The Effect of Chalcopyrite Composition on Semiconducting Properties

Sarah Patterson, Julian Battaglia, Ariel Rieffer, Zafer Mutlu, Andrew Wessman, and Isabel Barton

Abstract Chalcopyrite ($CuFeS_2$) is a common copper ore mineral that displays variable but often poor leaching behavior under typical heap leach conditions. Ongoing research has provided inconsistent magnitudes of activation energy and dissolution mechanisms, even for chalcopyrite leached in the same chemical systems. This is possibly due to variations in crystallography, impurities such as Zn, Ag, Co, and Se, which natural chalcopyrite readily accommodates, or interference from additional sulfides, like cubanite, haycockite, mooihoekite, putoranite, or talnakhite, which have similar crystallographic signatures and optical properties. Additional contributors to these observations are unconstrained variations in chalcopyrite semiconducting properties, such as charge carrier type, density, and resistivity. Little is known about these in natural chalcopyrites. Currently, most natural chalcopyrites are considered n-type semiconductors, while an estimated 3–5% of the species are weak to moderate p-type; measured resistivities reported in the literature range from 10^{-5} to 150 Ω-cm. However, measurements of natural samples are uncommon and typically uncorrelated with composition. Previous attempts to correlate chalcopyrite composition and semiconducting properties have yielded ambiguous results, largely due to limited numbers of samples and limited methods of characterization. This paper reports preliminary results from an ongoing study of the relationship between chalcopyrite composition and semiconducting properties. The results shown are based on 9 whole-rock chalcopyrite samples, characterized by electron microprobe and four-probe station for sample composition, resistivity, charge carrier density, and resistivity. These natural rock samples were found to have averages of 4.11 Ω-cm resistivity (median 0.35 Ω-cm) and mobility of 15.09 cm^2/V-sec (median 8.95 cm^2/V-sec). These preliminary results show a potential inverse correlation between chalcopyrite Ag concentration and charge mobility, while other elements cover a wide range with no clear effects. This may be due to the effect of fine-scale non-chalcopyrite sulfide impurities in the

---

S. Patterson · I. Barton (✉)
Department of Mining and Geological Engineering, University of Arizona, Tucson, AZ, USA
e-mail: fay1@arizona.edu

J. Battaglia · A. Rieffer · Z. Mutlu · A. Wessman
Department of Materials Science and Engineering, University of Arizona, Tucson, AZ, USA

The Metallurgy and Materials Society of CIM et al. (eds.), *12th International Copper Conference*, https://doi.org/10.1007/978-3-032-00102-3_72

samples, which affect the semiconducting properties, but not mineral composition measurements.

Keywords Chalcopyrite · Semiconductors · Resistivity · Chalcopyrite characterization

1 Introduction

1.1 Background

Pyrometallurgical processing of chalcopyrite-dominated ore is the current industry standard, but is expensive and emissions-heavy compared to hydrometallurgical approaches [1]. Unfortunately, leaching attempts have been challenging due to low solubility and inconsistent behavior of chalcopyrite in most common, non-exotic lixiviant-oxidant systems: anecdotally, chalcopyrite recovery at room-temperature is generally low but highly variable.

The reason for this variable behavior has never been firmly established. One major potential contributor is inherent variation within chalcopyrite ores. This includes a wide range of galvanically active accompanying minerals, such as pyrite, cubanite, or sphalerite; sulfide impurities like bornite, or covellite that leach and release catalyzing Cu^{2+} into solution; confusion with close relatives of chalcopyrite like mooihoekite, haycockite, and talnakhite; and 4–5 orders of magnitude variation in the trace-element contents [2]. Since chalcopyrite is a natural semiconductor, some of the variability is also due to distinctions in semiconducting properties such as resistivity, band gap size, and charge carrier mobility (Hiskey 1993). Mobility in particular explains how electrons move through a material and oxidizes–via holes from missing electrons (p-type), or donations from extra electrons (n-type)–and is determined by trace element impurities within the chalcopyrite itself. Most lab-scale research on chalcopyrite leaching does not account for these variations in composition or semiconducting properties [3]. Thus, the chalcopyrite leaching literature contains multiple, highly varying, sometimes conflicting results for activation energies, leaching kinetics, and total recoveries, even for the same lixiviant-oxidant combinations working on ore classified as chalcopyrite.

