Geologica Macedonica, Vol. **21**, pp. 87–91 (2007)
GEOME 2
ISSN 0352 – 1206
Manuscript received: March 30, 2007
UDC: 549.08:553.43(497.7)
Accepted: October 7, 2007

Original scientific paper

ELEMENT COMPOSITION OF SOME COPPER MINERALS FROM THE REPUBLIC OF MACEDONIA*

Radojko Jaćimović[1], Milena Taseska[2], Vekoslava Stibilj[1], Petre Makreski[2], Trajče Stafilov[2], Gligor Jovanovski[2]

[1]*Jožef Stefan Institute,*
P.O. Box 3000, SI-1001 Ljubljana, Slovenia
[2]*Institute of Chemistry, Faculty of Science, SS. Cyril and Methodius University,*
P.O. Box 162, MK-1001 Skopje, Republic of Macedonia
radojko.jacimovic@ijs.si

A b s t r a c t: The trace and major element contents in five copper minerals was determined using the k_0-method of instrumental neutron activation analysis (k_0-INAA). Four of the studied minerals, brochantite [$Cu_4SO_4(OH)_6$], chalcanthite [$CuSO_4 \cdot 5H_2O$], chalcopyrite [$CuFeS_2$] and native Cu were obtained from the Republic of Macedonia, while the fifth mineral, covellite [CuS], was obtained from Bor, Serbia. The total number of elements determined (with intermediate/medium and long half-life radionuclides) in the studied minerals was thirty nine. It was shown that the concentration of Fe is higher compared to the other elements. The contents of As, K, Na and U in brochantite, Ca, Co, Na and Zn in chalcanthite, Ag, As, Se and Zn in chalcopyrite and As and Se in covellite are higher compared to the other investigated trace elements. It was also found that native Cu contains low amounts of trace elements.

Key words: brochantite; chalcanthite; chalcopyrite; covellite; native Cu; composition; Macedonia; k_0-INAA

INTRODUCTION

Minerals are naturally-occurring inorganic substances. Over a long geological period it is not possible to obtain absolutely pure minerals without any contamination. This means that most minerals contain extraneous substances that might change some of their characteristics.

There are a number of elements that are quite easily interchangeable, making the transformation of one mineral into another plausible.

Therefore, there are many reasons to analyze trace elements in minerals, including the determination of their purity, as well as the presence of very rare and important elements that could be extracted and used to obtain important information about the geology of the mines and mineral localities. Copper minerals are widespread and modern civilization and life is heavily dependent on copper and copper products. Copper ore can be found in large deposits, relatively close to the surface, and amenable to relatively low cost bulk mining methods. The combination of its physical properties, abundance, and low cost make it a valuable commodity. Native copper is a relatively rare mineral. Most copper in nature is found in minerals associated with sulfur or in the oxidized products of these minerals. It is very important to know the content of trace elements in its minerals samples since copper is produced from these ore deposits. There are a limited number of studies concerning the determination of elements in similar geological samples by various methods such as atomic absorption spectrometry after the separation and concentration of the elements of interest (Taseska et al., 2005), atomic emission spectrometry with inductively coupled plasma (ICP-AES) (Li et al, 2005) or laser ablation microprobe-inductively coupled plasma-mass spectrometry (LAM-ICP-MS) (Huminicki et al, 2005). Instrumental methods (INAA, XRF, PIXE) are rarely used to determine trace elements due to matrix and inter-element in-

*Dedicated to Academician Bojan Šoptrajanov, the leader of the Spectroscopy Group in Macedonia, on the occasion of his 70th birthday.

terferences and background effects (Todorov T., 1991; Frantz et al., 1994; Jaćimović et al., 2002; Nečemer et al., 2003; Jaćimović et al., 2005).

In this work, the k_0-method of instrumental neutron activation analysis (k_0-INAA) was used for direct determination of major and trace elements in five copper minerals (four from the Republic of Macedonia and one from Serbia).

EXPERIMENTAL

Samples

Brochantite [$Cu_4SO_4(OH)_6$], originated from the Sasa mine, chalcanthite [$CuSO_4 \cdot 5H_2O$], chalcopyrite [$CuFeS_2$] and native Cu were collected from Bučim (both are active mines in the Republic of Macedonia), while covellite [CuS] was collected from Bor, Serbia. Mineral specimens were carefully hand-picked under an optical microscope from the ore samples and ground to powder.

k_0-Instrumental neutron activation analysis (k_0-INAA)

About 100 mg of the powder was sealed into a pure polyethylene ampoule (SPRONK system, Lexmond, The Netherlands). A sample and a standard (Al-0.1%Au IRMM-530 disc 6 mm in diameter and 0.2 mm high) were stacked together and fixed in the polyethylene ampoule in sandwich form and irradiated for 20 hours in the carousel facility (CF) of the 250 kW TRIGA Mark II reactor of the Jožef Stefan Institute with a thermal neutron flux of $1.1 \cdot 10^{12}$ $cm^{-2}s^{-1}$.

