Minerals Engineering 23 (2010) 652–658

Contents lists available at ScienceDirect

Minerals Engineering

journal homepage: www.elsevier.com/locate/mineng

Mössbauer quantification of pyrrhotite in relation to self-heating

A. Navarra [a,*], J.T. Graham [b], S. Somot [c,1], D.H. Ryan [b], J.A. Finch [c]

[a] *École Polytechnique de Montréal, 2500 chemin de Polytechnique, Montreal, QC, Canada H3T 1J4*
[b] *Physics Department, McGill University, 3600 University St., Montreal, QC, Canada H3A 2T8*
[c] *Mining and Materials Engineering Department, McGill University, 3610 University St., Montreal, QC, Canada H3A 2B2*

ARTICLE INFO

Article history:
Received 30 December 2009
Accepted 31 March 2010
Available online 18 April 2010

Keywords:
Analytical methods
Mass balancing
Sulphide ores
Ore handling
Ore mineralogy

ABSTRACT

Pyrrhotite (Po) is widely considered the most significant mineral in the self-heating of sulphide ores and concentrates. It is therefore desirable to determine the amount of Po in a sample. This is commonly accomplished through X-ray diffraction (XRD) or quantitative evaluation of materials by scanning electron microscopy (QEM–SEM), neither of which are suited to oxidizing samples such as Po. The sample preparation for these methods often requires heating and drying, which may alter the composition. This paper introduces another quantitative method based on Mössbauer analysis, whose sample preparation is limited, and not as likely to alter the sample. The technique is tested using binary and ternary mixtures containing pyrrhotite with pentlandite (Pn), pyrite (Py) and sphalerite (Sp). A detection limit of 2 wt.% Po is easily obtained in the Po–Pn binary mixtures. The Po is also successfully measured in Pn–Po–Py and Sp–Po–Py mixtures; however, the presence of sphalerite increases the time required for an accurate measurement. The time required to measure Po in complex samples may be optimized through future work.

1. Introduction

1.1. Significance of pyrrhotite

Although pyrrhotite (Po) is believed to be the most significant mineral in the self-heating of sulphides (Rosenblum and Spira, 2001; Somot and Finch, 2006; Sudbury and Petkovich, 1961), there is debate regarding the mechanisms of self-heating, which may indeed vary with the nature of the samples. Even without a complete understanding, industry has adopted a rule of thumb: stockpiles containing more than 10 wt.% Po are at high risk of self-heating and/or self-igniting (Rosenblum and Spira, 2001). The self-heating phenomenon is often accompanied by the release of noxious gasses (H_2S, SO, SO_2) and acid drainage. Although the rule of thumb is supported by case studies, it is clearly insufficient: Bayah et al. (1984) observed pyrrhotite driven self-heating with only 7 wt.% Po, and it has been shown that the phenomenon may occur with less than 4.5 wt.% Po (Somot and Finch, 2006). The 10 wt.% limit is especially questionable because of the high quantification limits (ca. 9 wt.%) inherent to the methodology of Rosenblum and Spira (2001).

To refine the industrial tolerances for Po content, an improved understanding of the self-heating phenomenon and more reliable quantification techniques are essential. A promising hypothesis was introduced by Somot and Finch (2006), suggesting that Po mobilizes the sulphur within the stockpiles. The sulphur may then be transported to oxygen-rich zones for the exothermic production of SO, SO_2, and H_2SO_4. The catalyzing effect of pyrrhotite may be related to its variable S/Fe atomic ratio.

Pyrrhotite is defined to be the group of minerals having the NiAs substructure, and the general formula $Fe_{1-x}S$, with x between 0 and 0.13 (Wang and Salveson, 2005). The sulphur poor Po ($0.00 < x < 0.10$) exhibits hexagonal crystal structures; the end-member having $x = 0$ is referred to as troilite. The sulphur rich Po ($0.09 < x < 0.13$) exhibits a monoclinic phase that is weakly magnetic; this monoclinic/magnetic phase co-exists with the hexagonal phase when $0.09 < x < 0.12$, and dominates for $0.12 < x < 0.13$. Po supports several stoichiometries, each with different sulphur content: FeS ($x = 0$), $Fe_{11}S_{12}$ ($x = 0.08$), $Fe_{10}S_{11}$ ($x = 0.09$), Fe_9S_{10} ($x = 0.10$), Fe_7S_8 ($x = 0.13$). Furthermore, these compounds can be blended into non-stoichiometric masses (Murch et al., 1974; Belzile et al., 2004; Wang and Salveson, 2005). By contrast, pyrite (Py) is presumed stoichiometric unless otherwise specified (FeS_2, $x = 0.50$), hence has a much narrower definition; it is not confused with its neighbour greigite (Fe_3S_4, $x = 0.25$), because of significant differences in physical properties.

