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SOLID SOLUTIONS IN THE ANNABERGITE – ERYTHRITE – HÖRNESITE SYNTHETIC SYSTEM

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ABSTRACT

Previous crystal-structure determination of magnesian annabergite $(Ni,Mg)_3(AsO_4)_2 \cdot 8H_2O$ indicated that ordering of Ni and Mg occurs in nonequivalent octahedral sites; such ordering supports the possibility of miscibility gaps on the $Ni_3(AsO_4)_2 \cdot 8H_2O$ – $Mg_3(AsO_4)_2 \cdot 8H_2O$ (annabergite – hörnesite) join. In a predecessor study based on compositions of natural specimens, it was proposed that solid solution is incomplete both for annabergite – hörnesite and annabergite – erythrite $[Co_3(AsO_4)_2 \cdot 8H_2O]$. In the current study, syntheses by a slow-addition technique at 70 and 95°C indicated that the annabergite – erythrite solid solution is complete, that no miscibility gap is present on the annabergite – hörnesite join to at least 58 mol% Mg, and that no miscibility gap occurs on the erythrite – hörnesite join to at least 53 mol% Mg. Furthermore, no miscibility gaps are evident in the low-Mg portion of the annabergite – erythrite – hörnesite ternary system. Thus, interpretation of the compositions of these phases in oxidized mill-tailings impoundments can be done with the normal precautions for homogeneity, and without the added concern of the possible presence of miscibility gaps in the ternary system.

Keywords: annabergite, erythrite, hörnesite, syntheses, solid solution, arsenic, environment, mill tailings.

SOMMAIRE

Les données disponibles sur la structure cristalline de l'annabergite magnésienne $(Ni,Mg)_3(AsO_4)_2 \cdot 8H_2O$ démontrent une mise en ordre impliquant des sites octaédriques non équivalents. Une telle mise en ordre entraîne la possibilité d'une lacune de miscibilité dans le système $Ni_3(AsO_4)_2 \cdot 8H_2O$ – $Mg_3(AsO_4)_2 \cdot 8H_2O$ (annabergite – hörnesite). Dans une étude préliminaire fondée sur la composition d'échantillons naturels, la solution solide semblait incomplète dans les systèmes annabergite – hörnesite et annabergite – erythrite $[Co_3(AsO_4)_2 \cdot 8H_2O]$. Dans ce travail, les synthèses effectuées par une technique d'addition lente à 70 et 95°C montrent que la solution solide entre annabergite et erythrite est complète, qu'il n'y a aucune lacune de miscibilité entre annabergite et hörnesite jusqu'à au moins 58% du pôle Mg (en termes molaires), ni entre erythrite et annabergite jusqu'à au moins 53% du pôle Mg. De plus, nous ne décelons aucune lacune de miscibilité dans la partie à faible proportion de Mg du système ternaire annabergite – erythrite – hörnesite. L'interprétation des compositions de ces phases dans les amas de rebuts oxydés du traitement de minerais peut donc procéder avec les précautions normales pour s'assurer de la homogénéité, et sans crainte à propos de la présence possible de lacunes de miscibilité dans le système ternaire.

(Traduit par la Rédaction)

Mots-clés: annabergite, erythrite, hörnesite, synthèses, solution solide, arsenic, environnement, rejets miniers.

INTRODUCTION

The mineral hosts of arsenic and their fate both in oxidizing conditions in the near-surface portions of wastes and in their underlying anoxic zones are of considerable concern in environmental mineralogy because of the well-known toxicity of even trace amounts of arsenic on biota. Arsenic in mine-related effluents is derived most commonly from the acidic dissolution of arsenopyrite FeAsS, and members of the tetrahedrite–tennantite series $(Cu,Fe)_{12}Sb_4S_{13}$ – $(Cu,Fe)_{12}As_4S_{13}$, all of which are of widespread occurrence in many base-metal and gold deposits. Other types of deposits, however, such as the vein-related five-element (Ag–Bi–Ni–Co–As) association and many uranium deposits, have the bulk of their arsenic contained in Ni–Co–Fe arsenides and sulfarsenides. Oxidation of these arsenides and sulfarsenides typically leads to the formation of secondary arsenates, which for Co and Ni are almost invariably pinkish and greenish coatings of, respectively, erythrite $Co_3(AsO_4)_2 \cdot 8H_2O$ and annabergite $Ni_3(AsO_4)_2 \cdot 8H_2O$.

Erythrite also has been identified as an abundant secondary phase in the cores of mill-tailings from the five-element-type silver deposits at Cobalt, northern Ontario (Dumaresq *et al.* 1994, Jambor 1994). Thus, crystallization of erythrite imposes a significant, if not dominant, control on the pore-water concentrations of both Co and As, but the extent of solid-solution toward annabergite in this specific occurrence is not known. In contrast to annabergite and erythrite, the analogous arsenates of Fe, Mg, and Zn are relatively rare in oxidized mineral deposits, and none of these minerals has as yet been identified as a secondary product in sulfide-rich tailings.