The activities of irradiated samples were measured after 6, 14 and 40 days cooling time on absolutely calibrated HPGe detectors (Canberra, USA) (Smodiš et al., 1988) with 45 % relative efficiency. Measurements were performed at such distances that the dead time was kept below 10 % with negligible random coincidences. The HPGe detector was connected to an EG&G ORTEC Spectrum Master high-rate multichannel analyzer.

For peak area evaluation, the HyperLab (HyperLab 2002 System, 2002) program was used. For determination of f (thermal to epithermal flux ratio) and α (parameter which measures the epithermal flux deviation from the ideal 1/E distribution), the "Cd-ratio" method for multimonitor was applied (Jaćimović et al., 2003). The values $f = 28.8$ and $\alpha = -0.005$ were used to calculate the element concentrations. For elemental concentrations and effective solid angle calculations a software package called KAYZERO/SOLCOI® (User's Manual KAYZERO/SOLCOI®, 2003) was employed.

RESULTS AND DISCUSSION

The results of the chemical composition of the investigated copper minerals obtained by k_0-INAA with their 1σ uncertainty (considering net peak area, nuclear data for a particular nuclide, neutron flux parameters, full-energy peak detection efficiency, etc.) are given in Table 1. Due to the relatively favourable nuclear characteristics of copper as the major element (cross-section, abundance, resonance integral), thirty nine elements were determined simultaneously in the studied minerals. It was also found that the contents of the major constituents obtained in all the studied minerals is lower than the expected value calculated from their formulas (brochantite, Cu: 54.99 % theoretical vs. 45.70 % experimental; chalchantite, Cu: 25.45 % theoretical vs. 20.80 % experimental, covellite, Cu: 66.50 % theoretical vs. 63.71 % experimental; native copper, Cu: 100 % theoretical vs. 89.45 % experimental and chalcopyrite, Cu: 34.6 % theoretical vs. 31.91 % experimental). It should be mentioned that in chalcopyrite [$CuFeS_2$] we obtained a little higher value for Fe compared to the formula (Fe: 30.4 % theoretical vs. 31.92 % experimental), but this could be due to experimental error in the method used. It was found that chalcopyrite from the Bučim mine is a relatively pure material. This cannot be stated for the chalcopyrite obtained from the Sasa mine, where the contents of the major constituents are lower than the expected values calculated from their formulas (Cu: 34.6 % theoretical vs. 25.68 % experimental; Fe: 30.4 % theoretical vs. 24.16 % experimental) (Jaćimović et al., 2005) which confirms that the impurities are present.

A comparison of the contents of the investigated elements obtained in this work (k_0-INAA) has shown that the content of Fe is higher than of other elements in all samples. The concentration of As and Se in covellite, of As, K, Na and U in brochantite, of Ca, Co, Na and Zn in chalcanthite and Ag, As, Se and Zn in chalcopyrite is higher compared to the other investigated trace elements. In the case of native Cu, most of the investigated elements (except Fe) are present in the order of a few mg/kg (Table 1). The validated k_0-INAA technique (Jaćimović et al., 2002; Jaćimović at al., 2003) was tested by its application to certified and reference materials from different producers (IRMM, NIST, IAEA, etc.).

Table 1

Chemical composition of the investigated copper minerals (mg/kg)

