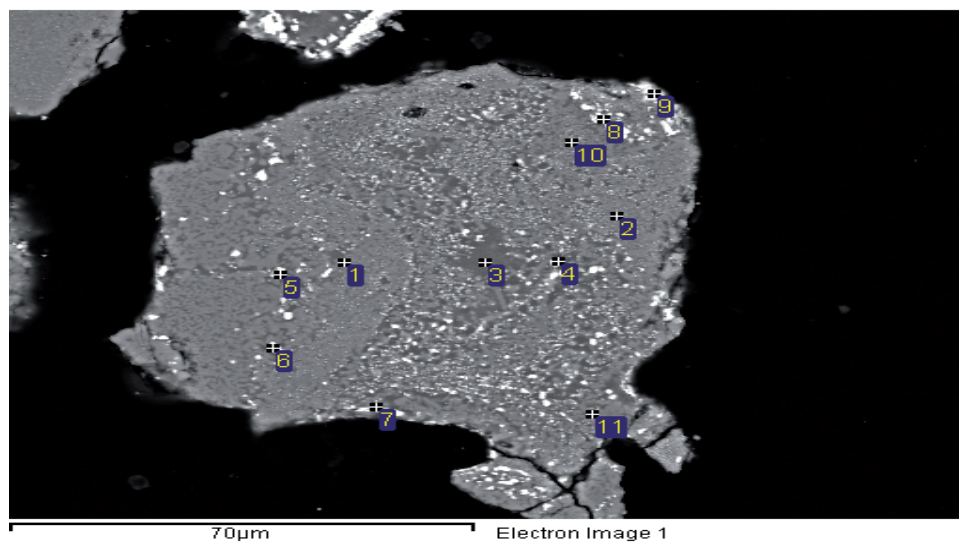


Figure 3: Microstructure of initial Ni-laterite ore Mirabela (1, 2, 3, 4, 8, 9, 11 Nickel-containing (Mg,Fe)-silicate (nepouite); 6 Iron silicate; 10, 13 Iron-containing Mg-silicate; 5, 7, 12 Quartz)



Spectrum	O	Na	Mg	Al	Si	K	Ca	Ti	Cr	Fe	Ni
1	46.36	0.16		0.77	26.52	0.17	0.17			8.50	2.37
2	44.14	0.08	10.99	1.13	24.09	0.13	0.12		0.32	15.99	3.01
3	53.61	0.31	0.34	1.27	41.75	0.21	0.52			1.99	
4	38.16	0.39	3.72	2.58	15.25	0.25	0.21		0.29	35.19	3.97
5	37.90		7.10	2.40	11.66	0.22		0.10	0.76	34.86	5.00
6	35.09	0.26	4.94	2.50	8.19	0.18		0.24	1.01	42.10	5.49
7	50.12		10.24	1.27	25.36	0.33	0.41		0.22	10.28	1.77
8	35.17	0.44	4.47	2.37	10.23	0.47			0.87	39.99	5.99
9	23.92		2.29	1.89	1.95	0.15		0.24	1.68	58.95	8.93
10	45.44	0.27	12.41	1.35	26.74	0.44	0.35			10.47	2.53
11	47.41		10.12	0.68	29.07				0.12	10.47	2.14

Figure 4: Microstructure and point analyses of Ni-laterite sample Mirabela after heat treatment up to 1300°C

