

Iron content variations in sphalerite and their effects on reflectance and internal reflections under reflected light

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Abstract Reflectance (R%) and internal reflections (IR) in the iron variant, sphalerite, are investigated by using the scanning electron microprobe and reflected light microscope. Iron contents in sphalerite positively affect reflectance and can be considered as a control factor of internal reflections color. Internal reflections of sphalerite grains that contain less than 10% Fe appear to be whitish yellow color but are with reddish brown color when Fe rises to 10% to 17%. This work is an effort for developing ore microscopy and ore petrography technique by using the optical properties as a geochemical tool for fast preliminary estimating iron content in sphalerite by using reflected light microscope.

Keywords Sphalerite · Reflectance · Internal reflections · Reflected light

Introduction

Some minerals are transparent and other completely opaque, with some being intermediate in their opacity. Therefore, the transparent phase is best studied as thin section under transmitted light, but the intermediate and opaque phases, of course, are best studied as polished section under reflected light. Sphalerite crystals are mostly opaque but sometimes show little transparency; consequently, they are examined more effectively on polished section under reflected light. It is generally recognized that impurity elements may be incorpo-

rated into mineral in several ways, one of these is substitution. The occurrence of zinc in sulfide ore deposits is generally accompanied by various iron minerals. Part of zinc in sphalerite is practically always isomorphously substituted by iron, often by manganese and cadmium (Ramdohr 1980). Iron content in sphalerite affects engineering extraction processes (Boulton et al. 2005) and on leaching (Xie et al. 2007).

The correlation of reflectance variations with compositional variations in minerals are important, but not yet fully explored field. The first contrasting test of this application of reflectance measurement is the use of reflectometric method for determining the silver content of natural gold–silver alloys (Sequair 1965; Eales 1967). Sphalerite has an average reflectivity percentage of 17.8. Reflectance (R%) of sphalerite increases with the increasing of iron content (Ramdohr 1980). Also, he mentioned that the internal reflections (IR) of sphalerite always very numerous; they are white in the iron poor sphalerite, in others yellow, light brown, and dark brown. No previous work has talked the ranges of reflectance and internal reflections by which the observer can directly estimate the iron content within sphalerite.

Iron content in sphalerite is quite considerable and effective on both physical and optical properties; on that basis, this work is aiming to develop a rapid microscopic technique for determining of approximately iron content in sphalerite depending on its reflectance and internal reflections. Therefore, this work is an effort to employ the physical properties and combine it with chemical composition.

Principles and definitions

Sphalerite phases that are sufficiently transparent allow plane-polarized reflected light to penetrate deep below the polished surface and be reflected back to the observer from

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Table 1 Chemical composition, reflectance (R%), and internal reflections (IR) of sphalerite

Spot no.	Zn%	Fe%	S%	Total%	Reflectance (R%) at 546 nm (λ)	Color of internal reflections (IR)
1	61.7630	4.5880	33.5080	99.8590	16.7	Yellowish white
2	61.7170	4.6000	33.3500	99.6670	16.7	
3	61.6070	4.6890	33.6780	99.9780	16.7	
4	61.5460	4.7190	33.4490	99.7140	16.7	
5	61.3090	4.7220	32.9480	98.9790	16.7	
6	61.1570	4.8370	33.3550	99.3490	16.7	
7	61.9200	4.9250	33.3310	99.5460	16.8	
8	61.4200	4.9350	33.4330	99.7880	16.8	
9	61.1160	4.9730	33.3490	99.4380	16.8	
10	61.5490	4.9800	33.6220	100.1510	16.8	
11	61.6600	4.9920	33.6470	100.1770	16.8	
12	60.9610	5.3510	33.7170	100.0290	16.8	
13	61.0640	5.3540	33.3790	99.7970	17.0	
14	60.6310	5.4880	33.5100	99.6290	17.0	
15	60.5450	5.5810	33.6830	99.8090	17.0	
16	60.3670	6.0160	33.4040	99.7870	17.0	
17	59.7740	6.0670	33.4370	99.2780	17.0	
18	59.8290	6.1370	33.4900	99.4560	17.0	
19	59.8610	6.2250	33.4600	99.2320	17.0	
20	59.7910	6.5780	33.6890	100.0580	17.0	
21	59.6540	6.7610	33.4080	99.8230	17.0	
22	59.1360	7.0320	33.6150	99.7830	17.0	
23	59.2930	7.2630	33.2860	99.8420	17.0	
24	58.8430	7.2930	33.3550	99.4910	17.0	
25	58.5710	7.4380	33.5710	99.5800	17.0	
26	58.6700	7.4760	33.4670	99.6130	17.0	
27	58.4120	7.4940	33.3550	99.3490	17.0	
28	58.7850	7.8490	33.6740	99.9480	17.0	
29	58.0960	8.1880	33.4000	99.6840	17.0	
30	57.0770	8.5250	33.7170	99.3190	17.0	
31	57.4710	8.5730	33.6150	99.7170	17.0	
32	57.4570	8.6300	33.7950	99.9720	17.0	
33	56.1960	9.8180	33.9570	99.9710	17.0	
34	55.7540	10.000	33.8370	99.6310	17.1	
35	55.1830	10.4090	33.8590	99.4510	17.1	
36	55.4480	10.5130	33.9270	99.8880	17.2	
37	54.8250	11.1640	33.9980	99.9870	17.2	
38	54.5400	11.6210	34.0820	100.243	17.22	
39	51.0660	14.6090	34.2660	99.9410	17.28	
40	50.6290	15.4720	34.1725	100.276	17.29	
41	50.5760	16.1830	34.5930	101.349	17.3	
42	49.679	16.2000	34.2220	100.101	17.32	
43	49.882	16.221	33.8960	99.999	17.35	
44	49.701	16.328	33.954	99.983	17.3	
45	49.760	16.330	33.893	99.885	17.34	
46	49.219	16.511	33.799	99.529	17.35	
47	49.212	16.573	34.055	100.020	17.37	
48	49.011	16.727	33.599	99.3370	17.36	
49	48.865	16.859	34.2350	99.9590	17.54	
50	49.807	16.957	33.3360	100.100	17.6	

