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X-RAY FLUORESCENCE ANALYSIS OF Fe, Mn, Cr and V
IN NATURAL SILICATE CRYSTALS

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V in Natural Silicate Crystals.

ABSTRACT

Concentrations of Fe, Mn, Cr and V were determined in samples of beryl, topaz, tourmaline and spodumene by measuring the first order K_{α} fluorescence lines. The intensity of these lines were calibrated by using beryl as the standard matrix. The matrices were prepared in the form of pressed pellets with 4:1 mixture of beryl and boric acid, where transition metal oxides were added.

RESUMO

Foram determinados as concentrações de Fe, Mn, Cr e V em amostras de berilo, topázio, turmalina e espodumênio através da medida de linhas de fluorescência de primeira ordem K_{α} . As intensidades destas linhas foram calibradas usando o berilo como matriz padrão. As matrizes foram preparadas na forma de pastilhas com mistura de berilo e ácido bórico na proporção de 4:1, e onde foram adicionados óxidos de metais de transição.

1. INTRODUCTION

It is the purpose of the present paper to report the results of a quantitative analysis of Fe, Mn, Cr and V in beryl, topaz, tourmaline and spodumene using x-Ray fluorescence spectroscopy. Beryl (Dana and Hurlbut, 1969), $Be_3 Al_2 [Si_6 O_{18}]$, is hexagonal with density 2.66-2.92. Topaz (Dana and Hurlbut, 1969), $Al_2 (OH, F)_2 [Si_6 O_{18}]$ is orthorhombic with density 3.49-3.57. Tourmaline (Dana and Hurlbut, 1969), $Na(Mg, Fe, Mn, Li, Al)_3 Al_6 [Si_6 O_{18}] (BO_3)_3 (OH, F)_4$, is trigonal with density 3.03-3.15. Spodumene (Dana and Hurlbut, 1969), $Li Al [Si_4 O_{10}]_2$, is monoclinic with density 3.03-3.22.

The fluorescent radiation depends on four groups of experimental factors (Müller, 1972; Kalman and Heller, 1962; Rose et al., 1963; Hooper, 1964) that must be considered in a quantitative analysis: (i) absorption by the sample; (ii) enhancement by the sample; (iii) inhomogeneities in the sample; (iv) instrumental instabilities.

The concentration, C_x of the element X, to be analysed are in general lower than several parts per thousand. Under this condition enhancement effects by the sample can be neglected.

The intensity of the fluorescent radiation, I_x , of the element X diluted in the matrix M is given by (Kalman and Heller, 1962; Sherman, 1955).

$$I_x = \frac{q}{\sin \phi} \int_{\lambda_c}^{\lambda} \frac{\lambda_x \omega_x C_x \mu_x(\lambda) N_o(\lambda) d\lambda}{\mu_M(\lambda)}$$

where

q = fraction of the fluorescent radiation passing through the colimator;

- ω_x = is related to the fluorescence yield;
 $N_o(\lambda)$ = intensity of exciting beam at wavelength λ ,
 $\mu_x(\lambda)$ = coefficient of absorption at wavelength λ of the element X ,
 $\overline{\mu_M(\lambda)}$ = $[\mu_M(\lambda)/\sin\phi + \mu_M(\lambda_o)/\sin\psi]$, coefficient of absorption at wavelength λ of the matrix M ,
 ϕ = angle of incidence of the exciting beam,
 ψ = angle of measurement of the fluorescent radiation,
 λ_o = wavelength of the fluorescent radiation,
 λ_c = critical absorption wavelength of element X,
 λ_x = shortest wavelength contributing to exciting beam.

In the derivation of this equation perfect homogeneity of the sample was assumed, and small concentration of X.

In a first order approximation, by considering that $\overline{\mu_M}$ varies slowly in the interval $[\lambda_c, \lambda_x]$, was obtained (Compton and Allison, 1935):

$$I_x = C_x k_x / \overline{\mu_M(\lambda)}$$

where

$$k_x = \frac{q}{\sin\phi} \int_{\lambda_c}^{\lambda_x} \omega_x \mu_x(\lambda) N_o(\lambda) d\lambda$$

$\bar{\lambda}$ = wavelength in the interval $[\lambda_c, \lambda_x]$.

