

THE DISCREDITATION OF HASTITE, THE ORTHORHOMBIC DIMORPH OF CoSe_2 , AND OBSERVATIONS ON TROGTALITE, CUBIC CoSe_2 , FROM THE TYPE LOCALITY

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ABSTRACT

“Hastite”, the orthorhombic dimorph of CoSe_2 , formerly considered as a valid mineral species occurring in the Trogtal quarries, Harz Mountains, Germany, is discredited as being identical with ferroselite, orthorhombic FeSe_2 . The discreditation has been unanimously approved by the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC) (IMA No. 07–E). We also provide observations on the composition, homogeneity, and origin of trogtalite (cubic CoSe_2) from its type locality.

Keywords: “hastite”, ferroselite, trogtalite, electron-microprobe data, reflectance data, Trogtal, Harz Mountains, Germany.

SOMMAIRE

La “hastite”, dimorphe orthorhombique de CoSe_2 , autrefois considéré comme une espèce minérale valide de la carrière de Trogtal, dans le massif de Harz, en Allemagne, est discréditée comme étant identique à la ferroselite, FeSe_2 orthorhombique. La discreditation a été approuvée à l’unanimité par la Commission IMA sur les Nouveaux Minéraux, leur Nomenclature et leur Classification (CNMNC) (IMA No. 07–E). Nous présentons aussi nos observations sur la composition, l’homogénéité, et l’origine de la trogtalite (CoSe_2 cubique) provenant de sa localité type.

Mots-clés: “hastite”, ferroselite, trogtalite, données de microsonde électronique, données de réflectance, Trogtal, montagnes Harz, Allemagne.

INTRODUCTION

Hastite, claimed to be orthorhombic CoSe_2 , was first described by Ramdohr and Schmitt in 1955 from the Trogtal quarry, near Lautenthal, Harz Mountains, Germany (Ramdohr & Schmitt 1955). A study of the type “hastite”, motivated by the lack of chemical characterization, revealed its identity with ferroselite,

orthorhombic FeSe_2 , a species described in the same year as “hastite” from the Ust’Uyuk deposit, Tuva, Siberia, Russia by Bur’yanova & Komkov (1955). The discreditation of hastite has been approved unanimously by the IMA Commission on New Minerals, Nomenclature and Classification (IMA No. 07–E). A study of trogtalite from the type locality also revealed pronounced heterogeneity in the Co, Cu and Ni content

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on a micrometric scale, which raises concerns about the validity of previous electron-microprobe results (Wallis 1994), as they may represent variable mixtures of homogeneous zones in “accidental” proportions.

BACKGROUND INFORMATION

The mineral hastite, claimed to be orthorhombic CoSe_2 (marcasite group), and named in honor of Dr. P.F. Hast, mining engineer, was first described by Ramdohr and Schmitt in 1955 from the Trogtal quarry, near Lautenthal, Harz Mountains, Germany (Ramdohr & Schmitt 1955). As it was described prior to 1959 (pre-IMA era), it received grandfathered status as a valid mineral species according to IMA practice. In the original paper on hastite, Ramdohr & Schmitt (1955) described four new minerals from Trogtal: trogtalite (cubic), with formula CoSe_2 , belonging to the pyrite group, hastite (orthorhombic), with formula CoSe_2 , belonging to the marcasite group, bornhardtite (cubic), with formula Co_3Se_4 , belonging to the linnaeite group, and the later named freboldite (hexagonal), with formula CoSe , belonging to the nickeline group. The authors characterized these minerals by using powder X-ray diffraction of drilled-out material containing a mixture of selenides, and also relied on the paragenesis, hardness, and the characteristic properties of these minerals in reflected light. At the time, electron-microprobe analysis was not available, and thus the determination (or better, assumption) that the minerals are cobalt selenides was made indirectly from (a) the presence of cobalt in the selenide ore from Trogtal (which consisted predominantly of clausthalite, PbSe), (b) the similarity of the diffraction patterns to synthetic material or chemically related compounds, and (c) the distinct violet to reddish brown color of cobalt minerals that, according to the authors, is hardly ever encountered in other minerals. In this light, it appeared possible and reasonable that the formulae given by Ramdohr & Schmitt (1955) were idealized, with potentially significant chemical substitution.

