GASPÉITE-MAGNESITE SOLID SOLUTIONS AND THEIR SIGNIFICANCE

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It is a surprising fact that, despite the increasing number of secondary minerals of Ni(II) recognized from oxidized base metal deposits (Anthony et al. 2003), the supergene chemistry responsible for their formation remains poorly understood. An understanding of this chemistry would be desirable in view of its importance with respect to geochemical exploration for the element, its behaviour in the regolith and the potential development of commercially exploitable secondary nickel resources. Of the secondary nickel minerals known, gaspéite, NiCO₃, is perhaps the most common and has been observed in a number of Western Australian deposits. Notable among these is the 132 pit at Widgiemooltha, near Kambalda, WA (Nickel et al. 1994). The supergene profile of the 132 pit consists of 5 zones: oxide, carbonate, violarite-pyrite, transition and primary zone. The carbonate zone is 3-12 m below surface and is characterized by the occurrence of a number of flat-lying to sub-horizontal veins of gaspéite that cut across altered wall rock comprising tremolite and goethite. These veins extend from what was a large sulfide body across the matrix layer. Single gaspéite veins have a size of 5 x 5 x 0.05 m on average and may occur in masses of up to 10 x 10 x 1 m; they are typically massive to either granular or fibrous. From the lower part of the carbonate zone upwards there is a progressive decrease in the amount of gaspéite and other carbonate minerals, and their respective nickel contents. The same is true from the carbonate zone to the top of the oxide zone. The lower part of the carbonate zone is dominated by gaspéite veins with minor amounts of goethite, nickeloan paratacamite, dolomite and huntite. (Nickel et al. 1994).

Gaspéite, seen as an important mineralogical control on the dispersion of nickel, is rarely, if ever, found as a pure end-member. It forms part of a complete solid solution series with magnesite, the Mg(II) analogue, and naturally occurring material invariably contains significant amounts of both Ni and Mg, together with other divalent cations. A study using SEM and microprobe techniques of material from the 132 deposit has revealed the extent of solid solution in this setting, the significance of cobalt substituted in the lattice and geochemical evidence for a number of mineralizing events.

Backscattered electron images (Figure 1) of polished sections of gaspéite reveal considerable zoning; characteristic compositions are given in Table 1. Significant Co contents are evident for some material. No Co was detected in earlier analyses (Nickel *et al.*1994, Kohls & Rodda 1966).

Description		Composition
Gaspéite	A	$(Ni_{0.737}Mg_{0.243}Ca_{0.010}Co_{0.010}Fe_{0.001})CO_3$
Gaspéite	В	$(Ni_{0.601}Mg_{0.375}Ca_{0.018}Co_{0.005}Fe_{0.001})CO_3$
Dolomite (С	$(Mg_{0.540}Ca_{0.427}Ni_{0.031}Co_{0.001})CO_3$
Magnesite	D	$(Mg_{0968}Ca_{0.026}Ni_{0.006}Co_{0.001})CO_3$
Gaspéite	Е	Vein not wide enough to analyse; brightness shows it to be Ni-rich
Magnesite	F	$(Mg_{0.983}Ca_{0.013}Ni_{0.003}Co_{0.001}Fe_{0.001})CO_3$

 Table 1: Characteristic compositions of zones in gaspéite-rich material from the 132 deposit (see Figure.1)

It should be noted that there is no smooth transition between regions of different composition in the sample. Rather, a number of abrupt phase changes are observed. In particular, Ni-rich areas are most pronounced, when they are embedded in material carrying more Mg. The sequence observed in order of decreasing age is Ni-rich > Ca- and Mg-rich > Mg-rich > Ni-rich >Mg-rich. In a carbonate-rich environment, Ni and Co are preferentially precipitated by virtue of the significant differences between their solubility products, as compared to values for MgCO₃ and CaCO₃. Values of pK_{so} at 25°C are -11.2, -7.46 and -8.35 for gaspéite, magnesite and dolomite, respectively. CoCO₃ has a value close to that of gaspéite at room temperature (Grauer R. 1999). The thermochemical data clearly indicate that gaspéite (or Ni-rich material at least) will be precipitated whenever Ni(II) is present in solution, rather than magnesite. That is to say, the distribution coefficient is very much different to unity. In this light, the narrow, Ni-rich band in Figure 1 is seen to be the result of a quite separate mineralizing event, as indeed are all the zones in the specimen. We draw attention to

the fact that this conclusion is reached solely on the basis of the more recent determination of an accurate solubility product for $NiCO_3$ (Grauer R. 1999); an inaccurate value that related to a hydrated phase has persisted in the literature for several decades.

Similar studies have been carried out on samples of nickel-rich magnesite from the New Find deposite at Mt. Clifford, north of Leonora, WA and from Murrin Murrin, west of Leonora. The behaviour of gaspéite and members of the gaspéite-magnesite solid solution series in the supergene zone can be described effectively using a simple equilibrium thermodynamic approach. However, it is emphasized that any comprehensive description of the low temperature geochemistry of Ni(II) must await the determination of the stabilities of a considerable number of other important phases, including several from the hydrotalcite series. Experimental work along these lines is currently under way.

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Figure 1: Backscattered image of a section of gaspéite-rich mineralization from the 132 deposit. The scale bar indicates size. Sections corresponding to analyses in Table 1 are shown alphabetically.