1.2 Problem Statement

Many of the disparities in the literature on chalcopyrite leaching were known long before the recent growth in professional publications multiplied them. The following section reviews some of the relevant previous work on the subject. Resolving these inconsistencies necessitates a combination of well-constrained and detailed mineralogy, measurement of trace elements, and correlation with semiconducting properties. This is the focus of an ongoing study at the University of Arizona with hopes to correlate the results to leaching behavior.

1.3 Previous Work

An early study in metallurgical engineering by Dutrizac [4], followed up by additional electrochemical results by McMillan et al. [5], illustrated the compositional and semiconducting differences among chalcopyrites from different sites. However, results were highly variable and showed no additional correlations with the leaching behavior.

Multiple authors in materials science have examined the connection between chalcopyrite composition and semiconducting properties. Teranishi and Sato [6] identified the compositions of chalcopyrite that correspond to n- versus p-type semiconduction. They found that the n-type chalcopyrites were typically those with major-element ratios and/or trace-element substitutions causing a slight excess of positive charge. This was supported by Ang et al. [7], who determined that the chalcopyrites with a deficiency of negative charges (through Cu-oversaturation coupled with Fe-undersaturation) were the ones that tended toward p-type behavior. Even so, the same authors found a wide range in semiconducting properties: Ang et al. [7] noted more than an order of magnitude variation in resistivity for a series of chalcopyrite samples that were all slightly Cu-oversaturated and Fe-undersaturated. However, most of these studies did not address potential implications for dissolution behavior.

The effect of major-element composition on leaching was examined by Rosso and Vaughan [8], who found that the stuffed structural derivatives of chalcopyrite (mooihoekite, talnakhite, or haycockite) dissolved noticeably faster in acid solutions than chalcopyrite with the normal proportion of vacant metal sites.

There has been some research on the effect of other sulfide impurities on chalcopyrite semiconducting properties or leaching behavior. Warren (1978) noted that small grains of cubanite would lower the resistivity of the host chalcopyrite substantially compared to pure samples. [9] suggested that abundant pyrite inclusions raise the rest potential of chalcopyrite. The implications of both for leaching, however, are mixed. For a long time pyrite was considered a catalyzing impurity in chalcopyrite ores (e.g. [10]), but recent studies have found little to no discernible effect [11]. This may relate to the choice of oxidant, since the catalysis of chalcopyrite dissolution appears to be specific to particular reagent combinations [11]. Alternatively, it may reflect the fact that pyrite varies in properties as much as chalcopyrite; the rest potential difference between the two species may range anywhere from 0 to 400 mV, which probably affects whether pyrite catalyzes chalcopyrite leaching or not.

1.4 Motivation for This Research

While often excellent in quality, most of the literature above covers only two of three attributes for chalcopyrite: composition, its semiconducting behavior, and its leaching behavior. The overall project goal at the University of Arizona attempts to link all three by using a large suite of well-characterized samples to constain the effects of major-, minor-, and trace-element compositions, resistivity, and charge mobility on leaching behavior. This paper outlines the first results of the relationship between semiconducting properties and compositional variations in chalcopyrite.

2 Methods and Materials

Natural chalcopyrite samples were obtained from Ward's Scientific and from existing collections at the University of Arizona at the locations shown in Table 1.

Each whole-rock chalcopyrite sample was mounted in a 1″ round epoxy mount and polished to 0.25-micron grit. These mounts were photographed in reflected light using a Nikon LV100 petrographic microscope and analyzed using a Cameca SX100 electron probe microanalyzer (EPMA) at the University of Arizona. Several point analysis were taken for each chalcopyrite sample and used for sulfide identification. These trace elements were averaged for each mineral within the samples, and used to support identification and rare mineral composition.

