

Received January 27, 2020; reviewed; accepted March 26, 2020

## Raman spectroscopy characterization of some Cu, Fe and Zn sulfides and their relevant surface chemical species for flotation

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**Abstract:** Raman spectroscopy as a high-resolution characterization technique was used to analyze various pure metal sulfides immersed in water, namely pyrite (FeS<sub>2</sub>), chalcopyrite (CuFeS<sub>2</sub>), sphalerite (ZnS), marmatite (Zn<sub>1-x</sub>Fe<sub>x</sub>S) and galena (PbS). The Raman characterization was undertaken in situ with the minerals immersed in water. Characteristic Raman spectrum that shows the vibrational modes of the atomic bonds in the mineral crystal structure is reported. This spectroscopic technique revealed that marmatite particles are composed of micro-size, perhaps nano-size, zones with different Fe and Zn content. With the intensity of the Fe-S and Zn-S Raman signals, the iron content of the zones was quantified. The copper ion up-take by marmatite particles was studied through this technique. It was found that the up-take of copper ions on the marmatite zones depended on their Fe content. Copper ion up-take occurred more preferentially on the zones of low Fe content than on those of high Fe content. The adsorption of the collector propyl xanthate on pyrite and chalcopyrite was also assessed by Raman spectroscopy. The Raman spectrum revealed that dixanthogen formed on the surface of these sulfides.

**Keywords:** Raman spectroscopy, marmatite, sphalerite, pyrite, chalcopyrite, galena, copper, activation

### 1. Introduction

Mineral characterization of sulfides is essential in many engineering fields related to minerals. In sulfide ore processing, it is an important tool that provides information to improve the efficiency of the concentration process and to upgrade the sulfide concentrates. In flotation research, it is of interest to characterize chemical species on sulfides to further understand the flotation process and delineate chemical schemes for the optimization of the process.

There are several techniques to characterize sulfide minerals in ores, such as optical microscopy (Pirard, 2004), scanning electron microscopy (Cornwell and Morse, 1987) and XRD analysis (Kumar and Rajkumar, 2014). To identify surface species on floating sulfides many techniques are available, namely FTIR spectroscopy, XPS, voltammetry (Salama et al., 2015), atomic force microscopy, calorimetry (Robledo-Cabrera et al., 2015; Robledo-Cabrera et al., 2018), zeta potential (Laskowski et al., 1997; Fuerstenau et al., 2007), time-of-flight mass spectrometry, ToF-SIMS, (Siew et al. 2008) and sum frequency spectroscopy (Jin et al. 2014). The surface chemical property of sulfides can also be studied using density functional theory, DFT (Chen et al., 2010). Raman spectroscopy has been recently applied to study a few sulfide minerals (Robledo-Cabrera et al., 2015; Chandra and Gerson, 2009).

Raman spectroscopy is a high-resolution technique that quickly provides information on the chemical and structure of organic and inorganic materials, allowing their identification. This technique has many advantages over those that are commonly used to characterize ores and surface species on

floating sulfide minerals. In Raman spectroscopy only a small amount of sample is needed, and the sample can be either a solid, liquid or a solid immersed in an aqueous solution. The sample does not require special preparation and can be in contact with water, which does not interfere in the characterization of the sample. It is possible to rapidly characterize inorganic and organic species and if an optical microscope is coupled to the instrument, it is possible to select specific domains on the mineral allowing a detail spatial characterization of the solid surface. White (2006) showed Raman spectroscopy has the advantage to provide a useful fingerprint for mineral identification, for example, sulphates can be easily distinguished from carbonates. In addition, unstable samples can be stored and analyzed on glass containers, without affecting their characterization. In addition, he showed that Raman spectroscopy is able to do in situ molecular identification of minerals in the ocean depths. White (2009) conducted studies to determine the characteristic spectral bands and the relative intensity of the Raman scattering of relevant minerals in hydrothermal sites of the seabed. Furthermore, he determined how the quality of the mineral spectra was affected by changes in excitation and sampling wavelength. The studied minerals were elemental sulfur, carbonates, sulfates and sulfides. High quality Raman spectra were obtained using the green excitation laser (532 nm) and no significant fluorescence was observed from the analyzed minerals. Bouchard and Smith (2003), presented a catalog of 45 mineral-related Raman spectra in the history of art or archeologies. Most of the minerals came from the Mineralogy Gallery at the Muse'um National d'Histoire Naturelle, France and were verified by X-ray diffraction to support the spectroscopic identification.

