Properties of iron sulphides from a copper mine in southern Brazil

Wagner N Mussel¹, Enver Murad¹, Natalie C Magalhães¹, Walter A P Abrahão², Jaime W V Mello² and José D Fabris¹

¹Departamento de Química, ICEx, Universidade Federal de Minas Gerais
Campus – Pampulha, 31270-901 Belo Horizonte, Minas Gerais, Brazil
²Departamento de Ciência do Solo, Universidade Federal de Viçosa, Avenida Peter Henry Rolfs, Campus Universitário, 36570-000 Viçosa, Minas Gerais, Brazil

E-mail: wdmussel@ufmg.br

Abstract. Chemical analysis, X-ray diffraction and Mössbauer spectroscopy showed two iron sulphide samples from a copper mine in Camaquã, Rio Grande do Sul, Brazil, to consist of essentially pure pyrite and chalcopyrite associated with a minor amount of pyrite and possibly some cubanite. While the pyrite was well crystallized and of simple mineralogy, Mössbauer data indicated the chalcopyrite contained in the second sample to consist of coexisting tetragonal and (remnant) cubic modifications, as has been previously described for another sample from this locality.

1. Introduction

Pyrite, (FeS₂), is a very common mineral that can be found in virtually all geological environments, whereas marcasite, the polymorph of pyrite, occurs mainly in sedimentary settings. Marcasite is orthorhombic and often has a tabular morphology that is distinctly different from that of (cubic) pyrite. Chalcopyrite, CuFeS₂, is another common iron-bearing sulphide that is often associated with pyrite and marcasite. When exposed to the atmosphere, these minerals can rapidly oxidize, leading to the formation of iron sulphates and abundant sulphuric acid. Mining wastes containing iron sulphides may thus cause “acid mine waters” and associated precipitates, and thereby severe environmental problems.

Because of its sulphur content, pyrite is of commercial interest and is currently used mainly as a starting material for the production of sulphur dioxide and sulphuric acid. High-quality pyrite powder is also used in lithium metal sulphide batteries, moulding compounds (resin-bonded grind wheels, brake linings etc), as well as in battery recycling discharge processes. Bioleaching of pyrite concentrates has been successfully used to liberate gold from the sulphide matrix for subsequent cyanidation [1], but cannot be recommended for leaching chalcopyrite concentrates for copper recovery since copper is a biocide. A somewhat exotic use of pyrite that has been suggested is the application as an amendment for calcareous soils, to which it can supply sulphur and iron as fertilizers and affect phosphorus sorption and dissolution [2]. Pyrite nanocrystals and nanorods also show promise for solar energy conversion devices, solid-state batteries and catalysis [3].

In the context of the industrial uses of pyrite and other iron sulphides, ⁵⁷Fe Mössbauer spectroscopy, being one of the most efficient methods for the characterization of Fe-bearing minerals, can play an important role as an analytical tool to characterize the principal iron-bearing phases and to
help identify impurities. To improve our knowledge of the physical properties of these minerals, we used X-ray diffraction with Rietveld analysis and Mössbauer spectroscopy in the present paper to characterize pyrite and chalcopyrite pyrite and chalcopyrite from a mine in southern Brazil that display slightly different spectral features from those reported earlier for samples from this deposit [4].

2. Materials and Methods
Two sulphide-rich samples from a copper mine in Camaquã (30° 30' 44" S 53° 29' 29" W), Rio Grande do Sul, Brazil [5], were selected with the purpose of identifying the main iron sulphide phases in samples from two stages of the industrial mining process. The samples were manually ground under acetone to prevent sulphide oxidation. X-ray diffraction was carried out by scanning from 5 to 80 °2θ at 0.025 °2θ per step on a Siemens D5000 diffractometer equipped with a Cu tube and a graphite diffracted-beam monochromator. Data evaluation was performed by Rietveld analysis. Total major and minor-element analyses were carried out by X-ray fluorescence on samples fused with a 2:1 mixture of Li$_2$B$_4$O$_7$ and LiBO$_2$ using a Rigaku spectrometer equipped with a Rh tube. Mössbauer spectra of both samples were taken at room temperature (298 K) and an additional spectrum of the chalcopyrite was taken at 110 K using a constant acceleration drive with a $^{57}$Co/Rh source. The experimental data were fitted using Lorentzian functions with a least-squares procedure based on the NORMOS program and calibration was effected relative to α-Fe.

3. Results
Chemical analyses given in table 1 show the pyrite (sample 1) to be associated with a minute amount of silica that could not be manually removed (possibly encapsulated quartz), whereas the other sample (sample 2) consists mainly of chalcopyrite with a subordinate admixture (6 wt%) of pyrite.

