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NICKELTYRRELLITE, CuNi_2Se_4 , A NEW MEMBER OF THE SPINEL SUPERGROUP FROM EL DRAGÓN, BOLIVIA

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ABSTRACT

Nickeltyrrellite, ideally CuNi_2Se_4 , is a new selenide species from the El Dragón mine, Department of Potosí, Bolivia. It most frequently occurs as anhedral to subhedral grains (up to 20 μm in size) in association with cerromojonite, klockmannite, clausthalite, and penroseite, forming fracture fillings in pre-existing krut'aite–penroseite solid solutions. Nickeltyrrellite is non-fluorescent, black and opaque with a metallic luster and black streak. It is brittle, with an irregular fracture and no obvious cleavage and parting. In plane-polarized incident light, nickeltyrrellite is cream to pale pinkish, displaying no internal reflections. Between crossed polarizers, it is isotropic. The reflectance values in air for the COM standard wavelengths are: 45.9 (470 nm), 47.6 (546 nm), 48.1 (589 nm), and 49.8 (650 nm). Electron-microprobe spot analyses ($n = 28$) of the grain populations used for the EBSD study yielded a mean composition Cu 13.01, Fe 0.27, Co 6.66, Ni 16.98, S 1.04, Se 61.91, total 99.87 wt%. The empirical formula, normalized to 7 apfu, is $\text{Cu}_{1.00}(\text{Ni}_{1.42}\text{Co}_{0.55}\text{Fe}_{0.02})_{\Sigma=1.99}(\text{Se}_{3.84}\text{S}_{0.16})_{\Sigma=4.00}$. The ideal formula is CuNi_2Se_4 , which requires (in wt.%) Cu 12.79, Ni 23.63, Se 63.58, total 100. EBSD patterns reveal nickeltyrrellite as cubic, space group $Fd\bar{3}m$, with $a = 9.99$ Å, $V = 997.0$ Å³, $Z = 8$. Calculated density is 7.36 g cm⁻³. It formed in response to alteration of quijarroite +

hansblockite + watkinsonite + clausenthalite + penroseite aggregates from oxidizing, low-*T*, Cu–Ni–Co–Pb-bearing fluids at a $f\text{Se}_2/f\text{S}_2$ ratio greater than unity. Nickeltyrrellite is a new selenide belonging to the tyrrellite subgroup of the spinel supergroup. The new species has been approved by the IMA-CNMNC (2018-110) and is named for constituting the Ni-analogue of tyrrellite.

INTRODUCTION

The ore mineralization at El Dragón, Province of Antonio Quijarro, in the Andes of Bolivia is the most spectacular occurrences of Se-bearing minerals on Earth known today. Although volumetrically very minor, a total of 29 selenides and selenates have been detected to date. The most recently discovered Se-species encompass eldragónite, $\text{Cu}_6\text{BiSe}_4(\text{Se}_2)$ (Paar *et al.* 2012), favreauite, $\text{PbBiCu}_6\text{O}_4(\text{SeO}_3)_4(\text{OH})\cdot\text{H}_2\text{O}$ (Mills *et al.* 2014), alfredopetrovite, $\text{Al}_2(\text{Se}^{4+}\text{O}_3)_3\cdot 6\text{H}_2\text{O}$ (Kampf *et al.* 2016), grundmannite, CuBiSe_2 (Förster *et al.* 2016a), quijarroite, $\text{Cu}_6\text{HgPb}_2\text{Bi}_4\text{Se}_{12}$ (Förster *et al.* 2016b), hansblockite, $(\text{Cu,Hg})(\text{Bi,Pb})\text{Se}_2$ (Förster *et al.* 2017), and cerromojonite, CuPbBiSe_3 (Förster *et al.* 2018). El Dragón also hosts the most recently IMA-CNMNC approved species luxembourgite, $\text{AgCuPbBi}_4\text{Se}_8$ (Philippo *et al.* 2019) (*cf.* Grundmann & Förster 2017, their Table 3)

This paper provides the description of a new species in the Cu–Co–Ni–Se system, nickeltyrrellite, ideally CuNi_2Se_4 , from El Dragón. The new mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the IMA, proposal 2018–110. The holotype polished section is housed in the collections of the Natural History Museum, London, catalogue number BM 2018, 19. Cotype material is stored at Mineralogical State Collection Munich–Museum Reich der Kristalle, inventory number MSM 73587. The name of the mineral indicates the Ni-analogue of tyrrellite, CuCo_2Se_4 (Robinson & Brooker 1952, Harris 1970).

