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Multi-elemental Characterization of Cuban Natural Zeolites.

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Abstract: Concentrations of 38 elements in samples from four important Cuban zeolite bed have beam obtained by Intrumental Neutron Activation (INAA) and X-Ray Fluorescence analyses (XRFA). In comparison with other analytical techniques good agreement was achieved. The concentration values of minor element Ba, Sr, Zn and Mn, and 25 trace element (including 9 REE) are at the first time reported in Cuban zeolite. It is important for the zeolite evaluation in different industrial uses.

INTRODUCTION

Natural zeolites, well know as the "XX Century Mineral" is extended used in many countries, thanks to their different applications: aciculated acid dried and purification, gases absorption, toluene extraction from benzene, dietetic compliment to animal food, residual water purification, sorbing of radioactive wastes, etc. (Gotardi *et al.*, 1985).

In the last decade, the use of natural zeolites in different economic sectors in Cuba was started, considering the abundance of this mineral resource in our country. For example, the construction of zeoponic plantations and the zeolite use as compliment to the animal diet are extended (Rodriguez, 1987), in increasing is their use in different process of the sugar industry. Zeolite is used as compliment in some pharmaceutical formulas (Rodriguez, 1993) and was studied to use in the radioactive wastes sorption (Chales *et al.*, 1987, 1988; Dominguez *et al.*, 1989).

INAA and XRFA have been widely used as multi-elemental technique for analyzing geological samples. Using these, it is possible to obtain the concentration of many major, minor and trace elements without contamination and, with INAA, without matrix effects.

Previous geochemical characterization, obtained by chemical (Novoa *et al.*, 1987) and nuclear (Sarria *et al.*,1990, Diaz *et al.*, 1990) analyses were dedicated only to the major elements. Then, the multi-elemental characterization, obtained by INAA in nuclear reactor and XRFA exposed in this article, is the most exhaustive analysis of Cuban natural zeolites. It may contribute to clarify their toxicology for agriculture and sugar and pharmaceutical indutries.

EXPERIMENTAL

The samples were taken from the principal Cubán zeolite bed: Piojillo (90% clinoptinolite), Palmarito (80-90% mordenite), Tasajera (40% mordenite + 40% clinoptinolite) and San Andrés (90% clinoptinolite). All samples were dried to 105 °C and mechanically powdered in an Agate mill. Table 1 shows the chemical composition for Piojillo and Palmarito, obtained by Atomic Absorption Spectroscopy (AAS) (Chales *et al.*, 1987).

For INAA, samples about 0.1 g (±0.01%) were prepared and packed in aluminum foils. Afterwards, specimen under study were placed in aluminum container with standards samples for relative analysis, and Zr monitor of neutron flux. Relative INAA was performed using the certified material IAEA/SOIL-7 as standard. The use of a soil standard for comparative INAA of zeolite was justified elsewhere.

Irradiations were performed an the thermal and epithermal channels in the "REGATA" facilities at reactor IBR-2 (16 MW, 1.10^{12} $n.cm^{-1}.s^{-2}$) at the Joint Institute for Nuclear Research, Dubna, Russia. The irradiation regimes were: a.-) T_i=1 min., T_d= 1 min., T_m= 2 min.; b.-) T_i= 10 min., T_d=15 min., T_m=30 min.; c.-) T_i=100 h, T_d= 7-10 d, 30 d, T_m=30 min.

Measurements of γ-ray spectra were performed using Ge(Li) detector with 2.5 keV resolution of the 1332 keV γ-ray line of ^{60}Co. Spectra were processed using PC/AT microcomputers and a modified version of ACTIV and SPAN codes. Elemental concentrations were obtained using FORTRAN programs.

Analytical peaks with statistical error ≤20%, at energies between 80 and 1800 keV, allowed the determination of 38 elements. The Sm analytical line at 103 keV was corrected from spectral unresolved lines ^{239}Np x-ray, when U was detected, and of ^{153}Gd. The k_o standardization method (De Corte *et al.*, 1989) was applied to the studied samples with good results for the majority of the elements. It allowed the concentrations of the elements not reported in the certified material (Gd, Tm, etc.).

