Vol.3 No.3 NUCLEAR SCIENCE AND TECHNIQUES Aug. 1992

A TOTAL CONTENT X– RAY FLUORESCENCE METHOD FOR COPPER PROSPECTING

Zhou Sichun (周四春), Xie Tingzhou (谢庭周) and Ge Liangquan (葛良全)

(Chengdu College of Geology, Chengdu 610059, China)

(Received September 1991)

ABSTRACT

A new method is proposed to prospect copper deposits with portable XRF analyzer. The method is based on the close relation between Cu and the chalcophile elements or some other elements in the geochemical anomalies of a Cu deposit. Applications of the technique in Northeast China are presented.

Keywords: Portable X-ray fluorescence analyzers Total content X-ray fluorescence method Prospecting for copper deposits

1 INTRODUCTION

An X-ray fluorescence (XRF) analyzer for geological survey enables one to do quick measurements with low cost *in situ*[1]. In searching for some mineral deposits, the method has been in great success from either geological or economic point of view. But so far it has made little progress in prospecting a copper deposit in China, due to the fact that a home-made portable XRF analyzer possesses an MDL (minimum detection limit) of only 100— 200 ppm, whereas the Cu Clarke value, i.e. the elemental abundance in the earth crust, is about 55 ppm[2]. In most cases, one is not able to find a copper deposit by detecting just the copper itself.

Based on principles of exploration geochemistry, we propose in this paper the total content XRF method to prospect copper deposits by detecting all the indicator elements. The physics and relevent techniques to realize the method are given, too.

2 GEOLOGICAL CONDITIONS FOR Cu PROSPECTING WITH XRF

It is seldom the case that a mineral deposit contains only one metal element, such as copper. Under a number of geological and geochemical conditions, the copper mineralizations are seen with groups of elements that feature the geochemical anomalies. Generally, there are seven types of copper deposits in the natural world[3] (see Table 1).

From Table 1, one finds that the chalcophile elements coexist with Cu in any of the copper deposits, which have a similar geochemical nature due to the same structures ($s^2p^6d^{10}$). Under most geophysical and geochemical circumstances, there are strong affinity between the chalcophile elements and the elements of the oxygen family, i.e. S, Se and Te, the sulphides or complicated sulphides of the chalcophile elements would be formed in a copper deposit. Therefore, chalcophile elements are desirable indicators to the copper. Something of note, too, is the transitional elements of Co and Ni. Both of them exist in all the geochemical anomalies of the copper deposits, and their Clarke values are high. Apparently, they are suitable indicators for Cu prospecting with the XRF method.

Table 1

Association of elements in geochemical anomalies of copper deposits[2-4]

Type of deposits	Association of elements
1. Shale copper deposits and their metamorphic ones	Cu, Ag, Zn, Cd, Pb, Mo, Re, Co, Ni, V, Mn, Se, As, Sb, Ba
2. Copper deposits in sandstone, arenaceous shale and conglomerate	Cu, Ag, Pb, Zn, Cd, Hg, V, U, Ni, Co, P, Cr, Mo, Re, Se, As, Sb, Mn, Ba
3. Porphyry copper deposits	Cu, Mo, Re, Fe, Ag, Au, As, Pb, Zn, B, Sb, W, K, Rb, Ba, Mn, Hg, Ni, Co
4. Skarn copper deposits	Cu, Fe, Mn, Zn, Pb, Ag, Cd, Mo, W, Au, Sn, Bi, Te, As, Ni, Co
5. Compact mass bearing-copper sulphides related to (ultra) basic rock	Cu, Ni, Co, Fe, As, Pt family, Au, Ag, Bi, Se, Te
6. Compact mass bearing-copper sulphides in volcanic sedimentary rocks	Cu, Zn, Pb, Cd, Ag, Fe, Hg, As, Sb, Au, Mo, W, Re, Co, Ni, B, Ga, In, Tl, Ge, Sn, Bi, Se, Te
7. Vein-typer copper deposits in different geological environments	Cu, Zn, Pb, Cd, Ag, Fe, Hg, As, Sb, Au, Mo, W, Re, Co, Ni, B, Ga, In, Tl, Ge, Sn, Bi, Se, Te

According to these facts, we developed the total content XRF method to measure the characteristic X-rays from an indicator group, such as Cu+Zn+Hg+As+Pb+Bi + Se, so as to solve the problems in Cu prospecting imposed by the MDL of an XRF analyzer. With this method, one is able to find out the geochemical anomalies of certain copper deposits.