Glass and water are weak Raman dispersers so spectra of minerals can be obtained from samples through glass and immersed in water. Hope et al. (2001) suggested the application of Raman spectroscopy to characterize minerals of importance in ore processing. Soumya and Hendry (2011) applied the technique to characterize different synthetic and natural phases of iron, found in the acid drainage of mines and slags, oxides (hematite,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>; magnetite, Fe<sub>3</sub>O<sub>4</sub>), hydroxides (ferrihydrite, 5Fe<sub>2</sub>O<sub>3</sub>·9H<sub>2</sub>O; goethite,  $\alpha$ -FeO(OH); lepidocrocite,  $\gamma$ -FeO(OH); akaganeite,  $\beta$ -FeO(OH,Cl)), carbonate (siderite, FeCO<sub>3</sub>), sulfate (natrojarosite, NaFe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) and ferric arsenates (scorodite, FeAsO<sub>4</sub>·2H<sub>2</sub>O; yukonite, Ca<sub>3</sub>Fe(AsO<sub>4</sub>)(OH)<sub>3</sub>·5H<sub>2</sub>O). They indicated that Raman spectroscopy can replace XRD for the characterization of minerals. Shapter et al. (2000) was able to characterize oxidation products on galena (PbS) such as oxysulfates (PbO, PbSO<sub>4</sub>, 3PbO·PbSO<sub>4</sub> and 4PbO·PbSO<sub>4</sub>), which formed by high-temperature oxidation of the galena induced by the high power density of the laser (25 mW at 514.5 nm).

Raman spectroscopy has not been limited for the characterization of minerals. Andreev and Barzev (2003) applied it to investigate surface species on chalcopyrite after treating the mineral with the collector isopropyl xanthate. At a high collector concentration, they reported chemisorbed cuprous xanthate and physisorbed isopropyl dixanthogen on chalcopyrite. At collector concentrations similar to those used in an industrial flotation process, cuprous xanthate was the only product found on the mineral.

The aim of this work was to further demonstrate that Raman spectroscopy is a straightforward and reliable technique to characterize sulfide minerals and the surface species on floating sulfides in a water environment. Pristine crystals of chalcopyrite, pyrite, galena, sphalerite and marmatite were used in this study. A very detail spectroscopy study was undertaken on the marmatite immersed in water with copper ions, which are used to activate the marmatite surface. Through copper activation, marmatite flotation improves with sulfhydrylic collectors. This work also involved the use of the technique to characterize the chemical species on pyrite and chalcopyrite after contacting them with propyl xanthate (PPX). Xanthates are common collector reagents to recover these minerals by flotation.

Marmatite (Zn<sub>1-x</sub>Fe<sub>x</sub>S), is a cubic polymorph mineral with a variable iron content. Fe<sup>2+</sup> ions exchange Zn<sup>2+</sup> ions in the mineral crystal structure. It is common in polymetallic ores. Its importance as a zinc source and its frequent occurrence in a wide variety of rock formation conditions has led to study the mineral through many experimental techniques. However, many details of the Zn-Fe isomorphism still remain unclear. One reason is the non-uniform distribution of Fe and Zn, even in individual grains of both pristine and synthetic marmatite (Osadchii and Gorbaty, 2010). They studied synthesized marmatites (Zn<sub>1-x</sub>Fe<sub>x</sub>S) with different Zn/Fe molar ratios, in the range of 0 < x < 0.5, through Raman spectroscopy. They reported differences in Raman band intensities throughout the concentration range, suggesting that these could be due to a change in the percolation state of the mineral crystal lattice. They

proposed that the intensity of the Raman band could be used to determine the chemical composition of marmatite.

## 2. Experimental methods

A ThermoScientific DXR Raman Spectrometer, with an optical microscope and a laser with a wavelength of 532 nm, was used in this work. The power amplitude to the laser was 10mW. Pristine crystals of chalcopyrite ( $\text{CuFeS}_2$ ), pyrite ( $\text{FeS}_2$ ), galena ( $\text{PbS}$ ) from Zacatecas, Mexico were used. The non-iron sphalerite ( $\text{ZnS}$ ), 99% pure synthetic sample, was obtained from Alfa AESAR. The marmatite ( $\text{Zn}_{1-x}\text{Fe}_x\text{S}$ ) sample was purchased from WARD'S Natural Science. For the Raman spectroscopic studies, the minerals were prepared to a size of approximately 5 mm by hand grinding using an agate pestle and mortar. One g mineral was conditioned in 100 mL deionized water at pH 8 for 10 min. In the case of sphalerite, the mineral was treated at pH 10.5. For pyrite and chalcopyrite treated with PPX, the sulfides were conditioned in an aqueous solution of  $10^{-3}$  mol/L PPX for 10 min. With a glass pipette, a very small volume of the mineral suspension was withdrawn and a few drops were placed on a glass slide, which was positioned under the Raman microscope to carry out the Raman analysis. The optical microscope, coupled to the spectrometer, allowed us to visualize and select the mineral areas to be analyzed. Each sulfide was characterized at three different areas. The Raman spectrum of  $\text{CuFeS}_2$ ,  $\text{FeS}_2$  and  $\text{ZnS}$  were identical in the examined areas, but in the Raman spectrum of  $\text{PbS}$ , a  $\text{SO}_4$  signal appeared, whose intensity depended on the exposure time to the Raman laser. To study the galena, the smallest power amplitude to the laser of the spectrometer was used to minimize the oxidation of the mineral surface. This was found to be less than 5 mW. pH 8 was selected because the flotation process of  $\text{PbS}$ ,  $\text{CuFeS}_2$  and  $\text{FeS}_2$  in polymetallic ores is undertaken about this pH value. For  $\text{ZnS}$ , the pH of 10.5 was chosen because this is the pH at which most flotation processes of  $\text{ZnS}$  are carried out.