For hastite, the authors noted that attempts to match the powder pattern with synthetic material were not possible, as efforts to synthesize an orthorhombic marcasite-group CoSe_2 failed. However, the authors were able to index all lines of the powder pattern by analogy to those of synthetic, orthorhombic marcasite-group FeSe_2 . Together with the color, thought to be characteristic of cobalt minerals, the paragenesis containing other cobalt selenides, the hardness, the observed type of twinning, the pleochroism, and the strong anisotropy, the authors concluded that they had identified the “ CoSe_2 – marcasite”, which they named hastite. They noted that small substitutions of Fe for Co and S for Se were possible. In addition, the authors noted that the unit-cell size was indistinguishable from that of synthetic FeSe_2 within the uncertainty of the measurement.

OTHER REPORTED OCCURRENCES OF “HASTITE”

Since the original description, minerals supposed to be “hastite” have been mentioned only sparingly. The most recent and well-documented description in the scientific literature of what has been suggested to be hastite was provided from the San Francisco deposit, Puerto Alegre, Sierra de Famatina, La Rioja, Argentina, by de Brodtkorb (1981). On the basis of the similarity of the optical properties to those described by Ramdohr & Schmitt (1955), the author initially concluded that the species is hastite. However, later electron-microprobe analysis unequivocally demonstrated that the material is ferroselite (de Brodtkorb 2002). Another record of “hastite” comes from the *Handbook of Mineralogy* (Anthony *et al.* 1990), where this mineral was mentioned from the LaSal mine, Beaver Mesa, Montrose County, Colorado, without a reference. Beaver Mesa is, however, in Mesa County, and in the book *Minerals of Colorado*, Eckel (1997) does not mention hastite at all, but instead he does mention ferroselite, as does Coleman (1959), who described ferroselite from numerous localities, including the La Sal mine. In only a single sample (from Utah), a 4% replacement of iron with cobalt was measured. Thus, the occurrence of hastite in the LaSal mine in Colorado is not unambiguously proven, and we tentatively suggest that it also has been mistaken for ferroselite.

SAMPLES

An initial investigation of hastite was undertaken on a sample of selenide ore from the Trogtal quarry in the collection of one of the authors (FNK). A phase that corresponds to the “hastite” of Ramdohr & Schmitt (1955) according to its optical properties was identified. Semiquantitative SEM–EDS analysis showed that the mineral is a Fe–Se species, with virtually no other elements present. Consequently, the holotype specimen of hastite, donated by Paul Ramdohr to the Smithsonian National Museum of Natural History in Washington (specimen #112811), was re-examined. In the type specimen, isotropic trogtalite and anisotropic “hastite” were identified according to their optical properties, as described by Ramdohr & Schmitt (1955). Both species form small grains included in clausthalite (Figs. 1, 2) and are spread over an area of about 1.5 mm^2 . Individual grains of the anhedral to subhedral hastite-appearing phase (standing out in relief) reach a maximum size of *ca.* $100 \mu\text{m}$. The grains of “hastite” are typically broken and “infiltrated” by clausthalite along cracks. The fragments “swim” in the clausthalite matrix and have in many cases become rounded along their rim. However, alteration of the hastite-appearing phase is mostly mechanical, and did not cause extensive dissolution, as is evident in trogtalite.

