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Additional data on reevesite and its Co-analogue, as a new member of the hydrotalcite group

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ABSTRACT: Reevesite, the Ni-Fe member of the hydrotalcite group, occurs as a secondary mineral in the serpentinized ultramafic rocks of the Kwangcheon area in Korea, replacing the pecoraite-magnetite-millerite-polydymite assemblages in small veins lining cracks and fracture zones. Chemical analyses for the reevesites indicate the presence of the Co-analogue of reevesite and the complete solid-solution between Fe^{3+} and Co^{3+}. The Co-analogue of the reevesite shows the approximate ratio of 3:1 of divalent to trivalent cations, which is in distinct contrast to the comblainite with the ratio of 2:1 reported by Piret & Deliens (1980). The presence of the complete solid-solution phase between Fe^{3+} and Co^{3+} is confirmed by synthesis at room temperature. On the basis of the results, the Co-analogue of the reevesite should be named as a new member of the hydrotalcite group, and thereby be distinguished from the comblainite. The partial substitutions of SO_4^{2-} for CO_3^{2-} in the interlayer region might affect the slight increase of the basal spacing in the reevesite. The synthesis performed suggests that the reevesite could be precipitated under either an alkaline or a neutral environment, if carbonate activity is high enough.

Reevesite ($Ni_6Fe_2(OH)_{16}(CO_3)\cdot 4H_2O$), the nickel analogue of pyroaurite, was first reported in the weathered Wolf Creek Meteorite (White *et al.*, 1967), as bright yellow fine-grained aggregates lining cavities and cracks, and in the nickel ore from the Bon Accord area in the Barberton Mountain Land, South Africa (De Waal & Viljeon, 1971). It is composed of positively charged brucite-like sheets and contains charge-compensating CO_3^{2-} anions and water molecules in the interlayers, which identify it as a member of the hydrotalcite group. The reevesite found in the serpentinized ultramafic rocks of the Kwangcheon area in Korea is characterized by pseudomorphic textures after a pecoraite-magnetite-millerite-polydymite assemblage (Song *et al.*, 1995) and the significant substitution of Co^{3+} for Fe^{3+} in the octahedral sites. Piret & Deliens (1980) described comblainite as the Co-analogue of reevesite in the hydrotalcite group. However, the ratio of divalent to trivalent cations is close to 2:1, significantly different from the common ratio of 3:1 in the hydrotalcite group. Mendiboure & Schöllhorn (1986) synthesized the Ni-Fe and the Ni-Co compounds by coprecipitation of the corresponding hydroxides in strong alkaline solutions, resulting in those with the common ratio of hydrotalcite group minerals. The hydrotalcite group mineral found in the Kwangcheon area shows not only the reevesite component but also its Co-analogue with the ratio 3:1. In addition, the complete 1:1 substitutional relation between Fe^{3+} and Co^{3+} is also observed. In this paper the presence of the Co-analogue of reevesite with the ratio of 3:1 in the hydrotalcite group and the complete solid-solution between reevesite and its Co-analogue is reported, and the physicochemical conditions of these materials through synthesis are discussed.

DESCRIPTION OF SAMPLES

The reevesite occurs as golden yellow fine-grained aggregates replacing early-formed pecoraite-magnetite-millerite-polydymite assemblages during the advanced weathering processes in the Buk-site of the Kwangcheon area (Song *et al.*, 1995). As the reevesite is mixed with these pre-existing minerals and is fine-grained, it is very difficult to separate cleanly from othe material in the samples. The pre-existing pecoraite-magnetite-millerite-polydymite assemblages, which are found in small vein-filled cracks and fractures in the serpentinized harzburgite and/or lherzolite, are observed as relicts less frequently in the Buk-site than in the Nam-site where the jamborite-like material is found. The Ni sulphides occur less frequently in the Buk-site than in the Nam-site. In addition, the relative proportion of the millerite is higher than that of polydymite, especially in the Buk-site (Song *et al.*, 1995). This occurrence is closely comparable with those of the Wolf Creek Meteorite (White *et al.*, 1967) and the nickel ore from the Ben Accord area (De Waal & Viljeon, 1971). However, the presence of the relict of pecoraite and magnetite indicates that this occurrence is different from those previously reported.

EXPERIMENTAL PROCEDURES

Preliminary separation of reevesite for X-ray diffraction (XRD) analysis was carried out using a binocular microscope by hand-picking the yellow-coloured materials in a small part of the altered rocks collected from the veins of serpentinized ultramafic rocks. These samples were mounted for scanning electron microscopic observation and polished thin-sections were made for petrographic and subsequent electron microprobe examination after epoxy resin impregnation. Scanning electron microscopic and electron microprobe examination were performed with a JEOL JCXA-733 WDS electron microprobe using a correction suggested by Bence & Albee (1968), a beam current of 3.0×10^{-8} A, beam diameter of 5 μm, and 90 s counting time. Natural silicates and oxide minerals were used for the standard materials: diopside for Si, almandine for Fe, olivine for Mg, anhydrite for S, and pure Ni and Co oxides for Ni and Co, respectively. X-ray diffraction traces were obtained from random powders using a MAC MXP-3 XRD system with Ni-filtered Cu-$K\alpha$ radiation at 0.02° 2θ s^{-1} and divergent and receiving slits of 1 mm and 0.15 mm, respectively. Infrared (IR) spectra were obtained using an Analet FX-6160 FT-Infrared Spectrometer and the KBr pellet technique. Differential thermal analysis (DTA) for synthetic material was performed with a MAC TG-DTA 2000S equipment with α-Al_2O_3 as standard material, increasing the temperature at 12°C/min from 25°C to 1100°C. Chemical analysis was also performed for synthetic material by using the ICP-AES (inductively coupled plasma emission spectrometry) method in Royal Holloway, University of London.