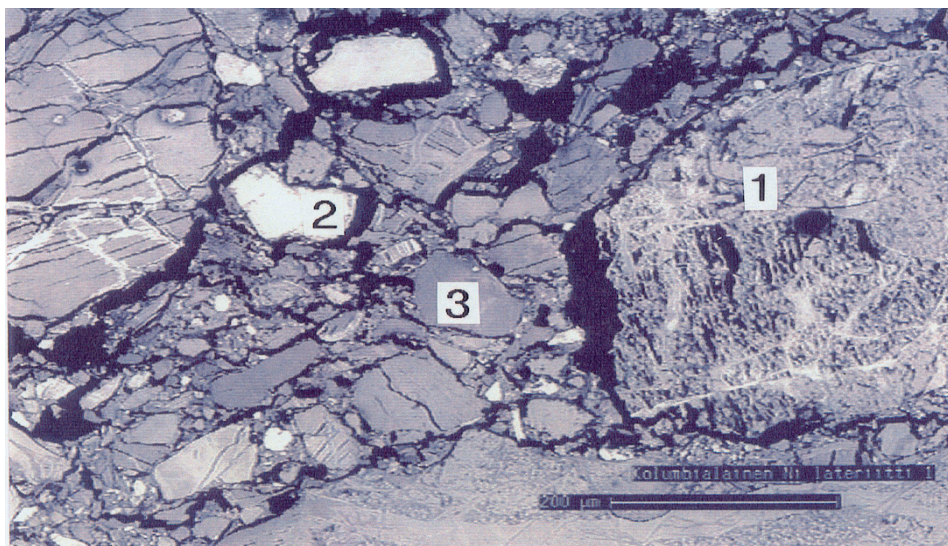
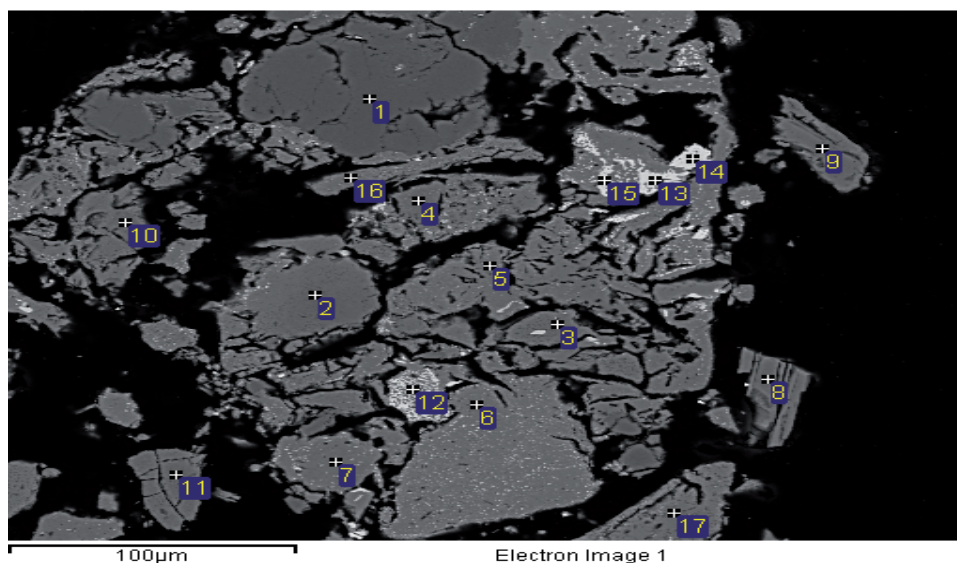


Figure 5: Microstructure of initial Ni-laterite ore Colombia-1 (1 Silicate; 2 Goethite; 3 Silica)



Spectrum	O	Mg	Al	Si	Ca	Cr	Mn	Fe	Ni
1	56.05			43.95					
2	48.81	17.27		29.21				3.86	0.85
3	48.52	15.97	0.20	28.02	0.57			6.16	0.57
4	46.64	22.02	0.03	22.72				8.16	0.43
5	45.82	20.32		22.35	0.12		0.58	8.18	2.64
6	45.16	16.97	0.18	24.69	0.24			11.45	1.31
7	44.05	25.36	0.03	19.01	0.18		0.32	9.02	2.03
8	48.12	19.71	0.29	26.26	0.28	0.39		4.62	0.33
9	45.08	28.15		18.80				7.59	0.38
10	45.40	24.74		21.38	0.25			7.54	0.69
11	45.71	26.09		20.32				7.19	0.69
12	33.66	3.97	1.27	8.30		2.72		44.34	5.73
13	29.27	2.89	1.02	0.43				64.56	1.83
14	30.99	2.91	2.02	1.72	0.35	0.70		58.75	2.58
15	31.41	6.01	0.74	4.05				56.68	1.11
16	47.61	13.85	0.71	27.18	0.23	0.21		8.91	1.30
17	47.02	17.52	0.21	26.25				8.28	0.72

Figure 6: Microstructure and point analyses of Ni-laterite sample Colombia-1 after heat treatment up to 1300°C

