

THE CANADIAN MINERALOGIST

The Canadian Mineralogist
Vol. 37, pp. 545-558 (1999)

CARROLLITE AND RELATED MINERALS OF THE LINNAEITE GROUP: SOLID SOLUTIONS AND NOMENCLATURE IN THE LIGHT OF NEW DATA FROM THE SIEGERLAND DISTRICT, GERMANY

THOMAS WAGNER¹

Mineralogisches Institut der Universität Würzburg, Am Hubland, D-97074 Würzburg, Germany

NIGEL J. COOK

Geological Survey of Norway, Boks 3006 Lade, N-7040 Trondheim, Norway

ABSTRACT

Carrollite, ideally CuCo_2S_4 , is a major component of "rejuvenation stage" mineralization in the Siegerland ore province, Germany. Carrollite from seven representative deposits has been analyzed. Combining this dataset with published data on carrollite and related minerals, the existence of a solid-solution series in the Cu–Co–Ni–S system, and the mechanisms of substitution responsible, are established. The characteristic feature of carrollite at Siegerland is a pronounced incorporation of Ni in the structure, reaching a maximum of 30.20 wt.% in the Eiserner Spies deposit, corresponding to 1.55 Ni atoms per formula unit (Me_3S_4). Concentrations of Ni display an ideal negative correlation with Co and Cu. Nickel thus apparently substitutes for both Co and Cu over the entire range of compositions represented by our dataset. This solid-solution series extends from end-member carrollite, CuCo_2S_4 , toward what we consider as cuprian siegenite, itself a member of an extensive solid-solution between linnaeite and polydymite. Our data show no evidence for solid-solution series between carrollite and fletcherite. The substitution scheme for the observed linear correlation trends relating Ni, Co and Cu involves at least two different mechanisms of substitution, each operating independently. Two alternative models are proposed: (1) substitution of Ni^{3+} for Co^{3+} at octahedral sites and of Ni^{2+} for Cu^{2+} at tetrahedral sites, and (2) substitution of Ni^{3+} for Co^{3+} at octahedral sites combined with the coupled substitution $\text{Cu}^{2+} + \text{Co}^{3+} \rightarrow \text{Ni}^{3+} + \text{Ni}^{2+}$. Our data suggest that the substitution of Ni^{3+} for Co^{3+} is dominant. Nickelian carrollite contains $\text{Ni}/(\text{Ni} + \text{Co} + \text{Cu}) > 0.05$, up to a maximum halfway along the $\text{CuCo}_2\text{S}_4 - \text{CoNi}_2\text{S}_4$ join at $\text{Cu}_{0.5}\text{Co}_{1.5}\text{Ni}_{1.0}$. Phases with $\text{Ni} > 1.0$ and $\text{Cu} < 0.5$ should be termed cuprian siegenite, so long as $\text{Cu}/(\text{Cu} + \text{Ni} + \text{Co})$ exceeds 0.05.

Keywords: carrollite, siegenite, micro-analytical data, solid solution, nomenclature, Siegerland, Germany.

SOMMAIRE

On trouve la carrollite, dont la composition idéale est CuCo_2S_4 , comme phase importante au stade de minéralisation dit "de ré-activation" dans la province minéralisée de Siegerland, en Allemagne. Nous avons analysé la carrollite provenant de sept gisements représentatifs. À la lumière de cette nouvelle information et des données déjà dans la littérature portant sur la carrollite et les minéraux associés, nous documentons l'existence d'une solution solide dans le système Cu–Co–Ni–S, et nous précisons les mécanismes de substitution responsables. La carrollite de Siegerland se distingue par l'incorporation de quantités importantes de Ni dans la structure, jusqu'à 30.20% (poids) dans le cas de la carrollite du gisement de Eiserner Spies, ce qui correspond à 1.55

¹ E-mail address: thomas.wagner@mail.uni-wuerzburg.de

atomes de Ni par unité formulaire (Me_3S_4). Les concentrations de Ni démontrent une corrélation négative idéale avec le Co et le Cu. Le nickel remplacerait donc à la fois le Co et le Cu sur l'intervalle complet de solution solide représenté par nos données. La solution solide s'étend à partir du pôle carrollite, $CuCo_2S_4$, vers ce que nous traitons de siegenite cuprifère, qui, à son tour, fait partie d'une solution solide étendue entre linnaeïte et polydymite. Nos données ne contiennent aucun indice d'une solution solide entre carrollite et fletcherite. Le schéma proposé pour rendre compte des corrélations linéaires observées impliquant Ni, Co et Cu implique au moins deux mécanismes de substitution, indépendants l'un de l'autre: (1) substitution du Ni^{3+} au Co^{3+} dans les sites à coordinence octaédrique et du Ni^{2+} au Cu^{2+} dans les sites à coordinence tétraédrique, et (2) substitution du Ni^{3+} au Co^{3+} dans les sites à coordinence octaédrique avec substitution couplée $Cu^{2+} + Co^{3+} \rightarrow Ni^{3+} + Ni^{2+}$. Nos données font penser que la substitution du Ni^{3+} au Co^{3+} est le mécanisme dominant. Dans la carrollite nickelifère, le rapport $Ni/(Ni + Co + Cu)$ dépasse 0.05, jusqu'à un maximum à mi-chemin le long de la série $CuCo_2S_4 - CoNi_2S_4$, à $Cu_{0.5}Co_{1.5}Ni_{1.0}$. On devrait se servir du terme "siegenite cuprifère" pour signifier une proportion de Ni dépassant 1.0 et de Cu inférieure à 0.5 dans les cas où le rapport $Cu/(Cu + Ni + Co)$ dépasse 0.05.

(Traduit par la Rédaction)

Mots-clés: carrollite, siegenite, données microanalytiques, solution solide, nomenclature, Siegerland, Allemagne.

INTRODUCTION

Thiospinel minerals of the linnaeite group include the following naturally occurring species in the system Cu-Fe-Co-Ni-S: carrollite $CuCo_2S_4$, linnaeite Co_3S_4 , siegenite $(Co,Ni)_3S_4$, polydymite Ni_3S_4 , fletcherite $Cu(Ni,Co)_2S_4$, violarite $FeNi_2S_4$, and greigite Fe_3S_4 . Compositional data reported in the literature, experimental determinations of phase relations in the subsystems Cu-Co-S and Fe-Ni-S, theoretical considerations based on molecular orbital (MO) calculations and models, and Mössbauer spectroscopic studies have indicated the existence of the following solid-solution series: linnaeite-carrollite, polydymite-violarite and linnaeite-polydymite (Craig 1971, Vaughan *et al.* 1971, Minceva-Stefanova & Kostov 1976, Craig *et al.* 1979, Vaughan & Tossell 1981, Vaughan & Craig 1985, Charnock *et al.* 1990).

Additional solid-solution fields have been proposed to exist between carrollite and siegenite and between violarite and siegenite. Intermediate compositions along these solid solutions have been referred to as cuprian siegenite, nickelian carrollite, ferroan siegenite and cobaltian violarite (Craig & Higgins 1975, Minceva-Stefanova & Kostov 1976, Craig & Vaughan 1979, Shadlun *et al.* 1979, Riley 1980, D'Orey 1983, Jessey 1983, Pignolet & Hagni 1983, Zakrzewski 1984). Although the thiospinels in the system Cu-Co-Ni-Fe-S have attracted considerable attention by these and other researchers, some uncertainties remain. The extent of solid solutions in naturally occurring samples remains poorly defined, as do some of the mechanisms of substitution involved. Observation of mineral associations, coupled with micro-analytical data derived from natural occurrences of linnaeite-group minerals, can provide some of this information, and by implication, permit better constraints on the range of geological and chemical conditions at which they form.