The structure of pyrrhotite is of longstanding interest, because of its importance in geology and mineral processing (Belzile et al., 2004; Wang and Salveson, 2005). There have been several X-ray and Mössbauer spectrographic studies (for a review, see Wang and Salveson, 2005). However, the relationship between Po transformation and the kinetics of self-heating is not well known;

---

[*] Corresponding author. Tel.: +1 514 567 0636.
E-mail address: alessandro.navarra@gmail.com (A. Navarra).
[1] Present address: COREM, 1180, rue de la Minéralogie, Quebec, QC, Canada G1N 1X7.

0892-6875/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.mineng.2010.03.022

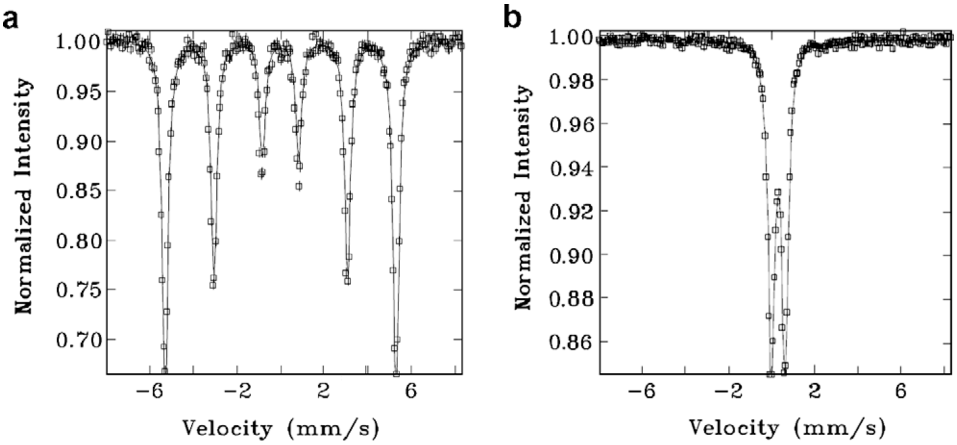

Fig. 1. Examples of Mössbauer spectra: (a) a magnetic sextet resulting from an iron sample, (b) a doublet resulting from a pyrite sample.

it is yet to be determined which sulphur-to-iron ratios are hazardous, and how their spatial distribution may change during self-heating. Hence, there are two points of interest: (1) determination of Po content in a sample, and (2) identification of S/Fe ratios (Arnold et al., 1966; Groves and Ford, 1963).

The current study focuses on the first of these two applications. This has opened discussions regarding the practicality of the technique in the industrial setting. The measurement of sulphur-to-iron ratios by Mössbauer analysis will be the subject of future work.

1.2. Mössbauer spectroscopy

Mössbauer spectroscopy has recognized applications in the minerals industry (Murad and Cashion, 2004) but is not widely used. The transmission Mössbauer technique shares a common basis with other spectral-absorption methods; in this case, gamma radiation is passed through a sample to a detector. The energy of the radiation is varied to produce a spectrum (a plot of Transmitted Intensity vs. Energy). As with other spectral-absorption techniques, (i) the sample behaves as a filter, selectively impeding the different components (energies) of the incident radiation, and (ii) the precision of a measurement is limited by the crystallinity of the sample.

The fine control over the source energy is obtained via the Doppler Effect (Serway et al., 2008); if the source is moving toward the sample (positive velocity), there is an increase in the frequency and energy. Likewise, if the source is moving away from the sample (negative velocity), the energy is lowered. In typical Mössbauer spectra (e.g. Fig. 1), the horizontal axis is the velocity of the source, which is merely a convenient measure of the energy.

Fig. 1 displays a sextet and a doublet, both of which are commonly produced by mineral samples. Sextets are typical of magnetically ordered minerals such as pyrrhotite (Po) and chalcopyrite (Cp). Doublets are observable spectral features of pyrite (Py), pentlandite (Pn) and certain pyrrhotite (Po) samples (Wincott and Vaughan, 2006). The signal that is transmitted by a mineral can be a superposition of several doublets and/or sextets. In the case of pyrrhotite, the intensity distribution between the spectral features depends on the S/Fe atomic ratio.

Mössbauer spectroscopy is analogous to X-ray transmission techniques, but with a caveat: the Mössbauer effect is a nucleus-to-nucleus interaction. Source nuclei are initially in an exited state, and are relaxed through the emission of gamma rays (as opposed to X-rays). The gamma rays occur at energies that are characteristic of the nuclear transitions; it is only this same nuclear species (isotope) that can reabsorb this radiation. Thus, the gamma rays cannot interact with any of the other nuclear isotopes in a sample, and are hence blind to all atomic elements, except for that of the source. For this reason, Mössbauer methods are less prone to matrix effects than X-ray techniques are.