El.	Native Cu (Bučim)		Chalcanthite $CuSO_4 \cdot 5H_2O$ (Bučim)		Chalcopyrite $CuFeS_2$ (Bučim)		Brochantite $Cu_4SO_4(OH)_6$ (Sasa)		Covellite CuS (Bor, Serbia)	
	Content	Unc.	Content	Unc.	Content	Unc.	Content	Unc.	Content	Unc.
Ag	0.16	0.01	< 0.4		96.6	2.8	0.71	0.04	0.96	0.04
As	< 0.76		2.78	0.23	140	5	70.7	2.6	110	4
Au	0.0060	0.0002	0.0062	0.0004	15.5	0.5	0.187	0.007	0.252	0.009
Ba	< 1		< 15		< 21		< 7		< 4	
Br	1.04	0.06	0.76	0.16	1.44	0.10	2.54	0.23	0.28	0.06
Ca	< 85		1698	340	< 1900		< 448		< 326	
Cd	< 0.3		< 3		< 5		< 3		< 2	
Ce	0.17	0.02	19.2	0.7	6.75	0.33	7.82	0.59	< 0.35	
Co	1.42	0.05	238	8	63.7	2.2	1.08	0.04	1.19	0.04
Cr	5.28	0.28	7.45	0.44	1.25	0.20	6.68	0.39	2.60	0.19
Cs	0.012	0.002	0.24	0.02	< 0.1		0.36	0.01	< 0.01	
Cu	894516	33101	207919	8127	319087	11942	457317	17328	637133	23685
Eu	0.042	0.005	1.65	0.07	0.080	0.005	0.95	0.04	< 0.004	
Fe	135	5	1944	70	319173	11172	936	34	1404	49
Ga	< 30		< 26		< 43		< 24		< 12	
Hf	< 0.003		0.087	0.014	< 0.1		0.112	0.008	< 0.018	
Hg	0.062	0.004	< 0.21		< 1		< 2.7		4.21	0.19
In	< 0.1		< 1		5.98	0.33	< 0.8		< 0.7	
K	< 2577		< 2187		< 1900		2010	402	< 1701	
La	< 0.03		3.70	0.24	3.31	0.14	5.94	1.13	< 0.02	
Mo	< 0.2		< 2		< 2.7		< 2		< 1	
Na	26.4	4.0	616	23	81.5	4.3	106	5	15.7	2.4
Nd	0.32	0.07	27.4	1	< 2.7		9.25	0.5	< 1	
Rb	< 0.14		4.35	1.03	< 6		11.8	0.5	< 0.4	
Sb	0.016	0.001	0.144	0.026	0.22	0.01	0.28	0.01	0.61	0.02
Sc	0.050	0.002	0.429	0.015	0.37	0.01	0.160	0.006	0.0040	0.0002
Se	0.18	0.01	2.15	0.12	49.3	1.7	17.9	0.7	67.5	2.4
Sm	0.15	0.01	11.3	0.5	0.80	0.04	6.08	0.3	< 0.027	
Sn	< 3		< 31		37.3	7.5	< 15		< 10	
Sr	< 3		< 38		< 62		< 17		< 7	
Ta	< 0.005		< 0.02		< 0.1		< 0.02		< 0.01	
Tb	0.096	0.003	2.38	0.08	0.100	0.007	1.20	0.04	<0.01	
Te	< 0.12		< 1.44		8.15	0.46	< 0.84		2.88	0.19
Th	0.69	0.02	3.61	0.13	< 0.01		2.05	0.07	< 0.03	
U	1.30	0.12	23.3	0.9	0.29	0.03	126	5	< 0.18	
W	< 2.38		< 1.08		20.5	0.9	2.64	0.49	< 1.66	
Yb	0.76	0.03	9.84	0.35	0.14	0.01	1.94	0.07	< 0.03	
Zn	3.05	0.12	59.9	2.4	195	7	2.73	0.18	2.48	0.14
Zr	< 3		< 45		< 102		< 14		< 6	

CONCLUSION

The k_0-method of instrumental neutron activation analysis was successfully applied for the determination of thirty nine elements in five copper minerals: brochantite [$Cu_4SO_4(OH)_6$], chalcanthite [$CuSO_4 \cdot 5H_2O$], chalcopyrite [$CuFeS_2$], native Cu and covellite [CuS]. Excellent homogeneity within each sample was observed. The content of Fe is higher than the other trace elements. The concentrations of the trace elements As and Se in covellite, of As, K, Na and U in brochantite, of Ca, Co, Na and Zn in chalcanthite and of Ag, As, Se and Zn in chalcopyrite are higher compared to the other investigated elements. In the case of native Cu, most of the investigated elements (except Fe) are present in the order of a few mg/kg.

Acknowledgment; The authors are grateful for financial support from the Ministry of Education and Science of the Republic of Macedonia and the Ministry of High Education, Science and Technology of the Republic of Slovenia.

REFERENCES

Frantz E., Palme H., Wolfgang T., El Goresy A., Pavićević M., 1994: Geochemistry of Tl-As minerals and host rocks at Allchar (Macedonia), *N. Jb. Miner. Abh*, **167**, 359–399.