BACKGROUND INFORMATION

Carrollite was originally described from Finksburg, Carroll County, Maryland, as a mineral with the com-

position $Cu_2Co_2S_4$ (Faber 1852). The subsequent discovery of a siegenite-like mineral that contains essential amounts of Cu, and especially Ni, from the Kohlenbach mine, Eiserfeld, Siegen, Germany, resulted in the proposal of a new species, named "sychnodymite" (Laspeyres 1891), although a possible relationship between "sychnodymite" and carrollite was recognized. The identities of carrollite and "sychnodymite" were later confirmed, the name "sychnodymite" being subsequently discredited. However, the name has been used to refer to a Ni-rich variety of carrollite (Craig *et al.* 1979).

Previous microscopic and mineral compositional studies of carrollite-bearing samples from the Siegerland district were mainly restricted to material from the occurrence at Kohlenbach, Eiserfeld (Stahl 1899, Berg 1928, Craig *et al.* 1979, Fenchel *et al.* 1985), although Rückert (1926) recognized a wider distribution of the mineral across the district. Our recent systematic studies of sample material from various localities throughout the Siegerland district have shown that carrollite is indeed very widespread, and present in most of the bornite-digenite-hematite-bearing samples from a number of occurrences. This has enabled us to obtain a relatively large body of new compositional data on carrollite from a number of Siegerland occurrences, allowing us to produce reliable evidence for extended solid-solution between carrollite and siegenite beyond the limits previously reported. We have also combined our new data with compositional data for other thiospinel minerals in the system Cu-Co-Ni-S available in the literature, leading to a series of models to account for observed variations in chemical composition.

THE SIEGERLAND DISTRICT

The Siegerland siderite district (Fig. 1) forms a part of the fold-and-thrust belt of the Rheinisches Schiefergebirge, belonging to the external zone of the Variscan orogenic belt (Oncken 1984, Franke & Oncken 1990). The siderite vein-type deposits are hosted within Lower Devonian pelitic to psammitic sedimentary rock sequences of Gedinnian to Siegenian age and are structur-

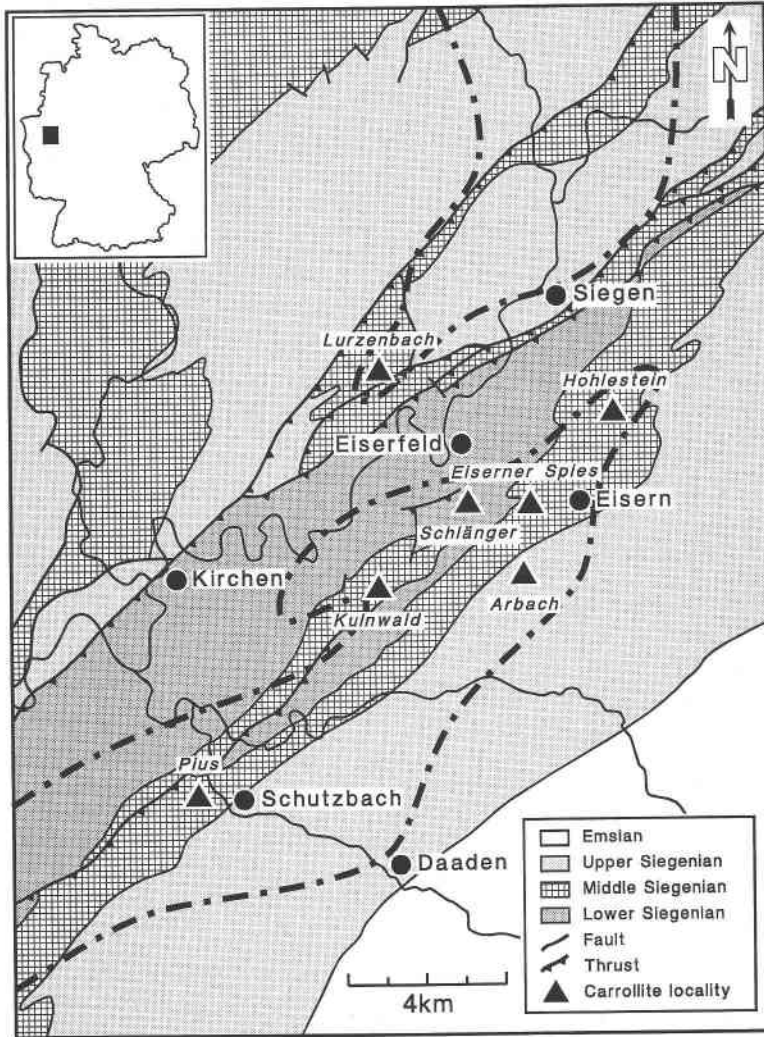


FIG. 1. Geological sketch map of the central portion of the Siegerland district, Germany, showing the location of the carrollite-bearing vein deposits sampled in this study. Redrawn and heavily modified after Fenchel *et al.* (1985). The thick dashed line indicates the boundary of the "rejuvenation stage" of mineralization (see text for explanation).

ally related to major fold- and thrust-zones. All individual veins represent mineralized parts of two sets of shear faults that are best developed in the sandstone-rich portions of the stratigraphy (Fenchel *et al.* 1985, Hein 1993). The principal sequence of mineralization is composed of three sequential stages, which can be related to tectonic movements during compressive deformation: (i) early stage (quartz – Co-rich arsenopyrite), (ii) main stage (siderite–quartz), and (iii) sulfide stage (sphalerite – chalcopyrite – galena). Stages (ii) and (iii) include mineral assemblages and associations that con-

tain Co–Ni minerals as minor constituents. The associations ullmannite–gersdorffite and siegenite – (polydymite) – millerite are typical of stages (ii) and (iii), respectively. The pattern of geographic distribution of these Co–Ni phases within the area seems random, but occurrences of siegenite are concentrated in the northern part of the district.

Subsequent postkinematic hydrothermal overprinting of the vein systems in the central portion of the Siegerland district (Fig. 1) resulted in the formation of a distinct and characteristic mineral assemblage domi-

nated by hematite, quartz, carrollite and various Cu–(Fe) sulfides. This so-called “rejuvenation stage” is associated with replacement of pre-existing vein assemblages by the influx of hot (300–350°C), oxidizing fluids along fracture zones cross-cutting the primary structures in the veins (Stadler 1959, Erlinghagen 1989). Intensive alteration of the wallrocks associated with this hydrothermal event led to (i) impregnation with hematite, (ii) formation of white mica, (iii) partial recrystallization of quartz grains, and (iv) replacement of dispersed siderite in the wallrock.