The current study employs the most common type of source, namely ^{57}Co, which decays into ^{57}Fe. The subsequent gamma rays can only interact with ^{57}Fe nuclei that may be present in the sample.[2] Therefore only iron containing compounds will produce signals, thus eliminating spectral distortion from non-iron minerals, such as pale sphalerite[3] (Sp) or galena (Ga). By the same token, the gamma radiation is immune to water, so Mössbauer samples do not need thermal drying. This is especially relevant to pyrrhotite, which oxidizes readily when heated in regular air environments.

2. Design of experiment and data processing

2.1. Mineral standards

The Mössbauer samples were composed of a Po standard (obtained from Horne Mine, Quebec), blended with varying degrees of specimen Pn, Py and Sp (purchased from WARD's Natural Science, Rochester, NY). Through the course of the study, the Mössbauer spectra revealed that the Po standard contained 92.9 wt.% Po. This was subsequently confirmed by a semi-quantitative XRD analysis performed at SGS Lakefield (Table 1). The overall iron content was found to be 58.91 wt.% by high-precision titrimetry, which was also performed at SGS Lakefield.

The pentlandite and pyrite samples were stoichiometric, represented by $Ni_{4.5}Fe_{4.5}S_8$ and FeS_2, respectively. Thus, the iron assay was 32.6 wt.% for the pentlandite and 46.5 wt.% for the pyrite. Lastly, the sphalerite did not contain any measurable iron.

2.2. Preparation of mixtures

Mössbauer analysis was performed on Po–Pn binary mixtures from less than 10 wt.% Po, to demonstrate the technique's ability to flag samples violating this industrially accepted threshold, to above 90 wt.% Po to demonstrate its wide application. Pyrrhotite is commonly associated with pentlandite (Somot and Finch, 2006), so Po–Pn mixtures are especially relevant.

---

[2] Note that natural elements have a fixed isotope distribution, e.g. naturally occurring Fe will always contain 2.17% of the ^{57}Fe isotope (Murad and Cashion, 2004; Gibb, 1976).

[3] Iron-rich sphalerites (Zn, Fe)S have a dark blackish color, and are sometimes referred to as marmatite. Pale sphalerite (ZnS) has a brownish-orange color.

Table 1
Semi-quantitative XRD analysis the pyrrhotite standard (in wt.%).

Pyrrhotite	Siderite	Chalcopyrite[a]	Pentlandite[a]	Magnetite[a]	Quartz[a]	Calcite[a]
92.6	4.3	0.7	0.7	0.6	0.5	0.5

[a] Tentative identification due to low concentration, diffraction line overlap or poor crystallinity.

Table 2
Sample composition (in wt.%).

	Po	Pn	Py	Sp
Po–Pn systems	92.9	–	–	–
	79.0	15.0	–	–
	76.2	18.0	–	–
	74.3	20.0	–	–
	37.2	60.0	–	–
	18.6	80.0	–	–
	7.4	92.0	–	–
	5.6	94.0	–	–
	1.9	98.0		
Po–Py systems	62.0	–	33.3	–
	30.7	–	66.7	–
Ternary systems	12.5	79.8	6.7	–
	12.4	–	6.9	79.9

Each mixture was composed of 100 mg of ground mineral powder (<300 μm), dispersed in a roughly equal volume of boron nitride. (The boron nitride is a dispersing agent, and does not contribute to the signal.) The experiments are summarized in Table 2, having taken into account the actual Po content of the Po standard. Each of the Po–Pn mixtures were analyzed for 12 h, producing two spectra per day.

An additional two binary samples demonstrated the contrast between pyrrhotite and pyrite. One of these samples was composed of two parts Po standard with one part Py; the other was two parts Py to one part Po standard. Again, boron nitride was used as the dispersal agent, and the samples were analyzed for 12 h.

Finally two ternary mixtures were prepared to simulate more complex samples:

$$80\%\ \text{Pn} - 13\%\ \text{Po} - 7\%\ \text{Py Standard}\ (100\ \text{mg})$$

$$80\%\ \text{Sp} - 13\%\ \text{Po} - 7\%\ \text{Py Standard}\ (200\ \text{mg})$$

The first of these ternary mixtures was run for 12 h. The second mixture employed a pale sphalerite, which was free of iron. It required 72 h, and a larger sample mass to give an adequate signal; this is discussed in Section 4.

Note that the Po Standard (92.9 wt.% Po) is a relevant data point for both the Po–Pn and Po–Py systems. Also, the Sp–Po–Py system is expected to give a spectrum similar to that of the 62% Po–33% Py, since the iron-poor sphalerite does not yield a signal.

The Mössbauer spectra were obtained at room temperature on a conventional spectrometer operated in constant-acceleration mode with a 25 mCi ^{57}CoRh source. The instrument was calibrated using a 10 μm thick pure (99.99%) Fe metal foil.