MINERALOGICAL AND CHEMICAL CHARACTERIZATION

X-ray powder diffraction

The X-ray powder diffraction result for a representative reevesite is reported in Table 1. The strong reflection of the reevesite is observed at 7.796 Å, and the other obvious reflections at 3.874 Å, 2.603 Å, 2.319 Å, 1.542 Å and 1.512 Å, which are slightly different from those of previous works (White *et al.*, 1967; De Waal & Viljeon, 1971) (7.60 Å), but are similar to those of the synthetic materials of Mendiboure & Schöllhorn (1986) who reported the strongest reflection at 7.749 Å. The discrepancy in the basal spacings of those reevesites will be discussed later. The unit-cell dimensions for the reevesite were computed on the basis of a three-layer hexagonal unit-cell by using the programme developed for the MAC

TABLE 1. X-ray powder diffraction data for the reevesite from the Kwangcheon area. Spacings in Å.

	Reevesite from the Kwangcheon area		
hkl	$d_{obs.}$	$d_{calc.}$	I/I_o
003	7.796	7.790	100
006	3.874	3.877	60
012	2.603	2.596	60
015	2.319	2.306	40
018	1.542	1.542	30
113	1.512	1.513	40
116		1.434	
119		1.323	

$a_o = 3.085$
$c_o = 23.355$

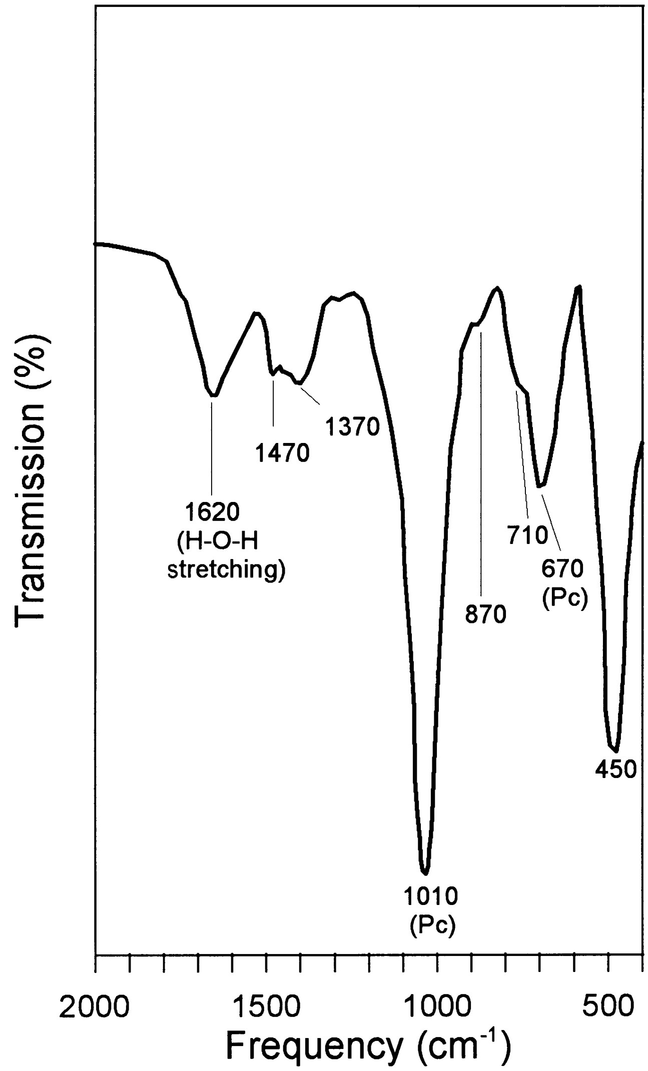

FIG. 1. FT-IR spectrum in the 2000–400 cm^{-1} range for the representative reevesite from the Kwangcheon area. Pc: pecoraite.

(Material Analysis and Characterisation Science Co., Ltd., Japan) system (Table 1). The results are a = 3.085 Å and c = 23.355 Å.

FT-infrared spectrum

Infrared spectroscopy can provide information for the charge-balancing anions in this material. The IR spectrum for the reevesite (Fig. 1) is characterized by several pronounced absorption peaks due to CO_3^{2-}. The CO_3^{2-} groups have three distinct bands below 1500 cm^{-1} frequency range due to internal vibrations; two of them are doubly degenerate asymmetric stretching of ν_3 at 1370–1470 cm^{-1} and planar bending of ν_4 at 710–715 cm^{-1}, one is non-degenerate out of plane bending of ν_2 at 850–900 cm^{-1} (Van der Marel & Beutelspacher, 1976). In spite of the high impurity and the low proportion of CO_3^{2-} in the material, the distinct double bands at 1370 and 1470 cm^{-1} (ν_3), and the shoulders at 870 cm^{-1} (ν_2) and 710 cm^{-1} (ν_4) are observed for the reevesite from the Kwangcheon area (Fig. 1), strongly indicating the presence of CO_3^{2-} as the charge-balancing anions. The splitting of the ν_3 frequency is similar to the spectra for takovite examined by Bish & Brindley (1977), but is different from other hydrotalcite group minerals, suggesting that the site symmetry of the CO_3^{2-} anion is lower in the Kwangcheon reevesite and takovite than the others (Bish & Brindley, 1977). An H_2O bending vibration occurs at 1620 cm^{-1}. The strong absorptions at 1010, 670, and 450 cm^{-1} can be attributed to cation-oxygen vibrations of associated pecoraite.