MINERAL ASSEMBLAGES OF THE SAMPLES INVESTIGATED

Investigation of samples from localities (Arbach, Eiserner Spies, Hohlestein, Kulnwald, Lurzenbach, Pius and Schlänger mines) in the Siegerland district has led to the recognition of a series of shared features that characterize the “rejuvenation stage” of mineralization, with respect to mineralogy, textural assemblages and paragenetic sequence. The vein mineralogy is dominated by hematite, quartz, bornite, chalcocite, djurleite, digenite and carrollite. Minor constituents are idaite, chalcopyrite, wittichenite, emplectite, native bismuth and native gold (Fenchel *et al.* 1985). Structurally controlled overprinting of the primary assemblages, oriented along microfractures, grain boundaries and other micro-scale discontinuities, led to the formation of hematite through oxidation of siderite, whereas Cu–(Fe)–(Co) sulfides have formed at the expense of pre-existing veinlets of chalcopyrite. As a consequence, carrollite is commonly associated with bornite and either digenite, djurleite or chalcocite, which usually occur as nest-like zoned aggregates surrounded by a narrow rim of hematite, composed of acicular and tabular crystals. The internal structures of the Cu–(Fe) sulfide aggregates are dominated by various textural features resulting from breakdown and replacement of high-temperature mineral assemblages. These include: (i) symplectitic intergrowths of bornite and either digenite, djurleite or chalcocite, (ii) bornite with exsolution lamellae of chalcopyrite, (iii) bornite with exsolution lamellae of idaite, (iv) patches of bornite hosted in a network of digenite veinlets, and (v) corroded relics of bornite in a matrix of chalcocite or djurleite.

Carrollite has typically formed preferentially along and close to grain boundaries between the Cu–(Fe) sulfides and hematite enclosing these minerals (Figs. 2a, b). The frequency of carrollite inclusions decreases continuously toward the inner portions of the Cu–(Fe) sulfides, the cores of larger aggregates being free of carrollite. In other samples, concentrations of carrollite are associated with irregular clusters of hematite grains enclosed in a matrix of bornite and digenite (Fig. 2c). Carrollite forms idiomorphic crystals (Figs. 2d, f), the aggregates being made up of large numbers of minute individual grains, which form either irregular clusters

or elongate alignments (Fig. 2b). The corroded contours of many larger crystals of carrollite indicate partial replacement by bornite and djurleite (Fig. 2e). In contrast, other grains of carrollite hosted within a symplectitic intergrowth of bornite and digenite indicate no substantial corrosion, except for infilling of minor microfractures by Cu–(Fe) sulfides (Fig. 2f). This is textural evidence in support of carrollite formation prior to the other Cu-bearing minerals, whereas most of the hematite apparently formed somewhat earlier still.

In reflected light, the optical properties of the Ni-rich varieties of carrollite are very close to those of other thiospinels of the linnæite series. Ni-rich carrollite is white with a slight pinkish tint, whereas Ni-poor carrollite is white with a slight creamy tint, the reflectivity appearing somewhat higher than that of Ni-rich carrollite.

Primary pyrite has been partly replaced by both the Cu–(Fe) sulfides and carrollite; it occurs as isolated relict inclusions inside these minerals. Carrollite displays no particular spatial association with the Bi–Au phases in the veins, although both may be found in the same polished section, though never together. Bornite grains hosting corroded inclusions of wittichenite are invariably free of carrollite. Emplectite, bismuth and gold are restricted to those parts of the veins dominated by massive hematite.

COMPOSITIONAL DATA

Electron-probe micro-analyses were carried out on carrollite from all seven occurrences using a CAMECA SX-50 instrument in Würzburg. Operating conditions were 15 kV at a beam current of 15 nA, a beam size of 1–2 µm and counting times of 20–30 s. The following standards were used: pure Cu ($K\alpha$), pure Co ($K\alpha$), pure Ni ($K\alpha$), pure Se ($L\alpha$), pure Te ($L\alpha$), pure FeS₂ ($FeK\alpha$, $SK\alpha$), pure Sb₂S₃ ($L\alpha$), pure MnTiO₃ ($MnK\alpha$), and pure GaAs ($AsL\alpha$).

In all samples investigated, carrollite contains essential Cu, Co, Ni, Fe and S; all other elements sought (Se, Te, Sb, Mn and As) lie below the limit of detection. The major compositional characteristic of all carrollite samples from the Siegerland is a significant extent of Ni incorporation, ranging from 2.01 (Pius) to 30.20 wt.% (Eiserner Spies). Mean compositions and minimum and maximum Ni concentrations for each deposit are given in Table 1; the formulae were calculated by normalization to three cations. Iron contents are relatively low in carrollite from most deposits, individual values varying between 0.2 and 1.0 wt.%. A single exception is shown by carrollite from the Hohlestein deposit, which has slightly higher Fe contents, in the range between 0.3 to a maximum of about 2 wt.%. Concentrations of both Co and Cu display a perfect negative correlation with the Ni content in most of the datasets, a feature best illustrated in the Eiserner Spies and Hohlestein deposits. Carrollite from these two localities