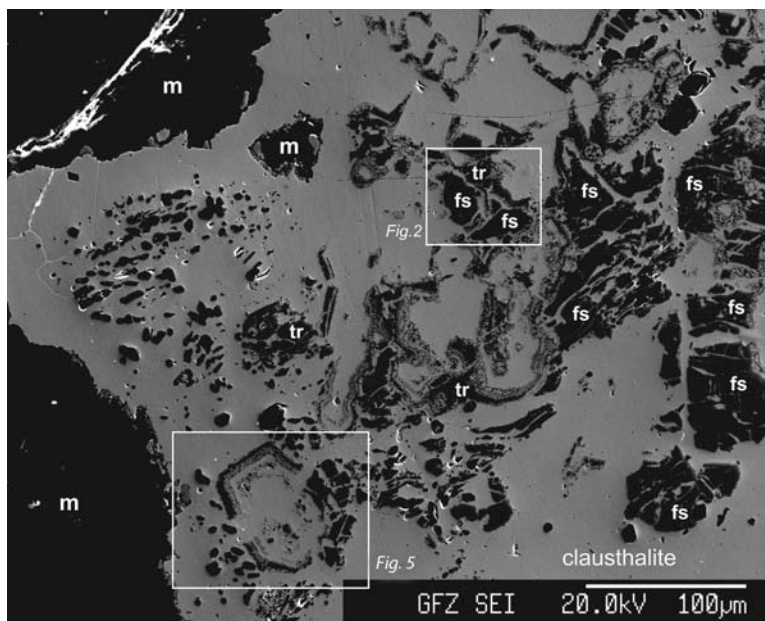


FIG. 1. Secondary-electron (SE) image of clausenthalite containing inclusions of the “hastite”-appearing, high-relief phase (fs), trogtalite (tr), hematite, and minor cerussite. Marked are only the largest grains of “hastite” and trogtalite. Trogtalite is typified by the extensive decomposition of the core and replacement by later-formed clausenthalite, generally leaving behind only the outermost rim. The white rectangles enclose the areas shown in more detail in Figures 2 and 4, respectively. m: carbonate matrix.

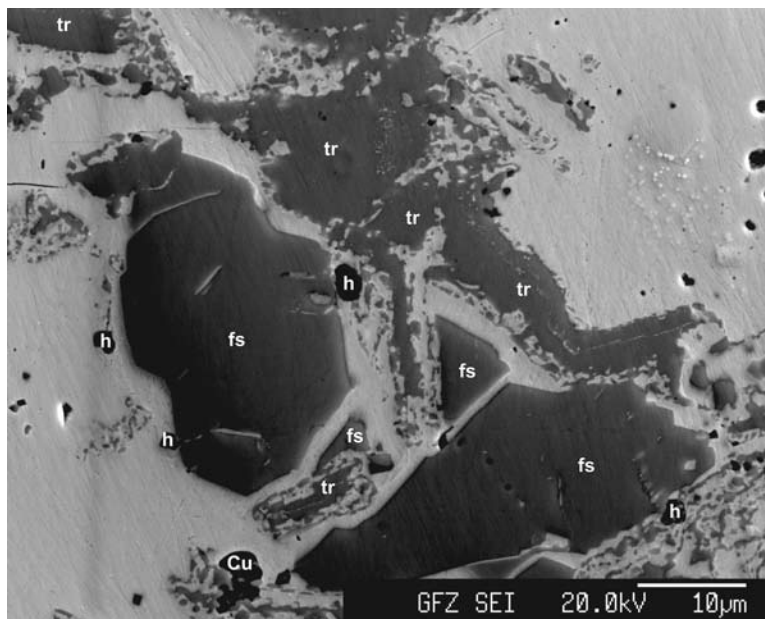


FIG. 2. SE image of “hastite” (fs) associated with trogtalite (tr), hematite (h), and an unspecified Cu selenide (Cu) in clausenthalite.

CHEMICAL COMPOSITION

The type specimen was analyzed at the Deutsches GeoForschungsZentrum in Potsdam using a JEOL thermal field-emission-type electron probe X-ray micro-analyzer (FE-EPMA) JXA-8500F (HYPERPROBE).

In addition to the “hastite” phase discussed below, the mineral assemblage comprises hematite, minor Cu selenides, cerussite, and native selenium, the latter two being breakdown products of clausthalite, and tiny grains of an unidentified Pb–Co selenide formed during the replacement of trogtalite by clausthalite.