Chemical data

Quantitative electron microprobe analyses of the representative reevesites from the Kwangcheon area are listed in Table 2. The results show that the reevesite contains NiO as a main constituent, ranging from 45.6 to 48.2 wt%, with Fe_2O_3 from 0.5 to 15.6 wt%, Co_2O_3 from 1.7 to 16.4 wt%, and SO_3 from 0.4 to 0.6 wt%. The small amount of SiO_2 may be due to the residual pecoraite impurity. In recalculating the structural formulae of the analyses, several assumptions have been made; (a) total Fe and Co are all trivalent; (b) to allow CO_3^{2-} to be calculated, the number of charge-balancing CO_3^{2-} and SO_4^{2-} ions equals half of the number of Fe^{3+} + Co^{3+}; and (c) the formulae have been calculated on the basis of $O_3(OH)_{16}$. The results are also listed in Table 2. The numbers of Fe^{3+} + Co^{3+} and Ni are 1.95–2.11 and 5.64–6.07, respectively. These results indicate that the formula of the reevesite agrees closely with that of the reevesite and of the reevesite-like compound synthesized by Mendiboure & Schöllhorn (1986), although the numbers of trivalent cations in the octahedral sites decrease slightly with increasing Co component in the unit-cell (Fig. 2A). The calculated CO_2 ranges from 4.2–4.9 wt%. The significant fact is that Co^{3+} continuously substitutes for Fe^{3+} in the octahedral sites and the almost pure Co end-

TABLE 2. Electron microprobe analyses and structural formulae for representative reevesites and their Co-analogues.

SiO_2	4.87	2.96	3.14	3.73	2.93	5.20	6.34
Fe_2O_3	0.47	1.96	6.92	11.28	13.61	14.54	15.58
MgO	0.66	0.55	0.23	0.31	0.28	0.48	0.46
NiO	48.18	48.45	47.53	46.57	45.67	45.84	47.17
Co_2O_3	16.37	14.83	10.84	6.84	4.68	3.12	1.69
CO_2*	4.19	4.24	4.54	4.59	4.70	4.54	4.38
SO_3	0.52	0.44	0.45	0.61	0.53	0.54	0.66
H_2O**	15.41	15.41	15.60	15.70	15.62	15.48	15.59
Total	90.67	88.84	89.25	89.63	88.02	89.74	91.87
Number of cations on the basis of $O_3(OH)_{16}$							
Si	0.758	0.461	0.483	0.570	0.450	0.806	0.975
Fe^{3+}	0.055	0.229	0.801	1.297	1.573	1.695	1.804
Co^{3+}	1.846	1.672	1.207	0.757	0.521	0.350	0.189
Sum	1.901	1.901	2.008	2.054	2.094	2.045	1.993
Mg	0.153	0.128	0.053	0.071	0.064	0.111	0.106
Ni	6.033	6.066	5.877	5.723	5.641	5.713	5.837
Sum	6.186	6.194	5.930	5.794	5.705	5.824	5.943
CO_3^{2-}	0.890	0.900	0.952	0.957	0.986	0.960	0.920
SO_4^{2-}	0.061	0.051	0.052	0.070	0.061	0.063	0.076
Sum	0.951	0.951	1.004	1.027	1.047	1.023	0.996

CO_2* and H_2O** are calculated values on the basis of assumptions mentioned in the text

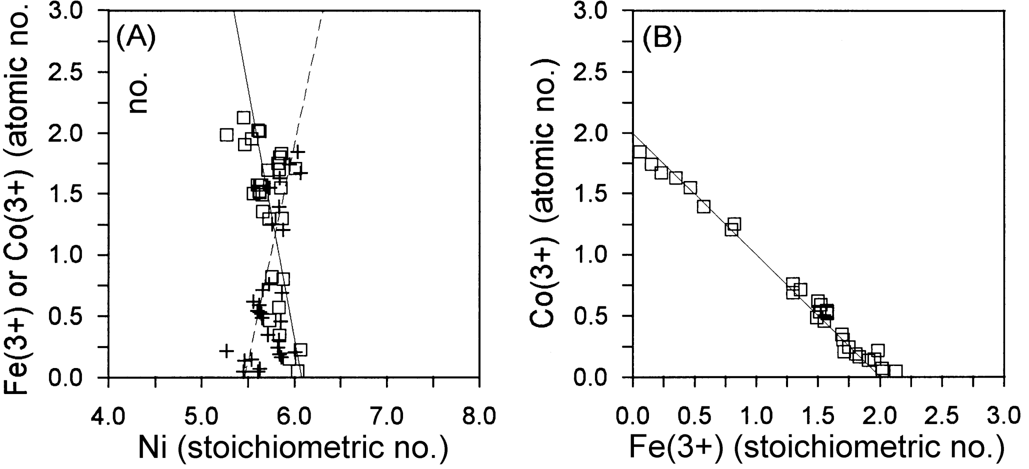

FIG. 2. Variational diagrams showing the compositional relations between Ni and Fe^{3+} (open rectangle) or Co^{3+} (cross) (A), and Fe^{3+} and Co^{3+} (B), respectively, in the natural reevesite from the Kwangcheon area.