The 1″ mounts were trimmed to fit in the four-probe station for charge carrier mobility and resistivity. Samples were mounted on a PCB holder and four probes

Table 1 Samples used in this study

Chalcopyrite locality	Texture/description	Deposit type	Accompanying sulfides
Ajo mine	Massive and in veins; small but abundant exsolutions, inclusions, or replacements of other sulfides	Porphyry Cu	Bornite, pyrite, minor covellite
Noranda	Massive, blocky with cubanite and sphalerite forming inclusions in chalcopyrite	Volcanic-hosted massive sulfide	Pyrite, sphalerite, trace cubanite
Sudbury	Massive, blocky with cubanite and sphalerite forming inclusions or close associations with chalcopyrite	Magmatic segregation	Pyrite, sphalerite, cubanite
Ward's scientific	Massive, blocky with a few veinlets of other sulfides	Unknown	Pyrite, sphalerite

were placed directly on the conductive samples without silver paste. Measurements were conducted using an HMS-5000 instrument with 0.55 T magnetic field and 1.00 mA current under ambient conditions. Each sample was measured 3 times for 25 rounds apiece at 1-min intervals. These measurements were averaged to produce single mobility and resistivity readings.

3 Methods and Materials

3.1 Overview of Samples

Figure 1 shows a representative sample of the natural chalcopyrite samples used in this study. As seen in the photomicrographs, most samples contain significant amounts of other minerals besides chalcopyrite. While some are inert and nonconductive species such as quartz and feldspar, other sulfides present include bornite, pyrite, sphalerite, minor covellite, and other minerals noted in Table 1.

All samples in this study are considered pure, high-grade chalcopyrite ores by industry standard, containing at least 85% chalcopyrite. However, additional sulfide impurities are common at the 1 cm scale. These non-chalcopyrite sulfides are expected to affect the semiconducting results as they are mixed below the scale of the 1–2 mm spacing between the probes. As research continues, leaching results are expected to be affected as well, due to copper-rich sulfides like bornite and digenite oxidizing before chalcopyrite [12]. Care will be taken to either minimize their reaction with non-reactive epoxy, or note their presence before and after. At present however, this explains much of the variability in our study and in most other metallurgical studies, which use samples that meet the mining industry's definition of high-grade chalcopyrite, but contain other sulfides at the experimental scale.

3.2 Sample Composition and Semiconducting Properties

Table 2 shows major-element compositions and semiconducting properties of the samples in this study. Minor elements are in Table 3.

As expected, resistivity and charge mobility show a strong inverse correlation for all samples. Beyond that, correlations are elusive. Based on literature, effects from galvanically active trace elements, such as Zn, Ag, and As could be expected, as well as some correlation between chalcopyrite Cu/Fe ratios and charge mobility [7, 13, 14]. As shown in Fig. 2, not all of these are apparent. There is a potential inverse correlation between Ag concentration and charge mobility, but most of the remaining relationships are too scattered to support firm conclusions.

Correlations were sought between charge mobilities and other elements from Table 3, but results were similarly inconclusive. No correlation was observed between