TABLE 1. MEMBERS OF THE VIVIANITE GROUP

arsenates		phosphates	
annabergite	$Ni_3(AsO_4)_2{\cdot}8H_2O$	arupite	$Ni_3(PO_4)_2{\cdot}8H_2O$
hörnesite	$Mg_3(AsO_4)_2{\cdot}8H_2O$	barićite	$(Mg,Fe^{2+})_3(PO_4)_2{\cdot}8H_2O$
parasymplesite	$Fe_3(AsO_4)_2{\cdot}8H_2O$	vivianite	$Fe_3(PO_4)_2{\cdot}8H_2O$
köttigite	$Zn_3(AsO_4)_2{\cdot}8H_2O$		
erythrite	$Co_3(AsO_4)_2{\cdot}8H_2O$		

Annabergite, erythrite, and hörnesite $Mg_3(AsO_4)_2{\cdot}8H_2O$, are members of the vivianite group of arsenates and phosphates (Table 1) that crystallize in the monoclinic system, space group *C2/m*. The crystal structures of various members of the group have been determined (Mori & Ito 1950, Hill 1979, Fejdi *et al.* 1980, Giuseppetti & Tadini 1982). Complete solid-solution between AsO_4 and PO_4, and among the transition-metal cations, would be expected from crystallochemical considerations. Giuseppetti & Tadini (1982), however, pointed out in their structural determination of "cabrerite" [= magnesian annabergite, $(Ni,Mg)_3(AsO_4)_2{\cdot}8H_2O$] that transition metals preferentially enter the more distorted *M*(1) octahedral sites, and Mg occupies the less deformed *M*(2) sites. Thus, significant Ni–Mg ordering was found in "cabrerite", and it could be inferred that ordered substitution or restricted substitution might occur in the series, with the potential for the development of miscibility gaps.

On the basis of a compilation of compositions of annabergite and erythrite, Yakhontova *et al.* (1981) proposed that miscibility gaps exist between approximately $Co_{40}Ni_{60}$ and $Co_{20}Ni_{80}$ along the join $Co_3(AsO_4)_2{\cdot}8H_2O$ – $Ni_3(AsO_4)_2{\cdot}8H_2O$, and that additional miscibility gaps occur if the binary is extended into a ternary system involving $Mg_3(AsO_4)_2{\cdot}8H_2O$ (Fig. 1). These gaps, if valid, should have a crystal-

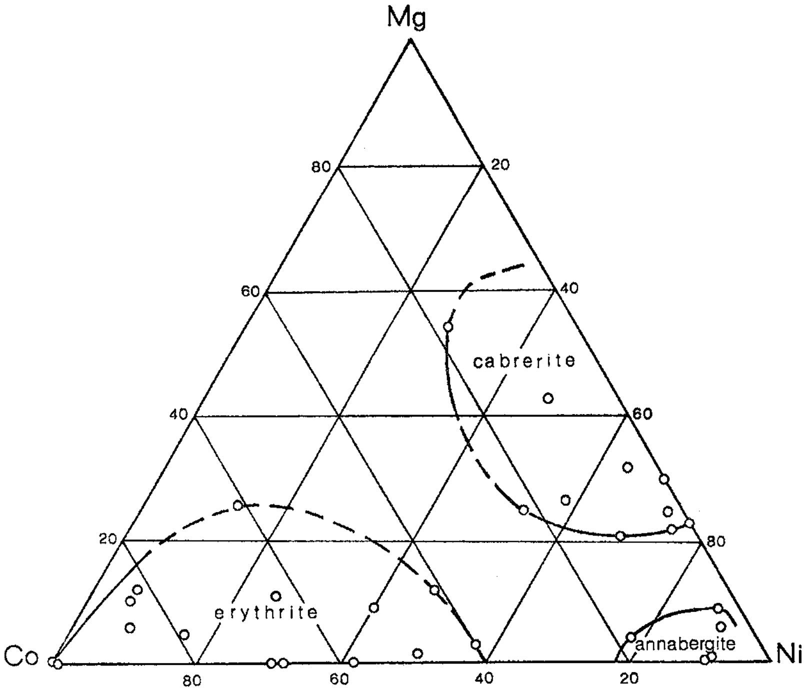

FIG. 1. Ternary diagram for the system $X(AsO_4)_2{\cdot}8H_2O$, showing the nomenclature and proposed limits of the solid-solution field, as derived from compositions of natural material (circles); redrawn from Yakhontova *et al.* (1981).