member is also detected in the limited part of the sample analysed. The compositional relation between Fe^{3+} and Co^{3+} was correlated in Fig. 2B. The small amount of SO_3 should be located in the interlayer region as SO_4^{2-} substituting for CO_3^{2-}, which indicates an increase of the honessite component (Bish & Livingstone, 1981; Nickel & Wildman, 1981).

SYNTHESIS AND CHARACTERIZATION

Synthesis

Some precipitates corresponding to the reevesite, Co-analogue, and Fe-Co solid-solutions were obtained by coprecipitation of hydroxides in an alkaline solution, which is basically similar to the method of Mendiboure & Schöllhorn (1986). The starting materials are Fe(III) nitrate and Ni(II) nitrate and CoF_3 was also used for Co^{3+} source material, precipitated as Co(III) hydroxide in H_2O solution, and then dissolved in concentrated HCl. Some mixtures of 1 M Ni, Fe, and Co solutions with appropriate ratios were prepared. Each solution was slowly added to a solution of 2 N Na_2CO_3 at room temperature. The precipitates which formed immediately from each mixed solution were centrifuged and thoroughly washed until the washing water reached a neutral pH, and dried at 40°C in an oven. A precipitate was also obtained from the Ni-Fe mixed solution under a neutral pH environment. The pH of the Na_2CO_3 solution was controlled through addition of concentrated HCl solution. Therefore, the absolute concentration of CO_3^{2-} was kept at a high level (generally, relative concentration of CO_3^{2-} is much lower than HCO_3^- and H_2CO_3 species in the neutral pH condition). The dried powders were yellow to brown for the Ni-Fe compound and dark green for the Ni-Co compound, and the gradual colour variations were clearly observed between Ni-Fe and Ni-Co compounds.

X-ray diffraction data

X-ray diffraction patterns for the synthetic materials are presented in Fig. 3. The reflections of the Ni-Fe compound are distinctly observed at 7.75 Å, 3.86 Å, 2.60 Å, 2.30 Å, 1.955 Å, 1.541 Å, and 1.513 Å. Comparison with the natural reevesite result in Table 1 indicates that a similar material has formed successfully. It also agrees well with the result of Mendiboure & Schöllhorn (1986). However, the intensity of the peaks gradually decreases with increasing substitution of Co^{3+} for Fe^{3+}, possibly due to the relatively low crystallinity of Co-rich compounds and to some amorphous phases containing Ni or Co which could be precipitated from the excess Ni or Co caused by inadequate ratio of Ni:Fe:Co. In spite of the low intensities of the diffraction patterns for Co-rich compounds, these indicate the formation of the

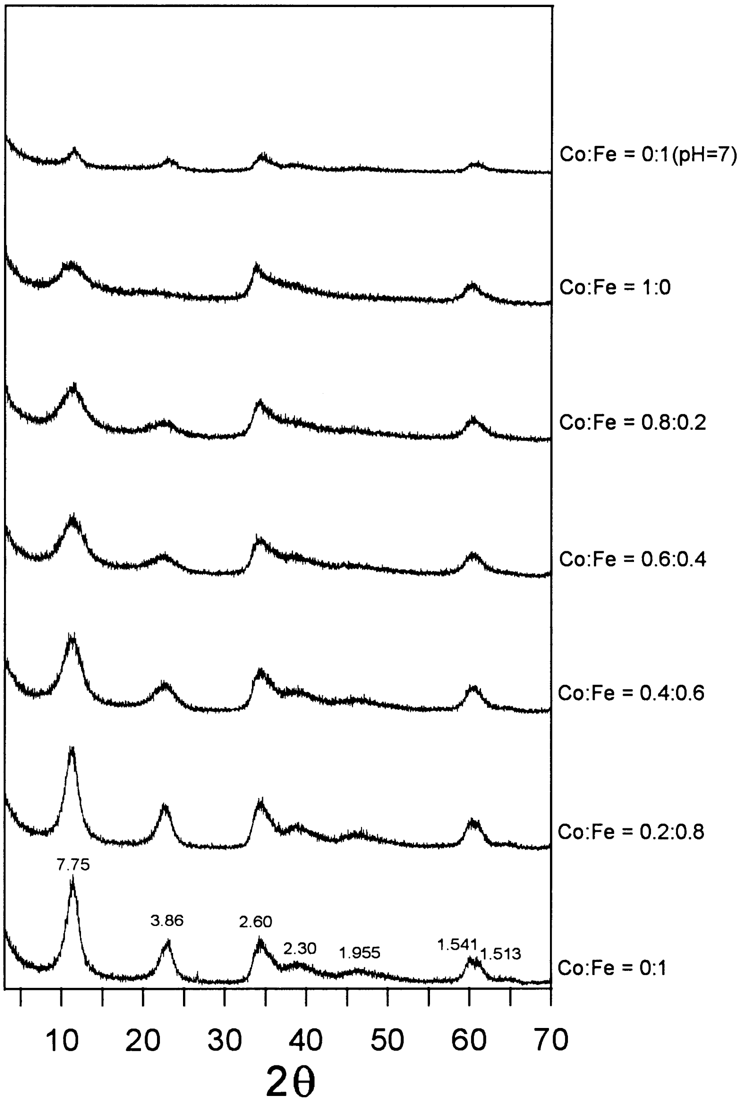

FIG. 3. X-ray diffraction patterns for the synthetic materials (Cu-$K\alpha$). Spacings in Å.