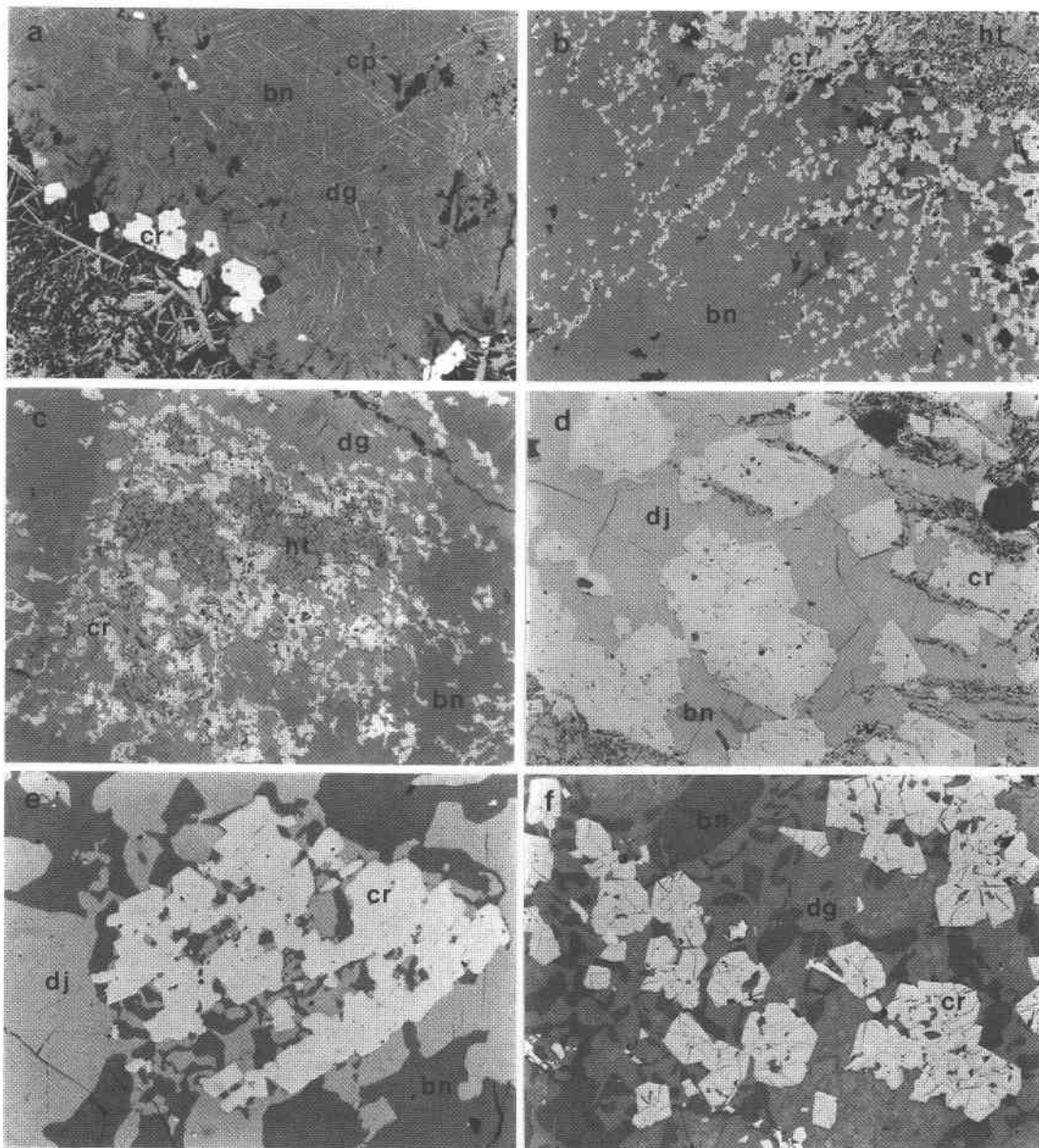


FIG. 2. Photomicrographs in reflected light showing various representative textural assemblages of carrollite in the Siegerland district. (a) Ni-rich carrollite (cr) preferentially formed along the grain boundary between the Cu-(Fe) sulfides and acicular hematite (bottom left of picture). Bornite (bn) is intimately intergrown with digenite (dg) and has exsolved crystallographically oriented lamellae of chalcopyrite (cp); Eiserner Spies (Eisefeld) deposit. Width of field: 310 μm . (b) Ni-rich carrollite (cr) concentrated along the grain boundaries between bornite (bn) and hematite (ht) and along crystallographic planes within bornite. Inner portions of bornite are almost free of carrollite inclusions; Hohlestein (Siegen) deposit. Width of field: 1.03 mm. (c) Clusters of intimately intergrown crystals of carrollite (cr) formed around hematite (ht). Later bornite (bn) and digenite (dg) have overgrown both minerals. Eiserner Spies (Eisefeld) deposit. Width of field: 900 μm . (d) Idiomorphic crystals of carrollite (cr) are hosted in a matrix of djurleite (dj) and minor bornite (bn); Schlänger (Eisefeld) deposit. Width of field: 600 μm . (e) Formation of a symplectitic intergrowth of bornite (bn) and djurleite (dj) resulted in the partial corrosion of the pre-existing crystals of carrollite (cr); Pius (Schutzbach) deposit. Width of field: 320 μm . (f) Clusters of idiomorphic crystals of carrollite (cr) hosted by a symplectitic intergrowth of bornite (bn) and digenite (dg); Arbach (Salchendorf) deposit. Width of field: 390 μm .

has the widest range of Ni substitution, which varies from 0.56 to 1.55 atoms per formula unit (*apfu*) at the Eiserner Spies (Fig. 3a) and 0.49 to 1.45 *apfu* at the Hohlestein deposit (Fig. 3b), which corresponds to Ni/(Ni + Co) values from 0.26 to 0.59 and from 0.22 to 0.56, respectively. Ni substitutes for both Co and Cu, and the proportion of Co and Cu (*apfu*) displays a dependency on the proportion of Ni atoms over the entire range of compositional variation.

The analytical datasets from the other five deposits display a narrower range of Ni incorporation and can be divided into two groups according to individual trends. Carrollite from the Arbach, Lurzenbach and Schlänger deposits displays compositional variations along the same linear solid-solution defined by the Eiserner Spies and Hohlestein data, but display a shift toward lower Ni

concentrations. The compositional limits are given by 0.33 to 0.56 *apfu* Ni at Arbach (Fig. 4a), 0.25 to 0.52 at Lurzenbach (Fig. 4b), and 0.11 to 0.24 at Schlänger (Fig. 4c), corresponding to Ni/(Ni + Co) values from 0.15 to 0.24, 0.11 to 0.23 and 0.05 to 0.11, respectively. In contrast to these deposits, carrollite from the remaining two datasets shows a rather different pattern of solid-solution trend, which deviates from the trends discussed above. At the Kulnwald (Fig. 4c) and Pius (Fig. 4d) deposits, Ni substitutes dominantly for Cu, the number of Co atoms per formula unit seeming to be relatively independent of the Ni content, thus favoring a simple homovalent substitution: $\text{Cu}^{2+} \rightarrow \text{Ni}^{2+}$. Compositional limits are given by Ni/(Ni + Co) values, from 0.10 to 0.28 at Kulnwald, and 0.08 to 0.12 at Pius.

The ratio of total metals to sulfur (*Me*:S) derived from all electron-microprobe analyses in this study lie close to the ideal proportion of 3:4 for carrollite, displaying a simple Gaussian frequency-distribution, with both lower and higher values in the range between 3:3.86 and 3:4.17 present in approximately equal numbers of samples (Fig. 5); 55.2% of the 290 individual analyses indicate between 3:3.95 to 3:4.05, whereas 89.7% have values of this ratio between 3:3.90 and 3:4.10.

DISCUSSION

Solid solution in the linnaeite series

Comparison of compositional data on linnaeite-group minerals documented in the literature with the new data from the Siegerland district provides new insights in the solid-solution trends in part of the complex system Cu–Fe–Co–Ni–S. In order to understand the underlying patterns of substitution, all available results of electron-microprobe analyses were recalculated to 3 cations and plotted in the four pseudoternary subsystems $\text{Cu}_3\text{S}_4\text{--Co}_3\text{S}_4\text{--Ni}_3\text{S}_4$, $\text{Cu}_3\text{S}_4\text{--Fe}_3\text{S}_4\text{--Co}_3\text{S}_4$, $\text{Cu}_3\text{S}_4\text{--Fe}_3\text{S}_4\text{--Ni}_3\text{S}_4$ and $\text{Fe}_3\text{S}_4\text{--Co}_3\text{S}_4\text{--Ni}_3\text{S}_4$ of the pseudo-quaternary system $\text{Cu}_3\text{S}_4\text{--Fe}_3\text{S}_4\text{--Co}_3\text{S}_4\text{--Ni}_3\text{S}_4$ according to their major components (Fig. 6), following the procedure described by Riley (1980). This method was considered appropriate in most cases, including all those from the Siegerland district, because the fourth component not represented in the respective diagrams is usually present at concentrations below 0.1 *apfu* (roughly equivalent to about 2 wt.%). The only major exception is shown by fletcherite reported from the Kalgoorlie area, Western Australia (Ostwald 1985), which has been assigned to the Cu–Fe–Ni subsystem, but also contains essential concentrations of Co.

We incorporated all literature data known to us; the distribution of carrollite compositions (Fig. 6) proves, in addition to the known solid-solution series with linnaeite (Craig *et al.* 1979), the existence of a broad range of Ni-for-Co, Cu substitution, extending from end-member carrollite, CuCo_2S_4 , toward cuprian siegenite. This interpretation is also supported by a number of in-

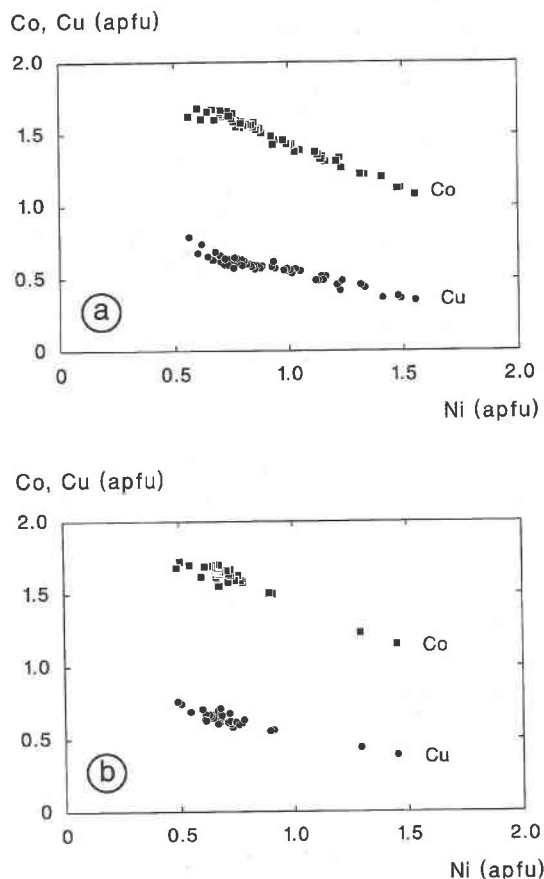


FIG. 3. Compositional ranges of carrollite from (a) Eiserner Spies (Eiserfeld) and (b) the Hohlestein (Siegen) deposits, the two deposits with the greatest range of Ni-for-Co, Cu substitution. The proportion of Co and Cu (*Me*₃S₄) is plotted as a function of the proportion of Ni (*apfu*).