2.3. Data processing

The Mössbauer spectra were fitted with a combination of singlets, doublets and sextets that are characteristic of the individual minerals (as documented by Wincott and Vaughan, (2006)). The individual dips were each modeled by a Lorentzian curve (Murad and Cashion, 2004). The initial parameter values were estimated visually and then refined using a conventional non-linear least-squares minimization routine.

At each stage of the refinement, additional parameters were released from their initial estimates and allowed to vary in order to minimize the final chi-squared χ^2 (Taylor, 1997; Lind et al., 2008). The order in which the parameters were released is important, because a misordering can cause the algorithm to fall onto a false (local) minimum. The first parameters to be included in the refinement are those which determine the location of the dips, i.e. the isomer shifts, the quadrupole splittings and the hyperfine fields (Murad and Cashion, 2004; Gibb, 1976); these are followed by the parameters that control the intensity and breadth of the peaks. The height of the baseline was generally the last parameter to be refined.

Mössbauer spectroscopy determines the iron-mass balance, as opposed to the net mass balance (see Section 1.1). Suppose that for a given sample, z is the fraction of the area of the spectrum associated with the Po component. This means that the corresponding fraction of the iron is associated with the Po. Therefore z can be converted into the wt.% Po, through the following formula:

$$\text{wt.\% Po} = z * (\text{wt.\% Fe in sample})/(\text{wt.\% Fe in Po}) \qquad (1)$$

The relative area associated with the Po component z is obtained via the refinement, and is then converted into wt.% Po, using Eq. (1).

3. Results and interpretation

3.1. Analysis of the standards

The pyrrhotite standard used in this study is fitted by three superimposed sextets (Fig. 2). On first inspection there appears to be only one sextet, partly because the hyperfine fields are similar (for a discussion of hyperfine fields, and the other spectral parameters, see Murad and Cashion, 2004; Gibb, 1976); the three sextets have relative areas of 22%, 37% and 41%, and their hyperfine fields are 23.6(8), 26.3(4) and 29.8(4) Tesla, respectively. At least two sextets can be resolved by eye, since the leftmost and rightmost dips are split into local "subdips." The error bars here and elsewhere in the paper span one standard error above and below the mean, i.e. the 68% confidence interval.

The pentlandite spectrum (Fig. 3a) was fitted to a sum of two contributions: a narrow doublet (82%) plus a singlet (18%) (Wincott and Vaughan, 2006). Since the singlet is positioned roughly in the center of the doublet, the net result has the appearance of a wide singlet. The pyrite signal is known to be a doublet (Wincott and Vaughan, 2006), as demonstrated in Fig. 3b. The Py and Pn features are both concentrated around the 0.5 mm/s region, so it may be preferable to distinguish between them with XRD analysis in

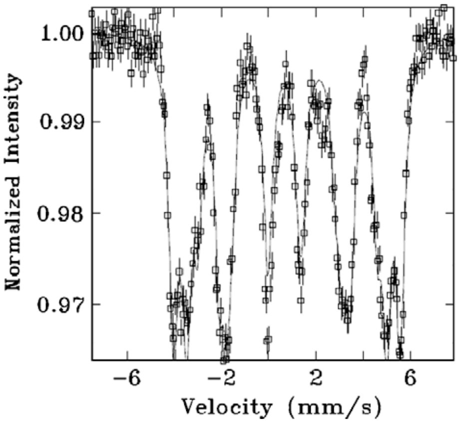

Fig. 2. Mössbauer spectrum of the pyrrhotite standard.

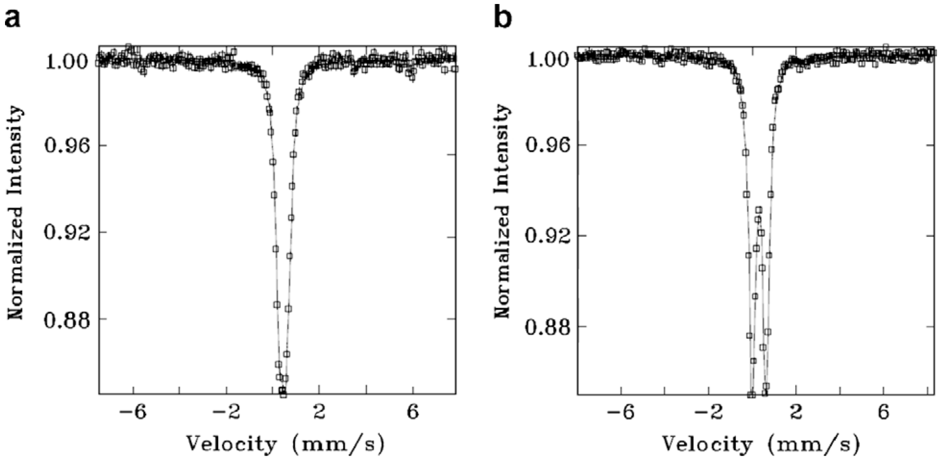

Fig. 3. Mössbauer spectra of the (a) pentlandite and (b) pyrite standards.

samples that may contain both. In contrast, the magnetically split pyrrhotite spectrum (Fig. 2) is spread over a much wider velocity range, and has several distinguishing peaks, so it is easily separated from the Pn and Py signals.