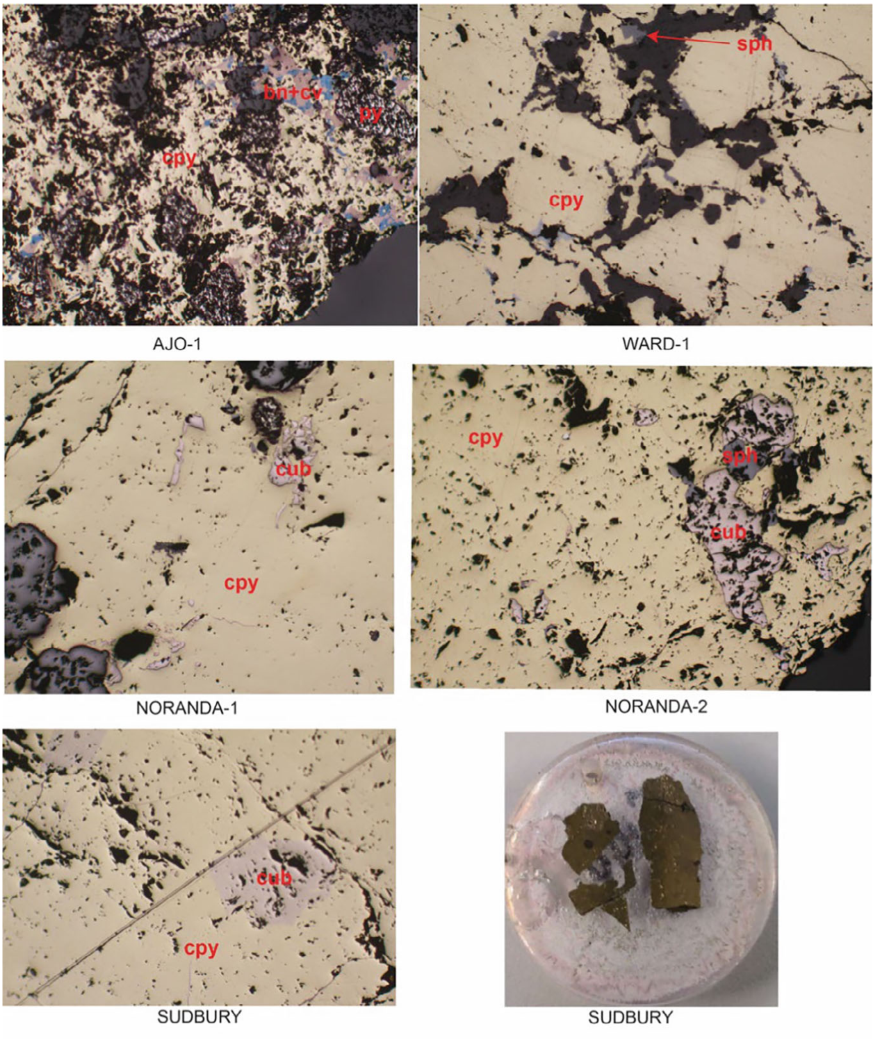

Fig. 1 Reflected-light photomicrographs of representative samples used in this study; see Table 1 for sample names. Cpy = chalcopyrite, bn = bornite, py = pyrite, sph = sphalerite, cub = cubanite, cv = covellite. Dark gray, high-relief areas of images are silicate minerals. All photomicrographs are at 5 × magnification with fields of view approximately 1mm wide; mount at bottom right is 2.5 cm (1″) in diameter

resisitivity or charge mobility and total trace-element contentration or major-element ratios. While Pridmore and Shuey [14] found a correlation between Cu/Fe ratio and resistivity, no such relationship was evident among our samples.

Table 2 Semiconducting properties and major-element composition of chalcopyrite samples in this study. For trace elements, see Table 3

Sample	Resistivity, ohm-cm	Charge mobility, cm^2/V*sec	Minerals	S, %	Fe, %	Cu, %	Zn, %	EPMA totals
Ajo-1	0.1667	26.099	Chalcopyrite	34.885	30.514	34.457	0.034	99.998
			Pyrite	53.488	46.845	0.014	0.040	100.648
			Bornite	27.186	12.439	59.287	0.053	99.110
			Digenite	28.220	1.123	72.233	0.024	101.814
Ajo-2	2.3516	2.9297	Chalcopyrite	33.507	30.223	34.546	0.025	98.404
			Bornite	26.609	12.573	62.010	0.031	101.376
			Pyrite	50.948	45.757	0.443	0.011	97.500
Ajo-3	0.1612	22.7299	Chalcopyrite	34.115	30.440	34.481	0.028	99.222
			Pyrite	51.520	45.653	0.057	0.004	97.612
			Bornite	26.147	12.191	61.653	0.049	100.158
Ajo-4	0.1933	18.6003	Chalcopyrite	34.528	30.432	34.529	0.031	99.622
			Bornite	25.999	11.235	63.711	0.051	101.119
Ajo-5	0.4341	8.9516	Chalcopyrite	34.279	30.455	34.411	0.034	99.286
			Pyrite	53.076	45.481	0.428	0.000	99.076
			Digenite	27.031	1.040	72.603	0.058	100.809
			Bornite	25.887	11.466	62.911	0.026	100.383
Noranda-1	0.021	48.9865	Chalcopyrite	34.038	30.560	34.308	0.071	99.157
			Pyrite	39.092	60.452	0.146	0.019	99.987
			Sphalerite	32.013	8.473	0.225	57.936	99.175
Noranda-2	0.3518	6.0752	Chalcopyrite	34.019	30.826	34.218	0.043	99.230
			Pyrite	38.796	60.637	0.060	0.000	99.667
Sudbury-1	1.7677	0.9581	Chalcopyrite	34.632	30.727	34.406	0.046	99.910
			Cubanite	35.034	41.201	23.228	0.019	99.587
			Sphalerite	32.109	8.404	0.729	55.829	99.235
Ward-1	31.545	0.4823	Chalcopyrite	34.659	30.040	34.261	0.026	99.114
			Sphalerite	32.617	1.359	0.896	64.268	100.613

