

## CHARACTERIZATION OF SOME IRON MINERALS FROM THE REPUBLIC OF MACEDONIA USING INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS

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**Abstract:** The major and trace element contents in three iron minerals collected from localities in the Republic of Macedonia using the  $k_0$ -method of instrumental neutron activation analysis ( $k_0$ -INAA) were determined. Two of them belong to the sulphide group [pyrite ( $\text{FeS}_2$ ) and chalcopyrite ( $\text{CuFeS}_2$ )], whereas the third one is an oxide mineral [hematite ( $\text{Fe}_2\text{O}_3$ )]. The total number of elements determined (with intermediate/medium and long half-life radionuclides) in the studied minerals was thirty nine. It was observed that the content of As, Se and Te in pyrite and of Ag, Cd and Zn in chalcopyrite, both from the Bučim locality, is higher compared to the other investigated trace elements. It was also found that hematite from Damjan contains lower amounts of trace elements.

**Key words:** pyrite; chalcopyrite; hematite; Macedonia;  $k_0$ -INAA

### INTRODUCTION

Although minerals are naturally-occurring inorganic substances with a definite chemical composition (and physical properties), they contain traces of other elements that could change some of their characteristics. Also, a variety of minerals are quite easily interchangeable, making it possible for one mineral to grade into another.

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 which could be extracted and used to obtain very important information on the geology of the mines and mineral localities.

Investigation of the purity of iron minerals is very important because of their utilization in iron and steel production. There are a number of studies concerning the determination of elements in similar geological samples by atomic absorption spectrometry, directly from the sample solution (Dulski & Bixler, 1977; Schrön et al., 1983; Castillo et al.,

1988; Barros, 1989; Lazaru & Stafilov, 1993; Stafilov, 2000), or after the separation and concentration of the elements of interest (Viets et al., 1984a; Viets et al., 1984b; Eidecker & Jackwerth, 1988; Stafilov et al., 1993; Kabil et al., 1996; Lazaru & Stafilov, 1998; Stafilov, 2000; Zendelovska & Stafilov, 2001). Instrumental methods (INAA, XRF, PIXE) are rarely used to determine trace elements due to matrix and inter-element interferences and background effects (Frantz et al., 1994; Jaćimović et al., 2002; Nečemer et al., 2003).

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 the investigated minerals without digestion of the sample. Due to the relatively favourable nuclear characteristics of the iron as a major element (cross-section, abundance, resonance integral), the number of elements determined simultaneously in the studied minerals was thirty nine.

## EXPERIMENTAL

*Samples*

Pyrite ( $\text{FeS}_2$ ), chalcopyrite ( $\text{CuFeS}_2$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ) mineral samples were collected from Bučim, Sasa (active mines) and Damjan (non-active). Mineral specimens were carefully hand-picked under an optical microscope from the ore samples and ground to powder.

 *$k_0$ -instrumental neutron activation analysis*

About 100 mg of 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 of 6 mm in diameter and 0.2 mm high) were stacked together and fixed in the polyethylene ampoule in sandwich form and irradiated for 17 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  $1.1 \cdot 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$ .

The activities of irradiated samples were measured after 7, 14 and 40 days cooling time on two absolutely calibrated HPGe detectors (Ortec

and Canberra, USA) (Smodiš et al., 1988) with 45 and 40 % relative efficiency. Measurements were performed at such distances that the dead time was kept below 10 % with negligible random coincidences. The detector with a 45 % relative efficiency was connected to an EG&G ORTEC Spectrum Master high-rate multichannel analyzer, while the detector with 40 % relative efficiency was connected to a CANBERRA S100 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  $\alpha$  (parameter which measures the epithermal flux deviation from the ideal  $1/E$  distribution), the "Cd-ratio" method for multi monitor is 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) is employed.

## RESULTS AND DISCUSSION

The results of the chemical composition of investigated iron minerals obtained by  $k_0$ -INAA are given with their  $1\sigma$  uncertainty (net peak area, nuclear data for particular nuclide, neutron flux parameters, full-energy peak detection efficiency, etc.) in Table 1. In order to test the homogeneity of each mineral, three independent measurements were made. The repeatability for the selected elements is presented in Table 2. It is evident that homogeneity is satisfactory for each mineral because the standard deviation is lower than uncertainty obtained by the  $k_0$ -INAA method (Table 1).

