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Atomic Spectroscopy

SAMPLE PREPARATION AND X-RAY FLUORESCENCE ANALYSIS OF SULFIDE ORES

Ming-Xing Ling,[1] Ying Liu,[1] Hong Zhang,[2] and Weidong Sun[3]
[1]*State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, The Chinese Academy of Sciences, Guangzhou, China*
[2]*Department of Geology, State Key Laboratory of Continental Dynamics, Northwest University, Xi'an, China*
[3]*CAS Key Laboratory of Mineralogy and Metallogeny, Guangzhou Institute of Geochemistry, The Chinese Academy of Sciences, Guangzhou, China*

Sulfide ores with varied concentrations, including four ore reference materials (zinc, copper, and iron sulfides) and two copper-nickel and iron sulfide samples, were used to develop an improved method for their analysis by X-ray fluorescence. The optimum conditions were established for the fusion of homogeneous stable glass disks. Different weights of silica were added to the samples, which were then fused with a lithium borate flux. The amount of silica varied from 1:20 for samples with low sulfur concentrations to 1:5 for those with high concentrations. The weight ratio of sample (including silica) to lithium tetraborate was 1:14. Lithium nitrate was used as a pre-oxidizing reagent to prevent degradation of platinum–gold crucibles. After pre-oxidation at 580° C for 13 minutes, the temperature was increased to 1100° C for 12 minutes. The relative standard deviations for major and trace elements were generally better than 5% and 10%, respectively.

INTRODUCTION

Sulfide ores deposits are one of the most important sources of metals for the global economy and industry, as well as of scientific significance (Green, Solomon, and Walshe 1981; Maclean and Kranidiotis 1987; Arndt, Lesher, and Czamanske 2005; Sun et al. 2008; Mishra and Bernhardt 2009). Consequently, there is an increased demand to analyze the materials. The compositions of sulfide ores are complicated (Zhao 2001), ranging from nickel-copper-rich magmatic ores to copper-zinc-lead-rich hydrothermal deposits (Green et al. 1981; Maclean and Kranidiotis 1987; Naldrett 1989; Arndt et al. 2005; Sun et al. 2008; Mishra and

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Address correspondence to Ming-Xing Ling or Weidong Sun, Guangzhou Institute of Geochemistry, The Chinese Academy of Sciences, Guangzhou 510640, China. E-mail: mxling@gig.ac.cn; weidongsun@gig.ac.cn

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Bernhardt 2009; Mao et al. 2011). It is always challenging to analyze sulfide ores. Due to the high sulfur contents of the ores, wet-chemical methods and atomic absorption spectrometry were previously used to determine their major element contents, but these methods are time-consuming and inefficient (Zhao 2001).

X-ray fluorescence (XRF) is a rapid, accurate, and precise method to determine elements in geological samples (Fabbi and Moore 1970). Although it has been used to analyze sulfide ores, sample preparation is difficult (Fabbi and Moore 1970; Johnson and Fleming 1987; Norrish and Thompson 1990). In general, two methods of sample preparation for XRF analysis are used, pressed powder pellets and fused glass disks. Pressed powder pellets have matrix effects (e.g., particle size and mineralogical effects), which increase analytical uncertainties, particularly in light elements, and hence fused glass disks are preferred when precise major element data are required (Baker 1982; Norrish and Thompson 1990).

The fused glass method allows major, minor, and trace elements to be determined in a wide range of materials (Vuchkova and Jordanov 2000). However, sulfide ores require special handling during sample preparation (Norman, Robinson, and Clark 2003), because elements such as copper, iron, and tin may be lost to the platinum–gold crucibles during fusion of glass disks (Norrish and Thompson 1990). In addition, sulfur is volatile and may be vaporized (Baker 1982; Norrish and Thompson 1990). In addition, sulfide can seriously damage the crucibles. These problems may be resolved if highly oxidizing conditions are used to retain sulfur and to protect the crucibles (Baker 1982). In the pre-oxidation treatment, KNO_3, Na_2O_2 (Fabbi and Moore 1970), $NaNO_3$ (Norrish and Thompson 1990), and $LiNO_3$ (Norman et al. 2003) have been used as oxidants to transform sulfides to sulfates. SiO_2 can also be added to sulfides as a glassing reagent to enhance fusion (Zhao 2001), but the optimum conditions are unknown.