BACKGROUND ON GEOLOGY

The geology and origin of the El Dragón selenide occurrence were comprehensively described by Grundmann & Förster (2017). The mine is located in southwestern Bolivia, in the Cordillera Oriental, some 30 km southwest of Cerro Rico de Potosí. The abandoned mine is positioned 19° 49' 23.90" S (latitude), 65° 55' 00.60" W (longitude), at an altitude of 4160 m above sea level. The almost vertical ore vein is located in the center of a 1.5-m-wide shear zone penetrating a series of thinly-stratified, pyrite-rich black shales and reddish-grey, hematite-bearing siltstones of probably Devonian age. The selenium mineralization consisted

of a single vein of small longitudinal extension (maximum 15-m-long gallery), ranging mostly from 0.5 to 2 cm in thickness.

APPEARANCE

Nickeltyrrellite occurs within two texturally different mineral assemblages, which are interpreted as pseudomorphs after quijarroite/hansblockite/watkinsonite/clausthalite/type-I cerromojonite/penroseite intersertal aggregates (Förster *et al.* 2016a, 2016b, 2017, 2018).

Type-I nickeltyrrellite (inclusion-free grain size $\leq 20\ \mu\text{m}$) is anhedral and occurs inside and/or at the margin of fine-grained granular or myrmekitic aggregates predominantly composed of penroseite, which generally show a finely branched network of shrinking cracks (Fig. 1).

Type-II nickeltyrrellite (inclusion-free grain-size $\leq 20\ \mu\text{m}$) is sub- to anhedral, rarely forms subhedral crystals (cube-octahedra), and crystallized inside and/or at the margin of lath-shaped or acicular type-II cerromojonite aggregates (Fig. 2), which may be intimately (sub-parallel) intergrown with relict quijarroite/hansblockite/watkinsonite and newly formed clausthalite and (according to energy-dispersive electron-microprobe analysis) two new Cu–(Ag)–Hg–Pb–Bi selenides (Förster *et al.* 2018).

PHYSICAL AND OPTICAL PROPERTIES

Nickeltyrrellite is non-fluorescent, black and opaque with a metallic luster and black streak. It is brittle, with an irregular fracture and no obvious parting and cleavage. Vickers hardness and density could not be measured because of the small grain size. Density calculated from EBSD data is $7.36\ \text{g} \cdot \text{cm}^{-3}$.

In plane-polarized incident light, nickeltyrrellite is cream against chalcopyrite, covellite, penroseite, krut'aite–penroseite solid solutions, and the unidentified alteration products (*cf.* Figs. 3 and 4). Nickeltyrrellite is pale pinkish against cerromojonite in the assemblage with klockmannite, penroseite, clausthalite, and krut'aite–penroseite (*cf.* Fig. 2). With crossed polarizers, nickeltyrrellite is isotropic.

Quantitative reflectance data were obtained in air relative to a Zeiss WTiC standard using a J and M TIDAS diode array spectrometer attached to a Zeiss Axiotron microscope. Reflectance values were measured in air on an area of $8\ \mu\text{m}$ by $8\ \mu\text{m}$ (asterisk in Figure 4b),

from which the chemical composition and EBSD data were obtained. The results are listed in Table 1.