The indicator elements in Table 1 can be divided into three groups as in Table 2. For each of the indicator group, it is practical for a portable XRF analyzer to detect the elements. From the information given in Ref.[2], the sum of the Clarke values of the elements in group I is about 240 ppm, which is higher than the MDL of an XRF analyzer. Thus, the XRF analyzer is well capable of determining the background values by measuring the group I elements. Practically, the occurance of a copper deposit is commonly seen in the areas where the background value of each element in the group is higher than its Clarke value. So, the total content is generally high enough to allow fast surveying for the copper deposits. For example, the second type of the copper deposits in Table 1 is always related to some special copper-bearing formations. Statistics indicate that the sandstones in China contain more than 100 ppm of Cu, and the abundances of Pb, Zn, Ag, As and Ni are much higher than their Clarke values[2].

Similarly, one is able to prospect a copper deposit by measuring the total content of the elements in group Ⅱ.

Table 2

Indicator element groups of copper deposits

Group	Indicator elements	Type of deposits
Ⅰ	Co, Ni, Cu, W, Zn, Hg, As, Pb, Bi, Se	1, 2, 3, 4, 6, 7
Ⅱ	Ag, Cd, In, Sn, Sb, Te, I, Ba	1, 2, 3
Ⅲ	Cu, Ni, Co	5

The third group of the indicator elements is designed to prospect the fifth type of the copper deposits, which are related to ultra basic and basic rocks. Cu-Ni deposits are commonly seen in this type of geological formations. Nickel usually exists in some form of sulphide. The Ni concentration and dispersion in magma are closely correlated with sulphur. With magmas of high S concentrations, Ni combines firstly with S, and then with Co, Cu and some Fe to form molten sulphides. As the magma becomes cooler, the molten sulphides tend to separate from silicates, and Cu-Ni deposits are formed under certain conditions. These deposits are characterized by their high contents of Ni, Co, and Cu, with the sum of their abundances well exceeding 300 ppm, or even more higher than the MDL of a portable XRF analyzer.

3 XRF METHOD AND APPLICATIONS

It has been proved that there is approximately a linear relation between the XRF intensity (I_i) from an element and its content (C_i) in a sample[5].

$$I_i = a_i + b_i C_i \tag{1}$$

where a_i and b_i are the intercept and the slope of the function. Therefore, for the same sample, the total XRF intensities and the elemental contents can be expressed as

$$\Sigma_{i=1}^{n} I_i = \Sigma(a_i + b_i C_i) = A + \Sigma b_i C_i \tag{2}$$

where $A = \Sigma a_i$. If the indicator elements in the Cu deposits are grouped in such a way that the energies of the characteristic X-ray are close to each other, the excitation functions and the detection efficiencies would be similar under the same measuring conditions (the source, detector and geometry). Thus, one has

$$b_1 \approx b_2 \approx b_3 \approx \cdots \approx b_n = B \tag{3}$$

and

$$\Sigma I_i = A + B \Sigma C_i \tag{4}$$

If A and B are determined experimentally, one is able to know, by measuring the total intensities, the total contents of the indicator group, hence the deposits.

Table 3

XRF parameters of different group of indicator elements

Element	$\text{Co}^{\mathrm{I,III}}$	$\text{Ni}^{\mathrm{I,III}}$	$\text{Cu}^{\mathrm{I,III}}$	W^{I}	Zn^{I}	Hg^{I}	As^{I}	Pb^{I}	Bi^{I}
Absorption edge (keV)	7.709	8.331	8.980	12.090	9.660	14.841	11.863	15.870	16.393
XRF (keV)	6.930	7.477	8.047	8.396	8.638	9.987	10.543	10.549	10.836
Element	Se^{I}	Ag^{II}	Cd^{II}	In^{II}	Sn^{II}	Sb^{II}	Te^{II}	I^{II}	Ba^{II}
Absorption edge (keV)	12.652	25.517	26.712	27.928	29.190	30.480	31.809	33.164	37.410
XRF (keV)	11.221	22.162	23.172	24.207	25.270	26.357	27.471	28.610	32.191

Notes: mark Ⅰ, Ⅱ, Ⅲ express the first, second and third group respectively

The elements in Table 2 are divided into groups according to the above assumption and the characteristic X-rays could be measured from the elements in each of the groups(see Table 3). For group Ⅰ, the characteristic energies are between 6.930 and 11.221 keV. X-rays from the group Ⅰ elements can be measured with a filter made of oxides of Mn and As, which offers a pass band from 6.537 to 11.863 keV (see Fig.1). To detect the elements in group Ⅱ and Ⅲ, Ru/I and Mn/Ni filters are used, and their absorption edges are at 22.118— 33.164 keV and 6.537— 8.331 keV, respectively.