It was also found that the content of the major constituents obtained in all studied minerals is remarkably lower than the expected value calculated from their formulas (pyrite, Fe: 46.5 % – theoretical vs. 34.0 % – experimental; chalcopyrite, Fe: 30.4 % – theoretical vs. 24.2 % – experimental; Cu: 34.6 % – theoretical vs. 25.7 % – experimental; hematite Fe: 69.9 % – theoretical vs. 60.3 % experimental). The content of the trace elements As, Se and Te in pyrite and of Ag, Cd, and Zn in chalcopyrite is higher than the remaining determined trace elements. This is not the case with hematite, where most of the investigated elements are present in the order of a few mg/kg (Table 1).

A comparison of the contents of Ag, Cd, Co, Cr and Zn obtained in this work ( $k_0$ -INAA) with other results for the corresponding iron minerals from Macedonia (Makreski et al., 2002; Stašilov & Zendelovska, 2002; Makreski et al., 2004; Taseska et al., 2005) is presented in Table 3. As seen from the Table, the content of Ag, Cd, Co, Cr and Zn is related to the origin of the minerals and the mineralization of its locality. Therefore, the contents of Ag, Cd and Zn in pyrite and chalcopyrite from Sasa are evidently higher compared to the corresponding values for the mineral samples collected in the Bučim locality (three different mineral samples). The higher content of Zn could be related to the contamination with sphalerite mineral ( $\text{ZnS}$ ) which is a major constituent in the Sasa mineralization (Dolenec et al., 2003). In this manner, the significant presence of Ag and Cd is also characteristic of this deposit (Aleksandrov et al., 1998).

On the other hand, the high content of Co in hematite from Ržanovo (two different samples) (390 mg/kg) is related to the abundance of Co in Fe/Ni mineralization (Boev & Stojanov, 1985; Boev & Janković, 1996).

Table 1

## Chemical composition of the investigated iron minerals (mg/kg)

El.	Minerals					
	Pyrite (FeS <sub>2</sub> )		Chalcopyrite (CuFeS <sub>2</sub> )		Hematite (Fe <sub>2</sub> O <sub>3</sub> )	
	Content	Uncertainty	Content	Uncertainty	Content	Uncertainty
Ag	6.77	0.25	378	13	< 0.4	
As	1 200	42	15.0	0.7	33.3	1.2
Au	2.14	0.08	0.0169	0.0014	< 0.003	
Ba	< 13.6		< 28		89.5	8.9
Br	2.78	0.17	< 0.7		8.02	0.32
Ca	< 1 615		< 1 523		< 1427	
Cd	< 4.8		90.1	3.5	< 4.1	
Ce	< 1.1		< 1.0		11.9	0.5
Co	18.3	0.6	28.9	1.0	3.64	0.13
Cr	9.98	0.68	30.0	1.9	29.3	2.1
Cs	< 0.10		< 0.09		0.41	0.04
Cu	< 278		256 829	9 627	< 668	
Eu	< 0.01		< 0.02		0.47	0.07
Fe	339 574	11 899	241 616	8 465	603 051	21 122
Ga	< 18		< 20		< 16	
Hf	< 0.1		< 0.2		< 0.2	
Hg	< 0.4		0.32	0.08	< 0.6	
In	< 2		10.4	0.6	< 3.0	
K	< 1 306		< 1 571		728	182
La	0.25	0.01	< 0.06		16.1	0.6
Mo	2.45	0.44	5.62	0.71	7.38	0.55
Na	47.3	2.6	26.5	2.6	37.4	3.0
Nd	< 2.6		< 2		10.1	2.1
Rb	< 5.3		< 5		< 6.9	
Sb	1.77	0.07	4.55	0.17	8.02	0.29
Sc	0.051	0.003	< 0.01		0.58	0.02
Se	27.5	1.0	0.67	0.17	< 0.9	
Sm	0.073	0.007	< 0.04		1.95	0.08
Sn	< 60		< 54		< 56.4	
Sr	< 65		< 79		117	27
Ta	< 0.03		< 0.06		< 0.1	
Tb	< 0.05		< 0.07		0.34	0.02
Te	36.9	1.5	< 3		< 1.8	
Th	< 0.07		< 0.11		0.12	0.02
U	< 0.14		< 0.3		1.87	0.08
W	< 0.66		5.18	0.60	8.64	0.47
Yb	< 0.11		< 0.1		0.30	0.03
Zn	3.57	0.89	6 836	241	22.0	1.7
Zr	< 60		< 83		< 165	