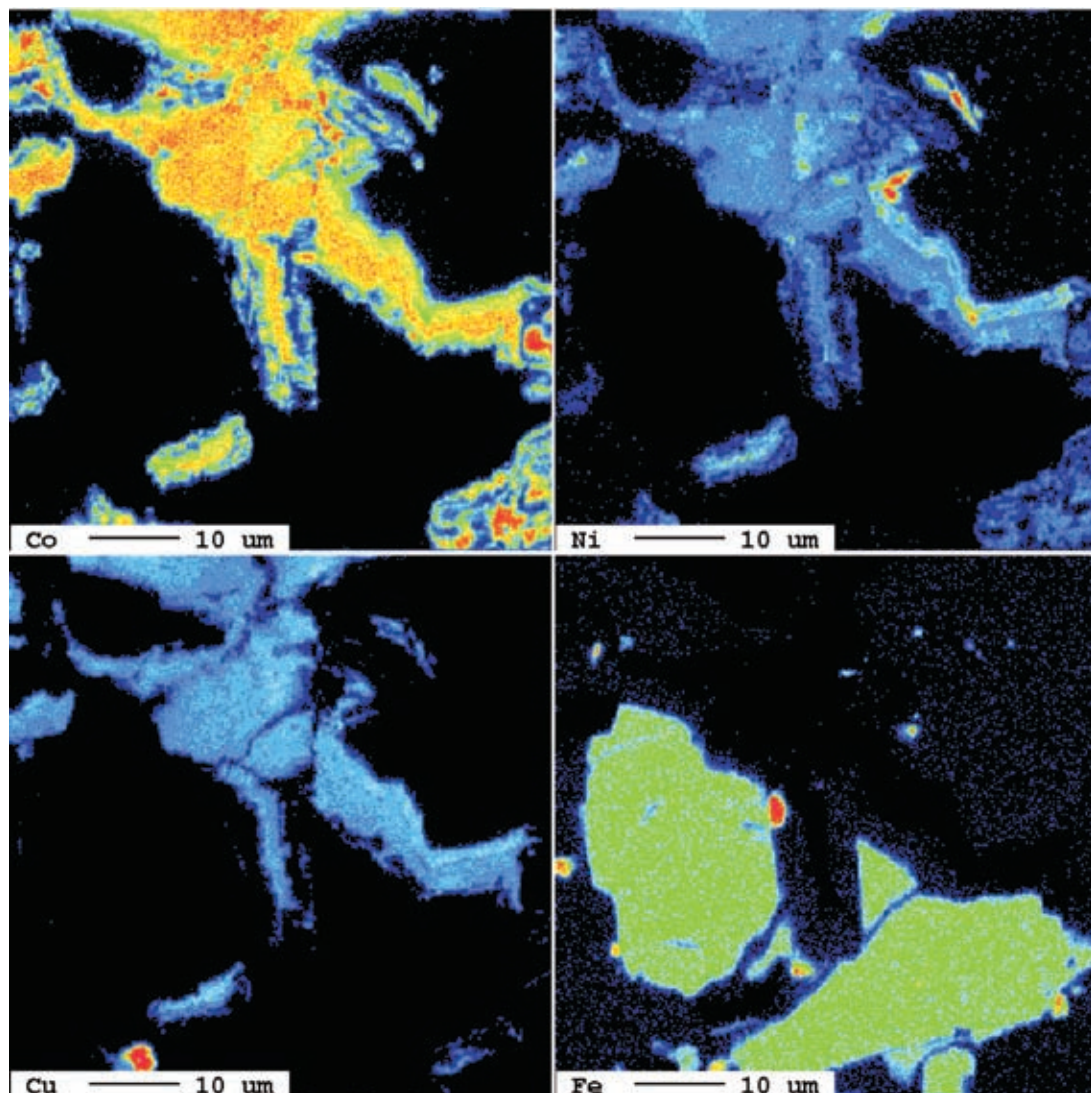


FIG. 3. X-ray element-distribution maps showing the distribution of Co, Ni, Cu, and Fe in the area shown in Figure 2 (20 kV, 15 nA, focused beam, 300×300 pixels, 300 ms counting time per pixel). Warm colors (yellow to red) denote high concentrations, cold colors (pink to blue), low concentrations. The misidentification of “hastite” for ferroselite is demonstrated in the Fe-distribution map, where Co-free ferroselite is highlighted in green. Ferroselite does contain only minor amounts of Co, Ni, Cu, and S (not shown) and, thus, is close to end-member composition FeSe_2 . The inhomogeneous nature of trogtalite is best shown in the Co- and Ni-distribution maps. The antipathetic relations of Co and Ni in trogtalite are clearly visible. Copper tends to parallel the behavior of Ni. The yellow-red spots in the Fe map denote minute grains of hematite. The red spot in the Cu map highlights the unspecified Cu mineral.