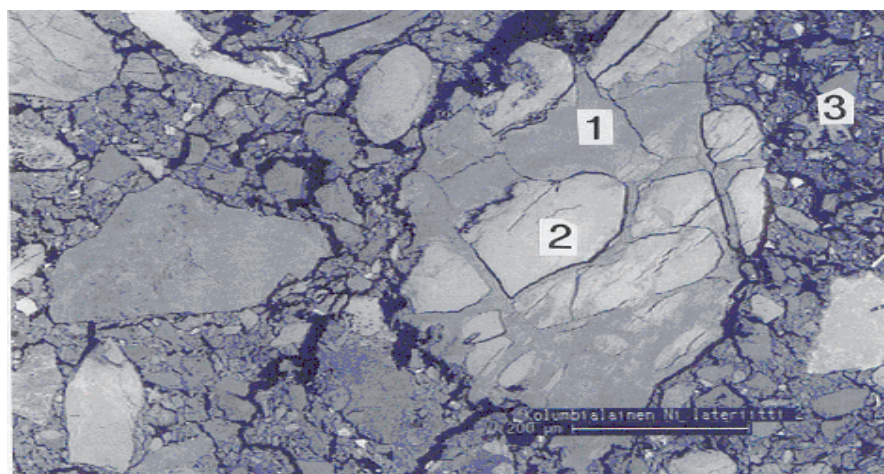
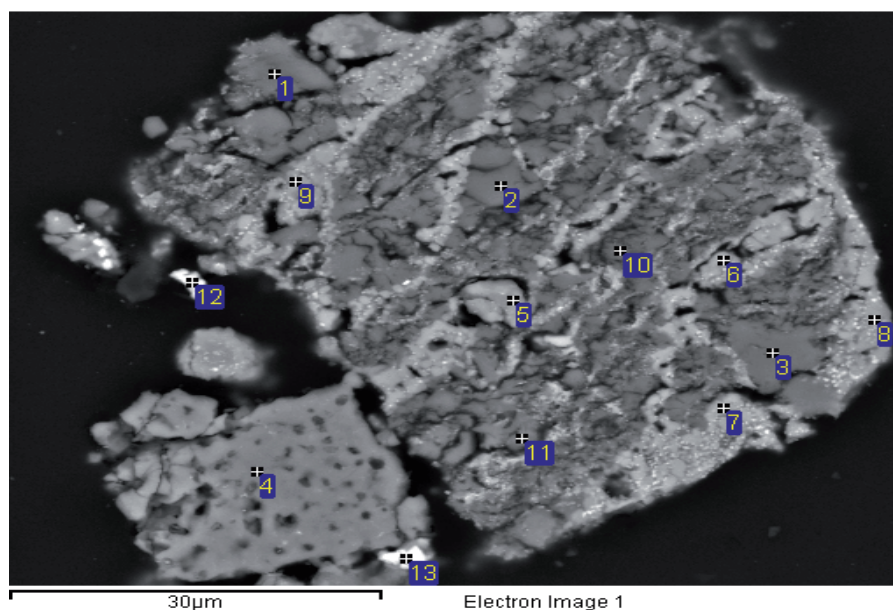


Figure 7: Microstructure of initial Ni-laterite ore Colombia-2 (1 Silicate; 2 Goethite; 3 Silica)



Spectrum	O	Mg	Al	Si	Ca	Cr	Fe	Ni
1	50.38			48.58			0.68	0.35
2	55.16	0.29		43.22			0.80	0.52
3	53.93	0.24		45.16			0.67	
4	46.22	21.85	0.23	23.60			7.07	1.03
5	43.39	17.33		22.18	0.19		7.26	9.65
6	41.53	17.23		21.41			7.43	12.40
7	42.75	16.49		20.70			7.75	12.30
8	43.07	17.84		21.24			8.05	9.81
9	43.88	13.78	0.25	23.28			10.60	8.21
10	52.58	1.02		43.41			1.78	1.21
11	53.24	0.84		39.75			2.46	3.70
12	39.98	3.28	1.09	13.68		0.71	36.86	4.41
13	35.24	6.29	1.92	4.98		3.26	44.13	4.17

Figure 8: Microstructure and point analyses of Ni-laterite sample Colombia-2 after heat treatment up to 1300°C