The determination of k_x and $\overline{\mu_M(\bar{\lambda})}$ is very complex, thus the use of standard M_p is very popular. If the measurements are done at the same experimental conditions we have:

$$C_x = \frac{I_{x_p}}{I_x} \frac{\overline{\mu_M(\bar{\lambda})}}{\overline{\mu_{M_p}(\bar{\lambda}_p)}} C_{x_p}$$

where I_{x_p} is the fluorescent intensity of the element X at a concentration C_{x_p} in the matrix M_p . From the universal absorption curve of Jönsson, we have the relation (Compton and Allison, 1935):

$$\mu = Z^{p+1} \lambda^p$$

where p decreases with the increasing of $Z\lambda$. The variation of p from $Z\lambda=5$ to $Z\lambda=60$ is smaller than 10%. Since the composition and density of our samples are similar $\overline{\mu_M(\bar{\lambda})}/\overline{\mu_{M_p}(\bar{\lambda}_p)}$ may be regarded as constant, provided that M_p is a silicate. Here we choose beryl for the preparation of standards, assuming $\overline{\mu_M(\bar{\lambda})}/\overline{\mu_{M_p}(\bar{\lambda}_p)} \sim 1$.

The size of the particles contributes to the fluorescent intensity, and in general the fluorescent intensity increases with diminishing the grain size. Even a long grinding period does not eliminate completely size effects. However, the powder method continues as one of the more popular methods of sample preparation, because the size effects can be reduced to some extent. Here we use the powder method, grinding the sample at the same conditions and time.

2. METHODOLOGY

a) Equipments

Preliminary analysis of rough samples were done at the Instituto de Química da Universidade de São Paulo. A Philips

X-Ray spectrometer was used with the following characteristics: generator, scintillation detector of NaI (Tl), crystal analyser LiF (200), Flat-Bed recorder, tungsten tube and operated with 30 KV and 20 mA electrom beam.

The quantitative analysis was done at the Laboratório de Espectrometria da Área de Processos Especiais of the Instituto de Pesquisas Energéticas e Nucleares de São Paulo. A RIGAKU-DENKI X-Ray spectrometer was used, with the following characteristics: Geigerflex generator, crystal analyser LiF (200), scintillation detector NaI (Tl). The experimental conditions of measurements are given in Table I. Measurements were done after stabilization of 1 hour to prevent equipment instability errors. The sample holder for six pellets enables simultaneous measurements of five pellets and one as equipment standard. All measurements were normalized to this equipment standard, eliminating instrumental fluctuations from one series of measurements to another.

The samples were powdered with a mechanical grinder SPEX Mixer-Mill with cylinders and spheres of tungsten for fifteen minutes. The powder pressed at 4 ton/cm² in HERZOG HTP-40 hydraulic press gives pellets of 25 mm diameter, 1.5 mm thickness and 1.5 g weight.

b) Sample Preparation

The rough samples were washed and treated in sulfuric acid for 10 minutes, eliminating metallic oxides in the surface of the samples.

The pellets prepared with powdered samples only, crack easily. The hardness of the pellets was improved by adding boric acid.

The lowest content of the boric acid to obtain hard enough pellets was about 25% in weight. In this way all pellets were prepared with a mixture of the sample and boric acid at 4:1 proportion.

Two kinds of standard pellets were prepared with beryl matrix, one for high concentrations of the Fe and low concentrations of Mn, Cr and V, with Anagês green beryl, and the other for low concentration of Fe with colorless beryl. The substances containing the metals were added in form of oxides. Due to small sizes of oxides, we assume that the distribution of the metals in the pellets are almost the same as of uniform distribution, that is, reabsorption of fluorescent radiation with small grains of the oxides are negligible.

3. RESULTS

In Tables II and III we give intensities of K_{α} fluorescence, already subtracted from back-ground radiation intensity, and the concentrations of added metals. The fluorescence intensity and concentration are correlated by a linear function:

$$y = ax + b$$

where y is the intensity of fluorescence, x is the concentration, a and b constants. These constants are shown in Table IV, together with the errors in a (δa) and in b (δb).

The constant b is due to the presence of metals in the matrices. By extrapolation to $x=0$, we obtained the following initial concentrations, y_0 :

[Fe] _o	:	170 ppm	in colorless beryl,
[Fe] _o	:	5200 ppm	in green beryl,
[Mn] _o	:	80 ppm	in green beryl,
[Cr]	:	760 ppm	in green beryl,
[V]	:	85 ppm	in green beryl.