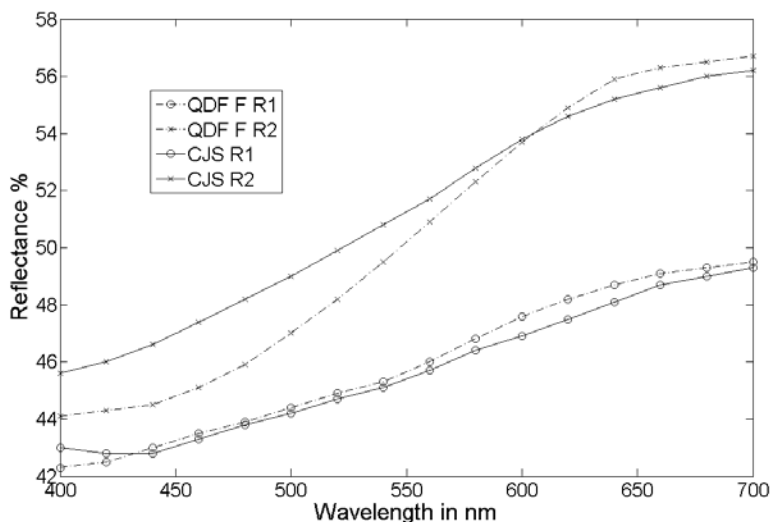


FIG. 4. Comparison of reflectance data for polished section #112811 (type specimen trogtalite—"hastite") from Trogtal, Harz Mountains, Germany (CJS) and ferroselite from the quantitative data file for ore minerals (QDF). The variability in data is attributable to measurements made on an orthorhombic mineral in different orientations.

TABLE 1. REPRESENTATIVE COMPOSITIONS OF FERROSELITE AND TROGTALITE FROM TROGTAL, HARZ MOUNTAINS, GERMANY

	ferroselite			early trogtalite			late trogtalite	
Cu wt%	0.11	0.11	0.08	6.35	7.39	6.90	2.40	0.22
Pb	0.33	0.22	0.47	0.62	0.6	0.54	2.89	2.12
Fe	25.79	25.79	26.18	0.04	0.09	0.20	0.87	0.50
Co	0.05	0.15	0.02	18.40	17.24	18.20	12.95	25.26
Ni	0.03	0	0	2.22	2.54	2.26	9.53	0.42
S	0.03	0.02	0	0	0	0	0	0.49
Se	73.11	73.1	73.43	71.8	71.88	71.52	69.85	69.42
Total	99.45	99.38	100.2	99.43	99.75	99.62	98.49	98.63
Cu <i>apfu</i>				0.22	0.26	0.24	0.08	0.01
Pb				0.01	0.01	0.01	0.03	0.02
Fe	0.99	0.99	1.00			0.01	0.04	0.02
Co		0.01		0.69	0.64	0.68	0.49	0.95
Ni				0.08	0.09	0.08	0.37	0.02
S								0.05
Se	1.99	1.99	1.99	2	2	1.99	1.99	1.94
Atoms	3	3	3	3	3	3	3	3

The analyses of polished section #112811 (type specimen for trogtalite and "hastite") were made with an electron microprobe (JXA-8500F, 15kV, 20 nA, WDS mode).

A qualitative chemical analysis of the type specimen by micro-area X-ray mapping corroborated the results of the previous SEM-EDS study of the Trogtal material and clearly demonstrated that the "hastite"-phase corresponds to a Fe-Se mineral virtually devoid of Co, Ni, Cu, and S (Fig. 3). A subsequent quantitative electron-microprobe analysis confirmed these findings

and further established unequivocally that the anisotropic "hastite" phase corresponds to an iron diselenide, FeSe₂ (Table 1). The composition of ferroselite from Trogtal is near the end-member, averaging (Fe_{0.99}Cu_{0.01})Σ_{1.00}Se_{1.99} (n = 10).