TABLE 1. REPRESENTATIVE ELECTRON-MICROPROBE DATA FOR Ni-RICH CARROLLITE FROM THE DEPOSITS STUDIED IN THE SIEGERLAND DISTRICT, GERMANY

	Cu	Fe	Co	Ni	S	Total	Cu	Fe	Co	Ni	S
ARBACH (n = 36)											
mean composition	15.12	0.27	34.47	8.40	41.41	99.67	0.74	0.01	1.81	0.44	3.99
σ	0.46	0.14	0.69	0.88	0.31						
composition with minimum Ni	15.67	0.50	35.62	6.31	41.24	99.34	0.76	0.03	1.87	0.33	3.99
composition with maximum Ni	13.95	0.11	33.06	10.43	41.82	99.37	0.69	0.01	1.75	0.56	4.08
EISERNER SPIES (n = 59)											
mean composition	11.68	0.45	28.37	17.34	41.67	99.51	0.57	0.02	1.49	0.91	4.03
σ	1.80	0.20	2.99	4.63	0.39						
composition with minimum Ni	15.97	0.62	30.67	10.60	40.48	98.34	0.78	0.03	1.62	0.56	3.93
composition with maximum Ni	7.28	0.45	21.01	30.20	42.30	101.24	0.35	0.02	1.08	1.55	3.98
HOHLESTEIN (n = 41)											
mean composition	12.90	0.62	30.64	13.35	41.36	98.87	0.63	0.03	1.62	0.71	4.03
σ	1.43	0.41	2.18	3.21	0.45						
composition with minimum Ni	15.78	1.37	32.32	9.43	40.63	99.53	0.76	0.07	1.68	0.49	3.87
composition with maximum Ni	7.84	0.32	21.66	27.38	41.65	98.85	0.38	0.02	1.14	1.45	4.05
KULNWALD (n = 28)											
mean composition	17.14	0.21	34.71	5.91	41.40	99.37	0.84	0.01	1.83	0.31	4.02
σ	0.97	0.15	1.15	1.35	0.43						
composition with minimum Ni	18.87	0.47	35.60	3.85	40.83	99.62	0.91	0.03	1.86	0.20	3.92
composition with maximum Ni	16.44	0.16	30.15	11.61	41.73	100.09	0.80	0.01	1.58	0.61	4.02
LURZENBACH (n = 35)											
mean composition	15.09	0.14	35.63	6.79	41.12	98.77	0.74	0.01	1.89	0.36	4.01
σ	0.59	0.12	0.64	1.15	0.36						
composition with minimum Ni	15.42	0.20	36.63	4.69	41.23	98.17	0.77	0.01	1.97	0.25	4.07
composition with maximum Ni	14.62	0.03	34.23	9.92	41.14	99.94	0.70	0.00	1.78	0.52	3.93
PIUS (n = 35)											
mean composition	18.38	0.18	36.17	3.94	41.08	99.75	0.89	0.01	1.89	0.21	3.95
σ	0.65	0.10	0.49	0.42	0.36						
composition with minimum Ni	20.01	0.22	35.29	2.96	40.05	98.53	0.98	0.01	1.86	0.16	3.87
composition with maximum Ni	18.61	0.25	35.68	4.51	41.42	100.47	0.90	0.01	1.85	0.24	3.96
SCHLÄNGER (n = 56)											
mean composition	16.85	0.16	37.20	3.86	41.37	99.44	0.82	0.01	1.96	0.20	4.01
σ	0.55	0.14	0.67	0.55	0.33						
composition with minimum Ni	17.77	0.50	38.08	2.01	40.88	99.24	0.87	0.03	2.00	0.11	3.95
composition with maximum Ni	16.59	0.42	37.36	4.65	41.42	100.44	0.80	0.02	1.94	0.24	3.95

The data in the first six columns are expressed in weight %, and the proportion of atoms, shown in columns 7 to 11, is expressed in atoms per formula unit.

intermediate compositions reported in the literature (Vokes 1967, Minceva-Stefanova 1975, 1978, Minceva-Stefanova & Kostov 1976, Rakhmedov *et al.* 1976, Ostwald 1978, Craig & Vaughan 1979, Shadlun *et al.* 1979, Riley 1980, Strashimirov 1982, Jessey 1983, Pignolet & Hagni 1983, Zakrzewski 1984, Filimonova *et al.* 1985, Yurgenson *et al.* 1985). In contrast to the wide variety of Ni substitution, the extent of possible Fe incorporation in this solid-solution series is relatively limited. This is reflected by only a slight scattering of the respective data-points in the subsystem Cu-Fe-Co around the stoichiometric composition of carrollite (Tsonev & Borodaev 1977, Riley 1980, Cagatay *et al.* 1982, Annels *et al.* 1983, Sovatzoglou-Skounakis 1984). Interestingly, most Ni-rich varieties of carrollite have very low concentrations of Fe, a consistent feature confirmed by the analytical data from the Siegerland district.

On the basis of Figure 6, there is no evidence for the existence of any solid-solution series between carrollite and fletcherite, as has been previously postulated (Craig & Carpenter 1977, Craig & Vaughan 1979). Moreover, the absence of intermediate compositions spanning the gap between siegenite and fletcherite would seem to make the existence of the "siegenite-fletcherite isomorphous series" proposed by Zakrzewski (1984) improbable. Fletcherite from both the original locality (Viburnum Trend, Missouri; Craig & Carpenter 1977) and from the Kalgoorlie area, Western Australia (Ostwald 1985), has a similar range of Cu/Ni values, but markedly differing concentrations of Fe and Co. The type material is Fe-poor (0.02 to 0.07 *apfu*), whereas Fe is a major component of the Kalgoorlie fletcherite, although Co is also present in significant amounts, in the range of 0.09 to 0.29 *apfu*. This would seem to suggest a possible substitution between Fe-poor and Fe-rich

