

## GERMANIUM-BEARING COLUSITE FROM THE WATERLOO VOLCANIC-ROCK-HOSTED MASSIVE SULFIDE DEPOSIT, AUSTRALIA: CRYSTAL CHEMISTRY AND FORMATION OF COLUSITE-GROUP MINERALS

THOMAS WAGNER<sup>§</sup>

*Institut für Geowissenschaften, Universität Tübingen, Wilhelmstraße 56, D-72074 Tübingen, Germany*

THOMAS MONECKE

*Geological Survey of Canada, Natural Resources Canada, 601 Booth Street, Ottawa, Ontario K1A 0E8, Canada*

### ABSTRACT

Bornite-bearing ores of the Waterloo volcanic-rock-hosted massive sulfide (VHMS) deposit, northern Queensland, Australia, host germanium-bearing colusite, ideally  $\text{Cu}_{24+x}\text{V}_2(\text{As,Sb})_{6-x}(\text{Sn,Ge})_x\text{S}_{32}$ , which has been studied by a combination of reflected-light microscopy, scanning electron microscopy and electron-microprobe (EMP) analysis. On the basis of textural criteria, colusite is associated with pyrite, chalcopyrite, sphalerite, tennantite and bornite. The EMP investigations showed that the colusite is chemically homogeneous, the concentrations of As, Sb, V, Sn and Ge being in the range of 3.42–4.08, 0.10–0.20, 1.86–2.19, 0.01–0.12 and 1.78–2.23 *apfu*, respectively. Data analysis demonstrates a statistically significant negative correlation between (As + Sb) and (Ge + Sn), in *apfu*. Moreover, the nominal number of vacancies per formula unit (*pfu*), calculated as  $34 - \Sigma\text{cations } apfu$ , was found to correlate negatively with (Cu + Fe + Zn). A compilation of literature data supports the existence of these two compositional trends in colusite-group minerals. However, the calculated nominal number of vacancies ranges between –2.0 and 2.5 *pfu*, indicating a significant deviation from the ideal crystal-chemical formulae proposed so far. The compositional range of the literature data can only be explained by the simultaneous operation of at least three different schemes of coupled substitution. Compositional discontinuities in the quaternary system As–Sb–Sn–Ge are interpreted to be indicative of the existence of miscibility gaps in the colusite group. Integration of the results of the present study and literature data with phase-equilibria constraints suggests that colusite-group minerals in VHMS deposits form under moderately oxidized conditions at distinctly high Cu:Fe activity ratios in the ore-forming hydrothermal fluids.

**Keywords:** colusite, germanium, solid solution, volcanic-rock-hosted massive sulfide deposits, Waterloo VHMS deposit, Queensland, Australia.

### SOMMAIRE

Dans le gisement à sulfures massifs volcanogéniques de Waterloo, dans le nord du territoire de Queensland, en Australie, le minerai contenant la bornite contient aussi de la colusite germanifère, de composition idéale  $\text{Cu}_{24+x}\text{V}_2(\text{As,Sb})_{6-x}(\text{Sn,Ge})_x\text{S}_{32}$ . Nous l'avons étudié par microscopie en lumière réfléchie, par microscopie électronique à balayage, et avec une microsonde électronique. À la lumière de critères texturaux, la colusite est associée à pyrite, chalcopyrite, sphalérite, tennantite et bornite. Les données obtenues avec la microsonde électronique montrent que la colusite est chimiquement homogène, avec des concentrations de As, Sb, V, Sn et Ge dans les intervalles 3.42–4.08, 0.10–0.20, 1.86–2.19, 0.01–0.12 et 1.78–2.23 *apfu*, respectivement. Il y a une corrélation négative entre (As + Sb) et (Ge + Sn), en atomes par unité formulaire. De plus, la proportion de lacunes, considérée égale à  $34 - \Sigma\text{cations}$ , montre une corrélation négative avec (Cu + Fe + Zn). Une compilation des données prises de la littérature renforce l'existence de ces deux aspects de la composition des minéraux du groupe de la colusite. Toutefois, la proportion calculée des lacunes varie entre –2.0 et 2.5 par unité formulaire, indiquant un écart important par rapport aux formules cristallographiques idéales déjà proposées. L'intervalle de composition observé dans la littérature ne peut s'expliquer que par opération simultanée d'au moins trois schémas distincts de substitution couplée. Des discontinuités compositionnelles dans le système quaternaire As–Sb–Sn–Ge témoigneraient de l'existence de lacunes de miscibilité dans le groupe de la colusite. D'après l'intégration de nos résultats et des données antérieures avec les contraintes imposées par les équilibres des phases, les minéraux du groupe de la colusite dans les gisements de sulfures massifs volcanogéniques se seraient formés en milieux relativement oxydants à partir de fluides hydrothermaux ayant un rapport élevé des activités de Cu et de Fe.

(Traduit par la Rédaction)

**Mots-clés:** colusite, germanium, solution solide, gisements de sulfures massifs volcanogéniques, gisement de Waterloo, Queensland, Australie.

<sup>§</sup> E-mail address: th.wagner@uni-tuebingen.de

## INTRODUCTION

Colusite is a rare copper vanadium sulfide of complex composition. It was recognized as a new species and named by Sales (1914) and described fully by Landon & Mogilnor (1933). Subsequent studies have established the existence of several structurally and chemically related phases (Table 1); colusite is now recognized to be the arsenic-dominant end-member of the colusite group (Mandarino 1992). The tin-dominant counterpart, nekrasovite, was defined by Kovalenker *et al.* (1984). Stibiocolusite represents the antimony-dominant analogue (Spiridonov *et al.* 1994) and germanocolusite is the germanium-dominant end-member (Spiridonov *et al.* 1992). Anisimova *et al.* (2002) reported the occurrence of anomalous concentrations of zinc in nekrasovite and suggested that a zinc-dominant end-member of the colusite group may also exist in nature. Possible further members of the colusite group are the recently approved molybdenum-bearing species maikainite and its tungsten-dominant analogue ovamboite (Spiridonov 2003). The four species colusite, nekrasovite, stibiocolusite and germanocolusite belong to the colusite group *sensu stricto* (Mandarino 1992) and are classified by Strunz & Nickel (2001) as members of the germanite–mooihoekite group. This group comprises a number of complex sulfides of Cu, Fe, V, Sn, Ge, As, Sb, which are all structurally related to sphalerite, but do not constitute an isostructural series with it (Strunz & Nickel 2001). Germanite is isostructural with the minerals of the colusite group *sensu stricto*, but is not considered a member of this group (Spry *et al.* 1994).

In the present contribution, results of new chemical analyses of germanium-bearing colusite are reported. This colusite-group mineral was discovered at the Waterloo volcanic-rock-hosted massive sulfide deposit, northern Queensland, Australia. On the basis of our analytical results and an extensive compilation of data presented by previous investigators, we have attempted to further constrain the crystal chemistry of the colusite-group minerals. In addition, we show that the chemical characteristics of these rare sulfides can be directly related to the environment of mineral precipitation. The chemical properties of colusite-group minerals, therefore, represent sensitive tracers that can be used in studies focusing on the genetic aspects of ore-forming systems.