4 Discussion

The goal of this study was to examine the correlations between chalcopyrite's chemical composition and its semiconducting properties. At this early stage, the preliminary results resemble those of Dutrizac [4], who found little or no correlation among chalcopyrite n- or p-typing, leaching rate, and trace-element composition for samples from different localities. However, his study (like this one) used a relatively small number of samples (11) and had incomplete resistivity and compositional characterization. Notably, Dutrizac [4] and McMillan et al. [5] did find that more silver-rich

Table 3 Minor-elements from sulfide samples in this study, by EPMA

Sample	Mineral	Zn	Ga	Ge	As	Se	Ni	Co	Ag	Te	Sn	Hg	Bi	Sb	Mn	Cd	Au
Ajo-1	Chalcopyrite	338	118	35	72	166	10	13	0	18	95	323	51	12	78	14	69
	Pyrite	396	183	0	0	294	210	1043	0	89	95	581	0	22	76	26	0
	Bornite	529	388	7	0	0	61	0	128	0	107	602	0	0	181	0	0
	Digenite	242	488	0	0	578	0	74	446	0	0	147	0	0	60	125	0
Ajo-2	Chalcopyrite	253	42	47	71	103	42	0	62	23	25	273	0	32	82	26	32
	Bornite	305	0	28	62	83	0	640	213	150	61	222	0	8	36	0	0
	Pyrite	108	0	0	7	172	622	1920	0	0	0	324	0	82	97	78	114
Ajo-3	Chalcopyrite	278	207	9	35	90	53	53	54	48	17	175	12	15	45	0	113
	Pyrite	40	0	47	0	130	854	1831	247	0	57	350	0	50	142	73	0
	Bornite	491.5	480	0	20	95	128	62	257	14	0	45	0	49	11	19	0
Ajo-4	Chalcopyrite	308	105	22	69	109	32	19	26	35	36	181	27	32	85	127	125
	Bornite	512	51	24	76	51	28	14	5	64	16	345	0	9	52	59	379
Ajo-5	Chalcopyrite	340	86	0	94	181	32	0	58	34	64	164	21	45	14	105	174
	Pyrite	0	134	129	0	148	77	0	127	0	15	41	0	0	75	67	105
	Digenite	581	0	0	0	0	11	0	250	0	0	73	0	0	135	115	44
	Bornite	261	0	163	97	260	42	0	0	224	0	0	0	0	146	0	0
Noranda-1	Chalcopyrite	709	48	17	85	399	0	0	90	29	63	279	33	17	61	87	5
	Pyrite	187	0	0	0	439	475	1231	0	0	73	192	0	176	120	83	0
	Sphalerite	Table 2	0	130	182	1356	6	790	0	0	0	345	0	0	56	2154	78
Noranda-2	Chalcopyrite	433	159	11	41	383	12	28	163	19	46	225	57	26	41	26	0
	Pyrite	0	167	34	0	529	137	561	61	22	69	0	0	23	48	0	96
Sudbury	Chalcopyrite	461	174	0	38	213	25	7	82	24	85	176	0	8	68	26	87

(continued)

Table 3 (continued)

Sample	Mineral	Zn	Ga	Ge	As	Se	Ni	Co	Ag	Te	Sn	Hg	Bi	Sb	Mn	Cd	Au
	Cubanite	285.3	34	47	41	26	0	55	108	57	187	0	3	66	83	60	0
	Sphalerite	Table 2	0	92	93	160	0	7	74	0	0	253	0	0	1067	19,622	0
Ward-1	Chalcopyrite	280	110	31	21	168	28	17	383	29	55	192	16	35	60	56	44
	Sphalerite	Table 2	5	21.3	116.3	260	47	197	135	0	57.3	402.3	0	0	71	11,641	0

All units are ppm. Pb and In were analyzed for, but not detected. Wt-percent values of sphalerite in Table 2