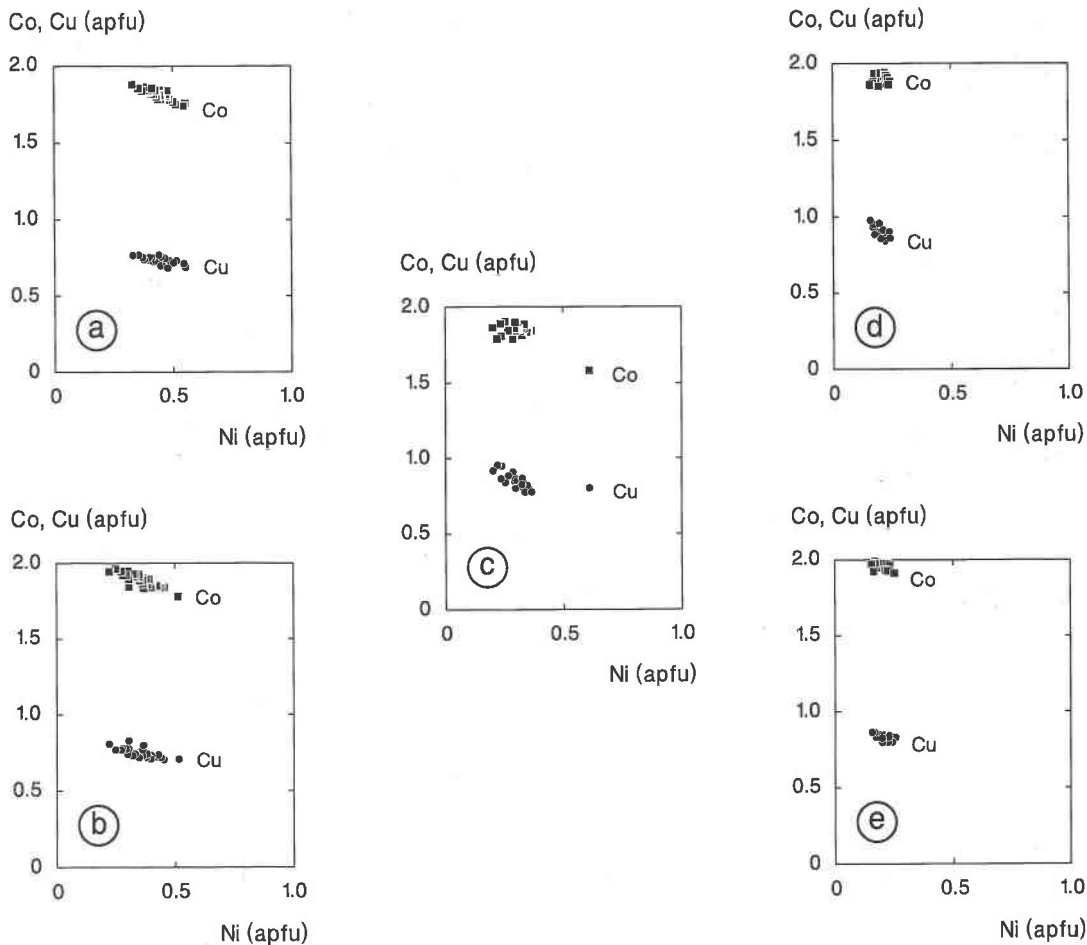


FIG. 4. Compositional ranges of carrollite from five deposits with a lower range of Ni-for-Co,Cu substitution. The proportion of Co and Cu is plotted as a function of Ni (apfu). (a) Arbach (Salchendorf) deposit. (b) Lurzenbach (Gosenbach) deposit. (c) Kulnwald (Dermbach) deposit. (d) Pius (Schutzbach) deposit. (e) Schlänger (Eiserfeld) deposit.

fletcherite, independent of other linnaeite-group solid-solution trends. Additional micro-analytical data are, however, required to fully substantiate this hypothesis.

The data indicate a relationship between Ni-rich carrollite and a phase with a composition close to CoNi_2S_4 , but this apparent solid-solution requires further explanation, owing to uncertainties as to the identity of relationships along the linnaeite–polydymite join and, by implication, that of siegenite itself. Two alternative concepts incorporating the crystal chemistry of the siegenite-group minerals with recommendations on nomenclature have been proposed in the literature. Complete solid-solution behavior between the two end-members linnaeite and polydymite has been favored by most investigators, in which the name “siegenite” is used for all intermediate members in this solid-solution

series. This model is based on the distribution patterns of natural compositions, calculations of the electronic structures, spectroscopic studies and the observations of continuous variation in the physical properties across the series (Vaughan *et al.* 1971, Craig *et al.* 1979, Vaughan & Tossell 1981, Vaughan & Craig 1985, Charnock *et al.* 1990). Minceva-Stefanova & Kostov (1976) have, however, suggested the existence of a significant miscibility gap within the linnaeite–polydymite series and postulated two distinct intermediate compositions with fixed stoichiometries, termed siegenite *sensu stricto*, Ni_2CoS_4 , and “nickellinnaeite”, Co_2NiS_4 . “Nickellinnaeite” is interpreted to be a normal spinel, whereas siegenite is assumed to be an inverse spinel, resulting in solid-solution fields extending to their respective structurally identical neighbors, *i.e.*, from

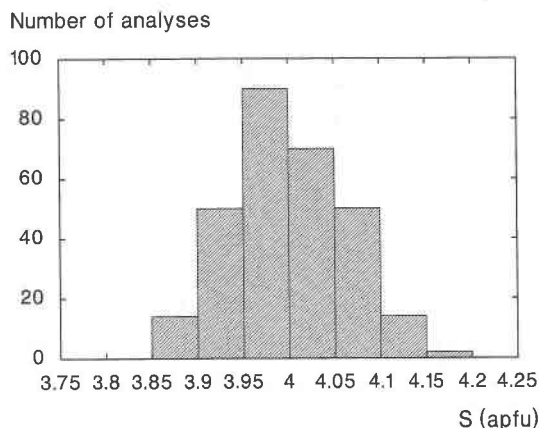


FIG. 5. Frequency distribution of *Me*:*S* ratios for carrollite from the Siegerland district.

"nickellinnaeite" to linnaeite and carrollite, and from siegenite to polydymite and violarite (Minceva-Stefanova 1978, 1986).

The solid-solution trend between Ni-poor and Ni-rich carrollite shown by the Siegerland data introduces an additional complication. It has been demonstrated that carrollite, linnaeite and synthetic Co_2NiS_4 all possess a normal spinel structure, whereas polydymite is an inverse spinel (Vaughan *et al.* 1971, Vaughan & Tossell 1981). The hypothesis of Minceva-Stefanova & Kostov (1976), in which siegenite is interpreted as an inverse spinel, should result in the existence of another miscibility gap between Ni_2CoS_4 and carrollite, which is seemingly not the case. The compositional variation of Ni-rich carrollite from the Siegerland deposits rather supports the concept of more-or-less complete solid-solution throughout the siegenite series, an observation concordant with the broad compositional range of siegenite minerals documented in the literature (Vokes 1967, Petruk *et al.* 1969, Sierra Lopez & de Vergara Schulze 1969, Rudashevskiy & Kondratiev 1972, Stoinova 1975, Ostwald 1978, Craig *et al.* 1979, Riley 1980, Shimada *et al.* 1981, Jessey 1981, 1983, Pignolet & Hagni 1983, Pignolet-Brandom & Hagni 1985, Bevins & Horak 1985, Bone & Ypma 1986, Hirata & Kato 1993, Ixer & Stanley 1996).

Mechanisms of substitution

As stated above, the Siegerland data strongly support the existence of a complete solid-solution series between Ni-rich and Ni-poor members of the series, with Ni substituting for both Co and Cu (Figs. 3, 4, 6). The substitution scheme for the two linear correlation trends relating Ni, Co and Cu can be expressed by the two equations:

$$\text{Co} = 2.07 - 0.63 \text{ Ni} \quad (1)$$

$$\text{Cu} = 0.92 - 0.37 \text{ Ni} \quad (2)$$

Such a solid-solution behavior cannot readily be explained by a simple cationic substitution of Ni into either Co or Cu sites, but would appear to involve a linear combination of at least two different mechanisms of substitution, which operate independently.