## REVIEW OF RECENT FINDINGS

Several authors have studied the structural and chemical properties of colusite, and views on the crystal chemistry of this rare sulfide have undergone substantial changes since its discovery (Zachariassen 1933, Berman & Gonyer 1939, Murdoch 1953, Dangel & Wuensch 1970, Orlandi *et al.* 1981, Spiridonov *et al.* 1986, Spry *et al.* 1994, Frank-Kamenetskaya *et al.*

2002). It is now well established that the colusite structure consists of  $\text{CuS}_4$  and  $\text{AsS}_4$  tetrahedra that are connected by corner sharing in a sphalerite-like framework. The number of Cu atoms in the metal positions varies from about 24 to over 26 per unit cell owing to the presence of vacancies. In addition to the sphalerite-like framework, colusite contains two V atoms per unit cell that are stuffed into the tetrahedral interstices in a sulvanite-like arrangement. In the colusite structure, the V atoms only occupy one of the two available interstitial sites. In a recent study, Frank-Kamenetskaya *et al.* (2002) have demonstrated that two structural modifications are possible, differing in the occupancy of the interstitial sites. Thus, a revision of the nomenclature of the colusite-group minerals may be required once additional data become available. In addition to this structural complication, Frank-Kamenetskaya *et al.* (2002) pointed out that several mechanisms of coupled substitution have previously not been recognized. However, because colusite-group minerals are comparatively rare in nature, currently relatively few data are available to constrain the relative importance of the different proposed mechanisms of substitution.

## OCCURRENCE OF COLUSITE-GROUP MINERALS

Initially, colusite was recognized at the Butte deposit in Montana (Sales 1914, Landon & Mogilnor 1933, Nelson 1939, Bideaux 1960, Lévy 1967, Springer 1969a, Kovalenker *et al.* 1984), but it is now known from several copper and copper–molybdenum porphyry systems and associated vein and skarn deposits. For instance, colusite has been identified at the Medet deposits in Bulgaria (Strashimirov 1982, Strashimirov *et al.* 2002), the Campbell orebody at Bisbee, Arizona (Harris *et al.* 1984), the Bor deposit in eastern Serbia (Cvetkovic *et al.* 1999), the Grasberg deposit in Indonesia (Pollard & Taylor 2002), and the Colquijirca deposit in central Peru (Bendezú & Fontboté 2002).

TABLE 1. GENERALIZED FORMULA OF COLUSITE-GROUP MINERALS AND OF RELATED PHASES

Mineral	Generalized formula	Reference
<b>Colusite-group minerals</b>		
Colusite	$\text{Cu}_{24+x}\text{V}_2(\text{As,Sb})_{6-x}(\text{Sn,Ge})_2\text{S}_{32}^*$	Spry <i>et al.</i> (1994)
Nekrasovite	$\text{Cu}_{26}\text{V}_2\text{Sn}_6\text{S}_{32}$	Kovalenker <i>et al.</i> (1984)
Stibiocolusite	$\text{Cu}_{26}\text{V}_2(\text{Sb,Sn,As})_6\text{S}_{32}$	Spiridonov <i>et al.</i> (1994)
Germanocolusite	$\text{Cu}_{26}\text{V}_2(\text{Ge,As})_6\text{S}_{32}$	Spiridonov <i>et al.</i> (1992)
Maikainite	$\text{Cu}_{26}(\text{Fe,Cu})_6\text{Mo}_2\text{Ge}_2\text{S}_{32}$	Spiridonov (2003)
Ovamboite	$\text{Cu}_{26}(\text{Fe,Cu,Zn})_6\text{W}_2\text{Ge}_2\text{S}_{32}$	Spiridonov (2003)
<b>Related phases</b>		
Germanite	$\text{Cu}_{26}\text{Fe}_4\text{Ge}_2\text{S}_{32}$	Tettenhorst & Corbató (1984)
Renierite	$\text{Cu}_{26}(\text{Zn}_{2-x}\text{Cu}_x\text{Ge}_{4-x}\text{As}_x)\text{Fe}_2\text{S}_{32}^*$	Bernstein (1986)
Vincienmite	$\text{Cu}_{22}\text{Sn}_2\text{As}_2\text{Fe}_2\text{S}_{32}$	Spry <i>et al.</i> (1994)

\* with  $0 \leq x \leq 2$ .

Several authors have noted the presence of colusite-group minerals in epithermal precious-metal deposits. For instance, colusite has been noticed at the Gies deposit, Montana (Spry *et al.* 1994, Zhang & Spry 1994). Colusite, nekrasovite and stibiocolusite are present in the Shin–Ohtoyo deposit, Hokkaido, Japan (Imai *et al.* 1999) and the Kairagach deposit, Uzbekistan (Kovalenker & Geynke 1984, Kovalenker *et al.* 1984, 2003, Spiridonov *et al.* 1984, 1994). Colusite, germanocolusite, nekrasovite and stibiocolusite have also been recognized at the Chelopech deposit, Bulgaria (Kovalenker *et al.* 1984, Spiridonov *et al.* 1994). An additional report on the occurrence of colusite in an epithermal deposit was given by Kesler *et al.* (1981).

Colusite-group minerals also occur in VHMS deposits (Matsukuma *et al.* 1974, Kase & Yamamoto 1988, Robinson *et al.* 1996). For instance, colusite has been described from the giant Kidd Creek deposit, Ontario, Canada (Thorpe *et al.* 1976, Hannington *et al.* 1999a, M.D. Hannington, pers. commun., 2004), and colusite as well as nekrasovite have been identified at the Neves–Corvo deposit, Portugal (Carvalho *et al.* 1999, Gaspar 2002). In addition, germanium-rich members of the colusite group were recognized in several VHMS deposits. For example, germanocolusite has been observed at the Urup deposit, Russia (Kachalovskaya *et al.* 1975, Spiridonov *et al.* 1992) and the Maykain deposit, Kazakhstan (Spiridonov *et al.* 1992). Germanium-bearing colusite has been described from the Gay deposit, southern Urals, Russia (Pshenichnyy *et al.* 1975), the San Fernando deposit, Cuba (Krapiva *et al.* 1986), the Yanahara mine, Japan (Kase *et al.* 1994) and the Bousquet deposit, Quebec, Canada (Tourigny *et al.* 1993). Colusite also is present in the Chizeuil deposit, Massif Central, France (Picot *et al.* 1963, Lévy 1967, Lecuyer & Picot 1984).

An additional well-described example is the Tsumeb mine, Namibia, where colusite and germanocolusite have been recognized in germanium-rich ore along with germanite and renierite (Springer 1969b, Geier & Ottemann 1970, Innes & Chaplin 1986, Spiridonov 1987, Spiridonov *et al.* 1992). Germanium- and tungsten-bearing colusite are present in trace quantities at the carbonate-hosted Khusib Springs deposit, Otavi Mountains, Namibia (Melcher *et al.* 2002). The occurrence of colusite in sulfide-bearing vugs in the Carrara area, Italy, has been described by Orlandi *et al.* (1981) and Spry *et al.* (1994). Additional descriptions of colusite-group minerals have been given by Mitryayeva *et al.* (1968), Yushkin *et al.* (1975), Yushko-Zakharova *et al.* (1982) and Lustig & Rosenzweig (1987).