Huminicki M. A. E., Sylvester P. J., Carbi L. J, Lesher C. M., Tubrett M., 2005: Quantitative hass balance of platinum group elements in the Kelly Lake Ni-Cu-PGE deposit Copper Cliff offset, Sudbury, *Economic Geology*, **100,**1631–1646.

HyperLab 2002 System, 2002: *Installation and quick start guide*, HyperLabs Software, Budapest, Hungary.

Jaćimović R., Lazaru A., Mihajlović D., Ilić R., Stafilov T., 2002: Determination of major and trace elements in some minerals by k_0-instrumental neutron activation analysis, *J. Radioanal. Nucl. Chem.*, **253**, 427–434.

Jaćimović R., Smodiš B., Bučar T., Stegnar P., 2003: k_0-NAA quality assessment by analysis of different certified reference materials using the KAYZERO/SOLCOI software. *J. Radioanal. Nucl. Chem.*, **257**, 659–663.

Jaćimović R., Makreski P. Stibilj V., Stafilov T., Jovanovski G., Characterization of some iron minerals from the Republic of Macedonia using instrumental neutron activation analysis, *Geologica Macedonica*, **19**, 33–38 (2005).

Li Q. L., Zhu J. X., Ying Q., Mao Z. W., Wang C. S., Chen J. L., 2005: The application of trace element analysis to the study of provenance of copper minerals in ancient bronzes, *Spectroscopy and Spectral analysis*, **25**, 1700–1702.

Nečemer, M., Kump P., Rajčevič M., Jaćimović R., Budič B., Ponikvar M., 2003: Determination of sulfur and chlorine in fodder by X-ray fluorescence spectral analysis and comparison with other analytical methods, *Spectrochim. Acta*, **58B**, 1367–1373.

Smodiš B., Jaćimović R., Jovanović S., Stegnar P., Vukotić P., 1988: Efficiency characterisation of HP Ge detectors for use in the k_0-method of neutron activation analysis, *Vestn. Slov. Kem. Druš.*, **35**, 397–408.

Taseska M., Stafilov T., Makreski P., Jovanovski G., 2005: Determination of trace elements in some copper minerals by atomic absorption spectrometry, *Ovidius University Annals of Chemistry*, **16**, 43–46.

Todorov T., 1991: NAA analysis of gold in minerals from upper cretaceous massive copper-deposits in Bulgaria, *Terra Nova,* **3,** 311-316.

User's Manual KAYZERO/SOLCOI® Version 5a software package, 2003: *KAYZERO/SOLCOI for reactor neutron activation analysis (NAA) using the k_0 standardization method*, Published by DSM Research, Geleen (NL), developed at the INW-RUG, Gent (B) and the KFKI, Budapest (H).

Р е з и м е

ХЕМИСКИ СОСТАВ НА НЕКОИ БАКАРНИ МИНЕРАЛИ ОД РЕПУБЛИКА МАКЕДОНИЈА

Радојко Јаќимовиќ[1], Милена Тасеска[2], Векослава Стибиљ[1], Петре Макрески[2] Трајче Стафилов[2], Глигор Јовановски[2]

[1]*Институт „Јожеф Стефан“,*
п. фах 3000, 1001 Љубљана, Словенија
[2]*Институт за хемија, Природно-математички факултет, Универзитет „Св. Кирил и Методиј“,*
п. фах 162, МК-1001 Скопје, Република Македонија
radojko.jacimovic@ijs.si

Клучни зборови: брошантит; халкантит; халкопирит; ковелин; самороден бакар, хемиски состав; k_0-ИНАА

Определена е содржината на главните составни елементи, како и на елементите во траги во пет бакарни минерали со примена на k_0-инструменталната неутронска активациона анализа. Четири од изучуваните минерали, бро-

шантит, $Cu_4SO_4(OH)_6$, халкантит, $CuSO_4 \cdot 5H_2O$, халкопирит, $CuFeS_2$, и самороден Cu се од Република Македонија, додека ковелинот (CuS) е од Бор, Србија. Вкупниот број на определени елементи (со кратко и долго полувреме на распаѓање на радионуклидите) во испитуваните минерали изнесува триесет и девет. Најдено е дека содржината на Fe е поголена во споредба со содржината на другите елементи. Содржината на As, K, Na и U во брошантитот, на Ca, Co, Na и Zn во халкантитот, на Ag, As, Se и Zn во халкопиритот и на As и Se во ковелинот е поголема од другите испитувани елементи во траги. Исто така е утврдено дека самородниот Cu има многу ниски содржини на елементите во траги.