When copper-activated marmatite was spectroscopically analyzed, the mineral was first conditioned at pH 10.5 in the absence of copper ions. The Raman analysis was performed on the marmatite under this condition. Afterwards, the particles were contacted with a few drops of a copper aqueous solution ( $10^{-3}$  mol/L  $\text{Cu}^{2+}$ , pH 10.5). This pH was selected because marmatite activation and flotation are carried out about this pH value.

All aqueous solutions were prepared with de-ionized water, which was obtained by passing distilled water through a Barnstead water purification system. The resistivity of the de-ionized water was 18  $\text{M}\Omega\text{-cm}$ . The pH of the aqueous solutions was adjusted using dilute  $\text{NaOH}$  solutions. Copper aqueous solutions were prepared with analytical-grade hydrated copper sulfate ( $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ ), from Alfa. Highly pure potassium propyl xanthate (PPX) was prepared from commercial PPX from Alkemin, México. Ethylic ether and acetone from J. T. Baker were used to purify the commercial xanthate. The commercial PPX was dissolved in acetone until saturation, followed by filtration of the PPX-acetone. Ethylic ether was added to the filtered acetone to precipitate the xanthate. This procedure was repeated three times. A xanthate with a purity of >99% was obtained.

## 3. Results and discussion

The Raman spectrum of the pure sulfides is presented showing the characteristic bands of their metal-sulfur bonds. Then, the Raman spectrum of marmatite is presented. This mineral was studied in detail because Raman bands of distinct intensities were obtained for various analyzed zones of the marmatite particle. This was found to be due to their distinct Fe and Zn content. Therefore, the behavior of zones with low and high Fe/Zn ratio for copper uptake was further spectroscopically analyzed. With the band intensity of the Fe-S bond, the Fe content of the zones was determined so as their copper uptake. Lastly, the Raman spectrum of  $\text{FeS}_2$  and  $\text{CuFeS}_2$  treated with PPX is presented showing not only the characteristic bands of the bonds in the sulfides but also the characteristic bands of the bonds in the alkyl  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-}$  non-polar, the  $\text{-OCS}_2$  polar group of the PPX and the bond S-S in the dixanthogen  $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OCS}_2\text{-S}_2\text{CO-CH}_2\text{-CH}_2\text{-CH}_3$  that formed on the sulfides through oxidation of the collector.

### 3.1. Chalcopyrite, $\text{CuFeS}_2$

In  $\text{CuFeS}_2$  the oxidation state of Cu, Fe and  $\text{S}_2$  is +1, +3 and -2, respectively. Fig. 1 shows the chalcopyrite Raman spectrum. As noted, 5 bands were identified, corresponding to the two metal-sulfur bonds in

the mineral crystal structure, Cu(I)-S ( $266\text{cm}^{-1}$  and  $475\text{cm}^{-1}$ ) and Fe(III)-S ( $291\text{cm}^{-1}$ ,  $320\text{cm}^{-1}$  and  $352\text{cm}^{-1}$ ). These bands are very close to those reported by White (2009), namely  $265\text{cm}^{-1}$  and  $471\text{cm}^{-1}$  for the Cu(I)-S bond and  $291\text{cm}^{-1}$ ,  $320\text{cm}^{-1}$  and  $352\text{cm}^{-1}$  for the Fe(III)-S bond.