OPTICAL DATA

Attempts to obtain reliable in situ XRD data to establish the structural identity of "hastite" with ferroselite were unsuccessful, as the lines of clausenthalite dominate in a way that any potential lines of "hastite" could not be properly separated. In order to gain further proof of identity of "hastite" with ferroselite, reflectance spectra of "hastite" in the type specimen were obtained using a Zeiss MPM800 microscope-spectrophotometer system relative to the spectra from a WTiC reflectance standard (Zeiss 314). Tabulated R1 and R2 (min/max) reflectance data characteristic of "hastite" and ferroselite (published) are given in Table 2 and are shown in Figure 4. The collected spectra are very close to published data for ferroselite (Criddle & Stanley 1993); variations are attributable to measurements taken in different orientations on an orthorhombic mineral.

DISCUSSION

The results of the quantitative chemical analysis demonstrate that holotype "hastite" corresponds to

FeSe₂, and the reflectance data show very good agreement with the literature values for ferroselite. In addition, Ramdohr & Schmitt (1955) were able to index all lines of the powder pattern they obtained by analogy to those of synthetic ferroselite, and they noted that the unit-cell size is the same, within the uncertainty of the measurement, as that of ferroselite. The unit-cell parameters reported for “hastite” (a 4.84, b 5.72, c 3.60 Å, V = 99.66 Å³) (Ramdohr & Schmitt 1955) and ferroselite (a 4.80, b 5.73, c 3.58 Å, V = 98.46 Å³) (Anthony *et al.* 1990) are indeed extremely similar. In contrast, a structural effect of the substitution of Co for Fe can be clearly observed in a comparison of the unit-cell parameters of trogtalite (a = 5.86 Å, V = 201.2 Å³) (Bindi *et al.* 2008) and dzharkenite (a = 5.78 Å, V = 193.0 Å³) (Yashunsky *et al.* 1995), and an effect on unit-cell size has also been reported for substitution of Co, Ni, and Cu in the pyrite-group diselenides (Bindi *et al.* 2008). Thus, the crystallographic results of Ramdohr & Schmitt (1955) in fact argue in favor of the similarity of “hastite” and ferroselite. These findings on the chemical and physical properties of “hastite” demonstrate that it is identical with ferroselite. This misidentification by two of the world’s leading experts in ore mineralogy, and in particular in reflected light microscopy, was a result of limitations in microchemical analytical methods in the

middle of the 20th century, as the authors had to infer the chemical composition. Therefore, and because no orthorhombic CoSe₂ phase has yet been unambiguously identified from any other occurrence, the discreditation of “hastite” in view of its identity with ferroselite has been approved unanimously by the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC) (IMA No. 07-E). “Hastite” and ferroselite were described in the same year; one might argue that the name “hastite” possibly has priority over ferroselite, as it was published several months earlier. However, the original publication of “hastite”, for understandable reasons, grossly mistook its chemical identity and thus, the discreditation of “hastite” instead of ferroselite is warranted.

COMMENTS ON TROGTALITE

Fine-scale X-ray mapping also revealed important insights into the chemical composition of isotropic trogtalite from Trogtal, suggested by Ramdohr & Schmidt (1955) to be nearly pure CoSe₂. In specimen #112811, in particular, the core of trogtalite grains was progressively and intensely cannibalized and replaced by clausthalite (Fig. 5). Trogtalite is strongly heterogeneous in composition (Fig. 6). Quasi-homogeneous