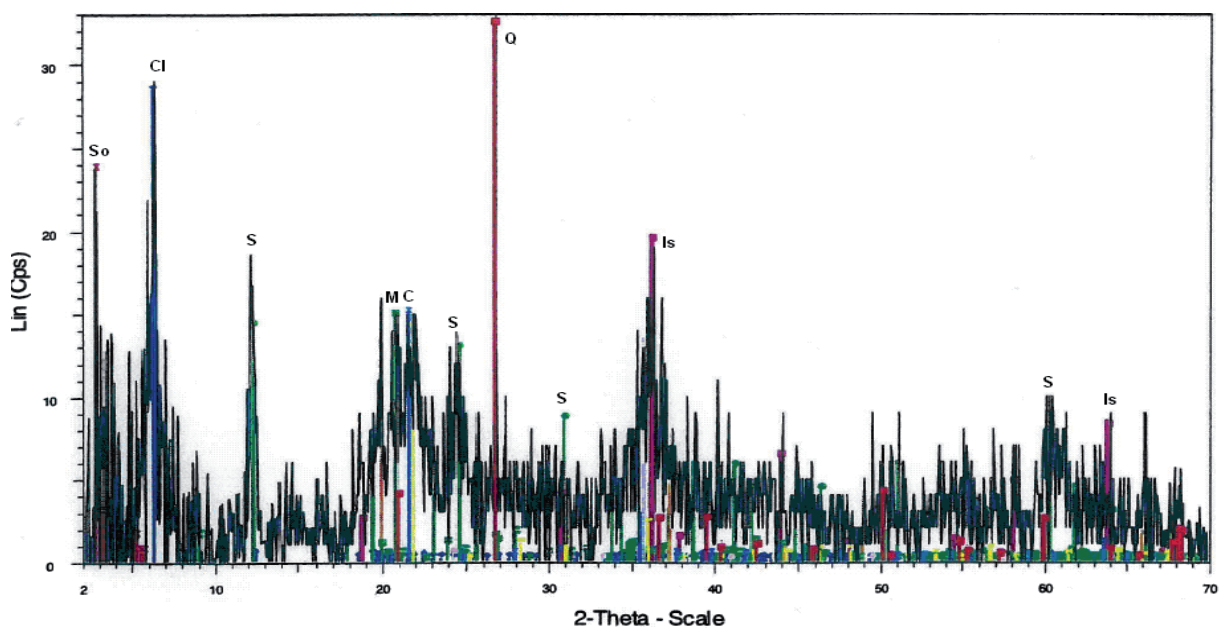
It can be seen from Figures 3, 5 and 7 that the initial structures of the ores are heterogeneous containing various different phases as was already seen in Table 1. As a result of heating, ore structures have been degraded due to dehydroxylation reactions (see Figures 4, 6 and 8). Also various new phases were formed, which can be distinguished by hues. Point analyses of the samples after heating showed, that nickel content varied from particle to particle and even within the same particle.

3.3 X-ray Diffraction Analyses

X-ray diffraction analyses were carried out for the samples to identify the phases present in the materials before and after heating. XRD patterns of samples before heating (Figures 9a, 10a and 11a) show that the samples are mixtures of serpentine, chlorite and clay minerals, which can be distinguished by different peak positions in X-ray diffraction pattern. The X-ray diffraction pattern peak around 12 on 2-theta scale is ascribed to serpentine minerals, while for clay minerals diffraction peak is around 6 on 2-theta-scale.

After heating samples were subjected to X-ray diffraction analysis, in order to determine mineralogical changes as a result of thermal reactions. The acquired representative diffractometer patterns for each of the samples are shown in Figures 9b, 10b and 11b. The high-temperature phases, namely enstatite as major phase and olivine, quartz and cristobalite as minor phases are formed in all samples, which is in accordance with the MgO-NiO-SiO₂ phase diagram at low nickel content [16].

a)



b)