CHEMICAL COMPOSITION

Nickeltyrrellite grains were routinely analyzed for concentrations of Cu, Ag, Pb, Hg, Fe, Co, Ni, As, Sb, Bi, S and Se. Quantitative chemical analyses were conducted in WDS mode, using a JEOL electron probe X-ray microanalyzer JXA-8230 at Deutsches GeoForschungsZentrum GFZ, Potsdam, Germany. The probe was operated at 20 kV, 20 nA, 1–2 μm beam size). The counting time on peak was 20–40 s, with half that time on background on both sides of the peak. The following emission lines and analyzing crystals (in parentheses) were used: Cu – $K\alpha$ (LIFL); Fe – $K\alpha$ (LIFH); Co – $K\alpha$ (LIFL); Ni – $K\alpha$ (LIFL); S – $K\alpha$ (PETJ); Se – $L\alpha$ (TAPH). The CITZAF routine in the JEOL software, which is based on the $\phi(\rho Z)$ method (Armstrong 1995), was used for data processing.

Chemical data (28 spots) acquired for the two grain type-II nickeltyrrellite populations from the holotype section subjected to structural study (*cf.* Figs. 3 and 4) are compiled in Table 2 and also listed in Table 3 (62/areas 2a and 2b). The grains are homogeneous within analytical error, but are slightly variable in composition in terms of Ni/Co and Se/S ratios. The empirical formula is $\text{Cu}_{1.00}(\text{Ni}_{1.42}\text{Co}_{0.55}\text{Fe}_{0.02})_{\Sigma=1.99}(\text{Se}_{3.84}\text{S}_{0.16})_{\Sigma=4.00}$ (based on 7 atoms *pfu*). The ideal formula is CuNi_2Se_4 , which requires (in wt.%) Cu 12.79, Ni 23.63, Se 63.58, total 100.

Altogether, 75 spot analyses were performed on both type-I and type-II nickeltyrrellite in three samples from El Dragón (Table 3). Detected components display the following range in concentration (in wt%): Cu 11.30 – 13.38; Fe 0.05 – 1.24; Co 1.90 – 9.12; Ni 14.09 – 22.24; S 0.03 – 2.18; Se 60.22 – 64.23. The mean formula ((based on 7 atoms *pfu*) derived from the 75 spots is $\text{Cu}_{0.97}(\text{Ni}_{1.52}\text{Co}_{0.47}\text{Fe}_{0.03})_{\Sigma=2.02}(\text{Se}_{3.92}\text{S}_{0.08})_{\Sigma=4.00}$.

Notably, grains from two areas (62/area 1 and 14/area 2a) are too low in Cu to completely fill the Cu-position. Conclusively, other cations (Fe, Co, and/or Ni) may have entered this position (see Discussion section).

EBSD STUDY

Conventional single-crystal X-ray and powder-diffraction studies could not be carried out because of the small crystal size. Alternatively, Electron Back-Scatter Diffraction (EBSD)

analyses of two fragments (Figs. 3 and 4) were performed using an HKL EBSD system on a ZEISS 1550VP Field-Emission SEM at Caltech, operated at 20 kV and 6 nA in focused-beam mode with a 70° tilted stage and in a variable pressure mode (25 Pa). The focused electron beam was several nanometers in diameter. The spatial resolution for diffracted backscatter electrons was ~30 nm in size. The EBSD system was calibrated using a single-crystal silicon standard. The determination of the cell parameters and suggestions on the possible crystal structure were obtained by matching the experimental EBSD patterns with structures of Cu–Ni–S, Cu–Co–Se, and Ni–Se phases.

The EBSD patterns are only indexed by the $Fd-3m$ spinel-type structure and give a best fit by the tyrrellite $[\text{Cu}(\text{Co}_{0.68}\text{Ni}_{0.32})_2\text{Se}_4]$ cell from Yang *et al.* (2007) (Fig. 5), with a mean angular deviation of 0.45°–0.56°, revealing the following cubic unit-cell parameters: $a = 9.99 \text{ \AA}$, $V = 997.0 \text{ \AA}^3$ and $Z = 8$.