The errors in y are almost given by δb , because $\delta a x \ll \delta b$, (see Tables II, III and IV).

The values of the concentrations of Fe, Cr, Mn and V in beryl, topaz, spodumene and tourmaline are given in Tables V, VI, VII and VIII.

4. DISCUSSION

In Table V we show the concentration of metal impurities in several samples of beryl. Looking only for colorless, green, blue and yellow beryl we see that largest concentration of V and Mn occur in colorless beryl. So, concentrations of Mn and V smaller than 100 ppm do not produce color in beryl. In the all samples, the concentrations of Cr is of the same order, showing that concentrations smaller than 100 ppm give no contribution for color in beryl. About concentrations of Fe, we note that green beryl have tonality stronger than of the blue. On the other hand Fe concentration in blue and colorless beryl are of the same order. These observations reinforce the suggestion (Blak, 1981) that the color depends on the site of Fe in the crystal. The Anagés and Carnaiba beryl are classified as emeralds due to the high contents of Cr. In

these samples we observe also a high concentration of Fe. So we suggest that the color in these emeralds is due to the combination of absorption bands of Cr and Fe.

In Table VI we show the impurity concentrations determined in samples of topaz. The colors brown and green were produced in colorless topaz by Co 60 γ -radiation. The blue results from heating at 200°C the irradiated samples. There is no correlation between type of color and concentration of Fe, Mn and Cr. A possible relation between iron concentration [Fe], and color intensity is in brown topaz. The [Fe] and brown color intensity in topaz B are larger than in topaz A.

In Table VII we show the impurity concentrations determined in samples of spodumene. The Cr concentration in the present samples are too low to contribute for coloration. In the samples lylac and colorless A spodumene the relation between the concentrations [Mn]/[Fe] are respectively 3 and 6. These samples when irradiated with ionizing radiation turn green, and lylac by heating at 200°C. The phosphorescence was observed to be strong. The B, C and D samples of spodumene show [Mn]/[Fe] relation of about 1. When irradiated they turn green but on heating at 200°C turn colorless or low lylac. The phosphorescence was observed to be low. The green spodumene does not change color with irradiation nor show phosphorescence. The present observations (Ito, 1981; Fujii, 1981) reinforce the suggestion that larger relation [Mn]/[Fe] favours the lylac color and phosphorescence. The low phosphorescence with increasing of [Fe] is expected because this ion can be a phosphorescence killer. We suggest, also, that the Fe³⁺ ion occupies sites of charge 3+ in competition with Mn³⁺, causing diminishing of lylac color with diminishing [Mn]/[Fe] relation.

In Table VIII we show impurity concentration determined in tourmaline. The concentrations of Cr are too low to contribute for coloration. In the varieties of pink tourmaline we observe a high concentration of Mn and low concentrations of [Fe] with $[Mn]/[Fe] \sim 30$. In green tourmaline we have $[Mn]/[Fe] \sim 1$ and in dark blue $[Mn]/[Fe] \sim 1/20$. From these observations we assign the pink color to the Mn^{3+} . When the concentrations of Fe increases the color goes from green to dark blue, indicating an inhibition of the pink color, by a mechanism similar to that observed in spodumene.

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TABLE I - Operation Conditions of the X-Ray Spectrometer

Characteristic Radiation	Excitation	Angular Peak	Background		
Fe(A) K_{α} , n=1 $\lambda = 1.936\text{\AA}$	20mA ; 30KV	57.54°	56.54°	and	54.54°
Fe(B) K_{α} , n=1 $\lambda = 1.936\text{\AA}$	40mA ; 40KV	57.54°	56.54°	and	58.54°
Mn K_{α} , n=1 $\lambda = 2.102\text{\AA}$	50mA ; 40KV	63.00°	62.00°	and	64.00°
Cr K_{α} , n=1 $\lambda = 2.289\text{\AA}$	50mA ; 40KV	69.37°	68.37°	and	70.37°
V K_{α} , n=1 $\lambda = 2.503\text{\AA}$	50mA ; 30KV	77.97°	76.97°	and	78.97°

Observations: Fe, Mn and Cr: Tungsten tube; V: Silver tube.