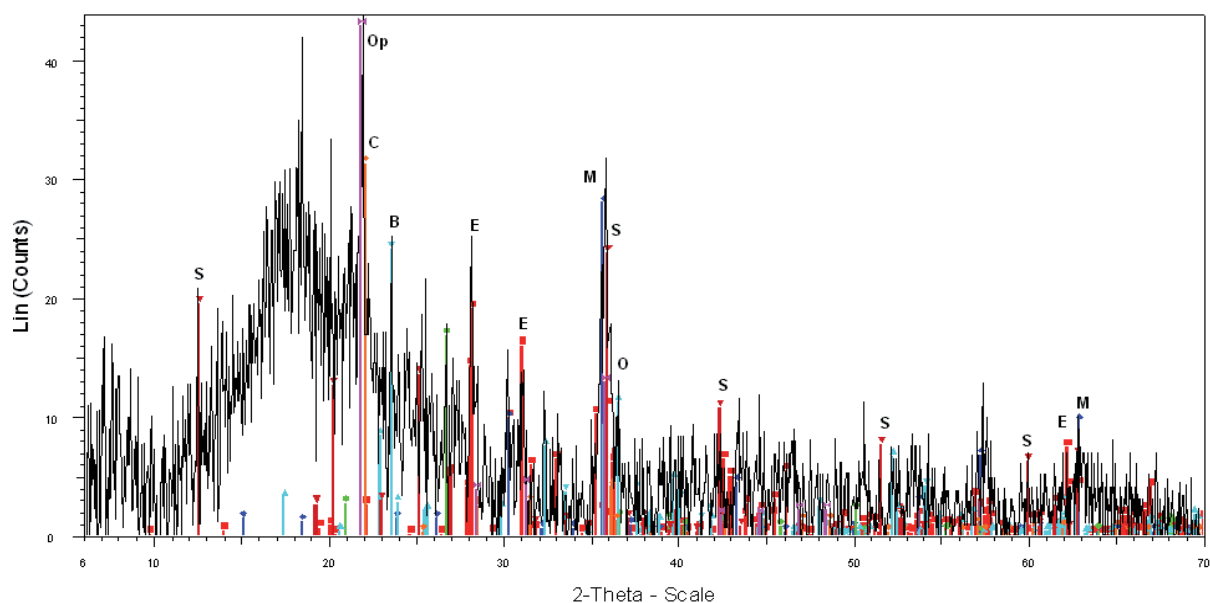


Figure 9: X-ray diffractometer pattern for Mirabela a) initial ore and b) after heat treatment at 1300°C. (C: cristobalite; B: bernalite (Fe-hydroxide mineral); Cl: clay; E: enstatite; Is: iron silicate; G: goethite; M: maghemite; O: olivine; Op: opal; Q: quartz; S: serpentine (Nepouite); So: silicon oxide)