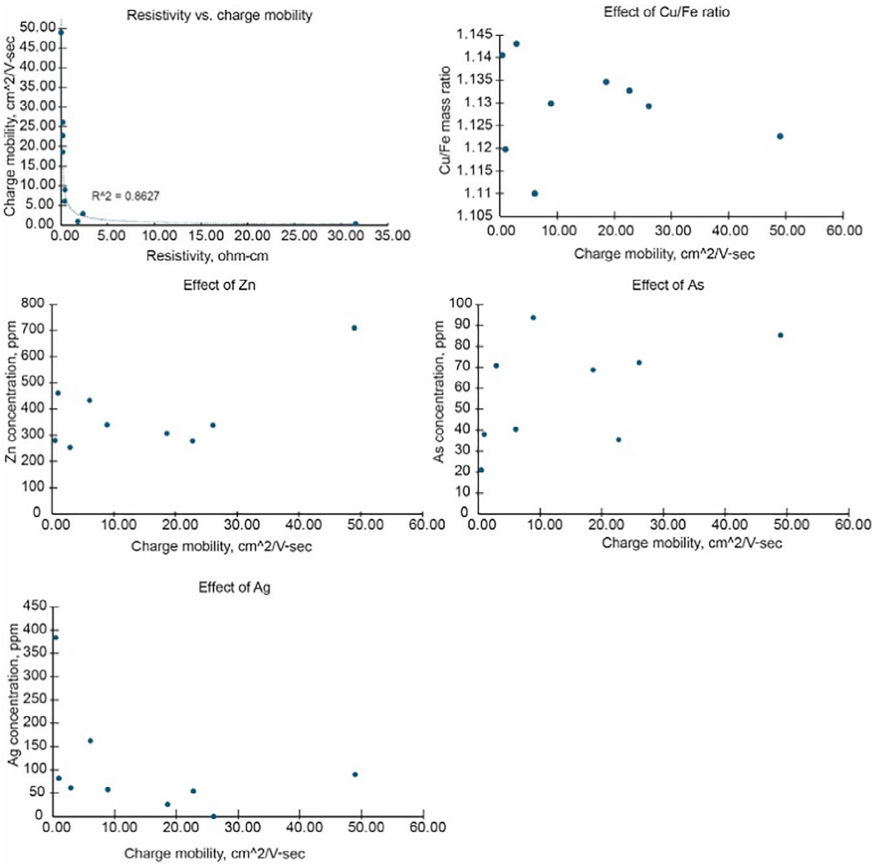

Fig. 2 Plots correlating the semiconducting properties of chalcopyrite and charge mobility

chalcopyrites showed slower leaching rates than comparable samples with less silver, which is consistent with the lower charge mobility for these samples noted in Fig. 1. This correlation is also supported by Wintenberger [15], who found that increased Ag substitution for Cu in chalcopyrites increased their resistivity.

Both studies used fairly small numbers of samples, which is one additional reason for the inconsistency, and also affects this study of 9 samples while testing continues. Another contributing factor is the diverse range of samples and accompanying sulfides. As Dutrizac [4] noted, declining sample purity—i.e. an increasing fraction of non-chalcopyrite sulfide minerals in the sample—corresponds to more erratic leaching behavior. These sulfides dissolve, releasing Cu^{2+} into the solution and increasing galvanic interactions. He also noted that at or below roughly 80% pure chalcopyrite, the observed leaching phenomena mostly reflect the dissolution behavior of the sulfide impurities. While all of our samples appear to be above the 80% threshold, the Cu-bearing and/or sulfide impurities in Fig. 1 likely affected semiconductor measurements. The four probes are placed at a distance of 3 mm apart, approximately 3 times larger than the representative fields of view for the photomicrographs in Fig. 1. It is possible and likely that the measured semiconducting properties of "chalcopyrite" in the literature actually reflect a combination of the properties of chalcopyrite and these other minerals, but this will require further correlations of samples with similar representative mineralogies to confirm.

Continued work on this project will focus on measuring additional samples to investigate these correlations and their impacts on leaching behavior.

5 Conclusions

Leaching tests on chalcopyrite ores tend to show highly variable results, with divergent findings on kinetics, activation energy, and ultimate recovery even for the same lixiviant-oxidant system. An ongoing UA project is examining how variability within chalcopyrite ores contributes to this problem via a large range of chalcopyrite trace-element compositions, semiconducting properties, accompanying sulfide impurities, and other features.