reevesite-like Ni-Fe-Co and Ni-Co compounds, which are also supported by the FT-IR and the DTA data presented later. The slurry obtained from the Ni-Fe mixed solution under the neutral environment (pH = 7) also can be interpreted as the reevesite-like compound (Fig. 3).

FT-infrared spectra

The IR spectra for the synthetic materials (Fig. 4) are characterized by typical pronounced absorption peaks due to CO_3^{2-}. The typical double peaks are observed at 1365 and 1470 cm^{-1} for the doubly degenerate vibrations of ν_3, and the typical band at 710–720 cm^{-1} due to the doubly degenerate vibrations of ν_4, which systematically changes from 720 to 710 cm^{-1} with the increase of the Co component in the materials. These are very similar to those of the natural reevesite after subtracting absorptions due to impurities. The splitting of the ν_3 frequency is also observed for all synthetic materials, strongly suggesting their structural

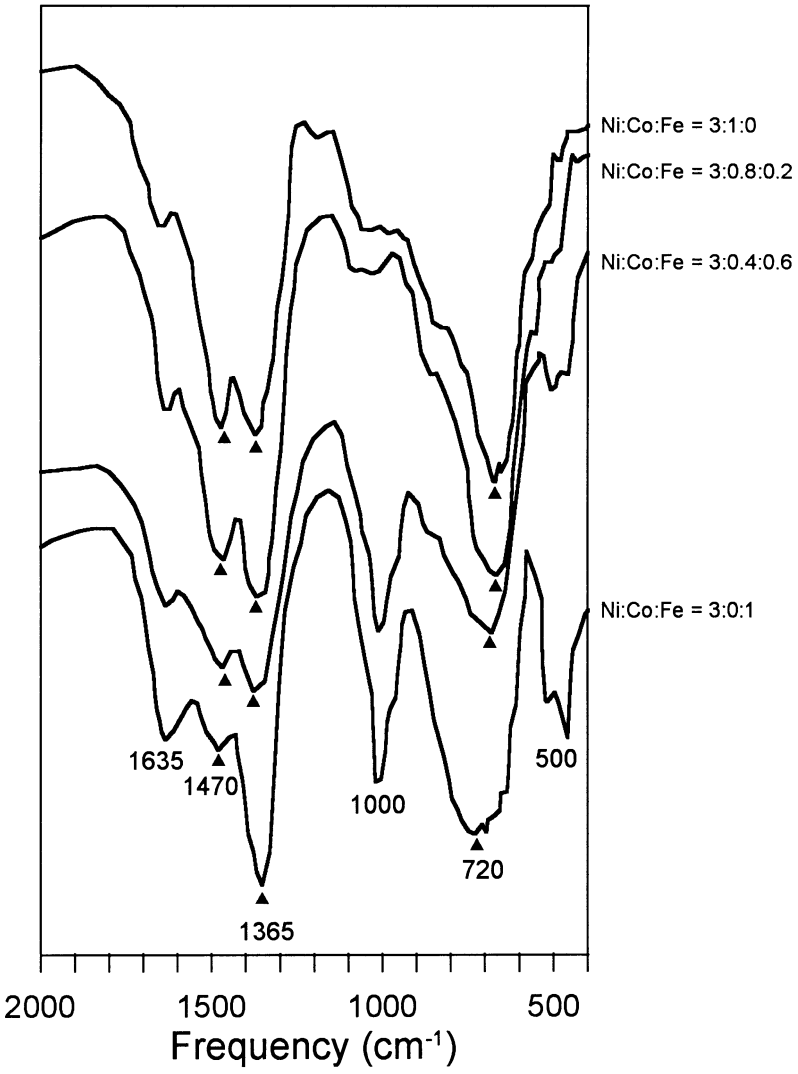

FIG. 4. FT-IR spectra in the 2000–400 cm^{-1} range for the representative synthetic materials.

similarity to the natural reevesite. An H_2O bending vibration occurs at 1635 cm^{-1}, too. The systematic variations of the ν_4 vibration might be interpreted as the systematic changes in the structure owing to the replacement of Co^{3+} for Fe^{3+}, suggesting that the solid-solution between Ni-Fe and Ni-Co end-members was successfully achieved. The absorptions at 1000 and 500 cm^{-1}, especially for the high Fe materials, are probably related to cation-oxygen vibrations.