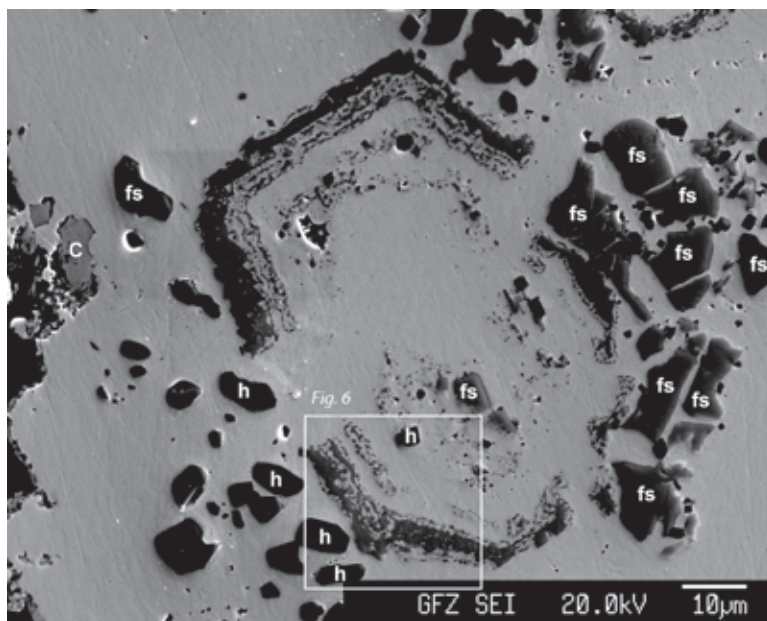


FIG. 5. SE image of a relict, formerly euhedral grain of trogtalite extensively metasomatized, disintegrated, and replaced by clausthalite. On its right-hand side, trogtalite is surrounded by several fragments of ferroselite, which probably originally formed one or two grains only. Other minerals shown comprise hematite (h) and cerussite (c). The white rectangle marks the part of the sample shown as Figure 6.