One gram targets for XRFA were prepared by pressing. Measurements were performed using a Si(Li) detector (180 eV resolution of the Mn-K_α-line) with annular sources of ^{55}Fe, ^{109}Cd and ^{241}Am. The Compton scattering radiation method (Tertian *et al.*, 1982) was applied, using the computer code "QXAS" for processing spectra and Tasajera zeolite as standard to obtain the concentration values of 19 elements.

AVERAGE VALUES OF ELEMENTAL CONTENTS

The average concentration values of the elements determinated by INAA is present in Table 2. The reported errors were calculate considering the statistical errors of the processed spectra and errors of the certified material. The detection limits were determinated using a (Currie, 1968) methodology.

XRFA results are shown in Table 3. The reported concentrations for Si, Al, Mg and Na are approximated. It is possible, because Compton scattering radiation method produce a partial compensation to the matrix effects of major elements presented in the analytical samples. The use of Tasajera zeolite as standard permit a better approximation between the determinated and real concentration values.

Elemental average concentration values are shown in Figure 1. The concentration of major elements (Ca, Al, Si, Fe, K, Mg and Na) are similar to values obtained by chemical analysis. As minor elements Ti, Ba, Sr, Zn, Mn and Zr were determinated. Except Ti, the rest is determinate at first time in Cuban natural zeolites. The presence of 25 trace element is relevant because they are reported for the first time too. The number of rare earth elements (Ce, La, Nd, Sm, Eu, Gd, Tb, Tm and Yb) is considerable. Their behaviour (Figure 2) is similar to the REE behaviour in rocks from Cuban petroleum wells (Herrera *et al.*, 1991).

TOXICOLOGICAL EVALUATION OF ELEMENTAL CONTENTS

The comparison of concentration values for Ba, Sr and Zn with the Permissible Concentration Levels (PCL) for soils and food (Bandman et al., 1988) and US zeolites approved by the NASA for space zeoponic plantations (Galindo et al., 1991) (Table 4), shows a great difference. Taking into account the INAA and XRFA can not determinate the chemical compounds with these elements, the difference between the Rusian and US norms, the lack of Cuban norms and the intensive use of zeolites in Cuba, its evident that a most exhaustive research of the toxicological levels for Ba, Sr and Zn in Cuban zeolites has to be performed.

On the other hand, the use of zeolite in different process of the sugar industry is not an impediment. The result of the nuclear analysis in different types of sugar and final molasses from Cuban sugar industry (Diaz Rizo *et al.*, 1992, 1996) shows the presence of these elements but in very low (in sugar) and normal (in molasses) levels (Figure 3).

The concentration values for all determinated trace elements (including the REE and high toxic elements as As, Hg, U, etc) must not limit the use of Cuban natural zeolites in agriculture and pharmaceutical and sugar industries.

CONCLUSIONS

This is the most exhaustive elemental analysis of Cuban natural zeolites, reporting at the first time the concentration values of minor elements Ba, Sr, Zn, Mn and Zr and 25 trace elements. The results shows the necessity of more detailed analysis of Ba, Sr and Zn in products whose maded using natural zeolites.

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Table 1.- Elemental content (in %) determinated by AAS (Chales *et al.*, 1987).

Element	Piojillo	Palmarito	Tasajera
SiO	64.17	65.78	57.69
TiO	0.36	0.27	0.3
Al_2O_3	10.89	10.81	9.9
Fe_2O_3	2.47	1.71	1.84
CaO	4.04	3.86	5.16
MgO	1.23	0.96	1.54
Na_2O	1.28	2.02	1.13
K_2O	0.90	0.79	1.1

Table 2.-INAA concentration values (in ppm) in Cuban natural zeolites. (Errors in %)