DISCUSSION

Relation to other species

The new mineral described here is the Ni-analogue of tyrrellite, CuCo_2Se_4 , resp. the Se-analogue of fletcherite, CuNi_2S_4 (Craig & Carpenter 1977). The scientific rationale for preferring the name nickeltyrrellite instead of selenofletcherite is explained below.

As pointed out in the recent classification of the spinel supergroup (Bosi *et al.* 2019), properly classifying Cu-bearing chalcospinel is quite challenging (Table 4). This is mainly due to the circumstance that confidence about the charge of ions in these minerals is lacking. Although Cu is usually considered as monovalent in sulfides, carrollite (CuCo_2S_4) has been traditionally considered a 2–3 species, $\text{Cu}^{2+}\text{Co}^{3+}_2(\text{S}^{2-})_4$ (*e.g.*, Charnock *et al.* 1990). Pattrick *et al.* (2008) and Buckley *et al.* (2009) studied spectroscopically the Co charge in carrollite and obtained contrasting results. Pattrick *et al.* (2008) suggested a Co charge between +2 and +3, giving rise to the formula $\text{Cu}^+(\text{Co}^{2+}\text{Co}^{3+})(\text{S}^{1.5-})_4$, whereas Buckley *et al.* (2009) proposed a low-spin Co^{3+} with a charge for S only 12.5% less negative than –2, which leads to $\text{Cu}^+\text{Co}^{3+}_2(\text{S}^{1.75-})_4$. As concerns fletcherite, CuNi_2S_4 , no information on the crystal structure and the formal ions charge is available. For tyrrellite, $\text{Cu}(\text{Co},\text{Ni})_2\text{Se}_4$, it was suggested that Cu is monovalent and Co or Ni exhibit a charge $> 3+$ (Yang *et al.* 2007, and references therein).

To classify chalcospinel, Bosi *et al.* (2019) assumed that the oxidation states of anions (S and Se) and Cu are –2 and +1, respectively. This implies the presence of Co^{3+} , Co^{4+} , Ni^{3+} and

Ni⁴⁺ leading to an overall charge for the octahedral cation of 3.5+. As a result, carrollite, fletcherite and tyrrellite fall into the subgroup 1–3.5 (Bosi *et al.* 2019). Tyrrellite has been considered as an isolated member of a *potential* “tyrrellite subgroup”, given the fact that the minimum requirement to have a mineral subgroup is that it contains at least two species (Mills *et al.* 2009). With the discovery of nickeltyrrellite, the “tyrrellite subgroup” gains its proper status.

The mineral described here compositionally resembles “unnamed phase CuNi₂Se₄“, already described from El Dragón by Grundmann & Förster (2017). In Figure 14 of this paper, penroseite was regrettably confused with the “unnamed phase CuNi₂Se₄“, that turned out to be type-I nickeltyrrellite which, in this case, partially replaced penroseite.

To display the presently known spread in composition of the nickeltyrrellite–tyrrellite solid-solution series, data for nickeltyrrellite from El Dragón and published information on tyrrellite are plotted in a Cu–Co–Ni ternary diagram of the system CuCu₂Se₄–CuCo₂Se₄–CuNi₂Se₄ (Fig. 6). This plot indicates that miscibility between tyrrellite and nickeltyrrellite is most likely complete. Moreover, “tyrrellite” from Hope’s Nose, UK, is in fact an intermediate member of the tyrrellite–nickeltyrrellite series. The most Ni-rich spot analysis listed by Stanley *et al.* (1990) yields the formula (based on 7 atoms *pfu*) Cu_{1.03}(Ni_{1.10}Co_{0.85})_{Σ=1.95}Se_{4.02} and, consequently, classifies as nickeltyrrellite.

