

# Germanium-rich Chalcopyrite from the Barrigão Remobilised Vein Deposit, Iberian Pyrite Belt, Portugal

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**Abstract:** Anomalously high germanium contents have been detected by means of whole-rock trace element analysis in remobilised vein type copper ores from the abandoned Barrigão mine, located in the Iberian Pyrite Belt, southern Portugal. The late-Variscan brecciated copper ores consist mainly of chalcopyrite, with minor tennantite, rare pyrite and arsenopyrite. The ores, investigated for elements increasingly used in several thin-film and other semiconductor high-technology applications (e.g. indium, selenium, tellurium and germanium), show germanium contents up to 280 ppm, with an average of 61 ppm from 10 samples. Electron Probe Microanalysis of Barrigão ore samples revealed that germanium is contained in chalcopyrite, with a range of 0.1 to 0.4 wt% (0.23 wt% average). High germanium contents seem to be linked to "dirty" chalcopyrite phases, showing irregular patchy zoning under the microscope and on back-scattered electron images.

**Keywords.** Germanium, chalcopyrite, Barrigão mine, remobilised vein, Iberian Pyrite Belt

## 1 Introduction

Germanium (Ge) is a geological all-round element, being distinctly lithophile, siderophile, chalcophile and organophile in different environments. Though geochemically scarce, Ge is not considered to be an extremely rare element. Its crustal average is estimated to be of about 1.6 ppm (Taylor and McLennan 1985). Though most Ge is dispersed through silicate phases, high Ge concentrations are normally found in zinc and copper-rich sulphide ore deposits or in coal and lignite.

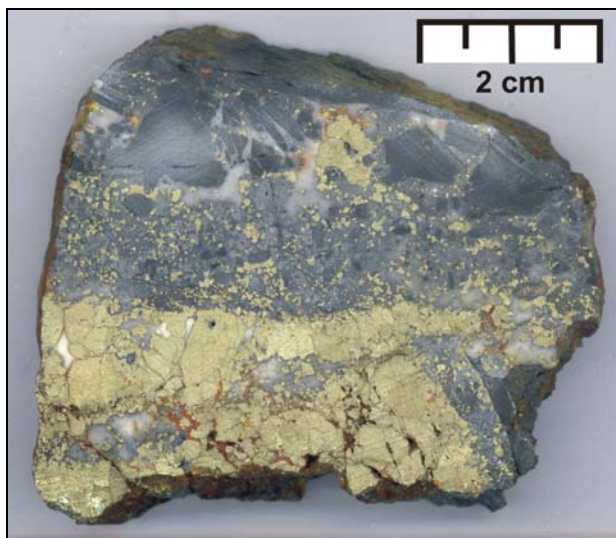
Germanium is also an element increasingly used for a range of high-tech applications, e.g. as a polymerisation catalyst, for infrared optics, fiber-optic systems, thin-film applications and electronic SiGe devices (USGS 2008). There is a strong growth potential for Ge uses, and

current global reserves are limited to 10000 metric tons (Feltrin and Freundlich 2008). Germanium does not form specific ore deposits but occurs in minor and trace amounts in a variety of ore types. Grades of a few tens to several hundred ppm of Ge are known from sulphide ore deposits (Höll et al. 2007), including volcanic-hosted massive sulphides, porphyry and vein-stockwork deposits, sediment-hosted massive sulfides, carbonate-hosted Zn-Pb and polymetallic Kipushi-type deposits. Germanium is mainly recovered as a by-product of zinc production from sphalerite ores. The estimated annual refinery amount of 100 metric tons in 2007 (USGS 2008) is about to increase because of growing Ge demand (International Mining 2008). Therefore, further exploration on finding potential Ge deposits is definitely important. Detailed investigations on a Ge-rich copper ore are currently being carried out for the Barrigão vein deposit, where Ge seems to be restricted to recrystallised chalcopyrite. The aim of this and further study is to find out how Ge enters chalcopyrite in these ores. Preliminary results are presented in this work.

## 2 Geological Overview

The Barrigão copper mine is located in southern Portugal, about 10 km southeast from Neves Corvo, in the Iberian Pyrite Belt. Structurally, the mine consists of two converging metric thick vein structures, extending approximately 1800m along strike (Matos and Rosa 2001; Matos et al. 2003). Several mine shafts were sunk down to a depth of 45m. The Barrigão copper ore is represented by fault breccias composed of chalcopyrite, minor tennantite, pyrite relics and arsenopyrite in a matrix of quartz and carbonates (Fig. 1). Host rocks are Viséan shales and greywackes of the Baixo Alentejo Flysch Group (Oliveira et al. 2006). The age of the

Barrigão mineralised structure and other similar copper structures present in the region (e.g. Brancanes, Ferrarias/Cova dos Mouros etc.) is considered late-Variscan and/or eo-Alpine (Mateus et al. 2003; Matos et al. 2003). These structures are intimately related with the main fault systems present in the SE sector of the South Portuguese Zone, striking generally NE-SW and NW-SE. The distribution of the copper mines and their location SE of Neves Corvo were considered an indication for massive sulphide exploration (Carvalho 1982). However, their sparse occurrence in the South Portuguese and Ossa Morena zones does not correlate directly with the presence of massive sulphide bodies. Exploitation of these veins took place mainly in the second part of the XIX century, sometimes down to a depth of 100 m.