Element	Piojillo	Palmarito	Tasajera	San Andrés
Ca	33002.3 (6)	25304.8 (6)	33261.3 (6)	20288.7 (6)
Al	34228.5 (11)	26481.4 (11)	38999.3 (4)	36517.2 (11)
Fe	11529.9 (3)	14392.1 (3)	13692.4 (3)	23567.1 (3)
K	6404.3 (7)	3831.2 (8)	6888.1 (7)	5657.1 (7)
Mg	6188.2 (11)	5740.0 (11)	7343.6 (4)	7337.2 (11)
Na	10445.3 (23)	11246.5 (23)	9382.1 (23)	5637.5 (24)
Ti	1172.7 (12)	<1508.0	1696.5 (17)	<1769.9
Mn	104.3 (11)	110.1 (9)	161.1 (6)	543.6 (5)
Zr	<100.0	107.0 (29)	83.8 (28)	<85.6
Ba	696.7 (27)	463.6 (27)	827.6 (26)	324.4 (27)
Sr	401.3 (27)	666.3 (27)	274.0 (28)	155.0 (29)
Zn	225.9 (8)	97.1 (8)	99.8 (8)	187.9 (8)
V	<17.9	12.3 (25)	<15.9	35.17 (17)
Ce	25.3 (11)	19.0 (11)	21.5 (11)	19.1 (11)
Cr	2.4 (29)	<4.6	<4.9	5.3 (20)
Rb	19.5 (13)	21.0 (12)	27.9 (12)	8.4 (20)
Nd	11.1(21)	20.3 (20)	42.9 (20)	6.7 (23)
La	15.2 (4)	11.4 (5)	11.1 (5)	16.9 (4)
As	<3.51	4.38 (25)	<3.6	5.4 (24)
Ga	10.8 (24)	8.2 (21)	8.4 (22)	17.5 (20)
Co	1.6 (14)	2.7 (12)	2.2 (12)	5.3 (11)
Sc	12.7(19)	6.6 (19)	8.4 (19)	12.5 (19)
Th	2.19 (14)	1.83 (14)	1.72 (14)	1.47 (14)
Br	<1.36	<1.65	0.68 (30)	1.9 (29)
Cs	0.5 (22)	0.3 (25)	0.3 (26)	0.1 (30)
Hf	4.1 (9)	4.6 (9)	5.4 (9)	2.0 (12)
Sm	4.4 (7)	3.0 (7)	3.6 (7)	5.2 (7)
U	4.5 (20)	1.6 (22)	2.2 (22)	3.7 (21)
Mo	<1.2	< 0.8	< 0.8	< 0.9
Yb	4.0 (20)	2.6 (20)	2.5 (25)	4.6 (19)
Sb	0.2 (15)	0.2 (15)	0.2 (15)	0.1 (22)
Eu	3.0 (25)	1.5 (27)	1.5 (27)	1.4 (28)
Ta	0.1 (28)	0.1 (28)	0.2 (27)	0.1 (28)
Tb	0.7 (22)	0.3 (26)	0.5 (23)	1.1 (20)
Hg	0.02 (30)	0.02 (30)	0.02 (30)	0.04 (30)
Gd	6.8 (30)	8.0 (30)	7.0 (30)	5.7 (30)
Tm	0.5 (30)	0.3 (30)	0.3 (30)	0.6 (30)

Table 3.- XRFA concentration values (in ppm) in Cuban natural zeolites. (Errors in %).

Element	Piojillo	Palmarito	San Andres
Si	378851.4 (7)	323250.6 (7)	264211.8 (7)
Ca	32547.6 (6)	29495.2 (6)	22265.8 (6)
Al	15637.4 (11)	9985.3 (11)	10173.7 (11)
Fe	10069.0 (4)	14461.7 (3)	33001.0 (3)
K	6958.2 (8)	5167.8 (9)	6092.8 (8)
Mg	12906.7 (15)	7788.5 (14)	18247.7 (12)
Na	8692.1 (24)	7174.5 (27)	10347.9 (20)
Ti	2533.8 (13)	1731.3 (16)	2213.7 (13)
Mn	162.6 (12)	161.0 (15)	549.0 (8)
Zr	163.9 (29)	180.8 (29)	162.7 (29)
Ba	747.6 (26)	575.9 (27)	327.2 (27)
Sr	271.2 (27)	502.9 (25)	160.5 (29)
Zn	199.5 (29)	101.5 (20)	165.4 (15)
V	17.6 (27)	17.4 (26)	22.3 (22)
Ce	27.5 (13)	18.3 (25)	22.6 (12)
Rb	20.2 (16)	25.0 (15)	11.3 (23)
La	12.2 (10)	10.2 (11)	15.3 (8)
As	< 3-5	< 3.3	< 3.4
Br	< 0.45	< 0.84	< 0.87

Table 4.- Permissible Concentration Levels (PCL) and concentration values for Ba, Sr and *Zn*, reported in Cuban and US zeolites (in ppm).