#### GEOLOGICAL FRAMEWORK

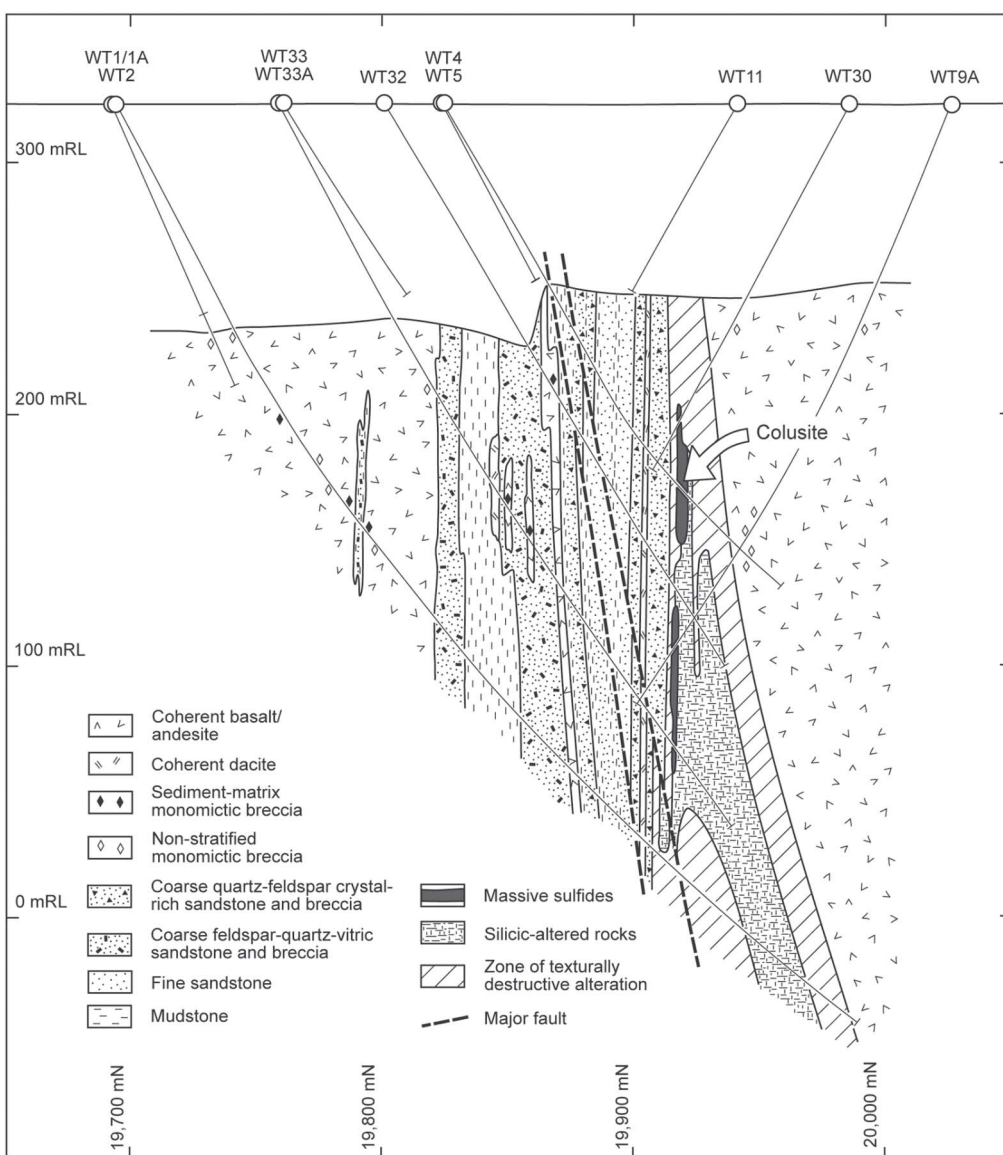
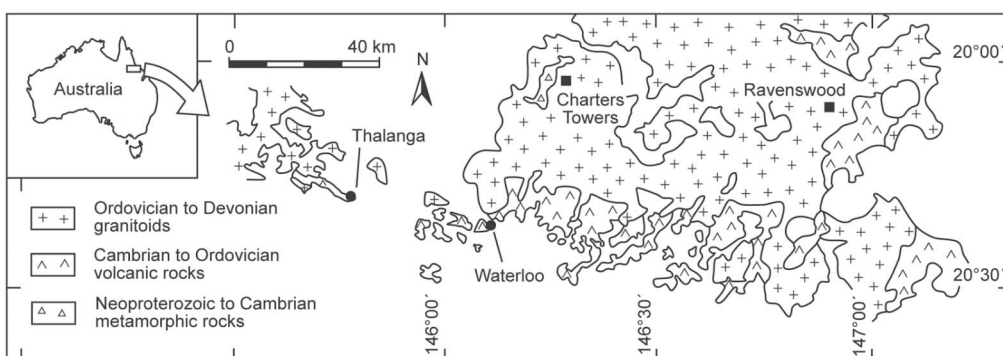
The Waterloo deposit is located in the Charters Towers region in north Queensland (Fig. 1). The massive sulfide mineralization is hosted by volcanic rocks belonging to the Seventy Mile Range Group, a major relic

of Cambro–Ordovician back-arc volcanism at the northern end of the Tasman Fold Belt System (Henderson 1986, Berry *et al.* 1992, Stolz 1995). The Waterloo deposit represents a small base-metal resource of 0.372 Mt at 3.8% Cu, 19.7% Zn, 2.8% Pb, 94 g/t Ag and 2 g/t Au (Berry *et al.* 1992, Huston *et al.* 1995). The mineralization comprises dismembered blanket-like lenses of massive pyrite – chalcopyrite – sphalerite – galena. In addition to these major components of the ore, the mineralization contains minor amounts of tennantite and traces of bornite, tellurides and arsenopyrite (Huston *et al.* 1995).

The blanket-like massive sulfide bodies are enveloped by a laterally extensive alteration halo (Fig. 1). In the footwall, the alteration halo exhibits a semiconformable mineralogical zonation that is defined by silicified rocks containing pyrite, quartz and muscovite, as well as phyllic-altered rocks that consist of pyrite, white mica, chlorite and quartz. Primary volcanic textures are not preserved in these two zones of intense hydrothermal alteration. In the outer alteration halo, the phyllic-altered rocks grade into propylitic-altered andesites that are characterized by the presence of substantial amounts of albite, chlorite, epidote, quartz, calcite and variable amounts of white mica and pyrite (Monecke *et al.* 2001). Weakly to moderately altered andesite of the outer alteration halo contains abundant relict volcanic textures, including evenly distributed phenocrysts and flow-aligned amygdules (Monecke *et al.* 2003).

The massive sulfide bodies are overlain by variably altered coarse quartz–feldspar crystal-rich sandstone and breccia. The hydrothermal alteration of the stratigraphically lower part of the volcanoclastic sedimentary units was feldspar-destructive, and lithic fragments are entirely or partially replaced by secondary minerals, such as white mica and quartz (Giorgetti *et al.* 2003). In contrast, primary textures are well preserved in the upper part of the volcanoclastic unit. The coarse quartz–feldspar crystal-rich sandstone and breccia hosts a large dacite cryptodome that also was subject to hydrothermal alteration (Giorgetti *et al.* 2003, Monecke *et al.* 2003). The top of the coarse volcanoclastic facies coincides with the upper limits of the hydrothermal hanging-wall alteration. The lower part of the unaltered hanging-wall succession comprises fine sandstone and greenish black mudstone. These fine-grained rocks contain a number of emplacement units of basaltic to andesitic composition. The upper part of the hanging wall is dominated by sandstone and breccia containing coarse feldspar, quartz and vitric particles and a thick coherent sequence of andesite and basalt.

The volcanic rocks hosting the Waterloo deposit were tilted into a subvertical position during north–south compression that is possibly Mid- to Late Ordovician in age (Berry *et al.* 1992). The massive sulfides and the surrounding volcanic rocks have been overprinted at lower greenschist-facies conditions during a regional metamorphic event. Peak conditions of metamorphism



reached during upper greenschist-facies metamorphism at the nearby Thalanga massive sulfide deposit were estimated to be 440 to 480°C at pressures below 3.5 kbar (Paulick & Franz 2001).

#### SAMPLING AND METHODS

Because the massive sulfides and their host rocks are not exposed in surface outcrop, sampling was restricted to diamond exploration drill-core that penetrated the blanket-like massive sulfide mineralization. On the basis of systematic logging of the available drill-core, representative samples were selected from all ore facies recognized at the Waterloo deposit. In the course of the study, a number of polished sections were studied by a combination of reflected-light microscopy, scanning electron microscopy (SEM) and electron-microprobe (EMP) analysis.