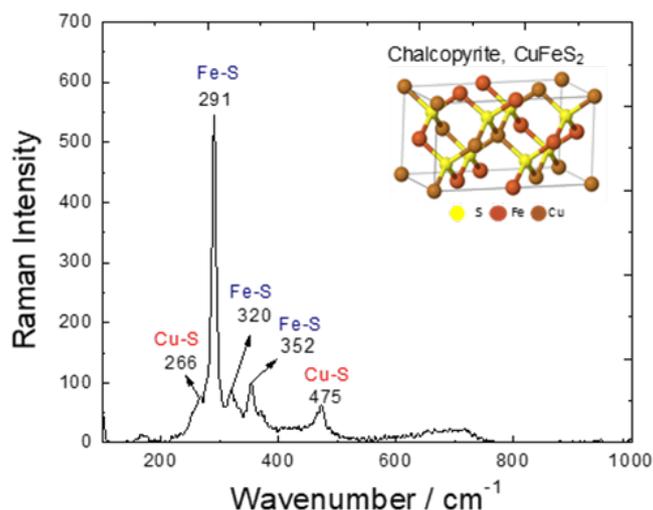


Fig. 1. Raman spectrum of chalcopyrite immersed in water

### 3.2. Pyrite, $\text{FeS}_2$

In Pyrite the oxidation state of Fe and  $\text{S}_2$  is  $2+$  and  $2-$ , respectively. Fig. 2 shows the pyrite Raman spectrum. Three bands were identified at  $343\text{cm}^{-1}$ ,  $379\text{cm}^{-1}$  and  $429\text{cm}^{-1}$ , which correspond to the  $E_g$ ,  $A_g$  and  $T_g$  vibrational modes in the di-anion S-S bond of  $\text{FeS}_2$  (Vogt et al., 1983). White (2009) reported similar signals.

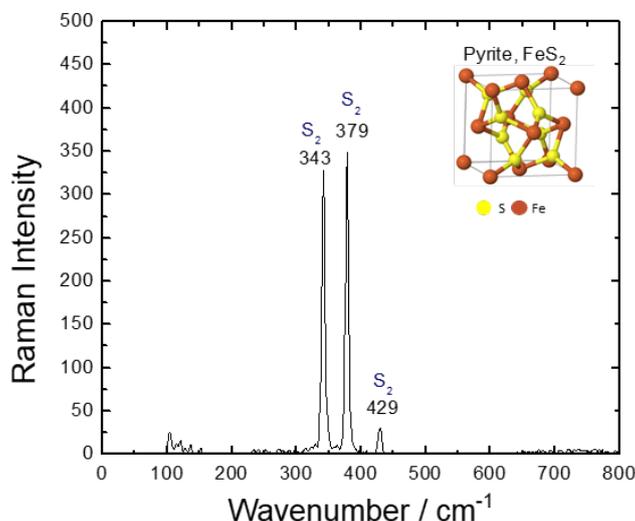


Fig. 2. Raman spectrum of pyrite immersed in water

### 3.3. Galena, $\text{PbS}$

The Raman spectrum of galena (Fig. 3) showed two bands corresponding to the Pb-S bonds in the mineral crystal structure, namely  $90\text{cm}^{-1}$  and  $138\text{cm}^{-1}$ . In addition, two bands were detected at  $430\text{cm}^{-1}$  and  $949\text{cm}^{-1}$ , which are due to  $\text{SO}_4$ . This indicated that the galena surface was oxidized where the oxidation can be accounted for by the laser beam and the dissolved oxygen in the aqueous solution. Galena rapidly oxidizes by oxygen and the oxidation rate increased with temperature (Shapter et al., 2000). The Raman bands reported here for  $\text{SO}_4$  are very close to those reported by Shapter et al. (2000) at  $438.5\text{cm}^{-1}$  and  $972\text{cm}^{-1}$  and Giudici et al. (2007) at  $436\text{cm}^{-1}$  and  $974\text{cm}^{-1}$ .

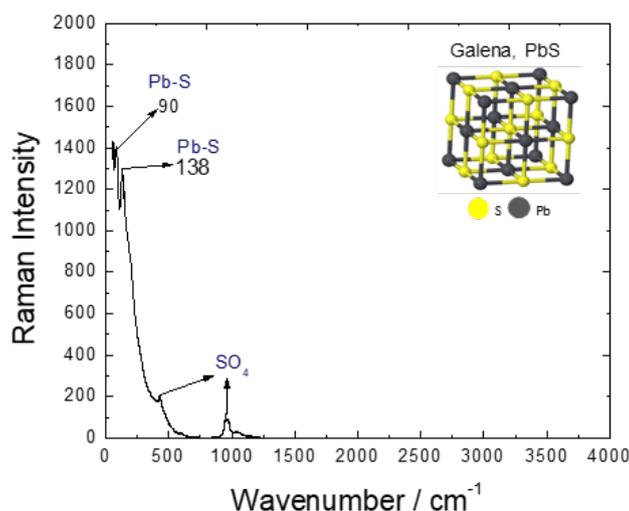


Fig. 3. Raman spectrum of galena immersed in water

### 3.4. Sphalerite, ZnS

Fig. 4 shows the Raman spectrum of sphalerite. Five bands were identified corresponding to the Zn-S bonds in the mineral crystal structure, namely 176 $\text{cm}^{-1}$ , 215 $\text{cm}^{-1}$ , 273 $\text{cm}^{-1}$ , 345 $\text{cm}^{-1}$  and 670 $\text{cm}^{-1}$ . These bands agree very well with those reported by Osadchii and Gorbaty (2010), and White (2009).