Differential thermal analysis

The DTA curves for the synthetic materials (Fig. 5) show that the volatiles are expelled at two different temperatures below 340°C. The first peaks observed at 206°C for the Ni-Fe compound and 128°C for the Ni-Co compound are probably associated with the loss of molecular water. The second endothermic band at 307°C for the Ni-Fe compound and 333°C for the Ni-Co compound

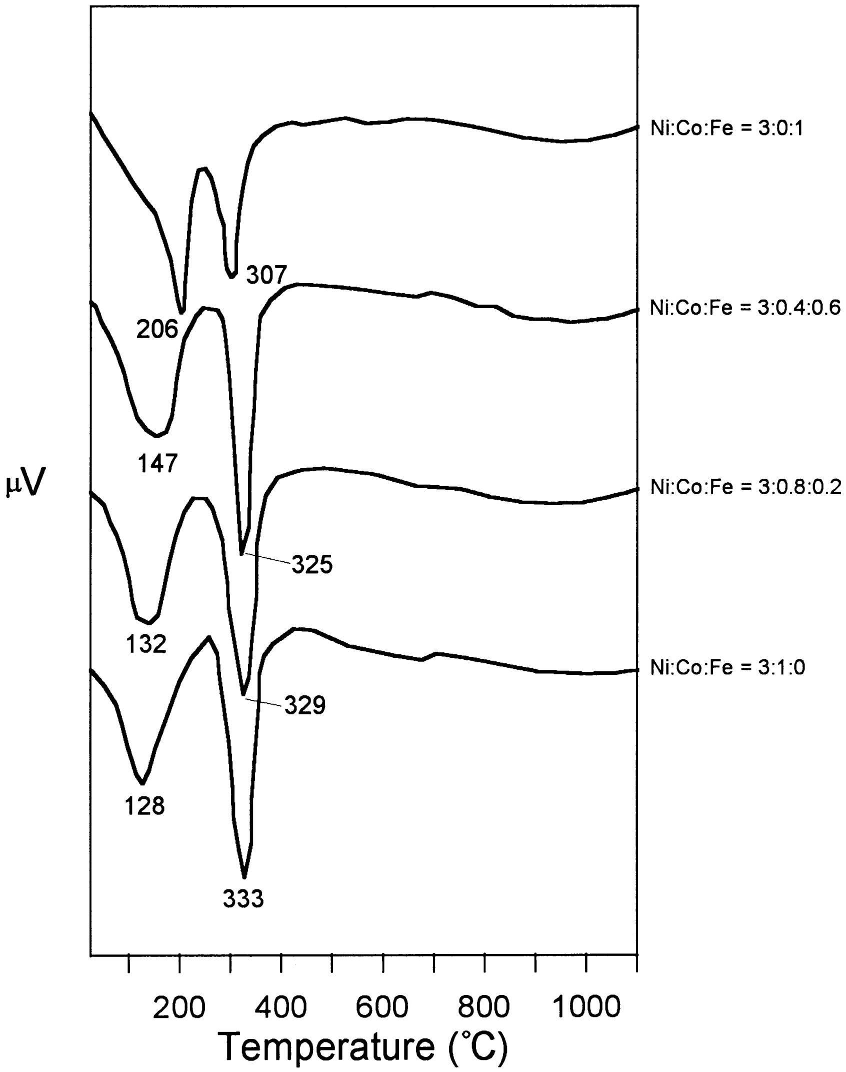

FIG. 5. Differential thermal analysis curves in the 25–1100°C temperature range for the representative synthetic materials.

probably represents dehydroxylation of structural water. These two reaction temperatures are in good agreement with the result for some takovite by Bish & Brindley (1977) who also confirmed that the loss of CO_2 was included in the second endothermic reaction. The systematic changes of the peaks, depending on the amount of Co^{3+} in the structure, corresponds to the results of the XRD and the FT-IR data.

Chemical analyses

The chemical analyses for the Ni-Fe, Ni-Co and Ni-Fe-Co synthetic materials are listed in Table 3. The chemical compositions of synthetic materials are similar to those of natural minerals: NiO ranges from 44.7 to 48.0 wt%, Fe_2O_3 from 1.3 to 17.6 wt%, and Co_2O_3 from 0.1 to 12.3 wt%. The structural formulae calculated on the same assump-

TABLE 3. Chemical analyses and structural formulae for the synthetic materials.

Fe_2O_3	17.62	14.51	10.93	8.47	5.50	1.33
NiO	44.70	45.35	45.64	46.17	45.76	47.96
Co_2O_3	0.05	2.08	3.99	6.56	8.83	12.30
CO_2*	4.87	4.55	4.07	4.08	3.86	3.63
H_2O**	15.09	14.73	14.06	14.16	13.77	13.82
Total	82.33	81.22	78.69	79.44	77.72	79.04
Number of cations on the basis of $O_3(OH)_{16}$						
Fe^{3+}	2.108	1.778	1.403	1.079	0.721	0.174
Co^{3+}	0.006	0.245	0.492	0.805	1.114	1.547
Sum	2.114	2.023	1.895	1.884	1.835	1.721
Ni	5.716	5.941	6.262	6.290	6.411	6.698
CO_3^{2-}	1.057	1.012	0.948	0.942	0.918	0.860

CO_2* and H_2O** are calculated values on the basis of assumptions mentioned in the text

tions as those for the natural samples are also listed in Table 3. The calculated structural formulae for the synthetic materials indicate that the total number of trivalent cations is getting lower, from 2.11 to 1.72, with the increase of the Co^{3+} contents in the octahedral sites, which is also observed in the natural samples. For the Ni-Co end-member, however, the substantial discrepancy of the Ni:Co ratio from 3:1 may be attributed to some underestimation of the Co concentration in solution by some loss during preparation of the Co^{3+}-containing solution from CoF_3; consequently, the excess Ni contents may be precipitated as a Ni hydroxide material. In spite of this, the variational trend in the compositions is similar to that of the natural samples.