The SEM work was performed on a JEOL JSM-6400 microscope equipped with a Tracor (Noran) series II energy-dispersion X-ray spectrometer. Routine operating conditions were 20 kV with a beam current of 700 pA. In addition, high-resolution back-scattered-electron (BSE) imaging was carried out on selected grains to test whether the colusite grains possess internal structures that could not be identified under routine operating conditions. The high-resolution BSE images were collected using a beam current of up to 5.5 nA at a working distance of only 16 mm.

The chemical composition of colusite was determined by wavelength-dispersion EMP analysis using a JEOL-8900 instrument. Operating conditions were 20 kV at a beam current of 20 nA (measured on Faraday cup), a beam diameter of 1–2 µm, and counting times of 20 s for all elements. Background count-rates were obtained on both sides of the peak using half the counting times. Matrix-correction procedures were performed with the CITZAF algorithm. The following standards and X-ray lines were used: CANMET arsenopyrite (FeK $\alpha$ , AsL $\beta$ ), synthetic vanadinite (VK $\beta$ ), CANMET CuS (SK $\alpha$ , CuK $\alpha$ ), synthetic SnO<sub>2</sub> (SnL $\alpha$ ), synthetic ZnS (ZnL $\alpha$ ), synthetic Bi<sub>12</sub>GeO<sub>20</sub> (GeK $\alpha$ ) and CANMET tetrahedrite (SbL $\alpha$ ). With the analytical conditions employed, the precision was approximately 1% for all major elements. The detection limits and their respective standard deviations (1 $\sigma$ ) have been calculated as: Fe: 548 (18) ppm; As: 899 (26) ppm; V: 2356 (79) ppm; S: 250 (10); Sn: 255 (3) ppm; Cu: 987 (24) ppm; Zn: 452 (14) ppm; Ge: 655 (8) ppm; Sb: 312 (4) ppm.

FIG. 1. Simplified geological cross-section and location of the Waterloo VHMS deposit. Note that the massive sulfides and the volcanic host-rocks were tilted into a subvertical position during regional deformation.

#### RESULTS

##### *Mineralogy and textures*

On the basis of ore-mineral associations and their textural relationships, three distinct types of massive sulfide ore can be distinguished, namely (1) sphalerite – galena – pyrite ore, (2) sphalerite – chalcopyrite – pyrite ore and (3) pyrite – (barite) ore. Both sphalerite-rich ore types occur as alternating discontinuous layers, mainly in the center of the ore lenses. The sphalerite – galena – pyrite ore is composed of a matrix of strongly recrystallized elongate grains of sphalerite, which show abundant galena infilling along the grain boundaries. Sphalerite hosts isolated euhedral and round porphyroblasts of pyrite and subordinate inclusions of elongate tennantite. The sphalerite – chalcopyrite – pyrite ore contains recrystallized sphalerite and chalcopyrite, with abundant patches of tennantite and pyrite. The pyrite patches are composed of several individual pyrite porphyroblasts, which show abundant evidence of fracturing. Chalcopyrite has been partly mobilized into pressure shadows between pyrite porphyroblasts. The pyrite–(barite) ore is exclusively found in the distal zone of the ore lenses. The mineralogy of this ore type is dominated by pyrite, which forms layers composed of numerous small grains of pyrite within a phyllosilicate-rich matrix. Pyrite has been subjected to extensive fracturing, with most of the microfractures showing infilling by chalcopyrite. Massive pyrite in some cases contains fractured euhedral crystals of barite.

The occurrence of germanium-bearing colusite is restricted to a transitional zone at the contact between sphalerite – galena – pyrite ore and sphalerite – chalcopyrite – pyrite ore (diamond drill-hole WT5 at 180 m below surface). Colusite forms round anhedral grains, which are present as isolated grains or as small clusters of 5–10 individual grains. Most grains of colusite are oval and show regular shapes, with only few grains being distinctly elongate and more irregular in shape. Grain sizes are in the range between 5 and 65 µm, with an average size of 25 ± 15 µm based on measurements on a total number of 108 grains. Most of the colusite occurs as individual grains within sphalerite or along the grain boundaries between sphalerite and chalcopyrite. Few grains of colusite are present as inclusions within tennantite and chalcopyrite or along the grain boundaries between sphalerite and galena. We note that the pyrite porphyroblasts within the colusite-bearing zone contain abundant inclusions of bornite and chalcopyrite. Neither colusite nor bornite have been observed in the pyrite–(barite) ore. The optical properties of colusite are comparable to those in most descriptions in the literature (*e.g.*, Orlandi *et al.* 1981, Spiridonov *et al.* 1992). In reflected light, germanium-bearing colusite from the Waterloo deposit has a cream color with a distinct brownish tint. All colusite grains are isotropic, and no internal reflections were observed. Conventional re-

flected-light microscopy did not reveal any compositional heterogeneity or distinct zonation within individual grains.

In contrast to reflected-light microscopy, the germanium-bearing colusite hosted by sphalerite was extremely difficult to identify with the SEM because both minerals exhibit very similar BSE contrasts. However, subtle variations in surface topography could be used to locate the grains of colusite; this mineral exhibits a slightly lower polishing-hardness than the surrounding sphalerite matrix. In contrast to grains contained in sphalerite, germanium-bearing colusite could be readily identified in other host minerals such as chalcopyrite (Fig. 2). BSE imaging at standard operating conditions as well as the high-resolution BSE imaging of selected grains of colusite confirmed the observation that the colusite is chemically homogeneous.

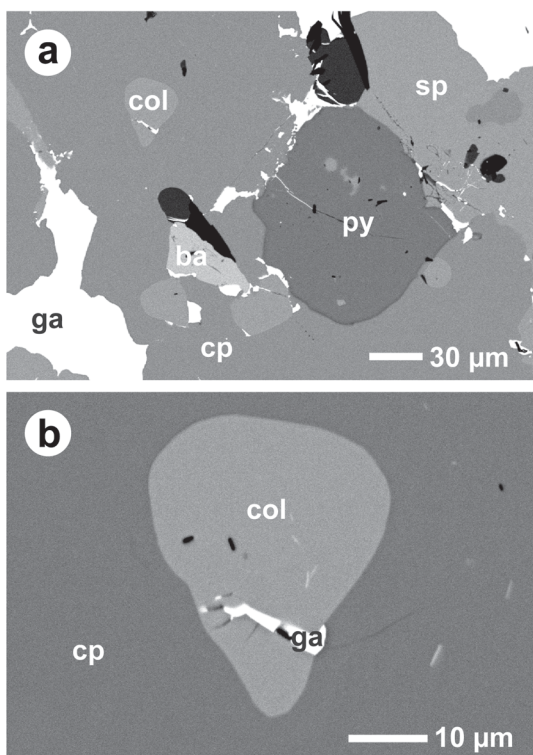


FIG. 2. Back-scattered electron (BSE) images of colusite from the Waterloo VHMS deposit. (a) Colusite (col) is hosted by a matrix of chalcopyrite (cp) and sphalerite (sp), which contains abundant porphyroblasts of pyrite (py) and galena (ga) infilling along the grain boundaries. Barite (ba) is locally present. (b) Enlarged view of a colusite (col) grain enclosed in chalcopyrite (cp). A microfracture in colusite has been infilled by galena (ga). The BSE images show that the individual grains of colusite are compositionally homogeneous.