This project presents preliminary results linking trace-element compositions to semiconductor properties using 9 well-characterized natural samples of varied type, provenance, and suite of accompanying sulfides. Comparison of EPMA in-situ chemical analysis and four-probe measurements shows a potential inverse relationship between chalcopyrite Ag content and charge carrier mobility, but few other observable correlations. Future work will continue to expand the study with additional samples and link compositional data to semiconductor properties and leaching behavior.

Acknowledgements We thank Freeport-McMoRan Inc. for supporting the research presented here. In particular, thanks to Jodie Robertson, Mitchell Catling, and VK Srivastava for sharing their insights and expertise.

References

1. Dreisinger D (2006) Copper leaching from primary sulfides: options for biological and chemical extraction of copper. Hydrometallurgy 83:10–20. https://doi.org/10.1016/j.hydromet.2006.03.032
2. George LL, Cook NJ, Crowe BBP, Ciobanu CL (2018) Trace elements in hydrothermal chalcopyrite. Mineral Mag 81(2):59–88. https://doi.org/10.1180/minmag.2017.081.021
3. Barton IF, Hiskey JB (2022) Chemical, crystallographic, and electromagnetic variability in natural chalcopyrite and implications for leaching. Miner Eng 189:107867. https://doi.org/10.1016/j.mineng.2022.107867
4. Dutrizac JE (1982) Ferric ion leaching of chalcopyrites from different localities. Metall Trans B 13B:303–309. https://doi.org/10.1007/BF02667745

5. McMillan RS, MacKinnon DJ, Dutrizac JE (1982) Anodic dissolution of n-type and p-type chalcopyrite. J Appl Electrochem 12:743–757. https://doi.org/10.1007/BF00617495
6. Teranishi T, Sato K (1975) Optical, electrical and magnetic properties of chalcopyrite, $CuFeS_2$. Journal de Physique Colloque 36:C3–149–C3–153. https://doi.org/10.1051/jphyscol:1975327
7. Ang R, Khan AU, Tsujii N, Takai K, Nakamura R, Mori T (2015) Thermoelectricity generation and electron-magnon scattering in a natural chalcopyrite mineral from a deep-sea hydrothermal vent. Angew Chem 127:13101–13105. https://doi.org/10.1002/anie.201505517
8. Rosso KM, Vaughan DJ (2006) Sulfide mineral surfaces. Rev Mineral Geochem 61:505–556. https://doi.org/10.2138/rmg.2006.61.9
9. Majuste D, Ciminelli VST, Osseo-Asare K, Dantas MSS (2012) Quantitative assessment of the effect of pyrite inclusions on chalcopyrite electrochemistry under oxidizing conditions. Hydrometallurgy 113–114:167–176. https://doi.org/10.1016/j.hydromet.2011.12.020
10. Abraitis PK, Pattrick RAD, Kelsall GH, Vaughan DJ (2004) Acid leaching and dissolution of major sulphide ore minerals: processes and galvanic effects in complex systems. Mineral Mag 68(2):343–351. https://doi.org/10.1180/0026461046820191
11. Nicol MJ (2022) Does galvanic coupling with pyrite increase the rate of dissolution of chalcopyrite under ambient conditions? An electrochemical study. Hydrometallurgy 208:105824. https://doi.org/10.1016/j.hydromet.2022.105824
12. Rosso KM, Vaughan DJ (2006) Reactivity of sulfide mineral surfaces. Rev Mineral Geochem 61(1):557–607. https://doi.org/10.2138/rmg.2006.61.10
13. Li L, Soleymani M, Ghahreman A (2021) New insights on the role of lattice-substituted silver in catalytic oxidation of chalcopyrite. Electrochim Acta 369:137652. https://doi.org/10.1016/j.electacta.2020.137652
14. Pridmore DF, Shuey RT (1975) The electrical resistivity of galena, pyrite, and chalcopyrite. Am Mineral 61:248–259. https://www.yumpu.com/en/document/view/8383458/the-electrical-resistivity-of-galena-pyrite-and-chalcopyrite
15. Wintenberger M (1962) Etude électrique et magnétique de composés sulfures et arséniés d'éléments de transition. Bulletin de la Société Française de Minéralogie et de Cristallographie 85(1):77–89. https://www.persee.fr/doc/bulmi_0037-9328_1962_num_85_1_5541