3.2. Po–Pn mixtures

A binary mixture containing 15.0 wt.% Pn and 79.0 wt.% Po produced a spectrum (Fig. 4a) in which both the pentlandite and pyrrhotite structures are clearly visible. The Po sextets extend well outside the central feature belonging to the pentlandite.

In Fig. 4b, the proportions of Pn and Po have been roughly reversed. The Po signal is thus comparatively weaker than the central Pn structure. Although the spectrum is dominated by the pentlandite contribution, the ability to quantify the pyrrhotite is not significantly affected. The error bars in Fig. 4b are not visible, given the scaling of the image. It is possible to zoom into the Po-dominated region and visually identify the features of the sextets; this is accomplished automatically through the numerical refinement.

The immediate quantitative outcome of the refinements is the relative areas corresponding to the individual minerals, which are converted to weight percentages as per Eq. (1). The results from the Pn–Po binary mixtures are summarized in Table 3 and Fig. 5.

The results show that Mössbauer spectroscopy can be used to quantify Po content over the full range, from <10 wt.% Po (i.e., well below the “threshold” range for self-heating), to >75 wt.%. The data could be fitted with a straight line having a slope consistent with unity (1.00 ± 0.05), and a y-intercept consistent with zero (-1 ± 3). The detection limit may be taken as the upper confidence limit of the y-intercept which is 2 wt.% Po. Smaller amounts could be detected with longer counting times.

Table 3
Summary of results for Po–Pn mixtures (in wt.%).

Pyrrhotite		Pentlandite	
Actual[a]	Mössbauer	Actual	Mössbauer
92.9	92.9 ± 1.8	–	–
79.0	76.8 ± 2.4	15.0	17.3 ± 2.6
76.2	74.9 ± 1.5	18.0	19.4 ± 1.6
74.3	73.1 ± 1.7	20.0	21.3 ± 1.9
37.2	34.8 ± 1.4	60.0	62.5 ± 1.5
18.6	16.6 ± 2.0	80.0	82.1 ± 2.2
7.4	7.0 ± 1.0	92.0	92.0 ± 1.1
5.6	5.0 ± 1.2	94.0	94.0 ± 1.3
1.9	1.0 ± 1.5	98.0	98.0 ± 1.7

[a] The actual (weighed) Po is calculated assuming 92.9% Po in the pyrrhotite standard (see Section 2.1).

3.3. Po–Py mixtures

The pyrite doublet is clearly visible in the center of Fig. 6a and b. There seems to be an asymmetry in the pyrite doublet of Fig. 6a,

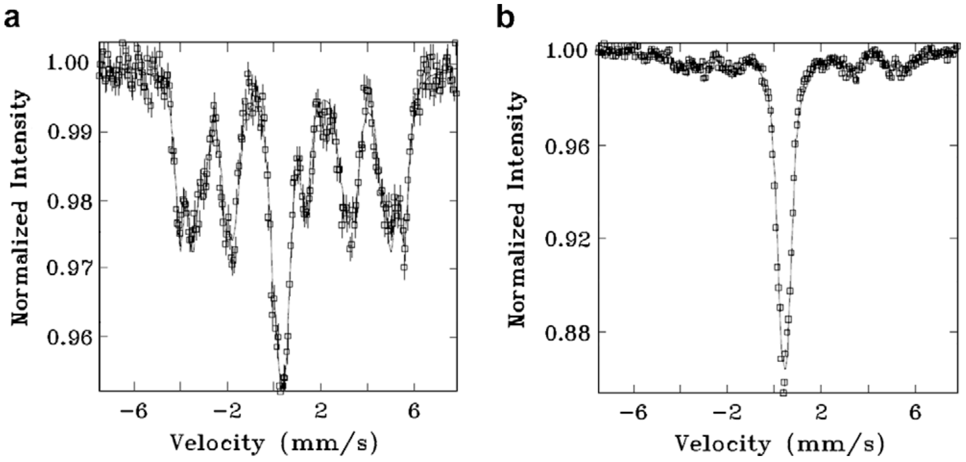

Fig. 4. Two experimental Mössbauer spectra: (a) 15.0 wt.% Pn mixed with 79.0 wt.% Po plus impurities, (b) 80.0 wt.% Pn mixed with 18.6 wt.% Po plus impurities.