### Chemical composition

A total of 29 colusite grains were analyzed; representative results of EMP analyses are given in Table 2. The different analyzed grains were found to exhibit relatively limited chemical variation. The germanium-bearing colusite contains essentially Cu, Fe, Zn, Sn, Ge, V, As, Sb and S; all other elements sought (Mn, Pb, Se, Te) lie below the respective limits of detection. The Cu concentrations are in the range between 48.05 and 50.14 wt.%, corresponding to 24.20 to 25.47 atoms per formula unit (*apfu*) calculated on the basis of 32 sulfur atoms. We found no clear correlation trend between the total Cu *apfu* and any other element or combination of elements, reflecting the complexity of the various mechanisms of substitution operating in colusite. The concentrations of As, Sb, V, Sn and Ge are in the range of 7.94–9.47 wt.% (3.42–4.08 *apfu*), 0.37–0.77 wt.% (0.10–0.20 *apfu*), 2.93–3.45 wt.% (1.86–2.19 *apfu*), 0.04–0.46 wt.% (0.01–0.12 *apfu*) and 4.01–5.03 wt.% (1.78–2.23 *apfu*), respectively. There is a statistically significant negative correlation between the total number of (As + Sb) *apfu* and (Sn + Ge) *apfu* (Fig. 3), indicating that these two groups of elements are related by at least one mechanism of coupled substitution. The proportion of V *apfu* shows no detectable correlation with the proportion of (As + Sb) *apfu* ( $R^2 = 0.05$ ) and (Sn + Ge) *apfu* ( $R^2 = 0.08$ ), which rules out a significant mechanism of coupled substitution involving V for the germanium-bearing colusite.

The grains of germanium-bearing colusite exhibit significant variations in their Fe contents. The Fe con-

TABLE 2. REPRESENTATIVE COMPOSITIONS OF GERMANIUM-BEARING COLUSITE FROM THE WATERLOO VHMS DEPOSIT

	1	2	3	4	5	6	7	8	9	10
Cu	49.01	49.35	49.57	48.80	49.96	49.36	49.28	50.14	49.20	49.73
Fe	0.10	0.07	0.09	0.13	0.09	1.05	1.16	0.78	0.43	0.59
Zn	0.89	0.54	0.48	1.06	0.71	1.00	0.95	0.12	1.06	0.39
Sn	0.33	0.32	0.42	0.33	0.41	0.31	0.31	0.04	0.34	0.42
Ge	4.66	4.24	4.31	5.01	4.52	4.89	4.83	4.11	4.88	4.18
V	3.13	3.38	3.39	3.13	3.28	2.99	3.20	3.08	3.02	3.31
As	8.45	8.76	8.64	7.98	8.20	8.19	8.36	9.47	8.36	8.76
Sb	0.65	0.48	0.66	0.68	0.77	0.61	0.67	0.37	0.69	0.59
S	31.89	31.77	31.73	31.87	32.07	31.99	31.83	31.79	32.16	31.88
Total	99.11	98.91	99.29	98.99	100.01	100.39	100.59	99.90	100.14	99.85
Cu	24.82	25.08	25.23	24.73	25.16	24.92	25.00	25.47	24.70	25.19
Fe	0.06	0.04	0.05	0.07	0.05	0.60	0.67	0.45	0.25	0.34
Zn	0.44	0.27	0.24	0.52	0.35	0.49	0.47	0.06	0.52	0.19
Sn	0.09	0.09	0.11	0.09	0.11	0.08	0.08	0.01	0.09	0.11
Ge	2.07	1.89	1.92	2.22	1.99	2.16	2.14	1.83	2.14	1.85
V	1.98	2.14	2.15	1.98	2.06	1.88	2.03	1.95	1.89	2.09
As	3.63	3.78	3.73	3.43	3.50	3.51	3.60	4.08	3.56	3.76
Sb	0.17	0.13	0.18	0.18	0.20	0.16	0.18	0.10	0.18	0.16
S	32	32	32	32	32	32	32	32	32	32

Electron-microprobe data, first reported in terms of wt.%, then in terms of atoms per formula unit, based on 32 atoms of sulfur. Columns 1–5: sphalerite-hosted colusite; columns 6–10: chalcopyrite-hosted colusite.

centrations show a clearly bimodal distribution, which reflects the different host-minerals of the respective grains. Sphalerite-hosted colusite has a mean Fe content of 0.09 ( $1\sigma = 0.03$ ) wt.%, whereas chalcopyrite-hosted colusite displays a significantly higher Fe content, 0.66 ( $1\sigma = 0.29$ ) wt.%. In contrast, the Zn concentrations of both populations are statistically indistinguishable, with mean values of 0.74 ( $1\sigma = 0.27$ ) wt.% and 0.75 ( $1\sigma = 0.30$ ) wt.% calculated for sphalerite-hosted and chalcopyrite-hosted colusite, respectively.

The crystal-chemical formulae for the different minerals of the colusite group are based on a maximum total number of 34 cations, calculated on the basis of 32 S atoms. Taking this value as a basis, the number of vacancies at cation sites in the structure can be calculated as  $34 - \sum \text{cations}$  for each individual analysis. The calculations reveal that the number of vacancies per formula unit (*pfu*) shows a statistically significant negative correlation with the total number of (Cu + Fe + Zn) *apfu* (Fig. 4). Most interestingly, some analytical data show a slightly negative nominal number of vacancies despite of the fact that these data points are perfectly situated on the regression line calculated on the basis of the entire dataset.

## DISCUSSION

### *Crystal chemistry of germanium-bearing colusite*

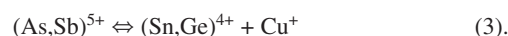
The minerals of the colusite group exhibit a number of crystal-chemical and structural complications. In order to explain the chemical variations observed, several homovalent and coupled substitution schemes have been proposed. The principal homovalent substitutions are



and



On the basis of a crystal-structural study of Sn-poor and Sn-rich colusite, Spry *et al.* (1994) showed that various members of the colusite group can be derived by a coupled substitution of the type



According to this substitution scheme, the incorporation of substantial amounts of tetravalent cations such as Sn and Ge in the colusite structure should be paralleled by an increase in the Cu content. Taking into account that

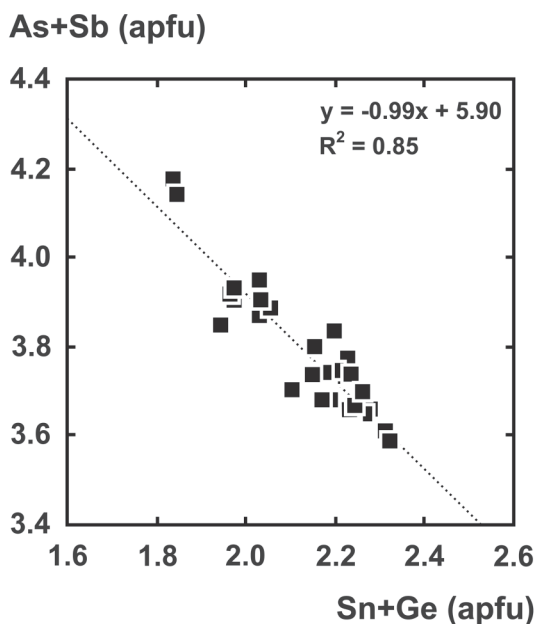


FIG. 3. Compositional ranges of germanium-bearing colusite from the Waterloo VHMS deposit. The numbers of (As + Sb) *apfu* are plotted as a function of the amount of (Sn + Ge) *apfu*.

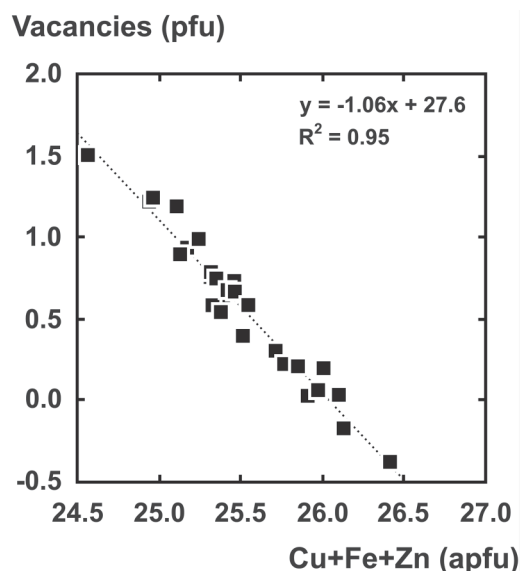


FIG. 4. Correlation between the nominal number of vacancies *pfu* and the amount of (Cu + Fe + Zn) *apfu* for germanium-bearing colusite from the Waterloo VHMS deposit. The vacancies were calculated as  $34 - \sum \text{cations}$  *apfu*.