This study focuses on solving technical problems for XRF analysis of sulfide ores. Several sulfide ore samples, including sulfide ore reference materials (lead–zinc, copper–nickel, and iron sulfides) and other copper–nickel and iron sulfide samples, were fused with a lithium borate flux for XRF analysis. By varying the pre-oxidation conditions and the proportions of SiO_2 to sulfide, optimum conditions were developed for the production of homogeneous stable glass disks for XRF analysis.

MATERIAL AND METHODS

Samples and Reagents

Sulfide ores in this study are described in Table 1. GBW07170 and GBW07171 are Chinese National copper and zinc sulfide reference materials. RTS-2 and RTS-3 are iron sulfide ore tailing reference materials, prepared and characterized by the Canadian Certified Reference Materials Project. BMZ-90 and I14-7 are iron and copper–nickel sulfide ores, respectively, collected in China. All reagents used are guaranteed reagents (99.9 wt%), including $LiNO_3$, SiO_2, $Li_2B_4O_7$, LiBr, and NH_4I.

Sample Preparation

The samples were ground to under 200 mesh. After drying at 100°C for 3 hours, the samples were stored in a desiccator. Different amounts of SiO_2 were

Table 1. Samples with different ratio of SiO_2 and fusion results

	Weight (g)					
Sample no.	Sample	SiO_2	$Li_2B_4O_7$	$LiNO_3$	SiO_2/Sample	Successful fusion
GBW07171 A	0.3573	0	5.0022	2.5000	0	No
GBW07171 a	0.4558	0	6.3811	2.5000	0	No
GBW07171 b	0.4039	0.0402	6.2173	2.5000	1/10	Yes
GBW07171 c	0.4010	0.0800	6.7338	2.5000	1/5	Yes
GBW07171 d	0.3502	0.1050	6.3728	2.5000	2/7	Yes
GBW07170 a	0.4555	0	6.3770	2.5000	0	Yes
GBW07170 b	0.4010	0.0400	6.1741	2.5000	1/10	Yes
GBW07170 c	0.3995	0.0800	6.7128	2.5000	1/5	Yes
GBW07170 d	0.3540	0.1051	6.4275	2.5000	2/7	Yes
RTS-3 a	0.4579	0	6.4104	2.5000	0	No
RTS-3 b	0.4002	0.0402	6.1652	2.5000	1/10	Yes
RTS-3 c	0.4005	0.0802	6.7300	2.5000	1/5	Yes
RTS-3 d	0.3494	0.1049	6.3598	2.5000	2/7	Yes
RTS-2 a	0.3200	0	4.4800	2.5000	0	No
RTS-2 b	0.3252	0.0177	4.8008	2.5000	1/20	Yes
RTS-2 c	0.3126	0.0329	4.8370	2.5000	1/10	Yes
BMZ-90 a	0.3192	0	4.4687	2.5000	0	No
BMZ-90 b	0.3008	0.0154	4.4268	2.5000	1/20	No
BMZ-90 c	0.2920	0.0279	4.4786	2.5000	1/10	No
BMZ-90 d	0.2726	0.0417	4.4002	2.5000	3/20	No
BMZ-90 e	0.2830	0.0553	4.7376	2.5000	1/5	Yes
I14-7 a	0.3159	0	4.4224	2.5000	0	No
I14-7 b	0.3225	0.0166	4.9701	2.5000	1/20	Yes
I14-7 c	0.3212	0.0325	4.4966	2.5000	1/10	Yes

added to the samples, which were then fluxed with $Li_2B_4O_7$. The weight ratio of sample, including SiO_2 content, to flux was 1:14. $LiNO_3$ was added to samples as an oxidant in order to protect the platinum–gold crucibles from corrosion by sulfides. A small amount of 1% LiBr-0.5% NH_4I was added as mixed releasing agent.

A V8C type automatic fusion machine with four stations, auto swirling, shaking, and programmable multi-step temperature control devices, produced by the Analymate Company in China, was used to prepare the glass disks. After pre-oxidation at 580°C for 13 minutes, the temperature was increased to 1100°C for 12 minutes.

The weights of sample, SiO_2, $Li_2B_4O_7$, and $LiNO_3$, as well as the fusion results (success or failure) are listed in Table 1. $LiNO_3$ (2.5 g) was added to fuse glass, as a pre-oxidizing reagent to protect the crucibles from destruction by sulfides. For RTS-2 and I14-7, SiO_2/sample (weight ratio) was larger than 1:20 to guarantee that glass fusion is successful, whereas for GBW07171, GBW07170, and RTS-3, the weight ratio was larger than 1:10, and even up to 1:5 for BMZ-90 (Table 1).

