

# Nickeloan hydrozincite: a new variety

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**SUMMARY.** Extensive substitution of Ni for Zn in hydrozincite from the Parc Mine, North Wales, has been observed. This is the first time that a substantial concentration of another transition metal in this mineral has been reported. The average composition of the nickeloan hydrozincite is  $Zn_{4.63}Ni_{0.37}(CO_3)_2(OH)_6$ . The relationship of this new variety to other secondary carbonate-containing nickel minerals is discussed, as is the possibility of substitution of other transition metal ions into the hydrozincite lattice.

DURING the course of a study (Alwan and Williams, 1979) on the formation of hydrozincite,  $Zn_5(CO_3)_2(OH)_6$ , from aqueous solution in the oxidized zone of base-metal ore-bodies we have had occasion to visit the Parc Mine in Gwynedd, North Wales (National Grid reference SH788602) in order to collect samples of the mineral and also aqueous solutions that were depositing hydrozincite on the surfaces of the old workings. In the No. 2 level, in a small cross-cut 620 metres from the adit entrance, hydrozincite forms coatings on the walls, stalactites in the back, and sheets and encrustations covering the floor. On one occasion it was noticed that some of the hydrozincite on the floor, cementing together and completely encasing in some cases small fragments of rubble derived from a shear zone, was stained a pale, but distinctly apple-green colour.

Palache *et al.* (1951) remarked that hydrozincite, which is crystallographically distinct from aurichalcite,  $(Zn,Cu)_5(CO_3)_2(OH)_6$  (Jambor and Pouliot, 1965), does not contain significant amounts of copper. Indeed it has been stated (Jambor and MacGregor, 1974) that 'copper substitution in hydrozincite is known to be negligible'. It was initially thought that the material collected could be copper-substituted hydrozincite in view of the fact that chalcopyrite is an accessory mineral in the ore assemblage. Subsequent studies, however, have shown that the mineral is in fact nickeloan hydrozincite, a new variety.

Two separate samples of the pale-green mineral were hand-picked under the microscope and separated mechanically from any contaminating material. The crusts of green hydrozincite in the

specimen are of the order of 1 mm in thickness and have a pure white streak. No difficulty was experienced in obtaining specimens suitable for analysis which were free from limonite, which is also present in large quantities in the workings as a result of oxidation of the sulphide orebody (Alwan and Williams, 1979). The material obtained was analysed by atomic absorption spectrophotometry, using a Varian AA6 instrument fitted with a carbon rod analyser, after dissolution in Analar® 0.05 mol dm<sup>-3</sup> HNO<sub>3</sub>. A summary of the analytical results are given in Table I. Very minor amounts of Cu and Fe were found to be present. Concentrations of Co, Ca, and Mg are less than the detection limit, and Al was not detected. The hydrozincite contains approximately 4% Ni by weight. The two samples have the stoichiometries indicated in the table. The results correspond to Ni/Zn ratios of 0.075 and 0.082.

TABLE I. *Partial chemical analyses of nickeloan hydrozincite samples*

	1	2
Ni	3.76	4.12
Cu	0.18	0.20
Fe	0.16	0.16
Co	0.01	0.01
Ca	0.02	0.02
Mg	0.02	0.02
Al	0.05	0.05

1.  $Zn_{4.65}Ni_{0.35}(CO_3)_2(OH)_6$ ; Ni/Zn = 0.075.

2.  $Zn_{4.62}Ni_{0.38}(CO_3)_2(OH)_6$ ; Ni/Zn = 0.082.

Thermogravimetric analyses of a sample of nickeloan hydrozincite was carried out with a Stanton Redcroft TG 750 temperature-programmed thermogravimetric balance. After loss of H<sub>2</sub>O and CO<sub>2</sub>, equilibrium weight was reached at 410° and was constant up to 900°. The equilibrium weight was 74.0% of the total. For pure hydrozincite the calculated equilibrium weight is 74.1%, corresponding to ZnO.