Cu does not exceed 26 *apfu* (Spry *et al.* 1994), this substitution scheme satisfactorily explains all colusite compositions involving the theoretical end-members  $\text{Cu}_{24}\text{V}_2\text{As}_6\text{S}_{32}$ ,  $\text{Cu}_{24}\text{V}_2\text{Sb}_6\text{S}_{32}$ ,  $\text{Cu}_{26}\text{V}_2\text{As}_4\text{Sn}_2\text{S}_{32}$  and  $\text{Cu}_{26}\text{V}_2\text{As}_4\text{Ge}_2\text{S}_{32}$  (Table 1).

Although most of the analytical data of colusite-group minerals in the literature are in agreement with this formula, a considerable number of data points exceed the maximum possible number of  $(\text{Sn} + \text{Ge}) = 2$  *apfu* (e.g., Kovalenker *et al.* 1984, Spiridonov *et al.* 1992, Tourigny *et al.* 1993, Hannington *et al.* 1999a, Imai *et al.* 1999). In these cases, a combination of tetravalent and divalent cations may enter the colusite structure according to the coupled substitution



as proposed by Frank-Kamenetskaya *et al.* (2002). The formula of colusite-group minerals then is  $\text{Cu}_{24+x-y}^{2+}\text{V}^{5+}_2(\text{As,Sb})^{5+}_{6-x-y}(\text{Sn,Ge})^{4+}_{x+y}(\text{Fe,Zn,Cu})^{2+}_y\text{S}_{32}$ , with  $0 \leq x \leq 2$  and  $0 \leq y \leq 6 - x$ .

Both the above schemes of coupled substitution should result in an ideal negative correlation between the number  $(\text{Sn} + \text{Ge})$  *apfu* and the  $(\text{As} + \text{Sb})$  *apfu* with a slope of  $-1$ . Extensive compilation of analytical data,

including the new dataset from the Waterloo VHMS deposit ( $n = 29$ ) and all EMP data in the literature available to us ( $n = 91$ ), demonstrates an excellent agreement between the compositional representations and the theoretical prediction (Figs. 3, 5). Only a relatively limited number of comparatively old EMP data (Mitryayeva *et al.* 1968, Kachalovskaya *et al.* 1975, Yushkin *et al.* 1975) show significant deviations from this trend and were not included in the regression analysis. Statistical analysis of the entire dataset shows that no significant correlation between the number of Cu *apfu* and the number of  $(\text{Ge} + \text{Sn})$  *apfu* ( $R^2 = 0.38$ ) and  $(\text{As} + \text{Sb})$  *apfu* ( $R^2 = 0.47$ ) exists. Both substitution schemes mentioned above are operating in colusite-group minerals. The possible incorporation of  $\text{Cu}^{2+}$  in the As position of the sphalerite-like framework substantially complicates the relationship between the number of cations in this position and the total Cu content of colusite-group minerals.

We have found a statistically significant negative correlation between the total number of  $(\text{Cu} + \text{Fe} + \text{Zn})$  *apfu* and the number of vacancies *pfu* for the Waterloo dataset, calculated on the basis of a maximum total number of 34 cations *apfu* in colusite (Fig. 4). If the number of vacancies *pfu* is calculated for the literature data as well, a similar relationship can be observed (Fig. 6). The

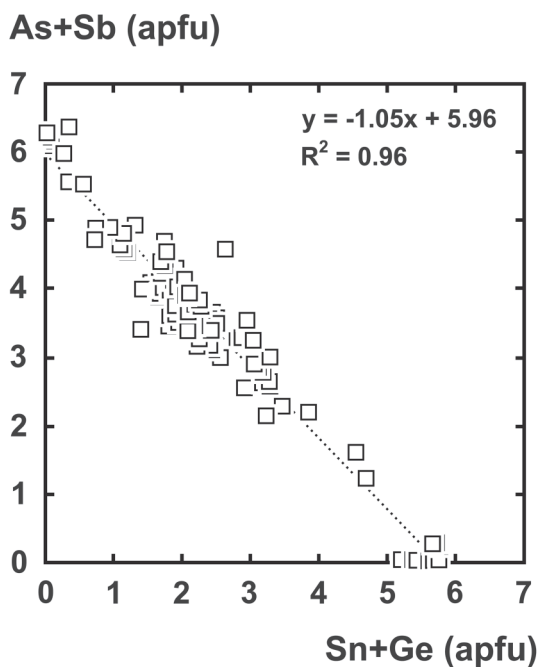


FIG. 5. Compositional ranges of colusite-group minerals expressed in terms of the numbers of  $(\text{As} + \text{Sb})$  *apfu* versus  $(\text{Sn} + \text{Ge})$  *apfu*. The diagram is based on our compilation of data from the literature ( $n = 91$ ).

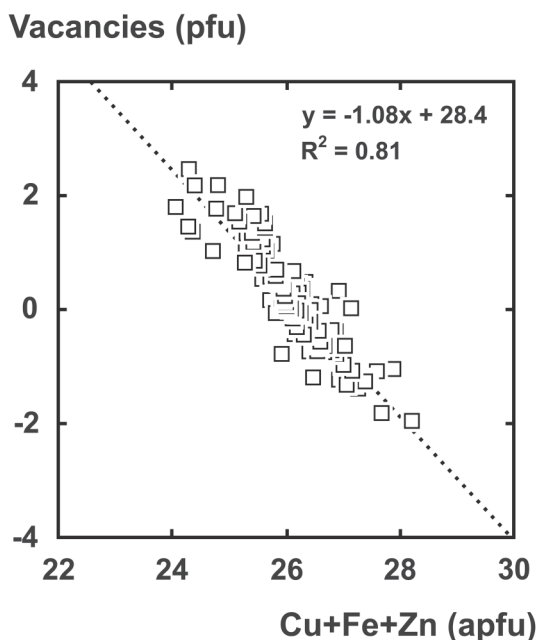
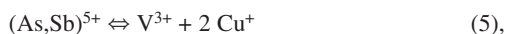


FIG. 6. Correlation between the number of vacancies *pfu* and the amount of  $(\text{Cu} + \text{Fe} + \text{Zn})$  *apfu*. The vacancies were calculated as  $34 - \sum \text{cations apfu}$ . The diagram is based on our compilation of data from the literature ( $n = 91$ ).



correlation trends displayed by both the Waterloo and the literature data sets intersect approximately at vacancies = 0 *pfu* and (Cu + Fe + Zn) = 26 *apfu*, consistent with the proposed crystal-chemical formulae for the fully substituted colusite-group minerals (*e.g.*, Kovalenker *et al.* 1984, Spiridonov *et al.* 1992, 1994, Spry *et al.* 1994). However, in contrast to the predictions from the general formula by Spry *et al.* (1994), which would only allow the number of vacancies to vary between 0 and 2 *pfu*, the calculated nominal number of vacancies ranges between -2.0 and approximately 2.5 *pfu* for the literature dataset. We note that almost half of the data points in the literature ( $n = 37$ ) have a negative nominal number of vacancies, suggesting that this latter trend constitutes a significant crystal-chemical feature of colusite-group minerals. The observed negative nominal numbers of vacancies *pfu* would seem to indicate that mechanisms of substitution other than those discussed above are at work in colusite from some localities, enabling incorporation of Cu in excess of 26 *apfu*.