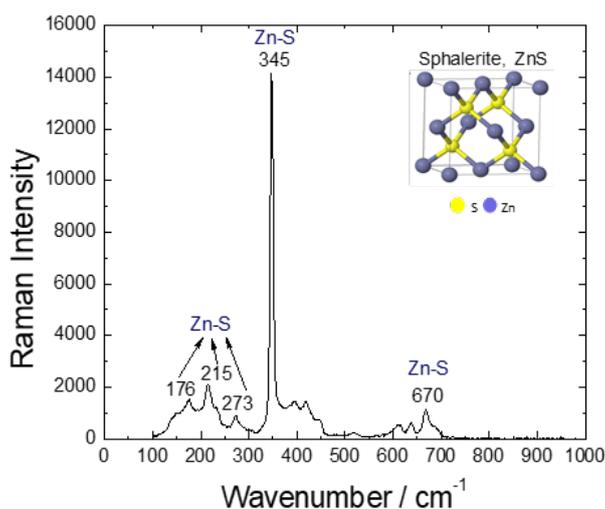


Fig. 4. Raman spectrum of sphalerite immersed in water

### 3.5. Marmatite, $\text{Zn}_{1-x}\text{Fe}_x\text{S}$

The Raman spectrum of marmatite is presented in Fig. 5 where six bands due to the Zn-S and Fe-S bonds in the mineral crystal structure were distinguished. The bands 176 $\text{cm}^{-1}$ , 215 $\text{cm}^{-1}$ , 350 $\text{cm}^{-1}$  and 665 $\text{cm}^{-1}$  correspond to Zn-S bond while the bands 298 $\text{cm}^{-1}$  and 328 $\text{cm}^{-1}$  are due to the Fe-S bond. Osadchii and Gorbaty (2010) reported the bands 298 $\text{cm}^{-1}$  and 328 $\text{cm}^{-1}$  for Fe-S and a 345 $\text{cm}^{-1}$  band for Zn-S.

Marmatites varied in their Zn and Fe content depending on the substitution degree of Zn by Fe in the marmatite crystal structure. This degree of Zn substitution can be up to 50%. The iron and zinc content in the marmatite affects the intensity of the Zn-S and Fe-S Raman bands as has been shown elsewhere (White, 2009, Osadchii and Gorbaty, 2010). In this study, many marmatite particles and distinct areas of the marmatite particles were spectroscopically analyzed. Different Raman intensities of both the Zn-S 350  $\text{cm}^{-1}$  band and the Fe-S 298  $\text{cm}^{-1}$  band were obtained from each of the particle and from each of the distinct analyzed areas of a particle. Fig. 5 presents representative spectra from areas with a low, intermediate and high Fe/Zn ratio. This Fe/Zn ratio is the Raman intensity of the Fe-S 298

$\text{cm}^{-1}$  band divided by Raman intensity of the Zn-S  $350 \text{ cm}^{-1}$  band. This Raman intensity ratio is shown as Fe/Zn in the figure. The Fe/Zn notation is used henceforth to represent such Raman Intensity ratio.

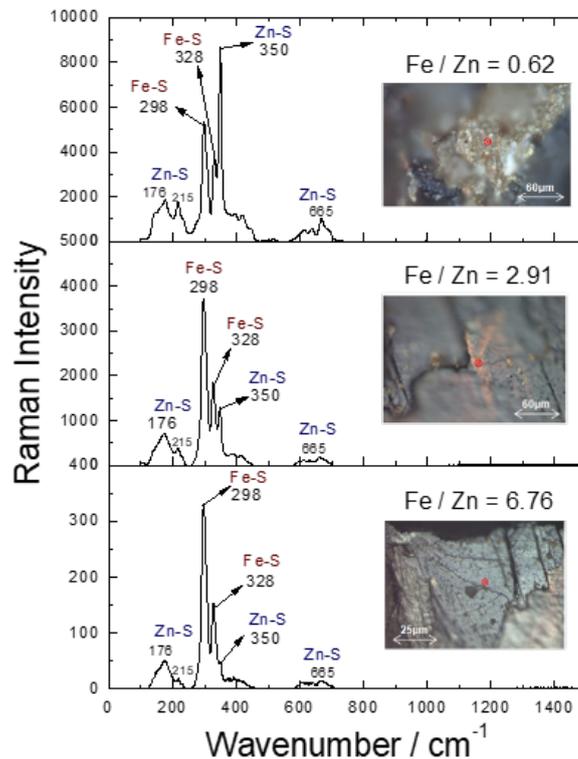


Fig. 5. Raman spectrum of 3 different areas of a marmatite particle immersed in water