Origin

Nickeltyrrellite from El Dragón is a late-stage mineral deposited during stage III (“fracture fillings”) as defined by Grundmann & Förster (2017) (Fig. 7). It formed in response to the alteration of quijarroite–hansblockite–watkinsonite–clausthalite–penroseite ± type-I cerromojonite aggregates by low-T, late-stage Cu–Co–Ni–Pb–Se-bearing oxidizing fluids. Type-I and type-II nickeltyrrellite containing mineral assemblages were deposited in the interstices or at the surface of fractured krut’aitite–penroseite solid solutions (Figs. 8–10). They precipitated during the same event, but from differently textured “mother” aggregates. Precursor of type-I nickeltyrrellite are fine-grained granular or myrmekitic aggregates, whereas type-II nickeltyrrellite is related to porous aggregates relatively richer in open spaces between the pre-existing lath-shaped or acicular grains of Cu–Ag–Hg–Pb–Bi selenides. These open spaces permitted type-II nickeltyrrellite to grow more freely and to locally develop crystal shapes (*cf.* Fig. 2). Associated type-II cerromojonite represents the alteration

product of the Bi selenides, with Ag and Hg being lost to the fluid phase. Overprinting may have been as intense as that the precursor Bi selenides were completely dissolved and the aggregates transformed into the assemblage nickeltyrrellite + penroseite + clausthalite + klockmannite (*cf.* Fig. 1).

Dissolution and partial replacement of Ni-Co-rich rim zones of angular krut'aite–penroseite solid solutions (k-p) by late clausthalite or penroseite (*cf.* Figs. 8 and 9) provide evidence that k-p grain surfaces have undergone local corrosion to release Cu, Ni, and Co, trapped by newly grown nickeltyrrellite and, probably, penroseite. Whether penroseite associated with nickeltyrrellite always formed simultaneously could not be securely answered, since “old” penroseite included in the precursor Bi-selenide aggregates share similar chemical signatures. Subsequent alteration of nickeltyrrellite, cerromojonite, and klockmannite assemblages by late chalcopyrite, covellite, and goethite caused strong fretting that significantly reduced the grain-size of nickeltyrrellite and penroseite (*cf.* Fig. 10).

Inferences on the physico-chemical environment of formation of nickeltyrrellite could be made from the type of Cu selenide, with which it is associated (clausthalite and penroseite have much larger stability fields). Its occurrence together with klockmannite implies high selenium fugacities above values defined by the umangite–klockmannite univariant reaction, but below those required to precipitate krut'aite. Assuming a T of 100 °C (which is probably too high) and an elevated oxygen fugacity defined by the magnetite–hematite buffer, this paragenetic relation is consistent with a range of $\log f_{\text{Se}_2}$ between -14.4 and -11.6 (Simon et al. 1996). The absence of krut'aite and sulfides (chalcopyrite, pyrite) defines the maximum $\log f_{\text{S}_2}$ to roughly -19 .

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Figures

FIG. 1. Type-I nickeltyrrellite (nt) in association with penroseite (p), klockmannite (kl) and clausenthalite (cl). Reflected light digital image. Width 200 μm .

FIG. 2. Type-II Nickeltyrrellite (nt) in association with type-II cerromojonite (ce) and klockmannite (kl). g = goethite, k-p = krut'aite-penroseite solid solution. Reflected light digital image. Width 200 μm .

FIG. 3. (a) Reflected light digital image (width 200 μm) and (b) corresponding SEM-BSE image of an altered type-I nickeltyrrellite (nt)/penroseite (p) aggregate mantled by chalcopyrite (ch) and covellite (co). The red rectangle encloses population 62/area 2a of nickeltyrrellite grains analysed for chemistry (cf. Tables 2 and 3). The red asterisk marks on of the two grains studied for crystal structure.

FIG. 4. Reflected light digital image (width 200 μm) and (b) corresponding SEM-BSE image of another altered type-I nickeltyrrellite (nt)/penroseite (p) assemblage overgrown by chalcopyrite (ch), covellite (co) and other unspecified alteration minerals. The red rectangle encloses population 62/area 2b of nickeltyrrellite grains analysed for chemistry (*cf.* Tables 2 and 3). The red asterisk marks the second grain studied for crystal structure. k-p = krut'aite–penroseite solid solutions.