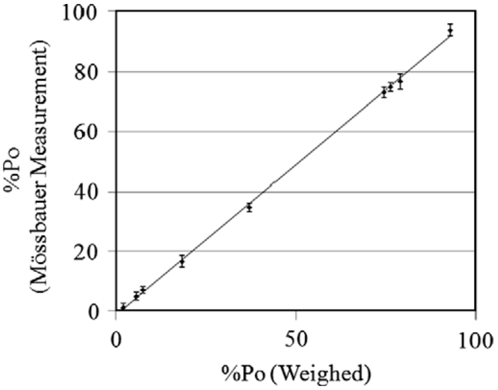

Fig. 5. wt.% Po values obtained by Mössbauer (*y*-axis) are compared with the weighed values (*x*-axis). Each point corresponds to a binary mixture composed of Pn and the Po standard. The data are fitted by a straight line with slope 1.00 ± 0.05 and a *y*-intercept −1 ± 3. The R^2 correlation coefficient was found to be 0.9992.

because the left side is superimposed with one of the Po dips. This is not the case in Fig. 6b, because the Py signal is much stronger than the Po signal.

In Fig. 7 the two Po–Py mixtures are plotted along with the Po standard (92.9 wt.% Po), and the Sp–Po–Py ternary mixture. Excluding the 79.9 wt.% Sp that acts as a diluent, the ternary system falls close to the corresponding 62.0 wt.% Po point. However, the error bar surrounding this point is much larger than the others, as discussed in the following section.

The Po–Py binary system was not explored with the same rigour as the Po–Pn system. However, it is clear that Mössbauer analysis can distinguish between samples having high and low Po–Py ratios. The results corresponding to Fig. 7 are included in Table 4.

3.4. Ternary systems

The Pn–Po–Py ternary spectrum in Fig. 8 may be compared to the Po–Pn spectrum in Fig. 3b. The pyrrhotite signal in Fig. 8, which surrounds the central pentlandite dip, is more subdued than in Fig. 3b because a third of the Po has been replaced by Py.

The Py signal suffers from confusion with Pn, but the refinement technique still gives a reasonable estimate of the pyrite, (5.2 ± 1.3) wt.% Py, compared to the known value of 6.7 wt.% Py. The ability to quantify the Po is of importance from the point of view of self-heating; the Mössbauer technique gave (11.8 ± 1.4) wt.% Po as compared to the known value of 12.5 wt.% Po.

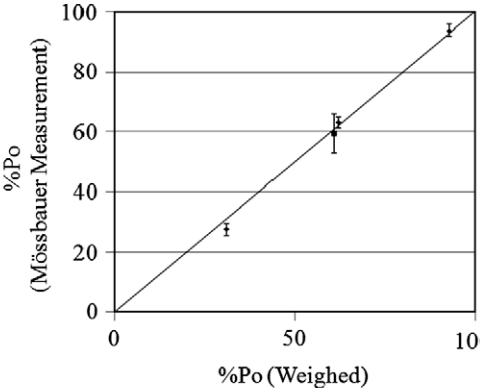

Fig. 7. wt.% Po values obtained by Mössbauer (*y*-axis) are compared with the known values (*x*-axis). The diamonds correspond to the Po–Py binary mixtures; the square represents the Sp–Po–Py ternary mixture in which the Sp component is ignored. The ideal line *y* = *x* is superimposed.

Table 4
Summary of results for Po–Py mixtures (in wt.%).

Pyrrhotite		Pyrite	
Actual[a]	Mössbauer	Actual	Mössbauer
62.0	63.2 ± 1.8	33.3	31.0 ± 1.9
30.7	27.5 ± 2.0	66.7	69.7 ± 2.2
61.0[b]	59.5 ± 6.5[b]	34.3[b]	26.0 ± 7.0[b]

[a] The actual Po is calculated assuming 92.9% Po in the pyrrhotite standard (see Section 2.1).

[b] Sample was 80% diluted in sphalerite.

The Sp–Po–Py spectrum (Fig. 9) has approximately the same underlying shape as that of Fig. 6a, because both samples included the same proportions of iron bearing minerals, roughly twice as much Po as Py. The sphalerite obstructs the gamma radiation without distinction, thus increasing the standard deviations. This results in the large error bars in Fig. 9, and the correspondingly large error bar in Fig. 7.

This additional uncertainty is taken into account in the χ^2 function, and its impact is minimized by the numerical refinement. Essentially, the errors are averaged out, and the spectrum in Fig. 9 is an accurate representation of the iron distribution, in spite of the noise. For instance, the central structure in Fig. 9 may still be correctly identified as the Py doublet. The Mössbauer technique measured (6.9 ± 1.4) wt.% Py and (12.0 ± 1.3) wt.% Po, as compared to known values of 6.9 wt.% Py and 12.4 wt.% Po.