XRF Analysis

Successfully fused glass disks were analyzed by a Rigaku 100e X-ray fluorescence spectrometer in the State Key Laboratory of Isotope Geochemistry, Guangzhou

Institute of Geochemistry, Chinese Academy of Sciences. Detailed working conditions of the XRF, for example, target, spectra, voltage, currency, crystal, 2θ angle, and types of corrections are listed in Table 2.

Table 2. Working conditions of XRF and spectral corrections

										Types of corrections	
Element	Target	Spectra	kV	mA	Crystal	2θ angle	Detector	Time (s)	PHA	Overlap corrections*	Absorption corrections*
Si	Rh	Kβ1	50	50	RX35	15.100	F-PC*	20	100–300	Zn, Pb, Cu Al	
Al	Rh	Kβ1	50	50	RX35	17.700	F-PC	20	99–330		Si, MgO ZnO, CuO
Na	Rh	Kα	40	70	RX35	25.401	F-PC	120	100–300	MgO, S, ZnO, Ni	
Mg	Rh	Kα	40	70	RX35	21.013	F-PC	20	100–300	Al_2O_3, Zn CuPb, Ni Na_2O	
Al	Rh	Kα	40	70	PET	144.655	F-PC	20	100–320	Na_2O, Fe_2O_3	
Si	Rh	Kα	40	70	PET	108.996	F-PC	20	100–300	Pb	
P	Rh	Kα	40	70	Ge	141.039	F-PC	120	119–300		
K	Rh	Kα	50	50	LiF1	136.777	F-PC	40	100–300	Pb	
Ca	Rh	Kα	50	50	LiF1	113.216	F-PC	20	100–300	Ni	
Fe	Rh	Kα	50	50	LiF1	57.501	SC*	20	100–300	CaO, SiO_2 MgO	MnO
Ti	Rh	Kα	50	50	LiF1	86.132	SC	40	100–300	Ba, V	
Mn	Rh	Kα	50	50	LiF1	62.944	SC	60	100–340	Cr, Ba	
V	Rh	Kα	50	50	LiF1	76.900	SC	40	99–330		TiO_2
Cr	Rh	Kα	50	50	LiF1	69.333	SC	30	99–330		V
Co	Rh	Kα	50	50	LiF1	52.759	SC	60	99–320		Fe_2O_3
Ni	Rh	Kα	50	50	LiF1	48.627	SC	30	100–300	Cu	
Cu	Rh	Kα	50	50	LiF1	44.994	SC	30	99–319		
Zn	Rh	Kα	50	50	LiF1	41.763	SC	30	100–300	Cu	
Pb	Rh	Lα	50	50	LiF1	33.903	SC	40	100–300		
S	Rh	Kα	40	70	Ge	110.670	F-PC	40	128–300	Mo, Pb	
Ba	Rh	Lα	50	50	Ge	50.400	SC	120	100–300		
Rb	Rh	Kα	50	50	LiF1	26.592	SC	60	100–300		
Sr	Rh	Kα	50	50	LiF1	25.133	SC	60	100–300		
Rh	Rh	Kα	50	50	LiF1	18.460	SC	20	100–300		
Bi	Rh	Lα	50	50	LiF1	32.993	SC	40	100–300		
Tl	Rh	Lα	50	50	LiF1	34.880	SC	30	100–300		
Mo	Rh	Kα	50	50	LiF1	20.321	SC	40	100–300		
W	Rh	Lα	50	50	LiF1	43.003	SC	40	100–300		
Cu	Rh	Lβ1	50	60	RX35	28.350	F-PC	40	159–300		
Zn	Rh	Lβ1	50	50	RX35	29.750	F-PC	40	100–300		
Br	Rh	Kα	50	50	LiF1	29.954	SC	20	100–300		
Rh	Rh	Lα	50	50	Ge	89.513	F-PC	40	100–300		

*Overlap corrections by intensity, absorption corrections by concentration; SC, scintillation counter; F-PC, gas flow type proportional counter; PHA, pulse height analyzer.