In order to explain the observed compositional trend relating carrollite and what we will choose to call cuprian siegenite, we have derived two solid-solution models, based on known cationic substitutions in the linnaeite group. The observed schemes of correlation relating Ni, Co and Cu described by equations (1) and (2) above can be solved by two different linear combinations of cationic substitutions. In the first model, we assume simple substitution of Ni^{3+} for Co^{3+} at octahedral sites, and of Ni^{2+} for Cu^{2+} at the tetrahedral sites. The respective correlations can be described by the equations:

$$\text{Co} = 2.07 - \text{Ni} \quad (3)$$

$$\text{Cu} = 0.92 \quad (4)$$

$$\text{Co} = 2.07 \quad (5)$$

$$\text{Cu} = 0.92 - \text{Ni} \quad (6)$$

Both individual mechanisms contribute fractions or coefficients, which are termed *a* and *b*, to the overall substitution. If it is assumed that only these two mechanisms are involved, it follows that $a + b = 1$ and $b = 1 - a$. The above equations form a linear set of equations, which can be readily solved to find *a* and *b*:

$$\text{Co} = 2.07 - 0.63 \text{ Ni} = a(3) + b(5) \quad (7)$$

$$\text{Co} = 2.07 - 0.63 \text{ Ni} = a(2.07 - \text{Ni}) + (1 - a) 2.07 \quad (8)$$

$$\text{Cu} = 0.92 - 0.37 \text{ Ni} = a(4) + b(6) \quad (9)$$

$$\text{Cu} = 0.92 - 0.37 \text{ Ni} = a(0.92 + (1 - a)(0.92 - \text{Ni})) \quad (10)$$

Solving the equations gives the values $a = 0.63$ and $b = 0.37$ and indicates that the substitution of Ni^{3+} for Co^{3+} at octahedral sites is the dominant of the two mechanisms governing incorporation of Ni in carrollite, although substitution of Ni^{2+} for Cu^{2+} at tetrahedral sites still accounts for about a third of the Ni content.

Taking into consideration that Ni^{2+} has a high octahedral site-preference energy, substitution of Ni^{2+} in carrollite should predominantly take place at the octahedral sites, which requires charge balance by simultaneous incorporation of Ni^{3+} at tetrahedral sites,

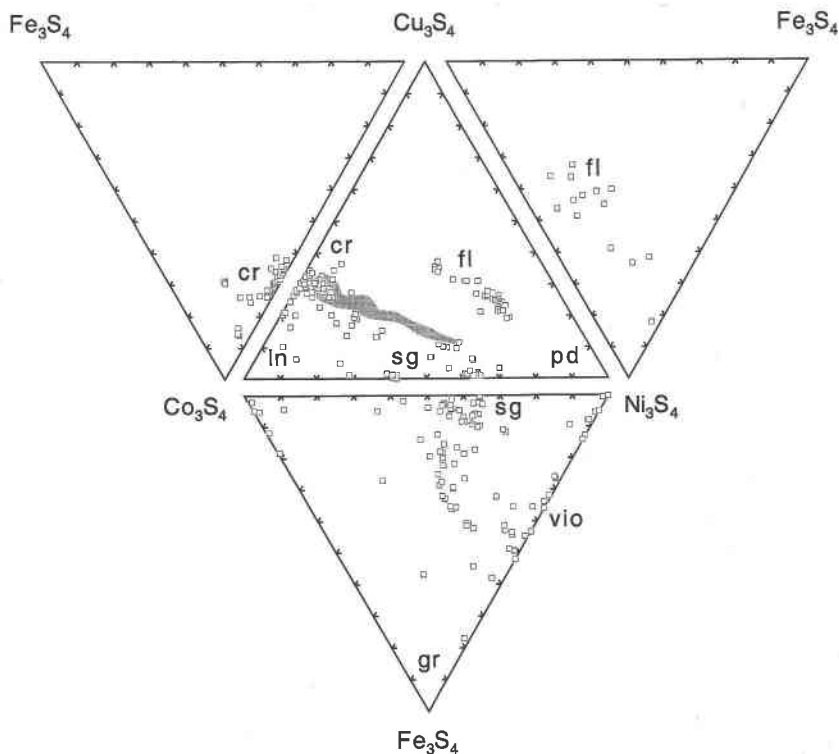


FIG. 6. Compositional representations of linnaeite-series minerals in the pseudoquaternary system Cu_3S_4 – Fe_3S_4 – Co_3S_4 – Ni_3S_4 . New data from the Siegerland are given as a single shaded area, whereas analytical data taken from the literature are indicated by open squares. All compositions were recalculated to 3 cations and plotted in the four pseudoternary subsystems according to their major components (Riley 1980). Abbreviations: (cr) carrollite, (fl) fletcherite, (ln) linnaeite, (sg) siegenite, (pd) polydymite, (vio) violarite, (gr) greigite.

concordant with the substitution scheme generally accepted for polydymite (Vaughan *et al.* 1971, Vaughan & Tossell 1981, Vaughan & Craig 1985). The resulting coupled substitution $\text{Cu}^{2+} + \text{Co}^{3+} \rightarrow \text{Ni}^{3+} + \text{Ni}^{2+}$ cannot explain the observed solid-solution trend in Ni-rich carrollite alone, but requires a linear combination with the secondary mechanism $\text{Co}^{3+} \rightarrow \text{Ni}^{3+}$. The respective correlations can be expressed by the equations:

$$\text{Co} = 2.07 - \text{Ni} \quad (11)$$

$$\text{Cu} = 0.92 \quad (12)$$

$$\text{Co} = 2.07 - 0.5 \text{ Ni} \quad (13)$$

$$\text{Cu} = 0.92 - 0.5 \text{ Ni} \quad (14)$$

$$\text{Co} = 2.07 - 0.63 \text{ Ni} = a (11) + b (13) \quad (15)$$

$$\text{Co} = 2.07 - 0.63 \text{ Ni} = a (2.07 - \text{Ni}) + (1 - a) (2.07 - 0.5 \text{ Ni}) \quad (16)$$

$$\text{Cu} = 0.92 - 0.37 \text{ Ni} = a (12) + b (14) \quad (17)$$

$$\text{Cu} = 0.92 - 0.37 \text{ Ni} = a 0.92 + (1 - a) (0.92 - 0.5 \text{ Ni}) \quad (18)$$

This approach now results in $a = 0.26$ and $b = 0.74$. Both crystal-chemical models are equally suited to explain the observed correlation trends in Ni-rich carrollite, but this second alternative displays a better concordance with the theoretical predictions.

An unequivocal solution to the problem in order to substantiate or negate the above arguments requires further research, notably involving spectroscopic studies carried out on various intermediate members of the series to prove site occupancies as well as further experi-

Solution of the linear set of equations is now carried out in a straightforward manner to give the two coefficients a and b :

mental determinations of phase relations in the complex system Cu–Co–Ni–S, as well as Cu–Co–Ni–Fe–S, which could confirm the location of substituting components and true nature of the solid-solution series.