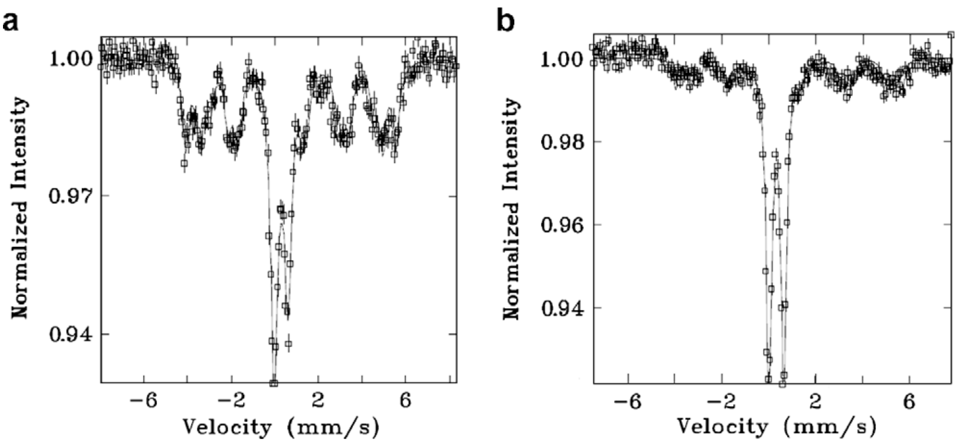

Fig. 6. Two experimental Mössbauer spectra: (a) 33.3 wt.% Py mixed with 62.0 wt.% Po plus impurities, (b) 66.7 wt.% Py mixed with 30.7 wt.% Po plus impurities.

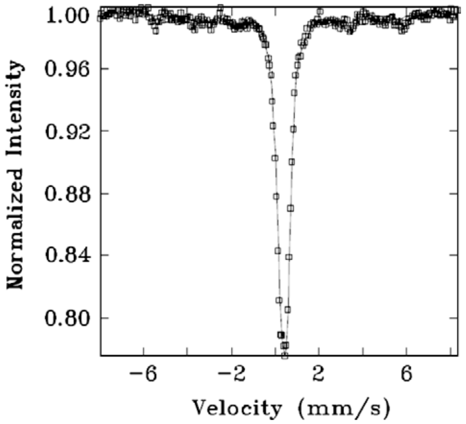

Fig. 8. Mössbauer spectrum resulting from 79.8 wt.% Pn, 12.5 wt.% Po and 6.7 wt.% Py.

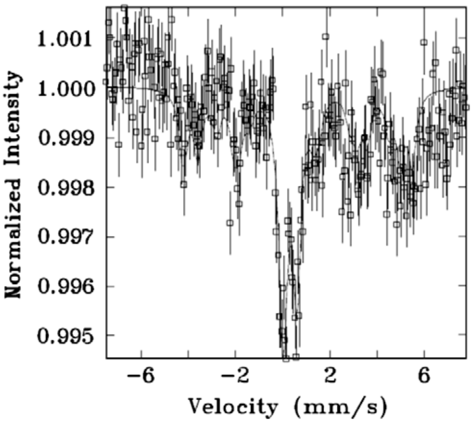

Fig. 9. Mössbauer spectrum resulting from 79.9 wt.% Sp, 12.4 wt.% Po and 6.9 wt.% Py.

4. Discussion

The Po–Pn results (Section 3.2) apply directly to the handling of nickeliferous sulphide ores, which are a prime concern in self-heating. Mössbauer spectroscopy easily measured pyrrhotite content below the 10 wt.% Po threshold, as depicted by Figs. 4 and 5. The contrast between the Po and Py was well demonstrated in Figs. 6 and 7; however the ternary Pn–Po–Py result of Fig. 8 did reveal a certain potential for confusion between Py and Pn signals, both of which occupy the same range in the spectrum, but the distinction between Py and Pn is accomplished by other techniques, such as XRD.

The Mössbauer technique may be applied to self-heating of other minerals, such as zinc bearing materials. Fig. 9 demonstrates the technique with 80 wt.% Sp (roughly 55 wt.% Zn), which is typical of Zn concentrates. In the initial attempt with 100 mg of the sphalerite-containing sample, there was insufficient iron in the sample to yield a discernable signal. The sample mass was doubled to 200 mg to increase the number of iron nuclei. However, this also increased the number of Zn and S nuclei, thus reducing the transmitted intensity. Consequently, the 200 mg sample had to be run for a longer time than in the case of high-Fe containing samples to obtain a usable count; it was run for roughly 72 h, given the available source.

A more in-depth study would establish the practical limits of Mössbauer spectroscopy in the presence of sphalerite and other minerals, and optimize the sample size and running time. Galena (PbS) containing samples, which are also prone to self-heating, would provide another test case. It is through continued experience with mineral samples that optimal running times and sample weights will be established for both iron and non-iron containing minerals.

The binary spectra were obtained after as few as 12 h, but it is likely that even less time would provide results that are sufficiently precise to identify hazardous self-heating materials. In an adaptive approach, less time would be spent on samples that are very high (low) in Po, because they can quickly be classified as hazardous (safe). More time may be spent on the samples whose Po content is close to the threshold. A rigorous study balancing the sample size and running time was beyond the scope of the current work, but could be important in the development of on-site diagnostic equipment.