**Figure 1.** Germanium-rich copper ore from the Barrigão mine. The breccia ore shows some indistinct layering of (from bottom to top) coarse-grained chalcopyrite, medium to fine-grained tennantite, partially replaced by chalcopyrite and clasts of dark schist with interstitial quartz and carbonate.

### 3 Germanium Mineralogy

Germanium was first detected in 1886 by the German chemist Clemens Winkler as a constituent of the silver sulphide mineral agyrodite. Germanium generally occurs in the tetravalent state, therefore developing tetrahedral coordination. Its high electronegativity favours covalent bonds and the similar ionic radius to silicon leads to isomorphous substitution for silicon in many silicates (Bernstein 1985). Germanium also occurs in six-fold coordination in some oxide and hydroxide minerals substituting Fe, e.g. goethite and stottite (Höll et al. 2007). But for considerations on Ge in chalcopyrite it is important to note that Ge is an essential component of a range of sulphide minerals like e.g. germanite, renierite, briartite or argyrodite. In Ge-bearing sulfides, Ge mostly occurs in tetrahedral coordination.

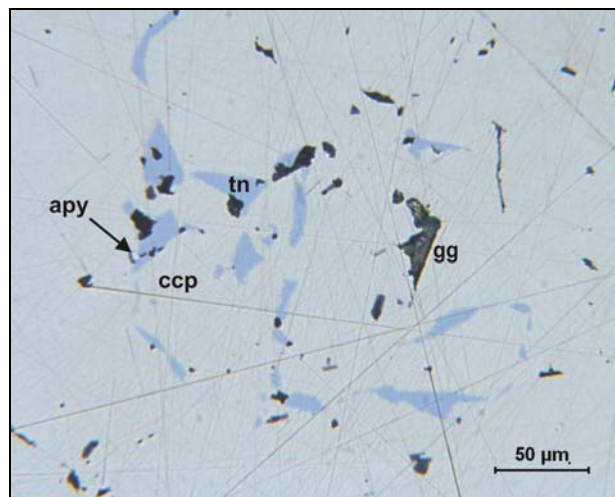
Germanium is also known to occur as significant trace element in some sulphide minerals. High trace concentrations were found in enargite (5000 ppm), sphalerite (3000 ppm), stannite (2830 ppm), tennantite (1500 ppm), colusite and sulvanite (up to 1000 ppm, data

from Höll et al. 2007). Most of these minerals have sphalerite or sphalerite-derivate structures.

### 4 Observations on Chalcopyrite

Whole-rock analysis for trace elements of 10 Barrigão ore samples collected from the mine tailings, revealed an average Ge content of 61 ppm, with a range of 4 to 280 ppm. The wide value range results from the sampling method: Some samples actually contain more gangue material than sulphide minerals, therefore exhibiting low Ge contents. Analysis for trace elements has been carried out through INAA and ICP-MS techniques at Actlabs Laboratories Ltd., Ancaster, Ontario (CA).

The studied Barrigão ore samples consist of chalcopyrite, with minor tennantite, rare pyrite and arsenopyrite. Textural evidence suggests that pyrite is the earliest formed mineral. Chalcopyrite occurs in two generations. Early chalcopyrite formed in equilibrium with tennantite. The second chalcopyrite generation partially replaces tennantite, showing typical textural features such as patchy zoned areas (only visible under xenon lighting) representing pervasive replacement (“dirty” chalcopyrite) and atoll-like structures (Fig. 2). Arsenopyrite occurs as a replacement by-product at the interface of chalcopyrite and tennantite.



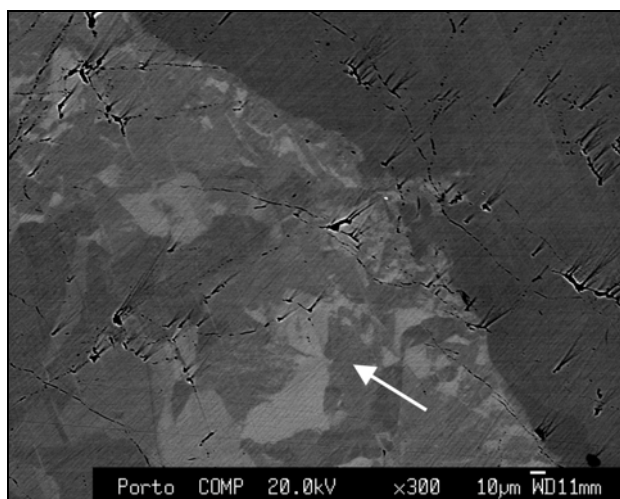
**Figure 2.** Photomicrograph of a polished section (sample BARR6) showing replacement texture of tennantite (tn), being nearly completely replaced by chalcopyrite (ccp). Small grains of arsenopyrite (apy) are often associated to these replacement textures. Gg is gangue.