Table 3. Major and trace element results by XRF

Sample No.	Al_2O_3 %	CaO %	$Fe_2O_3^T$ %	MgO %	SiO_2 %	TiO_2 %	Co ppm	Ni ppm	Cu ppm	Zn ppm	S ppm	Bi ppm
GBW07171 b	4.12	16.23	13.50	1.25	35.83	0.14	51	82	4254	84798	68485	547
GBW07171 c	4.07	16.44	13.73	1.39	34.20	0.13	59	105	4417	87711	66770	559
GBW07171 d	4.06	16.82	14.09	1.41	32.97	0.14	58	93	4516	90765	61284	578
Average	4.09	16.50	13.78	1.35	34.33	0.14	56	93	4396	87758	65513	561
RSD (%)*	0.83	1.81	2.16	6.23	4.17	1.57	7.80	12.60	3.00	3.40	5.74	2.78
Recommended value	3.87	15.67	13.97	1.30	36.76	0.13			4700	87100	67700	607
Relative error#	5.57	5.28	−1.39	3.97	−6.60	5.07			−6.47	0.76	−3.23	−7.59
GBW07170 a	4.11	23.46	11.98	2.14	24.64	0.19	204	362	117316	9788	94887	3342
GBW07170 b	4.32	24.12	12.31	2.21	20.76	0.20	221	363	122829	10197	94378	3567
GBW07170 c	4.38	24.27	12.44	2.26	21.93	0.20	214	335	125506	10383	94419	3676
GBW07170 d	4.48	24.63	12.67	2.33	21.53	0.21	222	319	128671	10698	83371	3850
Average	4.32	24.12	12.35	2.23	22.22	0.20	215	345	123581	10266	91764	3609
RSD (%)	3.65	2.03	2.32	3.51	7.61	4.06	3.95	6.25	3.89	3.70	6.10	5.90
Recommended value	4.64	24.49	12.76	2.48	23.12	0.21	221	376	125900	12100	99100	3600
Relative error	−6.82	−1.51	−3.22	−9.92	−3.91	−5.99	−2.52	−8.29	−1.84	−15.16	−7.40	0.25
RTS-3 b	8.56	3.35	30.43	3.81	34.01	0.51	245		2208	1157	88883	145
RTS-3 c	9.49	3.70	33.70	4.18	37.11	0.55	270		2330	1293	9082	133
RTS-3 d	9.57	3.74	34.02	4.34	36.69	0.55	277		2359	1281	4748	127
Average	9.21	3.60	32.72	4.11	35.94	0.54	264		2299	1244	34238	135
RSD (%)	6.11	5.89	6.08	6.65	4.68	4.36	6.34		3.50	6.03	138.37	6.94
Recommended value	9.05	2.95	30.60	4.06	34.22	0.53	260		2820	1850	99800	100
Relative error	1.71	22.11	6.94	1.12	5.00	0.68	1.54		−18	−33	−66	35
RTS-2 b	1.53	0.76	52.91	0.53	8.61	0.27	71	2396	261	N.D.	151292	
RTS-2 c	1.58	0.78	54.25	0.60	8.53	0.28	72	2397	266	N.D.	149516	
Average	1.56	0.77	53.58	0.56	8.57	0.27	71	2396	263		150404	
RSD (%)	2.44	2.10	1.77	8.00	0.67	0.30	1.02	0.02	1.48		0.83	
Recommended value	1.57	0.71	53.47	0.58	6.25	0.27	72	2430	670	117	189500	
Relative error	−0.79	8.41	0.20	−3.09	37.18	3.02	−1.15	−1.39	−60.71		−20.63	
BMZ-90 e	0.13	0.27	52.16	5.64	1.38	0.10	954	22634	12924	N.D.	206198	43
I14-7 b	1.06	0.16	24.53	12.42	28.34	0.11	448	18997	18547	N.D.	75677	21
I14-7 c	1.05	0.14	26.53	12.77	35.79	0.12	482	21459	19455	N.D.	74472	2

*RSD, relative standard deviation, calculated from the results of the same sample; #Relative error, error of average in this study relative to recommended value in literature; N.D., not detected.

RESULTS AND DISCUSSION

Results

The major and trace element results, including Al_2O_3, CaO, $Fe_2O_3^T$, MgO, SiO_2, TiO_2, Co, Ni, Cu, Zn, S, and Bi, are reported in Table 3, together with the recommended values of the reference materials. Relative standard deviations (RSD) for major elements are typically better than 5%, with some 6 to 8% (Fig. 1 and Table 3). The RSD values for trace elements are generally better than 10% (Fig. 2). Compared to the recommended values, the majority of results have relative