In this study, the detection limit in the Po–Pn mixtures was found to be 2 wt.% Po, which is well below the 10% threshold that is in current use (Rosenblum and Spira, 2001). According to Poisson statistics (Lind et al., 2008), the detection limit may easily be brought to below 1 wt.% by increasing the counting time to between 24 and 36 h, and using a more active source. The evidence points to Mössbauer spectroscopy being a useful addition to the techniques available for pyrrhotite analysis, and may provide new insight into the self-heating phenomenon.

Having introduced Mössbauer analysis as a viable means to differentiate Po from other Fe-sulphides, the next step will be a speciation study that will correlate the Mössbauer signals of Po specimens to their S/Fe atomic ratio. Eventually, Mössbauer analysis may be used to study the mobilization of sulphur as the Po self-heats.

5. Conclusion

This study demonstrates the practicality of pyrrhotite quantification by Mössbauer spectroscopy, which will aid in the correlation of sulphide mineral composition and self-heating. In binary mixtures with pentlandite, the pyrrhotite content was accurately determined over the full range, with a lower detection limit estimated to be 2 wt.% Po. (With longer counting times, this limit can likely be decreased.) Pyrrhotite was also successfully quantified in ternary mixtures with pentlandite, pyrite and sphalerite.

Acknowledgements

Funding for this project was provided through CAMIRO-MPD (Canadian Mining Industry Research Organization-Mineral Processing Division) and NSERC (Natural Sciences and Engineering Research Council of Canada) under the CRD (Collaborative Research and Development), as well as Discovery Grant programs and Fonds québécois de la recherche sur la nature et les technologies. The authors wish to thank Dr. Jeanne Paquette (Associate Professor in the McGill Department of Earth and Planetary Sciences) who generously searched and provided us with a pyrrhotite standard from Horne Mine (Quebec, Canada), that had been donated by Dr. Peter Tarasoff (Honorary Curator at McGill's Redpath Museum).

References

Arnold, R.G., 1966. Mixtures of hexagonal and monoclinic pyrrhotite and the measurement of the metal contents of pyrrhotite by X-ray diffraction. The American Mineralogist 51, 1221–1227.

Bayah, J., Meech, J.A., Stewart, G., 1984. Oxygen depletion of the static air by backfill material at the Thompson mine. Mining Science and Technology 1 (2), 93–107.

Belzile, N., Chen, Y., Cai, M., Li, Y., 2004. A review on pyrrhotite oxidation. Journal of Geochemical Exploration 84 (2), 65–76.

Gibb, T.C., 1976. Principles of Mössbauer Spectroscopy. Chapman and Hall, London.

Groves, D.I., Ford, R.J., 1963. Note on the measurement of pyrrhotite composition in both hexagonal and monoclinic phases. The American Mineralogist 48, 911–913.

Lind, D.A., Marchal, W.G., Wathen, S.A., 2008. Basic Statistics for Business and Economics, 13th ed. McGraw-Hill/Irwin, New York.

Murad, E., Cashion, J., 2004. Mössbauer Spectroscopy of Environmental Materials and their Industrial Utilization. Kluwer Academic Publishers, Norwell.

Murch, G.E., Rolls, J.M., Bruin, H.J., 1974. Diffusion in non-stoichiometric solids – a Monte Carlo analysis for pyrrhotite. Philosophical Magazine 29 (2), 337–348.

Rosenblum, F., Spira, P., 2001. Evaluation and control of self-heating in sulphide concentrates. CIM Bulletin 94 (1056), 92–99.

Serway, R.A., Faughn, J.S., Vuille, C., 2008. College Physics, eighth ed., Brooks/Cole Centage Learning, Belmont.

Somot, S., Finch, J.A., 2006. High self-heating rate of pyrrhotite-rich material – H_2S as a fuel? In: Proceedings of the 38th Annual Meeting of the Canadian Mineral Processors of CIM. Ottawa, pp. 83–92.

Sudbury, M.P., Petkovich, F., 1961. Exothermic hardening of Cu–Ni sulfide agglomerates, transactions of the American institute of mining. Metallurgy and Petroleum Engineers 220, 477–484.

Taylor, J.R., 1997. An Introduction to Error Analysis, second ed. University Science Books, Sausalito.

Wang, H., Salveson, I., 2005. A review on the mineral chemistry of the non-stoichiometric iron sulphide $Fe_{1-x}S$. Phase Transitions 78 (7–8), 547–567.

Wincott, P.L., Vaughan, D.J., 2006. Spectroscopic studies of sulphides. In: Vaughan, D.J., (Ed.), Sulphide Mineralogy and Geochemistry. Mineralogical Society of America, Chantilli, pp. 181–221.