Table 1. Chemical analyses of samples 1 (pure pyrite) and 2 (chalcopyrite and pyrite) and theoretical (idealized) compositions of pyrite and chalcopyrite.

| Element/ wt% | Fe        | Cu  | S        | Si   |
|--------------|-----------|-----|----------|------|
| Sample 1     | 46.4(2)   | –   | 53.6(2)  | 0.002(1) |
| Theory       | 46.55     | –   | 53.45    | –    |
| Sample 2     | 33.60(3)  | 27.53(3) | 41.87(5) | –    |
| Theory       | 30.43     | 34.63 | 34.94    | –    |

X-ray diffraction indicates sample 1 to consist exclusively of pyrite and sample 2 to consist predominantly of chalcopyrite. On the basis of line widths and lattice parameters, sample 1 is well crystallized, whereas sample 2 has an average particle size of 42 nm.

The room-temperature Mössbauer spectrum of sample 1 consists of the low-spin Fe$^{2+}$ doublet that is characteristic for pyrite (table 2 and figure 1a). At room temperature the chalcopyrite sample displays a broad sextet indicating a wide distribution of magnetic hyperfine fields and a poorly-defined central component (figure 1b). At 110 K (figure 1c), the spectrum of this sample still has rather high line widths, whereas the central component now is less pronounced than at room temperature. A quadrupole-distribution fit (figure 2a) to the central portion of the spectrum of sample 2 at 110 K has a complex appearance with a major maximum at 0.61 mm/s that can be attributed to pyrite and a subordinate maximum at ~ 1.36 mm/s that may result from an associated superparamagnetic iron sulphide, a superparamagnetic iron oxide, or a paramagnetic iron-bearing silicate that was not detected by X-ray diffraction, or it could be a fitting artefact. This spectrum was additionally fit with a magnetic field distribution to look into the possibility of coexisting tetragonal and cubic chalcopyrite phases. The resultant hyperfine distribution (figure 2b) is dominated by a broad maximum that can be broken up into a major maximum at 36.9(1) T and a subordinate maximum at 35.5(1) T. Another minor maximum, at 33.2(2) T, agrees well with published values on cubanite, CuFe$_2$S$_3$, at liquid-nitrogen temperature [6,7].
Table 2. Mössbauer data. The chalcopyrite spectrum (sample 2) at 110 K was fit with hyperfine field and quadrupole splitting distributions.

| Sample     | Room Temperature | 110 K |
|------------|------------------|-------|
|            | $B_{hf}$  | $\delta$ | $\Delta$ | $B_{hf}$  | $\delta$ | $\Delta$ | $A$ |
| Pyrite     | –       | 0.32(1) | 0.59(1) |             |         |         |     |
| Chalcopyrite| 35.5(2) | 0.36(1) | 0.00(1) | 0.69(3)     |         |         |     |
|            | 36.9(1) | 0.31(2) | 0.00(0) | 0.27(1)     |         |         |     |
|            | –       | 0.33(1) | 1.10(4) | 0.04(1)     |         |         |     |

Magnetic hyperfine fields ($B_{hf}$) in Tesla; isomer shifts ($\delta$) relative to $\alpha$-Fe, quadrupole splitting and quadrupole shifts ($\Delta$) in mm/s, fractional areas ($A$). Errors on the last digit are given in parentheses.

Figure 1. Mössbauer spectra at 298 K of samples 1 (a) and 2 (b) and of sample 2 at 110 K (c).

4. Discussion

Chemical analysis, quantitative X-ray analysis and room-temperature Mössbauer spectrum of sample 1 (table 2 and figure 1a) are consistent in showing the sample to consist almost exclusively of pyrite. The minor admixture of a silicate revealed by chemical analysis has no influence on these data. Similarly, the X-ray diffraction data and Mössbauer spectra of sample 2 (figures 1b,c) are dominated by chalcopyrite, and an apparent “deficit” in Cu shown by the chemical analysis (table 1) can be attributed to the presence of pyrite.

A narrowing of the sextet lines and concurrent reduction of the paramagnetic component between room temperature and 110 K indicates some effect of particle size at room temperature. The relatively broad hyperfine field distribution of the principal component at 110 K is attributed to the presence of two chalcopyrite phases that differ somewhat in their physical properties. We associate these with two
The coexistence of two chalcopyrite modifications may be due to an inhibited transformation of the original cubic constituent to the low-temperature tetragonal modification [4]. The presence of a further component with a hyperfine field of 33.2(2) T indicates sample 2 to contain cubanite, while a minor bulge near 40 T could either be a fitting artefact or result from a small amount of poorly-ordered goethite as a sulphide oxidation product.

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