Frank-Kamenetskaya *et al.* (2002) have already pointed out that the total number of cations in colusite-group minerals varies between 30.6 and 36.4 *apfu*, calculated on the basis of 32 sulfur atoms. Based on their crystal-structure determinations, which indicated the presence of significant amounts of a lighter element at the As positions of the sphalerite-like framework of colusite, they suggested an additional mechanism of substitution,



resulting in the more complex crystal-structural formula of colusite,  $\text{Cu}^{+}_{24+x-y+2z} \text{V}^{5+}_2 (\text{As,Sb})^{5+}_{6-x-y-z} (\text{Sn,Ge})^{4+}_{x+y} \text{V}^{3+}_z (\text{Fe,Zn,Cu})^{2+}_y \text{S}_{32}$ , with  $0 \leq x \leq 2$ ,  $0 \leq y \leq 6 - x$ , and  $0 \leq z \leq 0.5$  (Frank-Kamenetskaya *et al.* 2002). Our compilation of literature data shows that the total V content of colusite-group minerals only rarely exceeds 2.2 *apfu*, indicating that  $0 \leq z \leq 0.2$  rather than  $0 \leq z \leq 0.5$ , a fact that agrees well with the excellent correlation observed in Figure 5. The calculated nominal number of vacancies then ranges only from -0.4 to 2.0 *pfu*, which does not explain the entire observed compositional range of colusite-group minerals. This finding indicates that the substitution scheme proposed by Frank-Kamenetskaya *et al.* (2002) is only of minor overall importance. Additional complications may arise from the suggested mixed valence of vanadium; it cannot be readily shown that  $\text{V}^{5+}$  and  $\text{V}^{3+}$  are indeed simultaneously present in colusite. A combination of  $\text{V}^{5+}$  and  $\text{V}^{4+}$  appears to be more likely from a geochemical point of view.

The observed variations in the calculated nominal number of vacancies of -2.0 to approximately 2.5 *pfu* for the literature dataset can only be accounted for by a new scheme of substitution. A possible explanation would be the mechanism



because this process does not result in an increase of the total amount of V present in colusite-group minerals and is consistent with the observed correlation of (Ge + Sn) *apfu* with (As + Sb) *apfu*. If the V content is approximately 2 *apfu*, the formula of colusite-group minerals should then be written  $\text{Cu}^{+}_{24+x-y+z} \text{V}^{5+}_{2-z} \text{V}^{4+}_z (\text{As,Sb})^{5+}_{6-x-y} (\text{Sn,Ge})^{4+}_{x+y} (\text{Fe,Zn,Cu})^{2+}_y \text{S}_{32}$ , with  $0 \leq x \leq 2$ ,  $0 \leq y \leq 6 - x$ , and  $0 \leq z \leq 2$ . The maximum number of cations per 32 S atoms is then 36 *apfu*. Considering such a substitution mechanism, the full range of chemical variation found in colusite-group minerals can be satisfactorily explained.

#### *Compositional trends of colusite-group minerals in the system As-Sb-Sn-Ge*

On the basis of a compilation of analytical data of colusite-group minerals, including the new dataset from the Waterloo VHMS deposit, compositional trends in the quaternary system As-Sb-Sn-Ge can be assessed. Instead of using a tetrahedron, where the proper *loci* of the analytical data-points would be difficult to visualize, we have plotted the data into the ternary subsystems As-Sb-Sn, As-Sb-Ge, As-Sn-Ge and Sb-Sn-Ge (Fig. 7). The recalculated data were uniquely assigned to these subsystems according to their three predominant components, similar to the procedure previously applied to thiospinel minerals (Riley 1980, Wagner & Cook 1999). We consider this method appropriate in the present case, because the fourth component not represented in the respective ternary diagrams is usually present at concentrations below about 2 mol.%. Only two analytical data-points, which were assigned to the subsystems As-Sb-Sn and As-Sn-Ge, have elevated Ge and Sb concentrations, 2.9 and 3.9 mol.%, respectively.

Considering all available data on colusite-group minerals, it appears that their chemical representations occupy only a relatively small portion of compositional space. In particular, note that only a few published data-points plot close to the compositions of the proposed end-members germanocolusite and nekrasovite. As expected from the above discussion of substitution mechanisms, those colusite-group minerals possessing high contents of tetravalent cations are also typified by the presence of substantial amounts of Fe and Zn. Inspection of the ternary diagrams in Figure 7 reveals that solid solution between colusite and germanocolusite, as well as between nekrasovite and stibicolusite, seems to be rather continuous. Although the synopsis of literature data strongly supports a continuity for these two solid-solution series, general conclusions drawn from the observed compositional trends require some caution. Most importantly, it is not always certain whether previous investigators have tested the grains for composi-

tional inhomogeneities prior to analysis. Fine-scale intergrowths of different colusite-group minerals, oscillatory zoning and replacement textures are common in hydrothermal ore deposits (*e.g.*, Nelson 1939, Harris *et al.* 1984, Spiridonov *et al.* 1992, Melcher *et al.* 2002). However, a fine-scale intergrowth could not be observed for the germanium-bearing colusite from the Waterloo VHMS deposit, implying that the colusite–germano-colusite solid-solution series is indeed continuous.

In contrast to the colusite–germanocolusite and nekrasovite–stibiocolusite series, intermediate compositions along the binary joins germanocolusite–nekrasovite and germanocolusite–stibiocolusite have not been reported so far (Fig. 7). Moreover, there seems to be a compositional discontinuity between colusite and stibiocolusite. With the exception of the few data given by Imai *et al.* (1999), no sample of distinctly antimony-rich colusite has been documented. Although the solid solution between colusite and nekrasovite is rather continuous, it appears to be limited to about 50 mol.% nekrasovite. The observed compositional discontinuities, which are most pronounced along the Ge–Sn and Ge–Sb joins, possibly correspond to miscibility gaps in the quaternary system As–Sb–Sn–Ge. Such miscibility gaps could be related to the thermodynamics of exchange reactions among the different end-members and order–disorder phenomena, as already suggested by Spry *et al.* (1994). Examples from other groups of sulfide and sulfosalts minerals show that avoidance of particular substitutions due to positive exchange-energies (*e.g.*, Sack & Loucks 1985, Ebel & Sack 1989, 1991, Harlov & Sack 1994, Ghosal & Sack 1999) and complex order–disorder transitions (*e.g.*,

Pring & Hyde 1987, Pring *et al.* 1999, Pring & Etschmann 2002, Cook & Ciobanu 2003) are widespread phenomena.

#### *Genetic controls on the formation of colusite-group minerals in VHMS deposits*

Figure 8 depicts the compositional ranges of colusite-group minerals from VHMS deposits in the ternary diagrams As–Ge–Sn and As–Sb–Sn. Inspection of the diagrams reveals that most examples from this type of ore deposit have a composition close to the colusite–germanocolusite join. The fact that the sulfides contain substantial amounts of arsenic agrees well with the observation that tennantite is an abundant minor component in many VHMS deposits, including the Waterloo deposit (Huston *et al.* 1995). In contrast, tetrahedrite or other antimony-bearing phases are not as frequent in VHMS deposits, probably explaining the observation that colusite-group minerals from these deposits lack a significant stibiocolusite component (Fig. 8).