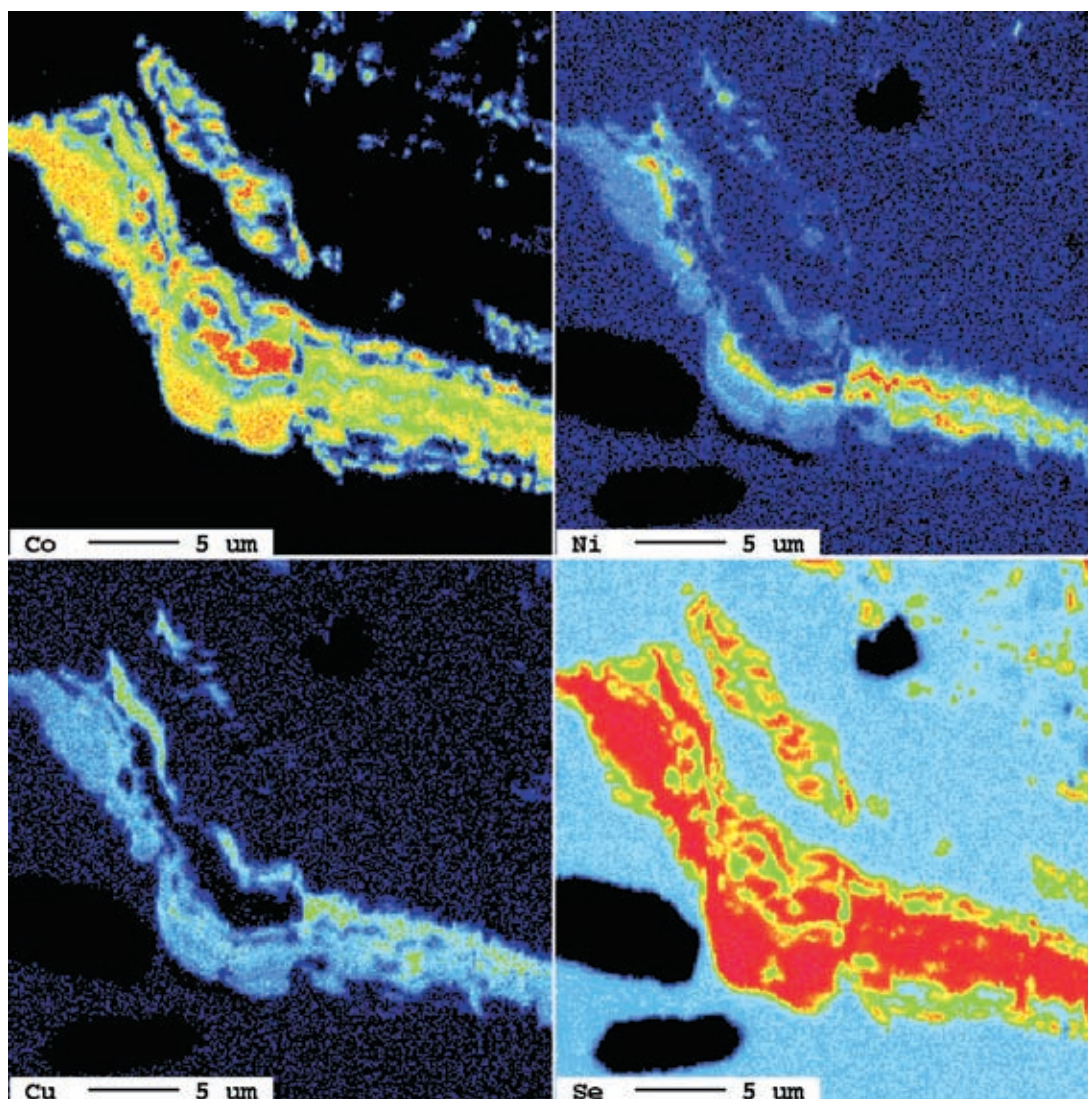


FIG. 6. X-ray element-distribution maps of Co, Ni, Cu, and Se (15 kV, 20 nA, focused beam, 300×300 pixels, 300 ms counting time per pixel) of the area enclosed by a white rectangle in Figure 5. The compositional heterogeneity of trogtalite at the μm scale is clearly displayed in the all four maps. Note that Co is inversely correlated with Ni and Cu. Co-rich spots devoid of Ni and Cu mark the location of unidentified Pb–Co–selenides newly formed in response to the alteration of CoSe_2 by PbSe.

areas are generally only a few μm^2 across. Trogtalite grains not affected by infiltrating Pb-bearing fluids correspond to CoSe_2 – NiSe_2 – CuSe_2 solid solutions and do not possess a near-end-member CoSe_2 composition. The trogtalite has the composition $(\text{Co}_{0.66 \pm 0.04} \text{Cu}_{0.24 \pm 0.02} \text{Ni}_{0.09 \pm 0.01} \text{Fe}_{0.01 \pm 0.00} \text{Pb}_{0.01 \pm 0.00}) \Sigma 1.01 \pm 0.01 \text{Se}_{2.00 \pm 0.01}$ ($n = 6$) (Table 1). Small zones less than a few μm^2 across of newly formed or re-equilibrated trogtalite display a variable composition, including Ni-rich CoSe_2 and near-

end-member CoSe_2 , both Pb-bearing (*cf.* Table 1). In tiny, more Ni-rich areas, Ni may even predominate over Co, thus probably representing penroseite, ideally NiSe_2 (*cf.* Fig. 6). Another sample from Trogtal investigated in this study (not shown here) revealed zones in trogtalite that appear to correspond to krutaite, $(\text{Cu,Co,Ni})\text{Se}_2$. The fine chemical heterogeneity of trogtalite from its type locality raises major concerns about the validity of previous microprobe analyses (Wallis 1994), which may

TABLE 2. REFLECTANCE VALUES FOR "HASTITE" (= FERROSELITE) AND FOR FERROSELITE

λ (nm)	CJS		QDF	
	R_1	R_2	R_1	R_2
400	43.0	45.6	42.3	44.1
420	42.8	46.0	42.5	44.3
440	42.8	46.6	43.0	44.5
460	43.3	47.4	43.5	45.1
480	43.8	48.2	43.9	45.9
500	44.2	49.0	44.4	47.0
520	44.7	49.9	44.9	48.2
540	45.1	50.8	45.3	49.5
560	45.7	51.7	46.0	50.9
580	46.4	52.8	46.8	52.3
600	46.9	53.8	47.6	53.7
620	47.5	54.6	48.2	54.9
640	48.1	55.2	48.7	55.9
660	48.7	55.6	49.1	56.3
680	49.0	56.0	49.3	56.5
700	49.3	56.2	49.5	56.7

Reflectance values were determined on polished section #112811 (type specimen of trogtalite and "hastite" from Trogtal, Harz Mountains, Germany (CJS), and taken from the Quantitative Data File for Ore Minerals (QDF; Criddle & Stanley 1993).

represent variable mixtures of homogeneous zones in "accidental" proportions. However, that trogtalite represents a valid IMA mineral has been confirmed several times (Paar *et al.* 1996, 2002, Roberts *et al.* 2002, Pirard & Hatert 2008) subsequently to its original description, and is not questioned here.

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