structure origin, and the effect on the mineral nomenclature of the ternary system would be profound. For this reason, and because of the significance of annabergite–erythrite with respect to environmental hydrogeochemistry, several specimens of the relevant minerals were obtained from the Systematic Reference Series of the National Mineral Collection housed at the Geological Survey of Canada, Ottawa. Portions of the specimens were mounted in polished sections and were quantitatively analyzed by electron microprobe. Although some solid solution was detected, most specimens proved to have compositions near those of the end members. As no new information concerning the miscibility gaps was obtained, synthesis experiments were undertaken to determine the extent of solid solution involving Ni–Co–Mg that can occur in the annabergite – erythrite – hörnesite ternary system, and especially along the annabergite–erythrite, annabergite–hörnesite, and erythrite–hörnesite joins. Mineralogical identification of secondary precipitates, and the specific compositions of these precipitates, generally are of critical importance in hydrogeochemical modeling of acidic mine-drainage systems. The secondary precipitates, however, are typically extremely fine-grained, and many are texturally complex and heterogeneous. Interpretation of the compositions, even if done by electron microprobe, therefore requires a cautious approach, especially where the results do not correspond to the compositions of known minerals or where previously defined limits of solid solution are exceeded. The latter can be encountered as a consequence of miscibility gaps in a series. This is the aspect that we evaluated in the annabergite – erythrite – hörnesite ternary system.

SYNTHESES

Preliminary experiments, wherein stoichiometric amounts of dissolved $Na_2HAsO_4{\cdot}xH_2O$ were mixed with 5 g/L Ni or Co nitrate solutions at pH 5 and 95°C, resulted in gel-like precipitates, the compositions of which were only approximately those of annabergite or erythrite. X-ray-diffraction analyses indicated very poorly crystallized phases. Similar results were realized for Ni, Co, and AsO_4 concentrations ranging from 0.2 to 25 g/L, for pH values from 3.2 to 7.0, and for temperatures from 25 to 140°C in the reaction vessel. Aging of the precipitates in their precipitation liquor for periods as long as 5 years failed to improve the crystallinity.

Because direct mixing of the reagents yielded gel-like products that did not crystallize on aging, we tried a slow-addition technique. In the general procedure, 250 mL of sodium arsenate solution, made by dissolving $Na_2HAsO_4{\cdot}xH_2O$ in water, are slowly pumped into 750 mL of solution containing the nitrate salt of Ni, Co, or Mg. The pH of both solutions is initially adjusted to 6.0 by the addition of NaOH or HNO_3. The 750 mL of solution are contained in a 2-L reaction kettle that is stirred on a temperature-controlled hot plate.

Preliminary experiments done with solutions at 95°C and containing 5 g/L Ni as the nitrate, chloride, or sulfate all yielded well-crystallized annabergite containing ~29% Ni, 46% AsO_4, and <0.1% NO_3, Cl, or SO_4. Nevertheless, all further tests were done using nitrate media to minimize the precipitation of impurity phases and to prevent the complexation of the metal ions at higher concentrations. Well-crystallized

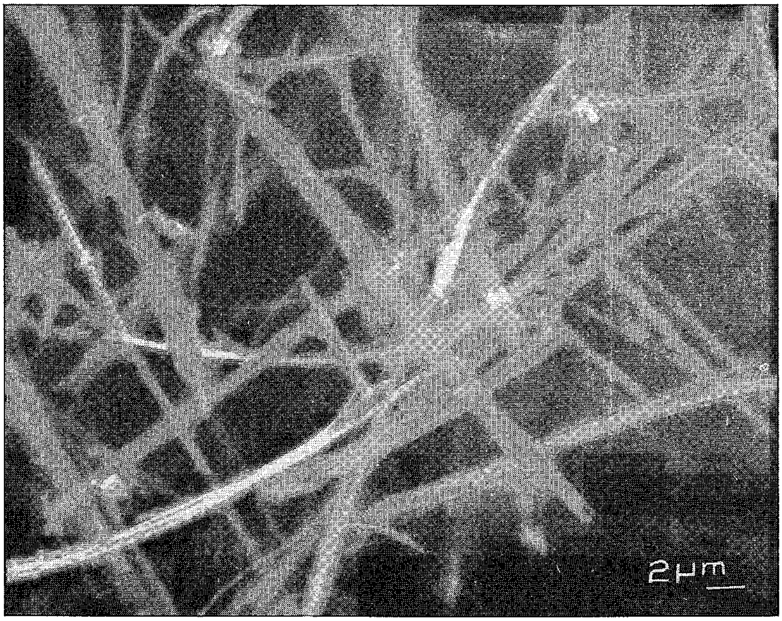

FIG. 2. Scanning electron-microscope photograph, showing the typical form and size of the synthesized products, in this case erythrite, sample F60.

annabergite or erythrite formed when the 250 mL of arsenate solution were pumped at 1.6 or 2 mL/h; a poorly crystallized product resulted when a pumping rate of 6 or 10 mL/h was used. The well-crystallized material consisted of fibrous crystals 1–2 μm across by 30–60 μm in length (Fig. 2). Reversing the pumping order, by pumping the metal nitrate solution into the hot stirred sodium arsenate medium, commonly yielded poorly crystallized material or arsenate phases other than annabergite – erythrite – hörnesite. Vigorous stirring of the nitrate solution was important to suppress the formation of gelatinous, poorly crystallized arsenate phases, and a stir bar was found more effective than a mechanical stirrer–agitator. A stirring speed of ~500 rotations min^{-1} was sufficient to yield well-crystallized material. In all of the experiments, the products were filtered, washed with copious amounts of water, and dried at 110°C for 24 h.