Reddish brown

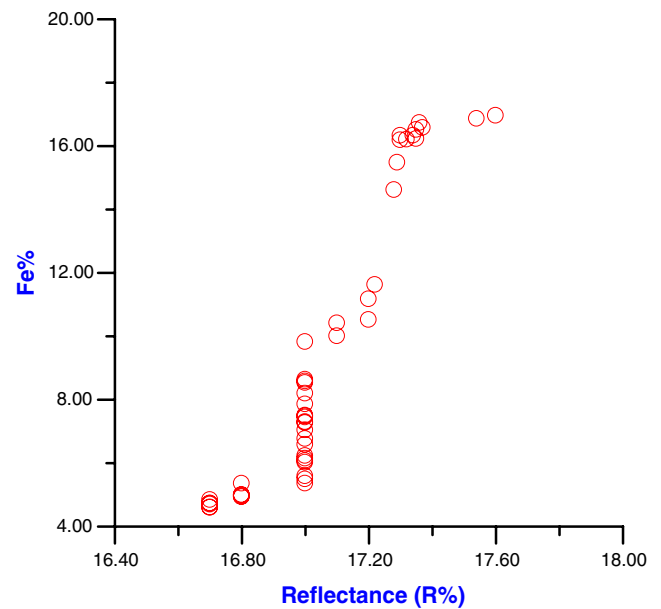


Fig. 1 The relationship between reflectance (R%) and Fe%

cracks, flows, and impurities within the crystals. Such light appears as diffused spots or patches known IR. Internal reflection can best be examined under crossed polars with intense illumination. They may also be visible under plane-polarized light (Craig and Vaughan 1981). The visibility of internal reflection is enhanced by using high power magnification. They are often best seen at the edges of grains or in small grains (Craig and Vaughan 1981).

Reflectivity is the term used previously in literature for reflectance (R%). It is a quantitative parameter represents a percentage of light at normal incidence reflected back to an observer (or instrumental observation system) from horizontal flat polished surface at a particular ore mineral. Absolute reflectance value depends on polishing surface and wave length of incident light. Sphalerite has very low

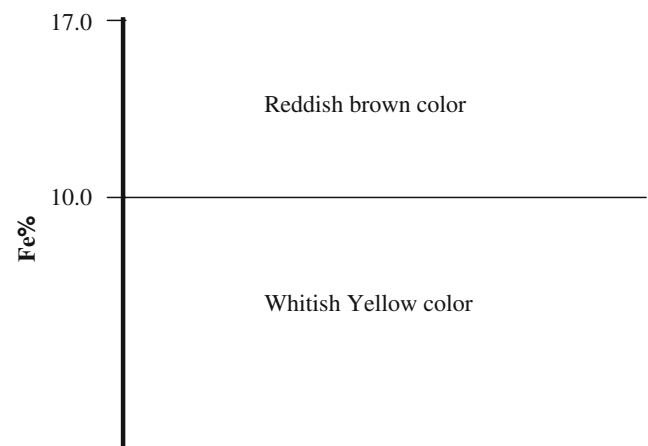


Fig. 2 The relationship between iron content in sphalerite and color of internal reflections