Osadchii and Gorbaty (2010) reported the Raman spectra of various synthetic marmatites with known composition of Fe and Zn. From their data, the Fe/Zn intensity ratio of the Raman spectrum of each marmatite type was plotted vs the corresponding Fe content in weight percent (Fig. 6). As noted a linear relationship is obtained:

$$\% \text{Fe} = 3.21(\text{Fe}/\text{Zn}) \quad (1)$$

where %Fe is the Fe-weight percent in the marmatite and Fe/S is the Raman intensity ratio as indicated above. With Eq. (1) and the Fe/Zn intensity ratio of the Raman spectrum presented in Fig. 5, the Fe content was calculated for the distinct analyzed areas of the marmatite particle that are shown in the figure. The Fe content was found to be 1.97, 9.33 and 21.68% for the 0.62, 2.91 and 6.76 Fe/Zn intensity ratio, respectively. Accordingly, a marmatite particle with a 5 mm size is an assembly of micro-size or even nano-size particles of marmatite differing in Fe and Zn content.

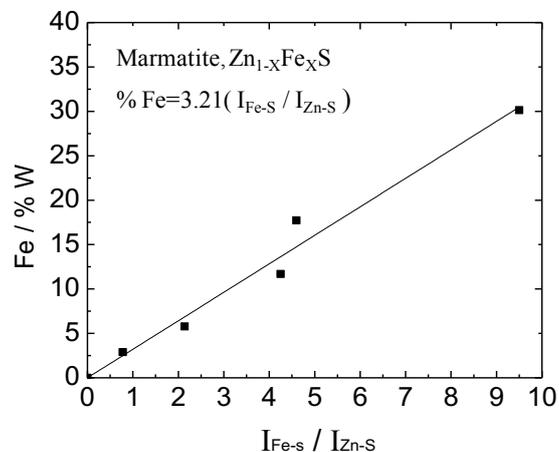


Fig. 6. Relationship between weight %Fe and intensity ratio of Raman bands of Fe-S Zn-S bonds. Data from Osadchii and Gorbaty (2010)

To corroborate that marmatite particles are constituted by micro-size entities of distinct Fe and Zn content, various marmatite particles were analyzed. Fig. 7 shows the Raman spectra of distinct areas of two marmite particles. The Fe/Zn intensity ratio was determined for each of the Raman spectrum. Through Eq. (1) the iron content of each analyzed area was calculated. It was found that the Fe content varied from 3.03% to 28.89%.

Marmatite is a difficult mineral to recover by flotation so the mineral needs to be activated with copper ions to enhance its flotation recovery (Tong et al., 2006, 2008; Long, 2020). Through this activation, copper sulfide species formed on the mineral surface (Hope et al., 2001). The flotation recovery of marmatite increased with the copper up-taking of the mineral surface. In this work, the Raman spectroscopy technique was used to assess the copper activation of the areas of marmatite particle with different Fe content. Accordingly, zones of low and high iron content were first identified on a marmatite particle. Then, copper ions were added to the marmite particles and the mineral was allowed to interact with the copper ions for 10 min. After this the zones with different Fe contents were analyzed again. Fig. 8 shows the Raman spectrum of areas with 3.8 and 24.4% Fe content. It is noted that only the zone with the lowest Fe content showed a Raman band at 470  $\text{cm}^{-1}$ , due to Cu-S bond. This signal did not appear in the spectrum of the zone with high iron content. Therefore, it can be said that Cu ions adsorb more preferentially on marmatite with a low iron content than on that with a high iron content. Our results are in agreement with those reported by Solecki et al. (1979) and Boulton et al. (2005).