The concentration of the 750 mL of heated nitrate solution played a dominant role in the syntheses, and the concentration was more critical for Co or Mg than for Ni. For example, when a stoichiometric amount of sodium arsenate was pumped at 2 mL/h into 750 mL of $Co(NO_3)_2$ solution at pH 6 and 95°C, well-crystallized erythrite formed where the nitrate solution contained less than 0.7 g Co. Where the solution contained more than 1 g Co, unidentifiable crystalline phases having AsO_4 contents of more than 60% were produced. It was not possible to synthesize the Mg end-member (hörnesite) regardless of the Mg concentration used. No product was formed from solutions containing less than 2 g/L Mg, and unidentifiable precipitates were made at higher concentrations of Mg. In contrast, well-crystallized annabergite was formed from solutions containing up to 25 g/L Ni. Increasing the pH of the nitrate solution from 5.0 to 7.0 had little effect on the composition of the product or its crystallinity, but yielded slightly more precipitate (~0.8 g). Additional phases were detected in some of the syntheses done at pH 8.0. The presence of up to 2*M* $NaNO_3$ in the initial solution did not affect the crystallinity of the precipitates, but did slightly reduce the product yield. The temperature of the nitrate solution had little effect on the crystallinity of the precipitates. Temperatures of less than 65°C, however, slightly reduced the amount of precipitate, and for this reason the remaining syntheses were done at 70°C or 95°C.

Increasing the ratio of AsO_4 directly increased the amount of precipitate. As long as the stoichiometric molar ratio of AsO_4 to Ni or Co was <1.5, well-crystallized annabergite or erythrite formed. Higher ratios, however, resulted in poorly crystallized precipitates or unidentifiable phases.

On the basis of the above screening experiments, the following conditions were used to prepare members in the annabergite–erythrite binary series. A volume of 250 mL of a solution containing 1.48 g of AsO_4 (as $Na_2HAsO_4 \cdot xH_2O$) at pH 6.0 was pumped at 2 mL/h

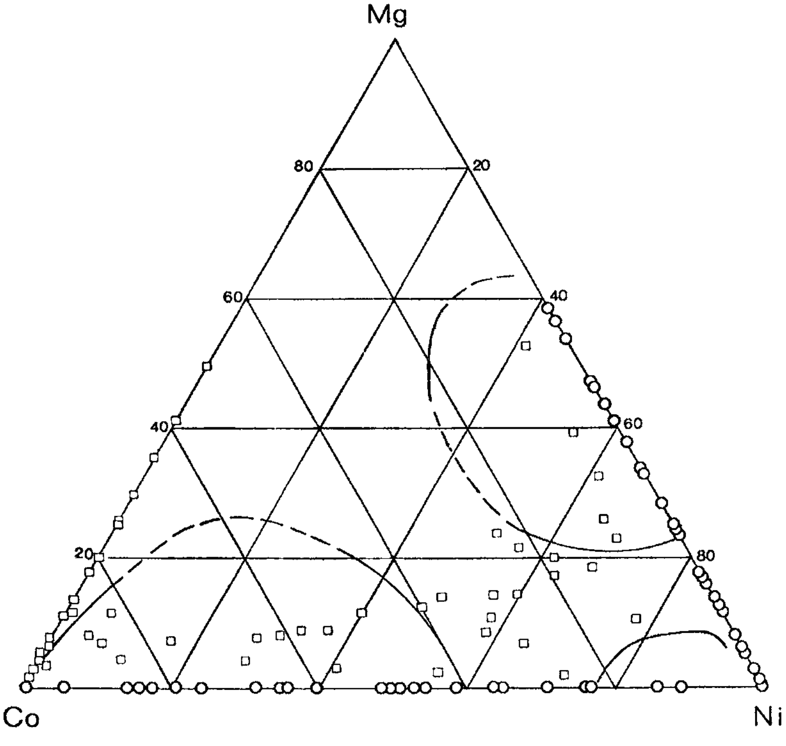

FIG. 3. Compositions synthesized (this study) along the Co–Ni (erythrite–annabergite) and Ni–Mg (annabergite–hörnesite) joins (circles), and along the Co–Mg join and within the ternary system (open squares). Outlines for the solid solutions proposed by Yakhontova *et al.* (1981) are as in Figure 1.

into 750 mL of vigorously stirred solution of Ni–Co nitrate at pH 6.0 and 70°C. The ratio of Ni to Co was varied, but with the condition that the mass of Ni+Co be equal to 0.5 g. The conditions used to prepare members in the annabergite–hörnesite series were identical, except that the mass of Ni+Mg was 0.8 g, and some tests were done at 95°C in addition to those carried out at 70°C. Members of the erythrite–hörnesite series were prepared at 70°C from solutions containing 0 to 0.5 g Co and 0 to 1.0 g Mg. The ternary compositions were synthesized at 70°C from solutions containing 0 to 0.8 g Mg and variable amounts of Ni and Co, but with the restriction that the mass of Ni+Co be equal to 0.5 g.