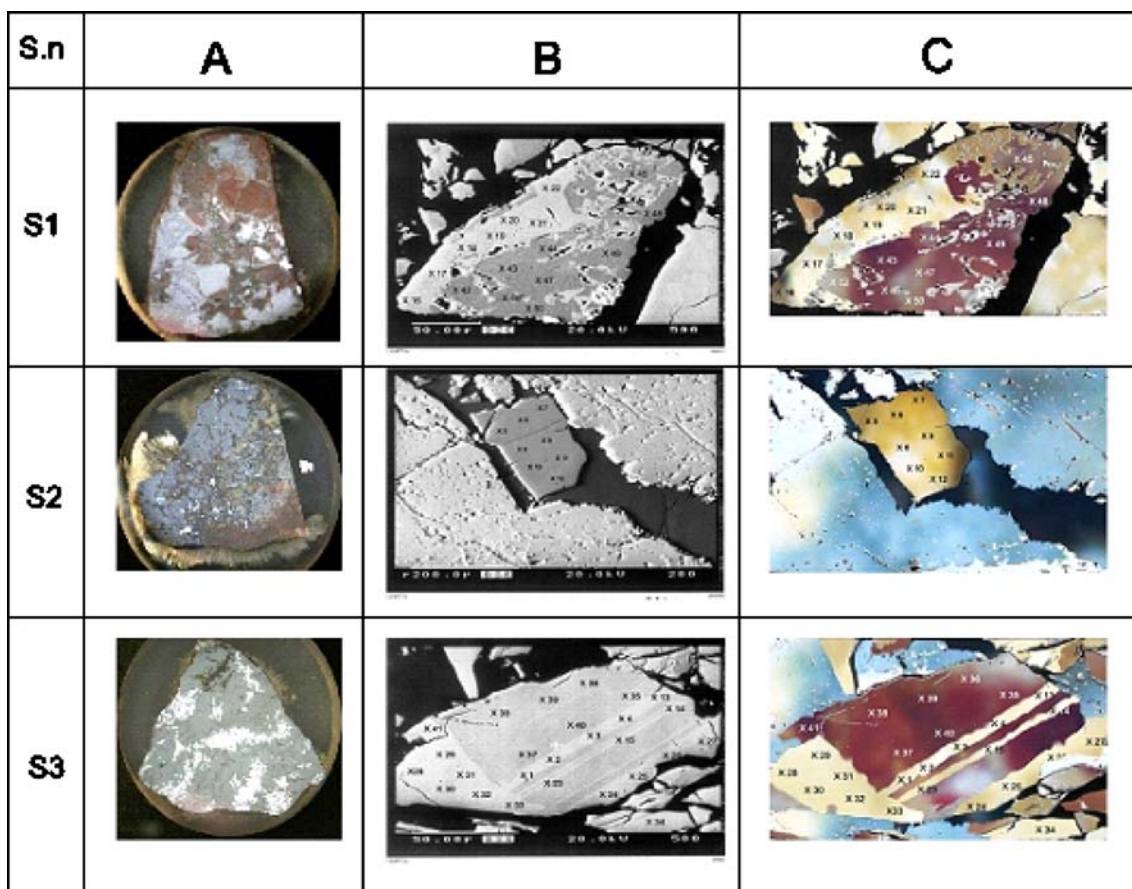


Fig. 3 Back scattered electron images (*column B*) and internal reflections images under high magnification power with cross-polar reflected light (+; *column C*) of three polished sections of sphalerite (*S1, S2, and S3; column A*)

reflectance and it is the lowest of the reasonably common sulfide ore minerals; it ranges from 17% to 20% (Uytenbogaardt and Burke 1973). Reflectance is one of the most important properties of an ore mineral, and its determination is part of a normal routine work (Craig and Vaughan 1981).

Methodology

Fifty spots on three polished sphalerite surfaces (Fig. 3) are investigated by scanning electron microprobe. These samples are collected from Lefan and Lower Banik localities in Northern Iraq. The investigated spots showed a wide range of iron content in sphalerite (Table 1). Reflectance (R%) and internal reflections (IR) are examined around these spots in order to monitor iron effects on the optical properties of sphalerite. All these measurements are conducted by Dr. H. J. Bernhardt at Ruhr University-Bochum in Turkey.