Counting time: Fe(B) and Cr: 20 seconds; Mn: 40 seconds; V: 200 seconds; Fe(A): 10 seconds.

TABLE II - Fluorescent Intensities and added concentrations of metal oxides in green beryl.

Pellets	Fe(A)		Cr		Mn		V	
	[Fe] (ppm)	Count	[Cr] (ppm)	Count	[Mn] (ppm)	Count	[V] (ppm)	Count
B ₁	-	46374	-	12558	-	6394	-	1070
B ₂	-	46509	-	12560	-	4173	-	1030
P ₁	205	43136	46	12536	49	13227	121	2381
P ₂	158	43026	47	12389	57	8874	246	3847
P ₃	839	51895	82	13352	86	15853	366	5332
P ₄	839	49929	78	13094	79	13823	486	6838
P ₅	2463	69186	163	15045	163	23618	-	-
P ₆	3894	85169	479	19052	249	25412	-	-
P ₇	9105	136728	813	25037	572	57417	-	-
P ₈	16052	195696	1606	37423	1219	112937	-	-
P ₉	32072	326152	2421	50413	1644	143365	-	-

TABLE III - Fluorescent Intensities and added concentrations of Fe oxide in colorless Beryl

Pellets	Fe(B)	
	[Fe] (ppm)	Count
B ₁	-	12262
P ₁	85	16759
P ₂	404	38207
P ₃	815	68773
P ₄	1628	125793
P ₅	3220	232358

TABLE IV - Constants a and b of the calibration curve.

Matrix	Metal	a	δa	b	δb
Green Beryl	Fe(A)	0.112	0.007	-5200	500
	Cr	0.063	0.002	- 760	30
	Mn	0.012	0.003	- 80	30
	V	0.084	0.003	- 85	5
Colorless Beryl	Fe(B)	0.0145	0.0005	- 170	20

TABLE V - Concentrations of Fe, Mn, Cr and V in Beryl***

Sample	Count	[Fe] (ppm)	Count	[Cr] (ppm)	Count	[Mn] (ppm)	Count	[V] (ppm)
Colorless	26576*	390	1376	90	9540	110	1874	160
Blue	31860*	460	1394	90	5505	70	1389	120
Yellow	42516*	620	1554	100	5435	70	322	30
Green	102484*	1490	1433	90	5431	70	454	40
Carnaiba	37670**	4220	11824	750	7039	90	860	70
Anagés	46441**	5200	12292	770	7217	90	1050	90

* Count condition B.

** Count condition A.

*** Errors assumed to be δb of table IV.

TABLE VI - Concentrations of Fe, Mn, Cr and V in Topaz*

Sample	Count	[Fe] (ppm)	Count	[Cr] (ppm)	Count	[Mn] (ppm)
Colorless	13935	200	1345	90	4788	60
Brown A	15864	230	1313	100	4818	60
Brown B	95148	1380	1551	100	4554	60
Green	8597	130	1540	100	4744	60
Blue A	19920	290	1570	100	4873	60
Blue B	26428	380	1461	90	4689	60
Imperial	69558	970	2501	160	5984	70

*Errors assumed to be δb of table IV; V was not detected.

TABLE VII - Concentrations of Fe, Mn, Cr and V in Spodumene*

Sample	Count	[Fe] (ppm)	Count	[Cr] (ppm)	Count	[Mn] (ppm)
Lylac	16369	240	1708	110	60965	730
Colorless A	9893	140	1450	90	51690	620
Colorless B	45372	660	1547	100	44304	530
Colorless C	17352	250	1537	100	23146	280
Colorless D	32852	480	1548	100	27926	340
Green	117699	1710	2464	160	45219	540

*Errors assumed to be δb of table IV; V was not detected.

TABLE VIII - Concentrations of Fe, Mn, Cr and V in Tourmaline***

Sample	Count	[Fe] (ppm)	Count	[Cr] (ppm)	Count	[Mn] (ppm)
Rose A	16932*	250	1589	100	724538	8690
Rose B	26599*	386	1594	100	920995	11050
Rose C	48269*	700	1643	100	979359	11750
Green	66550**	7450	1667	110	766295	9200
Dark Blue	393360**	44056	1641	100	180148	2160

* Count Condition B.

** Count Condition A.

*** Errors assumed to be δb of table IV; V was not detected.