RESULTS

All of the products were chemically analyzed for Ni, Co, and Mg, and many also were analyzed for As. All of the products were checked for homogeneity using Guinier – de Wolff X-ray patterns and Co radiation. Cell dimensions of selected samples were obtained by least-squares refinements of measurements from 114.54-mm Debye–Scherrer films obtained with Co radiation; corrections for shrinkage were derived either from back-reflections of the arsenate product, or by addition of MgO as an internal standard. Cell dimensions of other selected samples were obtained by slow scan using a Rigaku automated diffractometer and Cu$K\alpha_1$ radiation, with the addition of MgO as an internal standard in some samples.

Annabergite–erythrite series

Compositions synthesized for the annabergite–erythrite binary are shown in Figure 3. The syntheses indicate that solid solution is complete for the Co–Ni binary system.

Cell dimensions calculated from the Debye–Scherrer films were less accurate than those obtained from the diffractometer measurements even though the level of precision obtained from the least-squares refinements were similar for both methods (Jambor & Dutrizac 1995). The reason for the difference is that

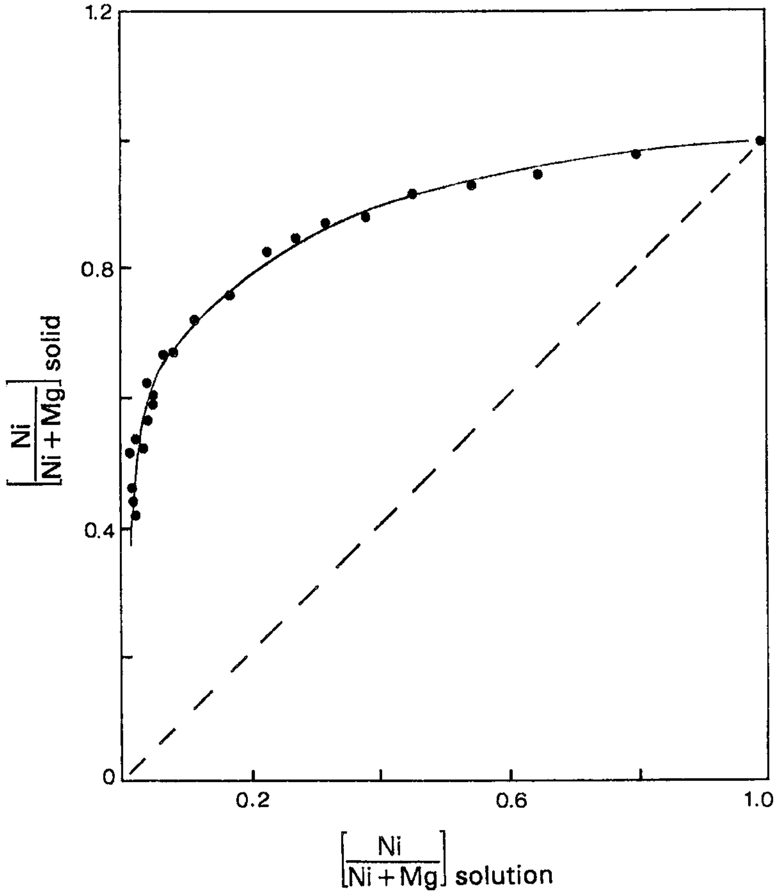

FIG. 4. Molar partitioning curve showing the variation of the Ni/(Ni + Mg) molar ratio of the precipitate with the Ni/(Ni + Mg) molar ratio of the initial solution.

13 to 20 diffraction lines were used to obtain the refinements for the Debye–Scherrer patterns, whereas for the diffractometer data, the smallest number of diffraction lines used for a refinement was 26 (one sample), and the average for all samples was 33. For the annabergite–erythrite series, the regression equations relating the mol% Ni and the diffractometer-determined cell parameters (in Å) are: $a = 10.1202 - 0.000615\ (x)$, $b = 13.4378 - 0.001287\ (x)$, $c \sin \beta = 4.6599 - 0.00056\ (x)$, and $V = 633.854 - 0.1832\ (x)$, where x is mol% Ni, β is in degrees, and V is in Å^3.