Reflectances were determined with a Vickers reflectance ore microscope at wave length of 546 nm in air, which is supplied with a photomultiplier and amplifier. A stabilized

selenium photocell run a high filament temperature of about 3,500°k for accuracy was used. Monochromator is inserted between light source and the specimen. Silicon carbide (SiC) which has R% (air) of about 20% at 546 nm was used as standard material. Standard specimens are both cleaned and leveled. Reflectance was measured under sharply focusing of the standard specimen using objective of ×16 magnification. Reflectance and internal reflections are checked again at the ore laboratory, Earth Sciences Department, College of Science, Baghdad University. Iron content, reflectance, and internal reflections are listed in Table 1.

Results and discussion

Electron microprobe analyses revealed that iron contents in sphalerite range from 4.588% to 16.957% (Table 1). The reflectance (R%) has been effected by these iron concentrations; it tends to increase slightly and systematically with the increasing of iron content (Fig. 1). Iron-poor sphalerite grains display a low reflectance and whitish yellow internal reflections color, whereas iron-rich sphalerite grains show

relatively higher reflectance and reddish brown internal reflections color (Figs. 2 and 3).

The whitish yellow internal reflection indicates average from almost pure zinc sulfide to sphalerite contains 10% iron as maximum (Fig. 3). The reddish brown internal reflection indicates considerable quantities of iron in sphalerite that have been determined to be ranging from 10% to 17% (Fig. 3).

The whitish yellow internal reflection indicates reflectance values range from 16.7% to 17.1% and iron content ranges from 4.6% to 10% (Table 1). Sphalerite grains that are characterized by reddish brown internal reflections appear to be rich in iron (10.4–16.95%) and reflect relatively highly reflectance (17.1% to 17.6%).

The general chemical formula of sphalerite is written (Zn,Fe)S to imply that the ratio of the two metals (Zn and Fe) is variable from one specimen to other, but the ratio of total metal to S remains constant. Zinc is ordinarily present in greater amount than Fe (Krauskopf 1979). Grains of conventional zinc concentrates typically contain 5–10% iron (Buban et al. 1999). Even though Zn^{++} and Fe^{++} have nearly the same ionic radii, because the Zn–S bond is more covalent than the Fe–S, only limited solid solution is possible between sphalerite and the hypothetical compound FeS with the sphalerite structure (Zielinski et al. 2000; Lusk and Caldar 2003). Consequently, the highest content of iron in sphalerite found to be (16.957%; Table 1). This ascribes to the electronic structure of minerals (Burns and Vaughan 1970; Craig and Vaughan 1981). The reflectance of the solid solution sphalerite is therefore interpreted in terms of their electronic structure, light absorption, and the transitions of electrons in the outer orbital. Electronic configuration of zinc reveals that the outer orbital $4s^2$ interferes with $3d^{10}$, while iron displays an electronic configuration in which the outer shell is formed from $4s^2$ interferes with $3d^6$. The electron density in the outer shell of zinc atom is higher than that of the iron atom. Thereafter, the absorption of incident light by iron-poor sphalerite is much greater than that of iron-rich sphalerite. Consequently, the quantity of reflected light from iron-poor sphalerite grain will be less than that reflected by iron-rich sphalerite. This also affects internal reflection color, but the detailed aspects of mechanism are not known yet.

The principle objective of this study is achieved with some useful points as listed below:

1. Electron microprobe analyses show that the iron present in sphalerite was part of sphalerite lattice and not as individual pyrite inclusions.
2. The compositional variation of sphalerite appears to be a controlled factor of internal reflections color and reflectance. There is a slightly systematic increasing in reflectance value whenever iron increased.

3. Sphalerite grains that are characterized by lowest reflectance (16.7–17.1%) with whitish yellow internal reflections confirm that the iron content does not exceed of 10%, whereas those characterized by a range of reflectance (17.1% to 17.6%) with reddish brown color indicate iron content range from 10.4% to 16.96%.
4. Iron content of 4.58% to 10% combined with whitish yellow internal reflections and iron content of 10% to 16.6% combined with the reddish brown internal reflections. These results allow us to use optical properties for estimating an approximate content of iron concentration in sphalerite.
5. Additional iron in sphalerite means a solid-phase diffusion of Fe ion throughout sphalerite structure with a constant quantity of sulfur in its unit cell.

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