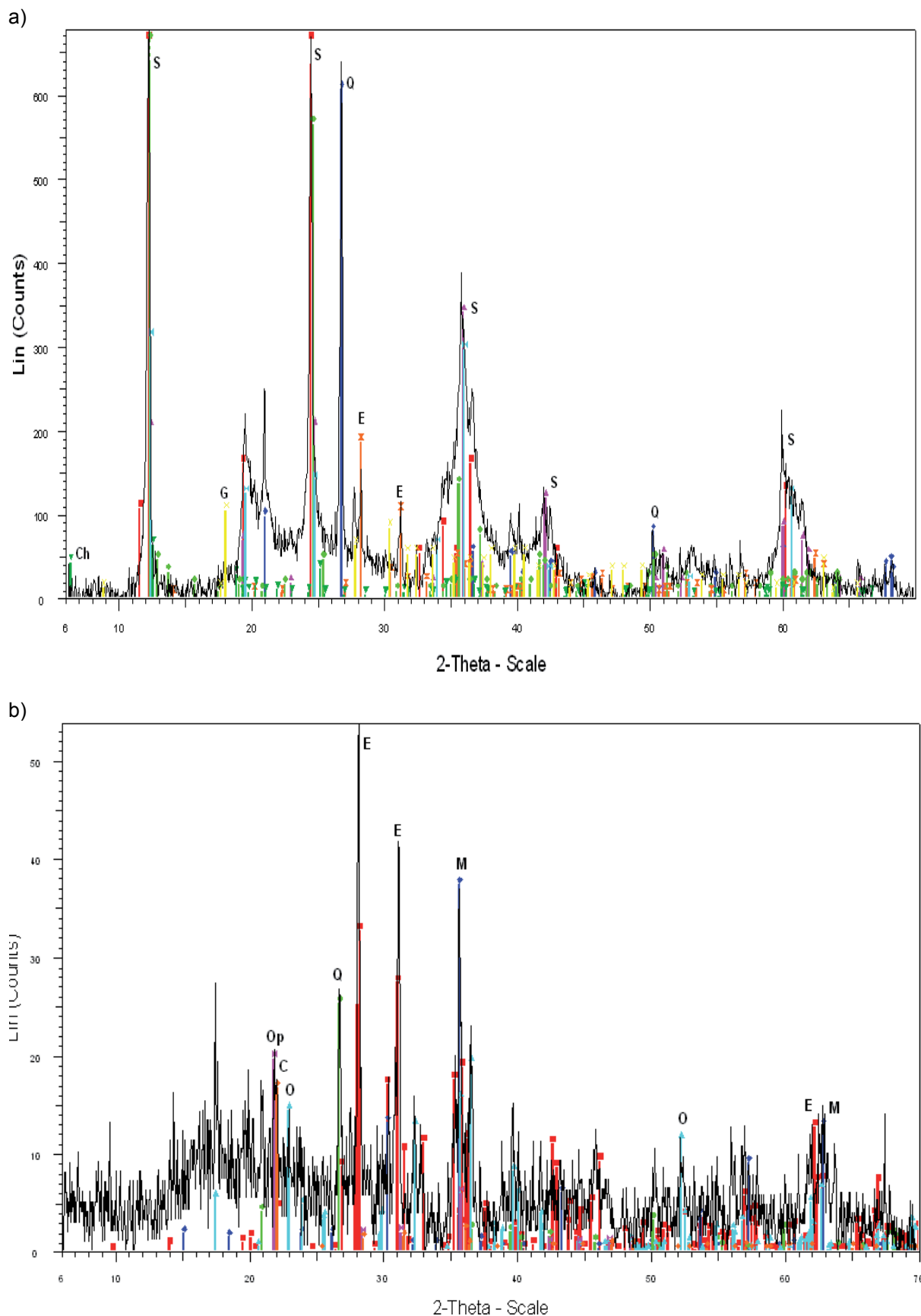


Figure 10: X-ray diffractometer pattern for Colombia-1 a) initial ore and b) after heat treatment at 1300°C. (C: cristobalite; Ch: chloride; E: enstatite; G: goethite; M: maghemite; O: olivine; Op: opal; Q: quartz; S: serpentine (Antigorite, Clinochrysotile, Lizardite, Nepouite))

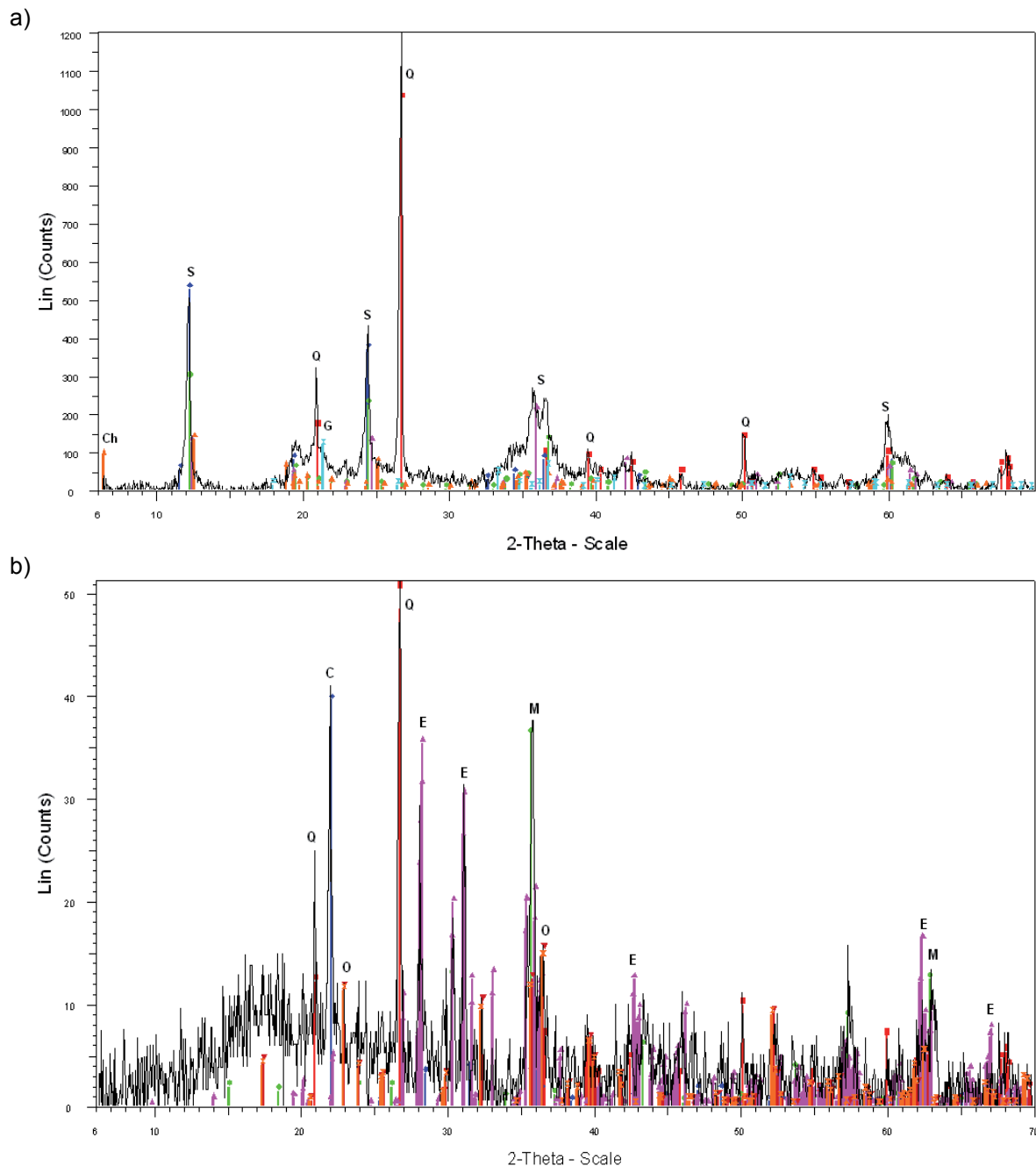
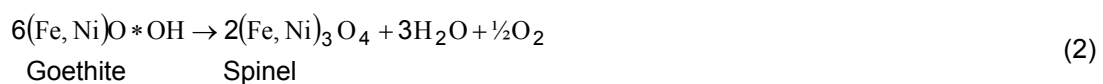
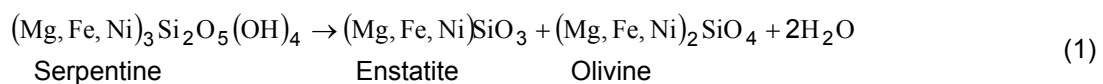