Annabergite–hörnesite series

Compositions synthesized for the annabergite–hörnesite binary (Fig. 3) extend across the previously proposed miscibility gap and show that solid solution is continuous to the limits of the syntheses. Extension toward the hörnesite end-point could not be accomplished in the syntheses because declining yields eventually led to insufficient quantities of material for chemical analyses. The problem is related to the strong tendency of Mg to remain in solution under the conditions of synthesis used. As the molar partitioning curve of Figure 4 shows, Ni is strongly precipitated with respect to Mg, and near-end-member annabergite is formed even from solutions containing 50 mol% Mg. Solutions very concentrated in Mg still yielded precipitates containing >40 mol% Ni. In addition, the amount of product decreased sharply in the Mg-rich media, and no product was formed from solutions containing only Mg.

Cell dimensions for seventeen of the samples in the annabergite–hörnesite series were obtained by diffractometer, as for the Ni–Co series; the number of diffraction lines used for the least-squares refinements, however, varied from 15 to 23, such that the accuracy is not as good as for the Ni–Co series. Nevertheless, trends are readily apparent, and indicate that the cell parameters increase with increasing substitution of Mg for Ni. Thus, cell volumes increase with increasing contents of Mg, whereas cell volumes in the annabergite–erythrite series decrease as the Ni content increases (Fig. 5). These trends are consistent with the ionic radii for Ni, Co, and Mg in octahedral coordination (Whittaker & Muntus 1970). For the annabergite–hörnesite series, the regression equations relating the mol% Mg and the cell parameters (in Å) are: $a = 10.039 + 0.000917\ (x)$, $b = 13.306 + 0.001474\ (x)$, $c \sin \beta = 4.621 + 0.000278\ (x)$, and $V = 617.343 + 0.163\ (x)$, where x is the mol% Mg, β is in degrees, and V is in Å^3.

Erythrite–hörnesite series

Results for the erythrite–hörnesite series (Fig. 3) indicate that solid solution is continuous up to the experimental limits at 52.8 mol% Mg. Plots of cell dimensions show that there is little variation with Co–Mg substitution, as is apparent simply from a visual inspection of the data in Table 2. The cell volume increases with increasing Mg content, but the

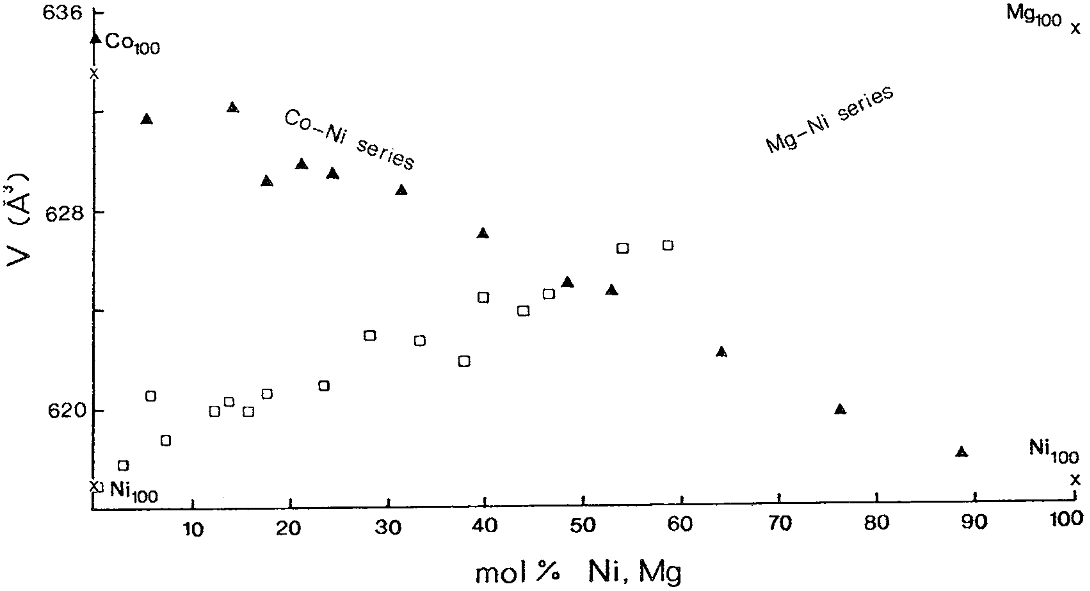

FIG. 5. Variations in cell volumes for the annabergite– erythrite and annabergite–hörnesite series, showing the increase in cell volume with increasing Mg substitution in the Mg–Ni series, and the decrease in cell volume with decreasing Co content in the Co–Ni series. NBS end-member points are shown as ×.