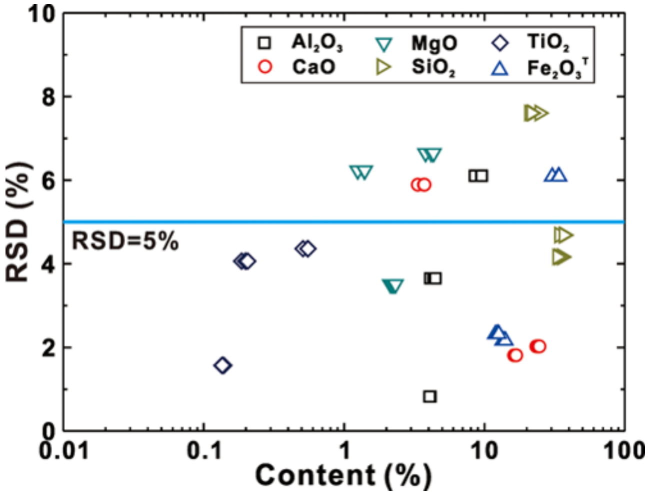

Figure 1. Relative standard deviation (%) vs. percent concentration of major elements.

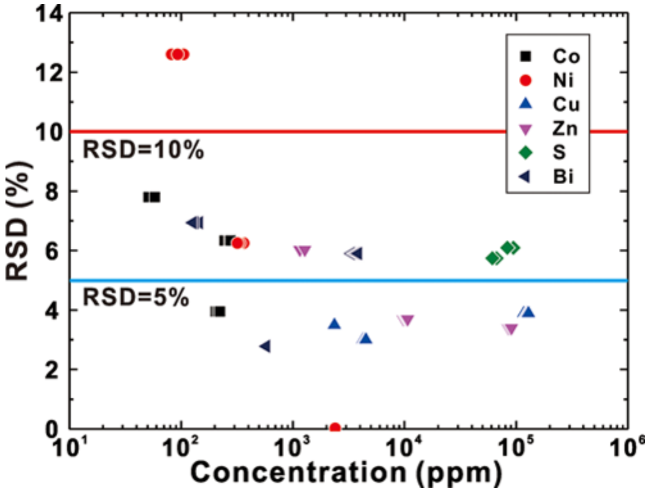

Figure 2. Relative standard deviation (%) vs. parts-per-million concentration of trace elements.

errors lower than 5%. The Chinese National Cu and Zn sulfide reference materials GBW07170 and GBW07171 exhibited reliable results with high precision and accuracy for nearly all elements listed in Table 3, close to the recommended values. Al_2O_3, CaO, $Fe_2O_3^T$, MgO, SiO_2, and TiO_2 contents of RTS-2 and RTS-3, both iron sulfide, also showed high precision and accuracy. The precision of cobalt, nickel, copper, zinc, and bismuth results for RTS-2 and RTS-3 are acceptable, but are far from the recommended values, especially the sulfur results.

Sulfur Loss by Volatilization

Sulfur is volatile during fusion (Baker 1982; Norrish and Thompson 1990) and may escape from the sample as S or SO_2. In this study, the results also showed sulfur loss in some analyses, especially for samples melted for a second or third time. For example, GBW07171 and GBW07170 have sulfur losses of 3.2% and 7.4%, respectively, compared with the recommended values. For iron sulfide reference materials (RTS-2 and RTS-3), the sulfur losses were much larger (Table 3). Sulfur can be determined by the pressed powder pellets method, which has no loss of sulfur.

Function of SiO_2

SiO_2 was shown to be a suitable glassing reagent for sulfide ores (Zhao 2001). Optimum conditions for the production of homogeneous stable glass disks by fusion were established. To fuse glass disks successfully, the weight ratio of SiO_2 to sample for RTS-2 and I14-7 was larger than 1:20, the ratio for GBW07171 and RTS-3 was larger than 1:10, and increases to 1:5 for BMZ-90. Given that RTS-2 and RTS-3 are both iron sulfides, the type of sulfide ores are not the essential reason that requires higher SiO_2 to achieve successful glass disks. Rather, the essential reason involves to sulfur content. The recommended values for these four samples show that increased SiO_2/sample ratios are required with increasing sulfur concentration (Table 3). The sample BMZ-90, which had the highest sulfur concentration (~20%), required the most SiO_2 (SiO_2/sample = 1:5) to fuse a glass disk.

CONCLUSIONS

Successful analysis of sulfide ores was accomplished by XRF. To prepare the glass disks for analysis, variable amounts of SiO_2 were added followed by oxidation using $LiNO_3$ to prevent corrosion of the platinum–gold crucibles. The amount of added SiO_2 varied from 1:20 for samples with low sulfur concentration to 1:5 for samples with high sulfur concentration. The relative standard deviations for major elements were generally better than 5%; for trace elements, better than 10%.

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