DISCUSSION

Co-analogue of reevesite

The most distinct feature of the reevesite in this study is that Co^{3+} continuously substitutes for Fe^{3+} in the octahedral sheets and the almost pure Co end-member is also detected. The structural formulae for these reevesite and Co-analogues agree closely with that of general hydrotalcite group minerals with 3:1 ratio for divalent:trivalent cations, although the numbers of trivalent cations in the octahedral sites decrease slightly with the increase in the Co^{3+} component in the unit-cell. The valence state of Co was not determined in this work. However, the assumption that all Co is treated as being trivalent is made on the basis of the distinct substitutional relationship between Fe and Co with only a little variation of NiO.

Piret & Deliens (1980) described comblainite as the Co-analogue of reevesite in the hydrotalcite group with a 2:1 ratio for divalent to trivalent cations, which is, however, substantially different from the common ratio of 3:1 in hydrotalcite group minerals. The Co-analogue of reevesite with 3:1 ratio of divalent to trivalent cations has been reported only in the synthesis performed by Mendiboure & Schöllhorn (1986). Therefore, the Co-analogue of the reevesite with 3:1 ratio from the Kwangcheon area is the first reported occurrence in nature. In addition, the complete 1:1 substitutional solid-solution between Fe^{3+} and Co^{3+} is also observed, and is synthesized at room temperature. Most hydrotalcite group minerals in nature show the ratio of 3:1 with only a little deviation (Ingram & Taylor, 1967; White *et al.*, 1967; De Waal & Viljeon, 1971; Bish & Brindley, 1977; Brindley, 1979; Bish & Livingstone, 1981; Hudson & Bussell, 1981; Nickel & Wildman, 1981). On the other hand, several hydrotalcite group minerals with unusual ratios of divalent to trivalent cations were also reported in nature previously; woodwardite with 1.7–2.0:1 for Cu:Al (Nickel, 1976), carrboydite with 1.45:1 for Ni:Al (Nickel & Clarke, 1976), eardleyite with 1.75:1 for Ni:Al (Nickel *et al.*, 1977), and motukoreaite with 1.7:1 for Mg:Al (Rogers *et al.*, 1977; Brindley, 1979). Different mineral names were given to them, thereby distinguishing them from the minerals with the 3:1 ratio. Consequently, for the Co-Ni material with the 3:1 ratio from Kwangcheon, the name 'comblainite' should not be applied, but a new mineral name should be given, as a new member of the hydrotalcite group.

Mineralogical characteristics

The reflections for the natural reevesite are similar to the synthetic materials reported by Mendiboure & Schöllhorn (1986) (7.749 Å) and by the authors in this study (7.75 Å) rather than the previous results (White *et al.*, 1967; De Waal & Viljeon, 1971) (7.60 Å). White *et al.* (1967) and De Waal & Viljeon (1971) observed some additional reflections with low intensities which can only be indexed with a double hexagonal unit-cell and they then interpreted the XRD data as a double hexagonal unit-cell. These additional peaks, however, are not observed for the reevesite in this study or for the synthetic materials. The absence of these peaks in the synthetic materials is consistent with the result of Mendiboure & Schöllhorn (1986), indicating that the materials consist of a structure corresponding to a simple hexagonal unit-cell in contrast to the natural reevesites mentioned by White *et al.* (1967) and De Waal & Viljeon (1971). They suggested that the synthesis is kinetically too rapid to allow cation ordering, and thus the statistical distribution of Ni and Fe in the structure results in a single unit-cell, while the thermodynamic conditions of the natural synthesis may lead to an ordering of Ni and Fe in the structure, resulting in a double unit-cell. On the other hand, Bookin *et al.* (1993) reinterpreted the XRD data and proposed that the natural reevesite contains two phases; $3R_1$ polytype reevesite, which is isostructural to $3R_1$ hydrotalcite, and $3H$ modified reevesite as a transitional phase to $3R_1$ reevesite, which obviously cannot be attributed to the CO_3^{2-}-bearing hydrotalcite group. According to the interpretation of Bookin *et al.* (1993), the natural reevesite with the additional peaks is relatively unstable compared to the synthetic one, which is contrary to the suggestion by Mendiboure & Schöllhorn (1986). And it also indicates that the natural and the synthetic reevesites in this study were possibly precipitated as relatively stable phases, i.e. they would be composed of the $3R_1$ single phase only without $3H$ modified reevesite; they would then show the basal spacing similar to that of the synthetic materials of Mendiboure & Schöllhorn (1986). The high impurity content and the relatively low crystallinity of the natural reevesite may also be responsible for the absence of the low intensity peaks.