FIG. 6. Co–Ni–Cu ternary diagram (mole%) of the system $(\text{Co,Ni,Cu})_3\text{Se}_4$. References: 1 – Stanley et al. (1990), 2 – Paar et al. (2002), 3 – Criddle & Stanley (1986), 4, 5 – Paar et al. (1996, 2016), 6 – Grundmann & Förster (2018). Designation of the six areas showing data from El Dragón correspond to the mean compositions in Table 3.

FIG. 7. Paragenetic sequence and crystallization/deformation diagram for the El Dragón selenium mineralization (modified from Grundmann & Förster 2017).

FIG. 8. Type-II nickeltyrrellite in association with penroseite (p), klockmannite (kl), type-II cerromojonite (ce) and clausenthalite (cl), interpreted as pseudomorph after a formerly angular network-like intersertal texture of quijarroite (qu), hansblockite, type-I cerromojonite, watkinsonite which was rich in penroseite. A replacement relic of quijarroite and penroseite surrounded by clausenthalite is shown on the right side of the image. k-p = krut'aite-penroseite solid solution. Reflected light digital image. Width 500 μ m.

FIG. 9. Aggregate of penroseite-poor, parallel crystallized Cu-Hg-Pb-Bi selenides partially altered to late klockmannite (kl), penroseite (p), type II cerromojonite (ce) and type-II

nickeltyrrellite (at right). cl = clausthalite, qu = quijarroite (qu), w = watkinsonite (w), k-p = krut'aite–penroseite solid solution. Reflected light digital image. Width 500 μm .

FIG. 10. (*left*) Partial replacement of Ni–Co-rich rim zones of angular krut'aite–penroseite solid solutions (k-p) by late clausthalite (cl) provides evidence that the concave surfaces have undergone corrosion to release Cu, Ni and Co, trapped by type-II nickeltyrrellite (nt) and possibly penroseite (p). (*centre*) Alteration of a type-II nickeltyrrellite + cerromojonite + klockmannite aggregate by chalcopyrite (ch). g = goethite. Reflected light digital image Width 200 μm .

Tables

TABLE 1. REFLECTANCE DATA FOR NICKELTYRRELLITE

λ (nm)	R (%)	λ (nm)	R (%)
400	42.1	640	49.7
420	43.3	660	50.1
440	44.4	680	50.5
460	45.4	700	51.0
480	46.2	Commission on Ore Mineralogy (COM) wavelengths	
500	46.7		
520	47.1		
540	47.5		
560	47.8		
580	48.3	470	45.9
600	48.8	546	47.6
620	49.9	589	48.1
		650	49.8

TABLE 2. CHEMICAL COMPOSITION (wt%) OF NICKELTYRRELLITE STUDIED FOR STRUCTURE

Constituent	Mean	Range	1 δ	Probe Standard
Cu	13.01	12.71 – 13.38	0.16	chalcopyrite
Fe	0.27	0.05 – 1.04	0.29	chalcopyrite
Co	6.66	3.10 – 8.83	1.86	cobaltite
Ni	16.98	14.36 – 20.10	1.67	pentlandite
S	1.04	0.03 – 2.18	0.69	chalcopyrite
Se	61.91	60.22 – 63.62	1.04	synthetic Bi ₂ Se ₃
Total	99.87	98.97 – 100.82	0.46	

1 δ = standard deviation.