Figure 8 shows that colusite-group minerals in some VHMS deposits are characterized by an elevated content of nekrasovite. These anomalous compositions were found at the Chizeuil deposit in the Massif Central of France and the Kidd Creek deposit in the Abitibi greenstone belt of Canada (Lévy 1967, Thorpe *et al.* 1976, Lecuyer & Picot 1984, Hannington *et al.* 1999a, M.D. Hannington, pers. commun., 2004). In contrast to other examples of massive sulfide mineralization, the ores of these two deposits are characterized by the abundant presence of tin-bearing minerals. For instance, Lecuyer & Picot (1984) noted that colusite occurs in association

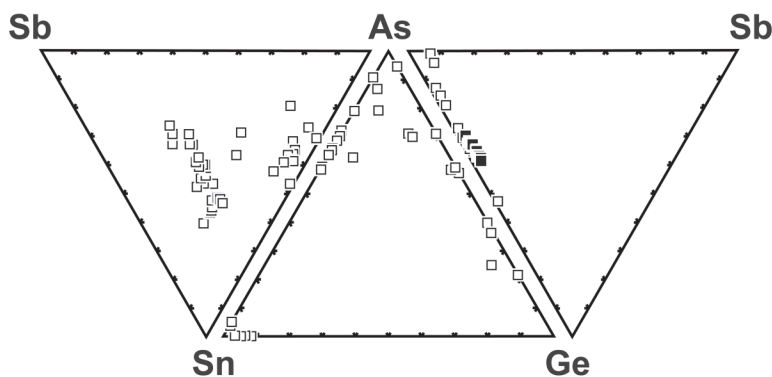


Fig. 7. Compositional representations of colusite-group minerals in the quaternary system As–Sb–Sn–Ge. New data from the Waterloo deposit are given as filled squares ( $n = 29$ ), whereas data taken from the literature ( $n = 91$ ) are indicated by open squares. All compositions were recalculated to 32 sulfur atoms and plotted in the ternary subsystems according to their three major components, *i.e.*, each composition is plotted onto only one of the four subsystems. The subsystem Sb–Sn–Ge is not included in the figure, because with the above procedure, no data point is located in this portion of compositional space.

with mawsonite, stannite and stannoidite at the Chizeuil deposit. In addition, tennantite is also found to be a common ore mineral associated with colusite. At the Kidd Creek deposit, Hannington *et al.* (1999a) showed that colusite primarily occurs in tennantite-rich bornite – pyrite – chalcopyrite ore containing tin-bearing minerals such as k esterite, mawsonite, stannite, stannoidite, vinciennite and minor cassiterite. In addition to these two localities, nekrasovite has been documented at the Neves Corvo VHMS deposit in Portugal (Carvalho *et al.* 1999). This giant massive sulfide deposit is also known for its anomalous tin content (Leistel *et al.* 1998, Carvalho *et al.* 1999).

Comparison of the available literature indicates that bornite is invariably present in cases of VHMS mineralization that contain colusite-group minerals. Although the paragenetic relationships between bornite and these rare sulfides are not always unequivocal, the presence of bornite may further constrain the chemical environment required for the formation of colusite-group minerals. Depending mainly on the temperature of mineralization and the total concentration of sulfur in the ore-forming fluids, the phase equilibria in the system Cu–Fe–S–O–H generally suggest moderately oxidizing conditions for bornite – chalcopyrite – pyrite assemblages in VHMS deposits (e.g., Ohmoto *et al.* 1983, Hannington *et al.* 1999b). The mineralogy of the alteration zones suggests that the hydrothermal fluids forming these ore deposits were acidic to near-neutral. We note that the Fe content of sphalerite in bornite-rich massive sulfide ores hosting colusite-group minerals tends to be comparatively low (e.g., Kase *et al.* 1994). Considering the constraints imposed by the sphalerite–pyrite phase equilibria (Scott & Barnes 1971), a low Fe content of sphalerite is also indicative of moderately oxidizing conditions (e.g., Hannington & Scott 1989). Hannington *et al.* (1999a) showed that the occurrence of bornite in massive sulfides indicates that the mineralizing hydrothermal fluids possessed a distinctly high activity ratio of copper to iron. The common occurrence of colusite-group minerals in bornite-bearing ores may, therefore, suggest that a comparably high Cu:Fe activity ratio is a prerequisite for the formation of these sulfides. This interpretation possibly explains the observation that the iron content of colusite-group minerals in massive sulfide deposits is generally quite low.

#### CONCLUSIONS

We have reported the occurrence of germanium-bearing colusite in the massive sulfide mineralization at the Waterloo volcanic-rock-hosted massive sulfide deposit, Australia. On the basis of EMP investigations, the crystal-chemical properties of this rare sulfide have been constrained and compared to literature data. The results of the present investigations suggest that at least three different schemes of coupled substitution are important in colusite-group minerals. Moreover, we propose that

the existence of chemical discontinuities within the colusite group is indicative of miscibility gaps between the respective end-members. The observed complex schemes of coupled substitution and the proposed existence of miscibility gaps show that the crystal chemistry of colusite-group minerals is rather complex and hitherto poorly understood. Although the major ore minerals that result from massive sulfide mineralization have been studied extensively, there is still considerable demand for microanalytical investigations on trace ore components.

Although colusite occurs only in trace amounts, we show that colusite-group minerals only form under spe-

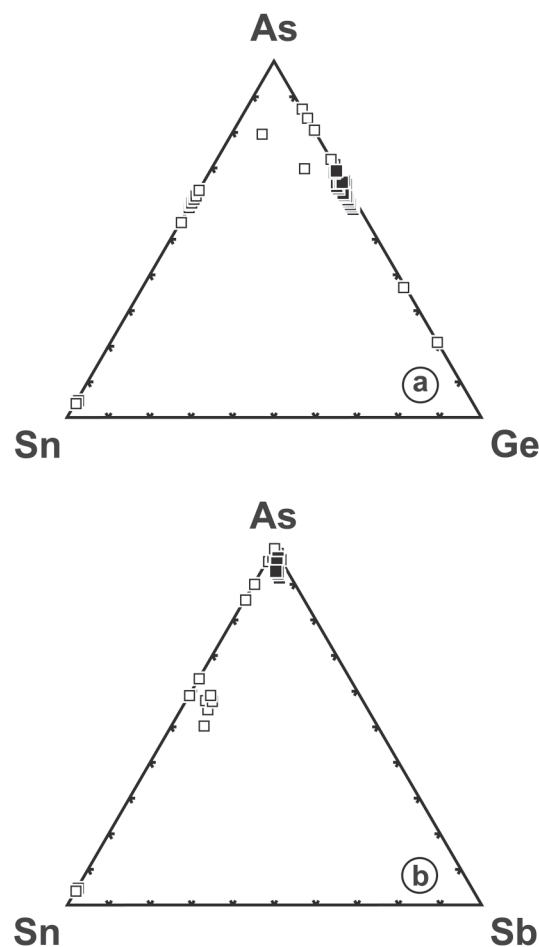


Fig. 8. Compositional representations of colusite-group minerals in the ternary systems (a) As–Ge–Sn and (b) As–Sb–Sn using only data from VHMS deposits. New data from the Waterloo deposit are given as filled squares ( $n = 29$ ), whereas data taken from the literature ( $n = 28$ ) are indicated by open squares.

sific physicochemical conditions. The occurrence in bornite- and chalcopyrite-bearing ores implies that colusite-group minerals form as a result of moderately oxidizing conditions. The association with bornite and low-Fe sphalerite further suggests that these rare sulfides precipitate only in an environment typified by a high Cu:Fe activity ratio. In general, colusite-group minerals are rich in arsenic in ores that contain substantial amounts of tennantite. In contrast, tin-bearing colusite and nekrasovite have only been reported from instances of volcanic-rock-hosted massive sulfide mineralization that possess an overall high tin content.

A particularly interesting feature of colusite-group minerals from volcanic-rock-hosted massive sulfide deposits is the anomalous germanium content, in view of the increasing demand for this high-technology metal. Taking into account that colusite may possess quite high germanium concentrations, it can be assumed that colusite-group minerals represent the principal host of this element in volcanic-rock-hosted massive sulfide deposits. Based on the findings of the present study, it appears possible that bornite-bearing massive sulfides are particularly promising as germanium resources. Recovery of germanium from these ores is probably favorable because this element is contained in a discrete mineral of reasonable grain-size. This would facilitate design of specific ore-dressing procedures designed to obtain germanium concentrates from such types of ore.

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