To determine the Ge-bearing mineral phases, preliminary Electron Probe Microanalysis (EPMA) of some ore samples was performed at the INETI Laboratory in São Mamede de Infesta, Portugal. Analysis was carried out using a fully automated JEOL JXA-8500F microprobe at 20 kV and 20 nA to produce an electron beam of 1 µm diameter for analysis of major and minor elements (S, Fe, Cu, Zn, Cd, As, Se, Sb, Bi) and trace elements (Mn, Ge, W, Ag, Hg, In, Sn). The results are shown in Table 1. The measurement totals are a little bit low. This is probably because some elements additionally contained in the examined chalcopyrites were not captured by the chosen analysis program.

**Table 1.** Compositions (in wt%) of chalcopyrite grains in Barrigão BARR1B, BARR6 and BARR1A ore samples.

	1B	1B	1B	6	1A	1A	1A	1A	1A
Hg	-	-	-	-	0,02	-	-	-	-
S	34,52	34,08	34,05	34,08	34,37	33,88	34,30	34,28	34,44
As	0,16	0,46	0,57	-	0,12	0,45	0,41	0,26	0,17
Fe	29,62	28,69	28,40	29,75	28,60	28,00	27,85	28,54	28,90
In	0,00	0,01	-	-	0,00	0,01	-	-	0,01
Cd	0,01	-	-	-	-	-	-	-	-
Se	-	-	-	-	0,01	-	-	-	-
Mn	0,00	-	0,00	-	-	0,01	0,01	-	-
Ag	0,01	-	-	0,01	0,00	-	-	0,01	0,00
Ge	<b>0,22</b>	<b>0,19</b>	<b>0,23</b>	<b>0,02</b>	<b>0,42</b>	<b>0,25</b>	<b>0,27</b>	<b>0,37</b>	<b>0,10</b>
Cu	33,66	34,51	34,05	34,18	34,21	34,52	34,37	34,01	34,00
Sn	0,16	0,73	1,07	0,01	0,55	1,39	1,37	0,72	0,37
Bi	0,15	0,07	0,08	0,09	0,12	0,09	0,12	0,09	0,10
Zn	0,04	0,05	0,07	-	0,02	0,05	-	0,00	0,03
Total	98,55	98,79	98,52	98,14	98,45	98,66	98,70	98,28	98,13

The EPMA analysis revealed that Ge is mainly present in “dirty” or patchy zoned chalcopyrite, which can contain up to 0.4 wt% (Fig. 3 and Table 1). Analysis of unaltered tennantites did not exhibit any Ge content. The Ge content in chalcopyrite seems to be coevally associated with significant contents of As and Bi, showing values up to 0.6 and 0.15 wt%, respectively.



**Figure 3.** Back-scattered electron image of a germanium-rich chalcopyrite (sample BARR1A) showing patchy, irregular zonation, adjacent to homogeneous, germanium-free chalcopyrite (dark grey). High germanium concentrations are restricted to areas with an intermediate shade of gray (arrow) in patchy chalcopyrite.

## 5 Discussion and Conclusions

Regarding the data, there emerges the question how Ge can be enclosed in chalcopyrite. One possibility is the occurrence of Ge-bearing submicroscopic phases within the chalcopyrite. It is also imaginable that Ge enters the chalcopyrite crystal lattice to some extent. For sphalerite, it has been proved that Ge substitutes for Zn (Höll et al. 2007; Bernstein 1985). Sphalerite and elemental Ge exhibit the same diamond lattice type (Bernstein 1985). The crystal structure of chalcopyrite, which is a sphalerite-derivate, suggests that Ge could potentially enter for Cu or Fe, though there is no direct evidence for such an assumption yet. Germanium entering chalcopyrite in such a way could also be imaginable by regarding the formula and crystal structure of briartite  $Cu_2(Fe,Zn)GeS_4$ , which is similar to

chalcopyrite and stannite. Briartite is the Ge-equivalent of the stannite-kesterite solid solution series, known to be able to incorporate Ge (Bernstein 1985). Briartite sometimes occurs as microscopic inclusions in tennantite. Other Ge-bearing inclusions in tennantite have been described, e.g. Ge-colusite (Melcher et al. 2006). The observed replacement texture (Fig. 2) suggests that Ge, previously contained in tennantite or in inclusions of other Ge-bearing phases therein, has been somehow adopted by or incorporated into the second generation of chalcopyrite. This approach will be pursued by the authors by means of further microscopic and EPMA investigation, considering also other Ge-bearing ores for comparison.

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