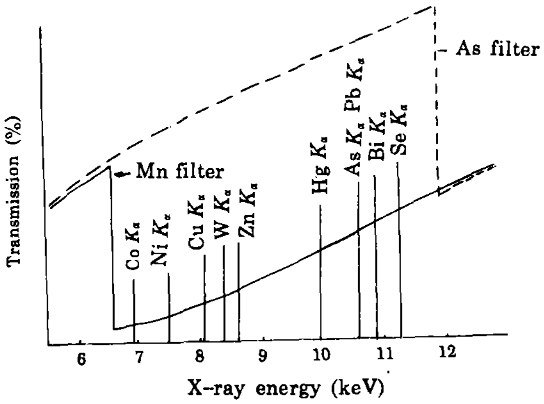

Fig.1 Principle of measuring total contents of the elements in group Ⅰ with the balanced filter

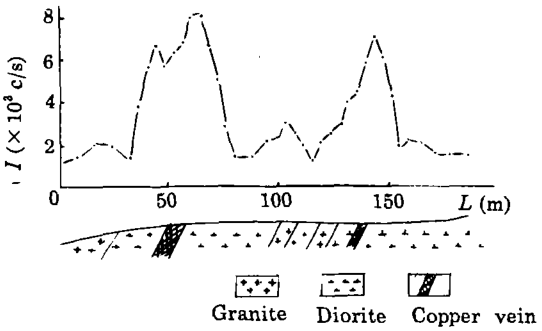

Fig.2 Section of the total XRF intensities measured in situ on survey line 1

The total content XRF method has been applied to several Cu prospecting projects and the results have been encouraging. In one of the field surveys in Northeast China, three survey lines were designed on the major veins of a geological structure. All the lines were perpendicular to the run of the veins. The measurements were carried out on bedrocks with a portable XRF analyzer (model HYX-1). According to the deposit type, we selected the group Ⅰ elements as indicators. Fig.2 is a section of the total XRF intensities. The statistical results of the three survey lines are given in Table 4. The results show that the total intensities of the characteristic X-rays are much higher than normal in areas of the copper mineralizations or ore veins. The ratios of the anomaly to background range from 3.55 to 6.95. Therefore, positions of the mineralizations or veins could be exactly determined by the anomalies observed.

Table 4

Statistical results of measurement on survey lines

Survey line	XRF intensities(Relative value) Background area	 Average value above mineralization area	Notes
1	0.9—3.0	6.39	Areal background: 1.8
2	0.6—2.8	8.21	Minimum of anomaly: 3.0
3	0.7—2.7	12.51	

4 DISCUSSION

The total content XRF method could achieve good geological benefits, as is described above. But one should notice that copper deposits usually occur in high Cu abundance areas. For some porphyry copper deposits, the minimum of the geochemical Cu anomalies may be over 100 ppm. If special measuring techniques are used, portable XRF analyzers are capable of detecting this level of copper contents. There are some other examples that the minimum Cu anomalies are higher than the MDL of an XRF analyzer. Therefore, it is necessary to do some experiments to select the simplest and the most effective technique for Cu prospecting in a new survey area.

On the other hand, one should choose the correct methods for field work of Cu prospecting with an XRF analyzer. This refers to different plans of the measuring technique, such as whether you are to measure powder samples or the soil *in situ,* how to correct geometry effects and matrix effects, how to design the survey points, *etc.* All these problems should be solved with a series of experiments. And when you do so, you go with success.

REFERENCES

[1] Zhang Ye, Li Shuyi. Contributions to the exploration geophysics and geochemistry, special issue– nuclear geophysical exploration. Beijing: Geological Publishing House, 1986.

[2] Liu Yingjun, Qiu Detong, Zhou Yadong *et al.* Exploration geochemistry. Beijing: Science Press, 1987.

[3] Xie Xuejing. Areal exploration geochemistry. Beijing: Geochemistry Publishing House, 1979.

[4] Department of Geology, University of Nanjing. Geochemistry. Revised edition. Beijing: Science Press, 1979.

[5] Zhang Ye,Xie Tingzhou, Liang Zhiyong *et al.* X–ray fluorescence exploration technique. Beijing: Geological Publishing House, 1984.