Another possibility can be found in its chemical composition. In the interlayer region of this reevesite, a small amount of CO_3^{2-} was substituted by SO_4^{2-} (0.4–0.6 wt%, listed in Table 2), indicating the presence of the honessite component, the sulphate analogue of reevesite (Bish & Livingstone, 1981; Nickel & Wildman, 1981). This could cause an increase in the basal spacing of the reevesite due to the difference in molecular geometry of carbonate and sulphate groups. Many previous works have reported some hydrotalcite group minerals with SO_4^{2-} and/or both of SO_4^{2-} and CO_3^{2-}, showing larger basal spacings than those with CO_3^{2-} (Nickel, 1976; Nickel & Clark, 1977; Rodger *et al.*, 1977; Bish & Livingstone, 1981; Nickel & Wildman, 1981; Hudson & Bussell, 1981). It is supported well by the results of the experimental exchange of CO_3^{2-} to SO_4^{2-} for the synthetic reevesite-like compounds by Mendiboure & Schöllhorn (1986). Brindley (1979) also showed a change in the basal spacing for a natural motukoreaite after anion exchange.

Physicochemical environment

It is evident that the reevesite was formed as a secondary alteration product after pecoraite-magnetite-millerite-polydymite assemblages. Considering the reevesite-forming processes, hydroxylation and decomposition of these assemblages, the oxidation of magnetite, and supply of CO_3^{2-} are required. The coexisting Ni sulphides should be dissolved to furnish some element, not only Ni, Fe and Co but also a small amount of SO_4^{2-}. The possible reactions for reevesite formation are as follows:

$$\underset{\text{pecoraite}}{12Ni_3Si_2O_5(OH)_4} + \underset{\text{magnetite}}{4FeO{\cdot}Fe_2O_3} + 6CO_2 + O_2 + 96H_2O \rightleftharpoons \underset{\text{reevesite}}{6Ni_6Fe_2(OH)_{16}(CO_3){\cdot}4H_2O} + 24H_4SiO_4(aq.)$$

$$\underset{\text{pecoraite}}{12Ni_3Si_2O_5(OH)_4} + \underset{\text{magnetite}}{4FeO{\cdot}Fe_2O_3} + 6CO_2 + 98H_2O \rightleftharpoons \underset{\text{reevesite}}{6Ni_6Fe_2(OH)_{16}(CO_3){\cdot}4H_2O} + 24H_4SiO_4(aq.) + 4H^+$$

As shown in the above reactions, the reevesite can be formed under a relatively oxidized and/or low hydrogen activity (alkaline) environment. It could be supported by the results of synthesis performed in a strong alkaline environment by Bish (1977), Bish & Brindley (1977), Brindley & Kikkawa (1979), Mendiboure & Schöllhorn (1986), and in this study. The reevesite-forming reactions also require the oxidation of Fe to the ferric state, which would be provided by the earth-surface environment. In addition, the necessity of CO_2 in the reactions also strongly suggests that the process must proceed under a high carbonate anion activity environment, which could be formed easily in an alkaline condition with low CO_2 partial pressure, but could also be obtained in a neutral or acidic condition with high CO_2 partial pressure. In a neutral or weak acidic condition, in spite of its extremely low proportion of the carbonate species, significant amounts of CO_3^{2-} could be provided for reevesite under high CO_2 partial pressure. The synthesis performed in a neutral solution (pH = 7) with a high carbonate anion activity condition in this study supports the above interpretation. These considerations suggest that the reevesite and the reevesite-like compounds might be formed both in an alkaline and in a neutral or a weak acidic environment, if a high carbonate acitivity is sustained.

Bish (1977) showed that the hydrotalcite group minerals have a marked chemical affinity for CO_3^{2-} over SO_4^{2-}, through synthesis for carbonate and sulphate forms of these minerals. Therefore, the substitution of SO_4^{2-} for CO_3^{2-}, in spite of its low proportion, indicates the existence of significant amounts of SO_4^{2-}, possibly provided from the oxidation of pre-existing Ni sulphides (Song *et al*., 1995).

CONCLUSIONS

The presence of the real Co-analogue of reevesite with a ratio of divalent to trivalent cations of 3:1 in the natural system is reported for the first time. It is significantly different from the comblainite described by Piret & Deliens (1980) in which the ratio of divalent to trivalent cations is close to 2:1. Therefore, the authors propose that the name comblainite for the mineral with the ratio of 2:1 should not be used for the Co-analogue of reevesite, and a new mineral name should be given to the Co-analogue of the reevesite from the Kwangcheon area, as a new member of hydrotalcite group. Another important fact is the presence of the complete solid-solution relationship between Fe^{3+} and Co^{3+} components in nature. The Co^{3+} component continuously and completely substitutes for Fe^{3+} in the octahedral sites. These solid-solutions with different ratios of Fe^{3+} to Co^{3+} were also synthesized in an alkaline solution and at room temperature.

The slight difference in the most intense reflections between the reevesite in this study and those of previous works, and the lack of some low-intensity peaks in the reevesite from Kwangcheon might be due to either the absence of 3*H* modified phase in the reevesite from Kwangcheon, the high impurity content, and the relatively low crystallinity, or the substitutions of SO_4^{2-} for CO_3^{2-} in the interlayer region of the reevesite.

The synthesis and the genetic considerations for the reevesite compound suggest that it could be precipitated under neutral as well as alkaline conditions, if there is a high carbonate activity.

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