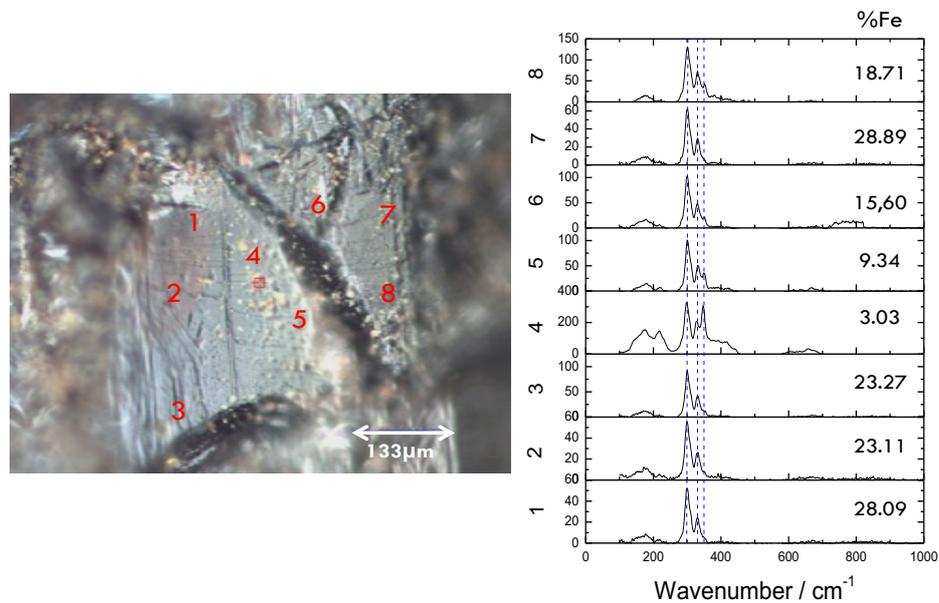


Fig. 7. Raman spectrum and iron content in different areas of marmatite particles

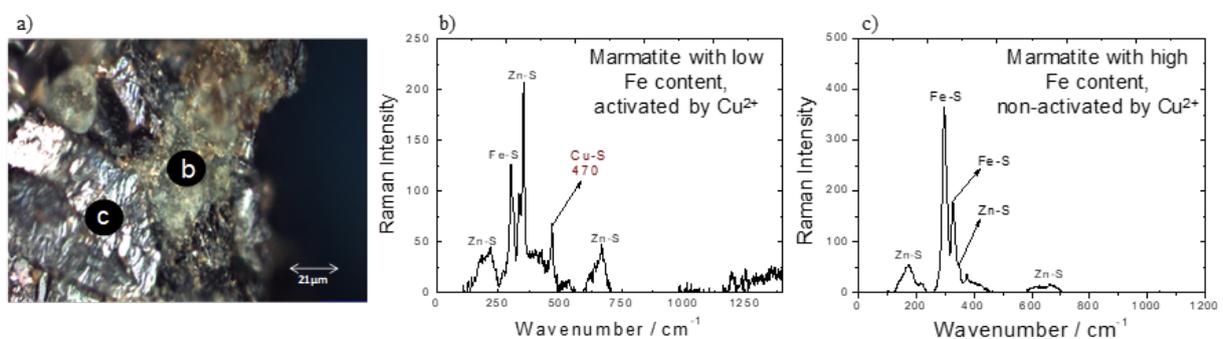


Fig. 8. (a) Photomicrograph of marmatite particle showing zones of low and high iron content analyzed by Raman spectroscopy, (b) Raman spectrum of marmatite in zone with low iron content (3.8%) activated by  $\text{Cu}^{2+}$  ions and (c) Raman spectrum of marmatite in zone with high iron content (24.4%) non-activated by  $\text{Cu}^{2+}$  ions

### 3.6. Adsorption of collectors on FeS<sub>2</sub> and CuFeS<sub>2</sub>

Xanthates are common in flotation of base-metal sulfides. They chemically and physically adsorb on the sulfide minerals. Characterization of the chemical compounds that formed from the xanthate-sulfide interaction is relevant for the mineral recovery by flotation. In this work Raman spectroscopy was used to identify the chemical species on pyrite and chalcopyrite once the minerals were contacted with PPX. First, the Raman spectrum of solid potassium propyl xanthate was obtained. Then, the sulfides in the presence of the collector were characterized. Fig. 9 shows the Raman spectrum of the PPX where bands due to the C-H bonds of the CH<sub>3</sub> and CH<sub>2</sub> of xanthate alkyl chain were clearly identified, as well as the bands corresponding to the C-S<sub>2</sub> and C-O-C bonds of the xanthate polar group. These bands agreed very well with those reported by Andreev and Barzev (2003) and by Hope et al. (2001).

Fig. 10 shows the Raman spectra of FeS<sub>2</sub> and CuFeS<sub>2</sub> in the absence and presence of the xanthate. For comparison purposes, the Raman spectra of the collector is also presented. In the Raman spectra of FeS<sub>2</sub> and CuFeS<sub>2</sub> with xanthate, the band at 500 cm<sup>-1</sup> is due to the S-S bond indicating the presence of dixanthogen (R-OCSS-SSCO-R; R is the collector alkyl chain) on the minerals. Dixanthogen resulted from the oxidation of the xanthate on the mineral surface and is physically attached on the mineral (Andreev and Barzev, 2003).