TABLE 3. MEAN COMPOSITION (wt%) AND FORMULA PROPORTIONS OF SIX GRAIN POPULATIONS OF NICKELTYRRELLITE FROM THREE SAMPLES

	62/area 2a		62/area 2b		62/area 1		123GG3/area2c		14/area1		14/area 2a	
	mean (21)	1d	mean (7)	1d	mean (8)	1d	mean (14)	1d	mean (9)	1d	mean (16)	1d
Cu (wt.%)	13.03	0.17	12.93	0.10	11.56	0.02	12.95	0.20	12.62	0.14	11.70	0.26
Fe	0.25	0.34	0.33	0.04	0.82	0.20	0.31	0.27	0.35	0.33	0.31	0.25
Co	7.67	0.62	3.64	0.34	2.41	0.01	8.31	0.63	4.29	0.49	3.88	0.87
Ni	16.11	0.74	19.58	0.46	21.51	0.16	15.13	0.53	18.86	0.72	20.30	0.59
S	1.38	0.42	0.05	0.03	0.12	0.04	0.40	0.14	0.18	0.12	0.14	0.08
Se	61.43	0.66	63.37	0.26	63.63	0.32	63.05	0.28	63.08	0.33	63.25	0.25
sum	99.86	0.48	99.90	0.43	100.04	0.28	100.16	0.34	99.38	0.72	99.57	0.50
Cu (<i>apfu</i>)	1.00	0.01	1.01	0.01	0.90	0.00	1.00	0.01	0.99	0.01	0.92	0.02
Fe	0.02	0.03	0.03	0.00	0.07	0.02	0.03	0.02	0.03	0.03	0.03	0.02
Co	0.63	0.05	0.31	0.03	0.20	0.00	0.70	0.05	0.36	0.04	0.33	0.07
Ni	1.34	0.06	1.66	0.04	1.81	0.01	1.27	0.04	1.60	0.06	1.72	0.05
S	0.21	0.06	0.01	0.00	0.02	0.01	0.06	0.02	0.03	0.02	0.02	0.01
Se	3.80	0.06	3.99	0.01	3.99	0.01	3.94	0.03	3.99	0.04	3.99	0.03

1d = 1d standard deviation; numbers in parentheses indicate the number of spots used for mean calculation. Formula proportions calculated according to 7 atoms *pfu*.

TABLE 4. CLASSIFICATION OF THE S/SE SPECIES IN THE SPINEL SUPERGROUP

Thiospinel group			
<u>carrollite subgroup</u> (1-3.5)	A¹⁺	B^{3.5+}	X
carrollite	Cu	Co ₂	S ₄
cuproiridsite	Cu	(Ir ³⁺ Ir ⁴⁺)	S ₄
cuprokalinitite	Cu	(Cr ³⁺ Cr ⁴⁺)	S ₄
fletcherite	Cu	Ni ₂	S ₄
florensovite	Cu	(Cr ³⁺ _{1.5} Sb ⁵⁺ _{0.5})	S ₄
malanite	Cu	(Ir ³⁺ Pt ⁴⁺)	S ₄
rhodostannite	Cu	(Fe ²⁺ _{0.5} Sn ⁴⁺ _{1.5})	S ₄
toyohaite	Ag	(Fe ²⁺ _{0.5} Sn ⁴⁺ _{1.5})	S ₄
<u>linnaeite subgroup</u> (2-3)	A²⁺	B³⁺	X
cadmoindite	Cd	In ₂	S ₄
cuprorhodsite	(Cu ⁺ _{0.5} Fe ³⁺ _{0.5})	Rh ₂	S ₄
daubréelite	Fe	Cr ₂	S ₄
greigite	Fe	Fe ₂	S ₄
indite	Fe	In ₂	S ₄
joegoldsteinite	Mn	Cr ₂	S ₄
kalinitite	Zn	Cr ₂	S ₄
linnaeite	Co	Co ₂	S ₄
polydymite	Ni	Ni ₂	S ₄
siegenite	Co	Ni ₂	S ₄
violarite	Fe	Ni ₂	S ₄
xingzhongite	Pb	Ir ₂	S ₄
Selenospinel group			
<u>tyrrellite subgroup</u> (1-3.5)	A¹⁺	B^{3.5+}	X
tyrrellite	Cu	(Co,Ni) ₂	Se ₄
nickeltyrrellite	Cu	Ni₂	Se₄
<u>bornhardtite subgroup</u> (2-3)	A²⁺	B³⁺	X
bornhardtite	Co	Co ₂	Se ₄
trüstedtite	Ni	Ni ₂	Se ₄