TABLE 2. CELL DIMENSIONS OF THE SYNTHETIC ERYTHRITE-HÖRNESITE SERIES

No.	*a* (Å)	*b* (Å)	*c* (Å)	β(°)	mol% Mg
NBS	10.118(5)	13.433(4)	4.762(2)	101.90(3)	–
G68	10.122(2)	13.436(2)	4.761(1)	101.96(1)	0.3
G69	10.122(2)	13.436(2)	4.762(1)	101.95(1)	0.7
G70	10.124(1)	13.438(2)	4.763(1)	101.96(1)	1.0
G71	10.121(1)	13.436(2)	4.764(1)	101.94(1)	1.6
G73	10.125(2)	13.440(2)	4.765(1)	101.95(1)	2.5
G74	10.122(1)	13.435(2)	4.762(1)	101.96(1)	2.8
G75	10.120(2)	13.437(2)	4.764(1)	101.95(2)	3.5
G76	10.124(1)	13.436(2)	4.761(1)	101.94(1)	4.9
G77	10.124(2)	13.437(2)	4.765(1)	101.95(2)	7.3
H83	10.119(1)	13.431(2)	4.760(1)	101.90(1)	10.6
G79	10.124(2)	13.439(2)	4.761(1)	101.88(1)	11.5
H82	10.123(2)	13.438(2)	4.760(1)	101.89(1)	13.7
G80	10.127(2)	13.441(2)	4.761(2)	101.84(1)	18.7
H81	10.119(1)	13.431(2)	4.759(1)	101.89(1)	18.7
H80	10.114(2)	13.424(2)	4.756(1)	101.88(1)	20.1
H78	10.123(2)	13.432(2)	4.759(1)	101.85(2)	25.4
H79	10.120(2)	13.431(2)	4.757(1)	101.87(2)	26.1
G78	10.122(1)	13.435(2)	4.761(1)	101.90(1)	29.7
H77	10.122(2)	13.434(2)	4.758(1)	101.80(2)	35.5
H76	10.125(2)	13.441(2)	4.759(1)	101.78(2)	41.3
H75	10.126(2)	13.443(2)	4.756(1)	101.78(1)	52.8
NBS	10.137(2)	13.445(2)	4.7542(10)	101.73(2)	100

NBS: National Bureau Standards (Morris *et al.* 1982)

This study: cell dimensions calculated by least-squares refinement of diffractometer data using Cu$K\alpha_1$ radiation, MgO internal standard; average of 39 diffraction lines (range 32 to 47) used for the refinements.

TABLE 3. CELL DIMENSIONS FOR SELECTED SAMPLES IN THE ANNABERGITE-ERYTHRITE-HÖRNESITE SERIES

					mol%		
No.	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	Mg	Ni	Co
F96	10.123(4)	13.430(2)	4.766(2)	101.94(3)	4.4	0.2	95.4
F97	10.121(5)	13.428(4)	4.761(3)	101.96(4)	4.4	11.1	84.5
F98	10.097(5)	13.407(4)	4.757(3)	101.97(3)	4.2	28.1	67.7
F99	10.087(4)	13.386(3)	4.752(2)	101.97(2)	3.0	41.0	56.0
F100	10.089(6)	13.369(4)	4.744(3)	102.01(4)	2.9	54.7	42.4
F101	10.060(7)	13.341(5)	4.736(4)	102.09(5)	1.9	72.5	25.6
F102	10.053(7)	13.307(5)	4.724(4)	102.09(5)	0.1	99.8	0.1

Diffractometer data as in Table 2; 19 to 24 diffraction lines used for the least-squares refinements.

change is less than 0.3% over the total composition span from erythrite to hörnesite. For the erythrite–hörnesite series, the equations relating the mol% Mg and the cell parameters (in Å) are: a = 10.121 + 0.000116 (x), b = 13.433 + 0.000147(x), $c \sin\beta$ = 4.659 – 0.000053 (x), and V = 633.473 + 0.007 (x), where x = mol% Mg, β is in degrees, and V is in Å^3.

Annabergite – erythrite – hörnesite series

Results for the annabergite – erythrite – hörnesite series do not indicate that a miscibility gap is present within the field of compositions that was synthesized (Fig. 3). Extension of the compositional range to members higher in Mg content was limited by low yields of the reaction product that were insufficient for chemical analysis. Although the individual particles were too small for meaningful electron-microprobe analysis, semiquantitative SEM–EDX analyses conducted at both 15 and 20 kV showed that all of the particles contained Ni, Co, and Mg, and that no variation in composition was detectable from crystal to crystal or along the length of the crystals.

Cell dimensions of a series of samples from near the annabergite–erythrite join are listed in Table 3. National Bureau of Standards data (Morris *et al.* 1982) for synthetic erythrite and hörnesite indicate that *a* and *b* increase by only 0.00019 Å and 0.00022 Å, respectively, per mol% Mg, and that *c* decreases by 0.0008 Å per mol% Mg. Thus, adjustments to the cell parameters of samples low in Mg can be taken as negligible; Figure 6 shows the decreases in cell dimensions and volume that result as the proportion of Ni in the mol ratio [Ni/(Co+Mg)] in these products increases.