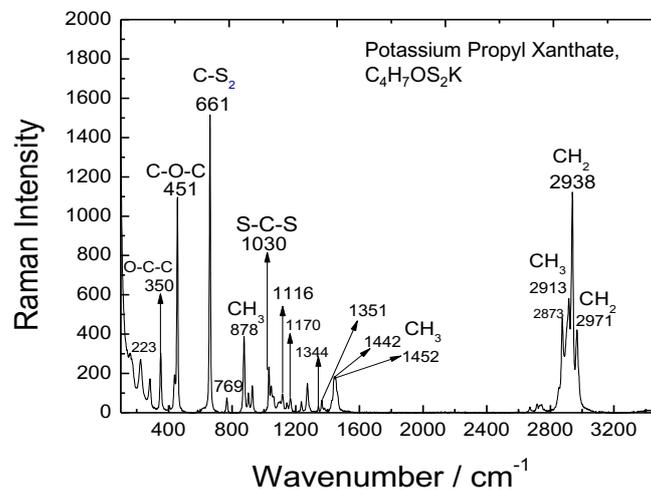


Fig. 9. Raman spectrum of potassium propyl xanthate (PPX)

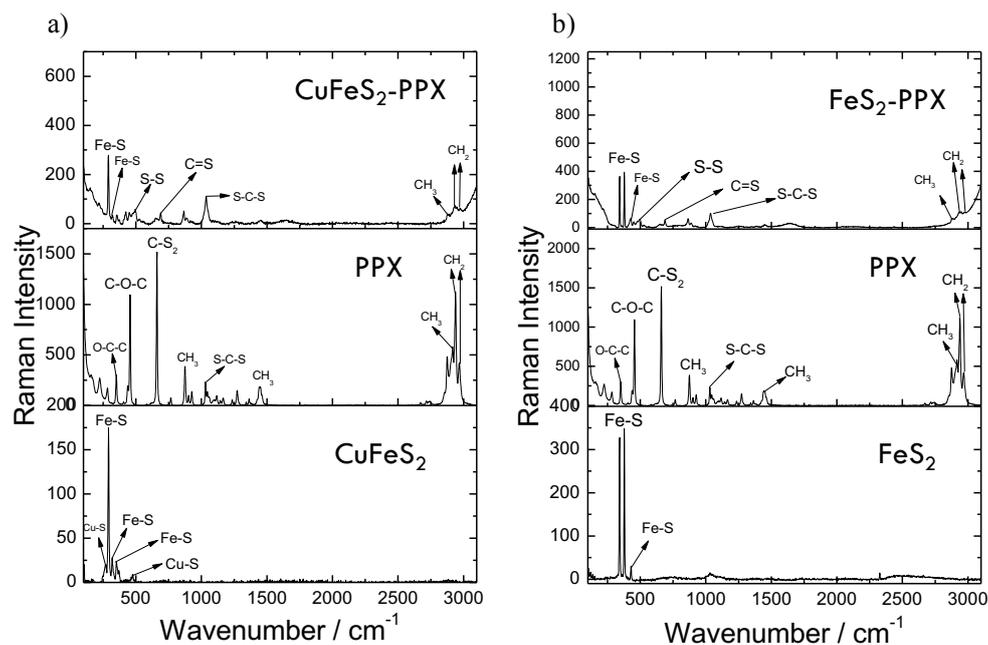


Fig 10. Raman spectra of: (a) Chalcopyrite and Chalcopyrite-potassium propyl xanthate and (b) Pyrite and pyrite-potassium propyl xanthate

#### 4. Conclusions

Raman spectroscopy is a reliable and straightforward technique to characterize sulfide minerals immersed in water and to determine chemical compounds on floating sulfides. The metal-S bonds in the crystal structure of the sulfides are clearly distinguished in the Raman spectrum of the mineral. This spectroscopic technique is able to reveal the compounds on the floating minerals after their interaction with sulfhydrylic collectors and activators. It also showed that marmatite particles of millimetric size are composed by micro-size, perhaps nano-size, marmatite entities with different Fe and Zn contents. In addition, it revealed that the marmatite entities with the lowest Fe content absorbed more copper ions than those with high Fe content.

#### Acknowledgements

E. E. Vázquez Sánchez gratefully acknowledges the National Council of Science and Technology (CONACYT), México for the Fellowship Grant No. 269106 to pursue Ph. D. studies in Materials Science and Engineering at Universidad Autónoma de San Luis Potosí, México.

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