These results, coupled with X-ray crystallographic and infra-red studies, establish that the mineral is nickel-substituted hydrozincite, and not a mixture of two compounds. Various nickel containing carbonate minerals have been found to occur in the oxidized zone of base metal ore bodies. These are gaspéite,  $\text{NiCO}_3$ , zaratite  $\text{Ni}_3\text{CO}_3(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ , otwayite,  $(\text{Ni,Mg})_2\text{CO}_3(\text{OH})_2 \cdot \text{H}_2\text{O}$ , reevesite,  $\text{Ni}_6\text{Fe}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ , takovite,  $\text{Ni}_6\text{Al}_2\text{CO}_3(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$ , eardleyite,  $\text{Ni}_{4.92}\text{Mg}_{0.10}\text{Ca}_{0.02}\text{Fe}_{0.13}\text{Al}_{2.81}(\text{CO}_3)_{2.27}(\text{OH})_{14.42} \cdot 5.42\text{H}_2\text{O}$ , carrboydite,  $(\text{Ni,Cu})_{6.90}\text{Al}_{4.48}(\text{SO}_4)_2(\text{CO}_3)_{2.78}(\text{OH})_{21.69} \cdot 3.67\text{H}_2\text{O}$ , and possibly nickelian calcite,  $(\text{Ca,Ni})\text{CO}_3$ . All of the minerals in this group were eliminated with the exceptions of gaspéite and zaratite on the basis of the analytical results. No sulphate could be detected in the mineral under examination so together with carrboydite, compounds such as jamborite,  $\text{Ni}_6\text{Ni}_2\text{SO}_4(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$  and honessite,  $(\text{Ni,Co,Fe})_6(\text{Fe,Ni})_2\text{SO}_4(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$  were also discounted.

TABLE II. Observed *d*-spacings (Å) of hydrozincite and nickeloan hydrozincite.  $\text{CuK}_\alpha$  radiation

Hydrozincite	Nickeloan hydrozincite
6.83*	6.80*
4.050	4.043
3.701	3.711
3.170*	3.161*
2.885	2.878
2.719*	2.720*
2.564	2.569
2.498	2.497
2.330	2.328
2.204	2.206
2.094	2.098
1.914	1.917
1.709	1.707
1.548	1.549

Powder X-ray crystallographic studies have also shown that neither gaspéite nor zaratite are present. Table II tabulates *d*-spacings for hydrozincite also from the Parc Mine together with the results for the nickel-containing mineral for comparison. Measurements of *d*-spacings agree well. The three strongest lines, marked with an asterisk in the table, correspond closely to those given in the literature (Roberts *et al.*, 1974) of 6.66, 2.72 and 3.14 Å for hydrozincite. Some variation in the strong low-angle reflection, where errors are greatest, has been noted in the past. Jambor and Pouliot (1965) give 6.77 Å for this line, which is in

fact fairly broad. None of the strong reflections of either zaratite (5.07, 8.93, 2.45 Å) or gaspéite (2.741, 1.692, 3.543 Å) was observed (Roberts *et al.*, 1974). Aurichalcite has three strong lines at 6.78, 3.68, and 2.61 Å (Jambor and Pouliot, 1965) but the two latter reflections were missing in the sample. Thus the possibility that the compound was a mixture of hydrozincite and a nickel-containing analogue of aurichalcite was discounted.

Analysis of the infra-red spectrum of the green mineral (Perkin Elmer 457 grating infra-red spectrometer calibrated against polystyrene) confirms the above findings. White (1974) has listed infra-red spectral data for zaratite, hydrozincite, and aurichalcite. The carbonate ion in hydrozincite has stretches at 837 ( $\nu_2$ ), 1400, 1515 ( $\nu_3$ ), and 710, 738 ( $\nu_4$ )  $\text{cm}^{-1}$ . In the nickel-containing sample absorptions occur at 836, 1510, 1400, 710, and 738  $\text{cm}^{-1}$ . Zaratite has  $\nu_2$  at 881 and 835  $\text{cm}^{-1}$  and aurichalcite  $\nu_2$  at 860, 835, and 821  $\text{cm}^{-1}$  and  $\nu_4$  at 742  $\text{cm}^{-1}$ . None of these frequencies is found in the spectrum of the nickel-containing compound. All of the evidence available therefore points to the fact that the green mineral is a nickel-rich hydrozincite.

This is the first time that substitution in the hydrozincite lattice by another transition metal ion has been proven. Ghose (1964) has determined the crystal structure of hydrozincite. The zinc atoms lie in three different coordination environments, one tetrahedral, and two different octahedral. While there seems little doubt that the nickel atoms in nickeloan hydrozincite lie in one of the latter sites, other metals such as Co(II) might substitute into the lattice in the tetrahedral site. Indeed, there appears to be no reason whatsoever against a wide variety of transition metal solid-solution in the hydrozincite lattice. Unfortunately very little analytical data on hydrozincites has been published with this possibility in mind.

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