CONCLUSIONS

The mineralogical characterization of secondary precipitates is of critical importance in the hydrogeochemical modeling of acidic mine-drainage systems. In most sulfide-rich mill-tailings impoundments, the main control of pore-water Ni and As concentrations has been found to be adsorption on goethite (Jambor & Blowes 1991, Jambor & Owens 1993, Alpers *et al.* 1994). In tailings from the arsenide–silver deposits at Cobalt, Ontario, erythrite is present as a secondary phase, and its precipitation would be expected to exert a significant, if not predominant, control on the pore-water concentrations of Co and As, and probably also on the concentrations of Ni, which substitutes for Co. Syntheses experiments have shown that Ni-for-Co and Ni-for-Mg substitutions occur to more than 50 mol% Mg without interruption along the binary joins in the synthetic system. Thus, it is likely that interpretation of the compositions of these phases in tailings can be done with the normal precautions for homogeneity, but without the added concern of the possible presence of miscibility gaps in the ternary system.

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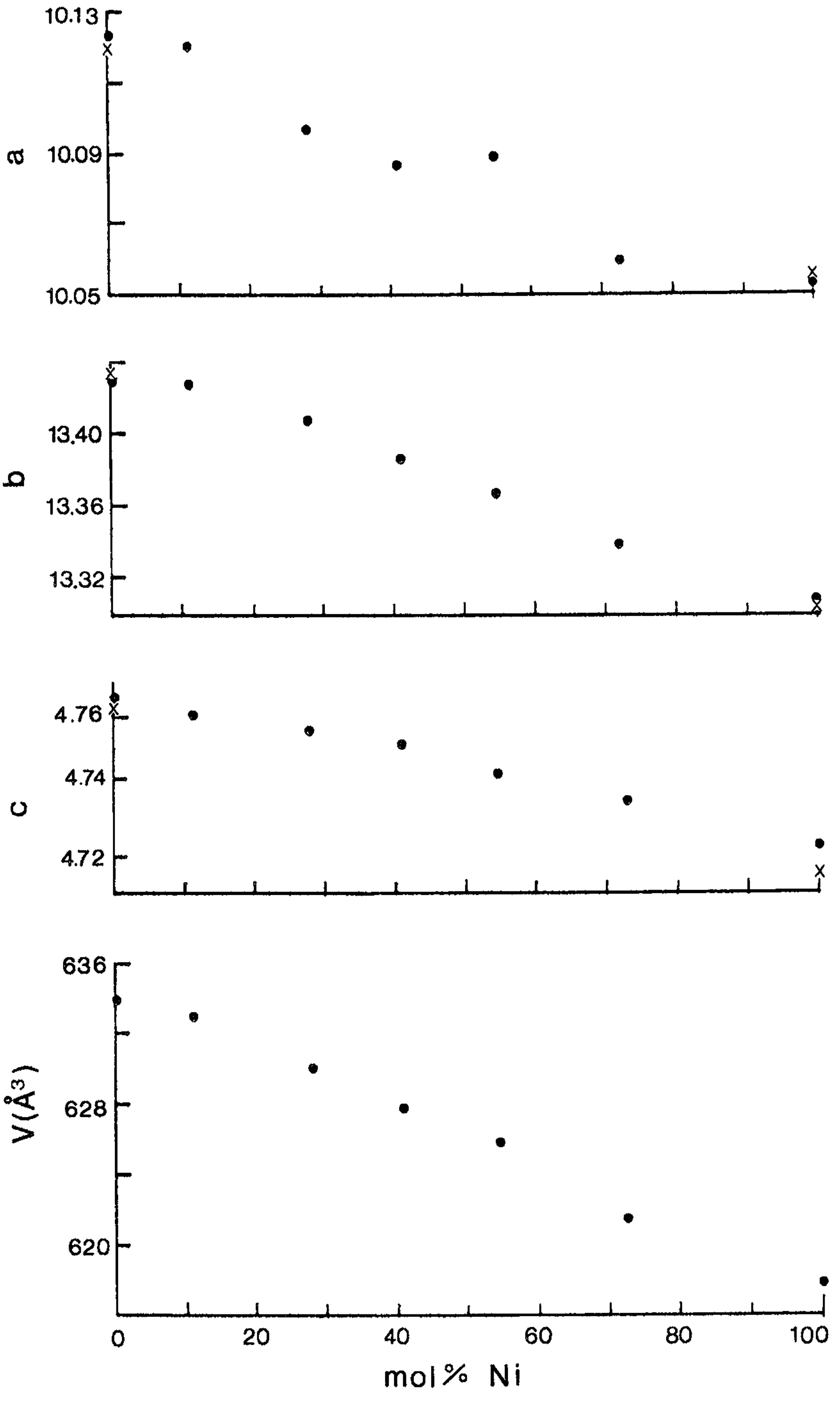

FIG. 6. Variation in cell dimensions (Å) and cell volume for the synthetic members of the annabergite – erythrite – hörnesite series listed in Table 3. NBS end-member points are shown as ×.

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