Table 2

*Homogeneity for selected elements in the iron minerals under investigation obtained from three independent measurements (mg/kg)*

El.	Minerals					
	Pyrite (FeS <sub>2</sub> )		Chalcopyrite (CuFeS <sub>2</sub> )		Hematite (Fe <sub>2</sub> O <sub>3</sub> )	
	Content	SD <sup>a</sup>	Content	SD	Content	SD
Ag			380	2		
As	1 188	16	15.1	0.4	33.3	0.1
Au	2.04	0.09				
Br	2.56	0.37			7.83	0.43
Cd			90.1	3.5		
Co	18.1	0.1	30.0	1.9	3.57	0.10
Cr	9.24	0.69			28.8	0.8
Cu			256 410	3 682		
Fe	335 946	3 380	242 467	901	602 585	579
Na	41.9	5.1	24.6	1.8	35.5	1.8
Sb	1.80	0.16	4.61	0.07	8.05	0.03
Se	26.1	1.4				
Sm	0.072	0.001			1.98	0.03
Te	35.0	2.4				
W			5.27	0.09	8.39	0.23
Zn			6 910	89		

<sup>a</sup> SD = standard deviation

Table 3

*Comparison of results obtained for Ag, Cd, Co, Cr and Zn in investigated iron minerals with literature data (mg/kg)*

Mineral	Locality	Elements					Reference
		Ag	Cd	Co	Cr	Zn	
Pyrite	Bučim	6.77	< 5	18.1	9.24	3.57	This work
	Bučim	0.13	0.52	17.3	9.2	249	Makreski et al., 2002
	Bučim			36.8	11.6	39.0	Stafilov & Zendelovska, 2002
	Sasa	29.0	142.0	< 0.01	58.9	175 300	Makreski et al., 2002
Chalcopyrite	Sasa	378	90.1	28.9	30.0	6 836	This work
	Bučim		54.9	19.5	80.3	947	Taseska et al., 2005
Hematite	Damjan	< 0.4	< 4	3.64	29.3	22.0	This work
	Damjan	< 0.05	< 0.05	0.53	18.2	138	Makreski et al., 2002
	Damjan	3.7	0.9	3.9		114	Makreski et al., 2004
	Damjan			1.79	16.4		Stafilov & Zendelovska, 2002
	Ržanovo					128	Stafilov & Zendelovska, 2002
	Ržanovo	0.9	< 0.05	390		125	Makreski et al., 2004

## CONCLUSION

The  $k_0$ -method of instrumental neutron activation analysis method was successfully applied for the determination of thirty nine elements in three iron minerals (pyrite, chalcopyrite and hematite) from the Republic of Macedonia. Although excellent homogeneity within each sample was observed, the content of the trace elements As, Se and Te in pyrite and Ag, Cd, and Zn in chalcopyrite is higher than the remaining determined trace elements. On the other hand, most of the investi-

gated elements in the hematite mineral specimen are present in the order of a few mg/kg (Table 1). The content of some of the investigated elements is related to the origin of the mineral and the mineralization of its locality.

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## Резиме

## КАРАКТЕРИЗАЦИЈА НА НЕКОИ ЖЕЛЕЗНИ МИНЕРАЛИ ОД РЕПУБЛИКА МАКЕДОНИЈА СО ПРИМЕНА НА ИНСТРУМЕНТАЛНА НЕУТРОНСКА АКТИВАЦИОНА АНАЛИЗА

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Клучни зборови: пирит; халкопирит; хематит; Македонија;  $k_0$ -INAA

Со  $k_0$ -инструментална неутронска активациона анализа е определена содржината на главните составни елементи, како и на елементите во траги во три железни минерали од локалитети од Република Македонија. Притоа два од минералите ѝ припаѓаат на сулфидната група [пирит ( $\text{FeS}_2$ ) и халкопирит ( $\text{CuFeS}_2$ )], а третиот е оксиден минерал [хематит ( $\text{Fe}_2\text{O}_3$ )]. Вкупниот број на определени елементи (со кратко и долго

полувреме на распаѓање на радиоуклидите) изнесува тринаесет и девет. Најдено е дека содржината на As, Se и Te во пиритот и Ag, Cd и Zn во халкопиритот (земени од локалитетот Бучим) е повисока споредена со другите испитувани елементи во траги. Кај хематитот од Дамјан е најдено помало присуство на елементите во траги.