Figure 11: X-ray diffractometer pattern for Colombia-2 a) initial ore and b) after heat treatment at 1300°C. (C: cristobalite; Ch: chloride; E: enstatite; G: goethite; M: maghemite; O: olivine; Op: opal; Q: quartz; S: serpentine (Clinochrysotile, Lizardite))

According to XRD analyses (Figures 9b, 10b and 11b) enstatite, olivine and maghemite (spinel) have been formed as a result of disintegration of minerals during the heating. It is suggested that the serpentine (antigorite, clinochrysotile, lizardite and nepouite) has been transformed to enstatite and olivine via the following reaction (1) whereas goethite and iron-rich nickel bearing minerals are transformed to the maghemite (spinel) by reaction (2).



4 CONCLUSION

According to the X-ray diffraction and initial chemical analyses of three different nickel laterite ores, it can be concluded that they are mixtures of minerals such as serpentine, clay and chlorite. The electron micrographs gave knowledge about morphology of minerals and suggested that they have complex and heterogeneous phase structure with various contents of elements such as Mg, Si, Fe, Ni, Al, Co, Mn, Cr..., which alternate from particle to particle and from mineral to mineral within the same mineral, conformable with the serpentine-clay-chloride mixture of materials.

DSC curves revealed that all samples have three endothermic peaks (100°C, 250°C and 550-650°C) caused by removal of free water, dissociation of goethite and by dehydroxylation reactions, respectively. The endothermic reactions are followed by an exothermic reaction at 850°C which is associated with crystallization of new phases. The composition the final phases are strongly dependent on the proportion of serpentine-like and clay-like layers in the initial ore.

SEM-images showed that as a result of heating, ore structures have been degraded due to dehydroxylation reactions and new phases formed. The formation of new phases during heating was also confirmed by XRD analyses, which showed that enstatite, olivine and maghemite (spinel) have been formed as a result of disintegration of minerals during the heating.

5 ACKNOWLEDGEMENTS

Outotec Research Oy and Outokumpu Oyj have been participating in this investigation. The authors are grateful to Outotec Research Oy for the mineralogical and microanalyses of samples.

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