Nomenclature

Our data have some implications for the nomenclature for thiospinel phases in part of the system Cu–Co–Ni–S, although no significant changes to current usage are necessary. We suggest that the variety name nickelian carrollite be used for carrollite that has a Ni:(Ni + Co + Cu) ratio in excess of 0.05. The upper compositional limit for nickelian carrollite is more problematic, owing to the uncertainties as to the compositional limits for siegenite, as have been outlined above. We suggest however, that this limit should lie exactly at the mid-point along the join $\text{CuCo}_2\text{S}_4 - \text{CoNi}_2\text{S}_4$, thus being dependent on the Cu content as well as the Ni:(Ni + Co) ratio. This places the upper limit for nickelian carrollite at $\text{Cu}_{0.5}\text{Co}_{1.5}\text{Ni}_{1.0}$. Those phases with more Ni and less Cu than these values are better described as cuprian siegenite. Deriving the lower limits in the same way as for nickelian carrollite, the variety name cuprian siegenite should be used for varieties that have Cu:(Cu + Ni + Co) in excess of 0.05.

Genetic considerations

The abundance of textural modifications resulting from the breakdown of high-temperature assemblages, microthermometric data available in the literature and constraints based on the given compositional limits permit us to evaluate the conditions of formation of carrollite. Fluid inclusions in quartz deposited contemporaneously with hematite indicate the presence of low-salinity fluids (3–7 wt.% NaCl-equivalent), with homogenization temperatures in the range of 230–330°C (Erlinghagen 1989, Hein 1993). This range defines the upper temperature limit for deposition of carrollite, which followed closely the formation of hematite from siderite.

The chemical variables $f(\text{S}_2)$, Eh and pH that governed the precipitation of carrollite in the Siegerland vein systems are difficult to estimate meaningfully. Available data on sulfidation reactions, which have been successfully used to constrain the sulfur fugacities in carrollite-bearing assemblages, especially in the Central African Copperbelt (Craig & Vaughan 1979, Annels *et al.* 1983), are not applicable, since equilibrium conditions have not been attained in the Siegerland deposits. Textures indicative of incomplete replacement, patterns of mineralogical zonation, and the high compositional variability of carrollite indicate the existence of physicochemical gradients inside the vein systems or evolution of some or all the chemical variables with time. Furthermore, the introduction of Ni as an addi-

tional component into the structure of carrollite generates an additional complication when applying stability data and sulfidation equilibria, although the general tendency for carrollite to form at conditions of relatively high $f(\text{S}_2)$ should persist.

Formation of Ni-rich carrollite after deposition of the stoichiometric end-member (*i.e.*, Ni-free) carrollite in MVT deposits in the Southeast Missouri Mining District has been explained by either an increased availability of Ni in evolved ore-forming fluids or by relative oxidation of the fluid system, thereby enabling Ni^{3+} to compete with Co^{3+} during precipitation of the ore components (Jessey 1981, 1983, Pignolet & Hagni 1983, Pignolet-Brandom & Hagni 1985). Such a mechanism can also be applied to the Siegerland deposits, as it coincides well with the observed formation of hematite *via* oxidation of siderite, thus reflecting a significant increase in $f(\text{O}_2)$ during the “rejuvenation stage” of mineralization. In contrast to the MVT deposits, however, Ni-rich carrollite in all vein systems studied in the Siegerland is characterized by very heterogeneous Ni/(Ni + Co) values, which indicates small-scale lateral compositional and physicochemical gradients in the ore-forming fluids. Such a scenario could be related to either interactions with the wallrock or to partial repeated remobilization of pre-existing ore components, including buffering through siderite dissolution. Additionally, some of the fluctuating Ni/(Ni + Co) values may have resulted from diffusion in the solid state. Formation of Cu–(Fe) sulfides following deposition of carrollite indicates a fluid evolution resulting in more reducing and sulfur-deficient conditions toward the end of the mineralization event, accompanied by significant cooling of the system.

The Ni content of the carrollite can readily be derived from partial corrosion of pre-existing Ni-rich pyrite, which is supported by Ni concentrations in the range of 1.02 to 4.33 wt.% in relict pyrite. Remobilization of primary ullmannite–gersdorffite and possibly also additional supply by the ore-forming fluids may also represent a source for part of the Ni concentrated in the thiospinel. Remobilization of chalcopyrite and fluid-assisted redistribution inside the vein systems are the most probable mechanisms of copper enrichment. In contrast to the readily identifiable sources of Ni and Cu, no Co-rich precursor mineral texturally associated with either carrollite, hematite or the Cu–(Fe) sulfides has yet been found in significant amounts. Some of the investigated deposits do contain Co-rich arsenopyrite within sets of veins that are spatially distinct from the veins affected by the “rejuvenation stage” of mineralization. However, even though a direct association cannot be demonstrated, the patterns of regional distribution of both the carrollite-bearing mineral assemblage and of the early-stage mineralization dominated by Co-rich arsenopyrite show a distinct spatial overlap.

CONCLUSIONS

1. Carrolite, a major component of the "rejuvenation stage" of mineralization in the Siegerland ore province, Germany, displays significant variation in composition, characterized by incorporation of Ni, up to a maximum of 1.55 Ni *apfu*, coupled with a decrease of Cu and Co in the structure.

2. This linear solid-solution trend indicates that Ni substitutes for both Co and Cu, and represents the greater part of a solid solution extending from end-member Ni-free carrolite, CuCo_2S_4 , to a composition close to the linnaeite-polydymite join and termed cuprian siegenite. This means that carrolite has an appreciably broader field of solid solution than has been previously recognized. The extent of iron incorporation in carrolite is insignificant as the Ni content increases.

3. Our data confirm the presence of a linnaeite-siegenite solid-solution series, but refute the existence of any solid solution between carrolite and fletcherite.

4. Incorporation of Ni into carrolite involves at least two different mechanisms of substitution that operate independently of one another. The main mechanism involves the simple substitution of Ni^{3+} for Co^{3+} at octahedral sites.

5. Our micro-analytical data and published data on other occurrences of carrolite suggest that this mechanism is either combined with substitution of Ni^{2+} for Cu^{2+} at tetrahedral sites or with the coupled substitution mechanism $\text{Cu}^{2+} + \text{Co}^{3+} \rightarrow \text{Ni}^{3+} + \text{Ni}^{2+}$. The addition of one of these mechanisms into the substitution model improves the fit to the observed data.

6. The formation of carrolite in the Siegerland deposits is consistent with the overprinting of existing Ni- and Cu-bearing mineral associations by relatively late oxidizing fluids during the final stage of vein development.

7. The following nomenclature for phases along the CuCo_2S_4 and CoNi_2S_4 join is suggested. The variety name nickelian carrolite should be used for carrolite with $\text{Ni}/(\text{Ni} + \text{Co} + \text{Cu}) > 0.05$, up to a maximum halfway along the join at $\text{Cu}_{0.5}\text{Co}_{1.5}\text{Ni}_{1.0}$. Phases with $\text{Ni} > 1.0$ and $\text{Cu} < 0.5$ (*apfu*) should be termed cuprian siegenite, so long as $\text{Cu}/(\text{Cu} + \text{Ni} + \text{Co})$ exceeds 0.05 *apfu*.

ACKNOWLEDGEMENTS

Messrs. A. Hellmann (Eisern), G. Helsper (Siegen) and H. Latsch (Grünebach) are thanked for providing a number of samples investigated in this study. The assistance of Mr. P. Spaethe with preparation of polished sections is gratefully appreciated. Mr. K.-P. Kelber is thanked for the black-and-white photographs. We thank the two referees, L.L.Y. Chang and J.R. Craig, as well as Robert F. Martin, for their comments. These have improved this paper. The investigation forms part of the doctorate project of the first author.

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Received October 11, 1998, revised manuscript accepted April 8, 1999.