Bed	Ba	Sr	Zn
Piojillo	697	401	226
Palmarito	464	666	97
Tasajera	828	274	100
San Andrés	324	155	188
PCL*	300	667	30
PCL*(soils)	230	600	23
Wyoming	906	421	-
Texas	198	1	-
California	360	2855	-

* In oxide compound.

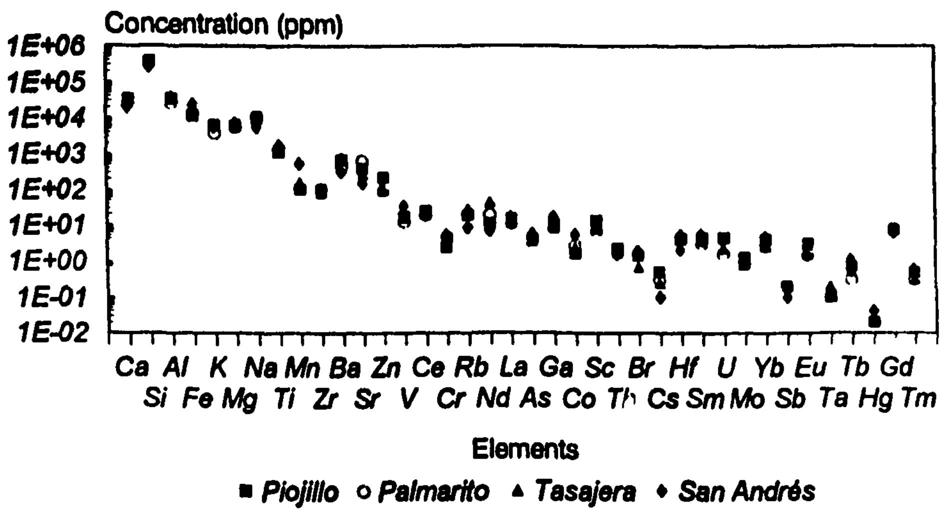

Figure 1.- INAA and XFRA results in Cuban natural zeolites.

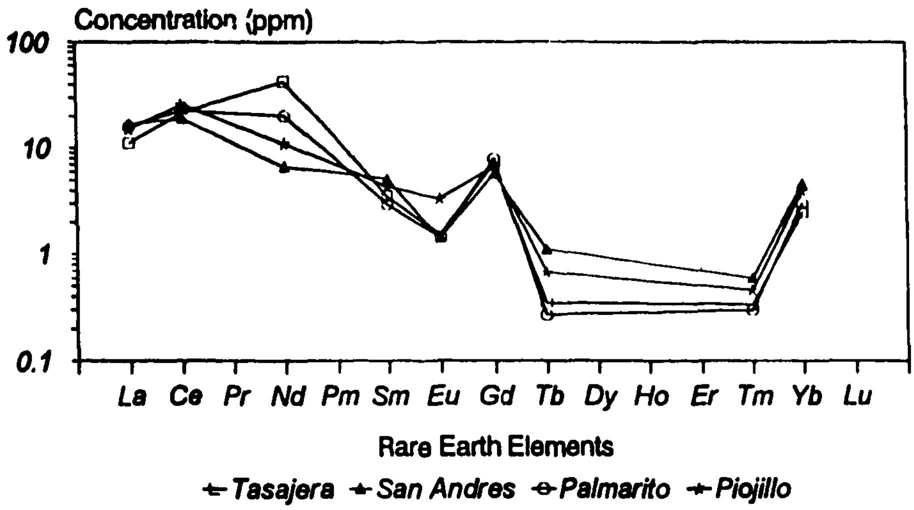

Figure 2.- Behaviour of REE determinated in Cuban natural zeolites.

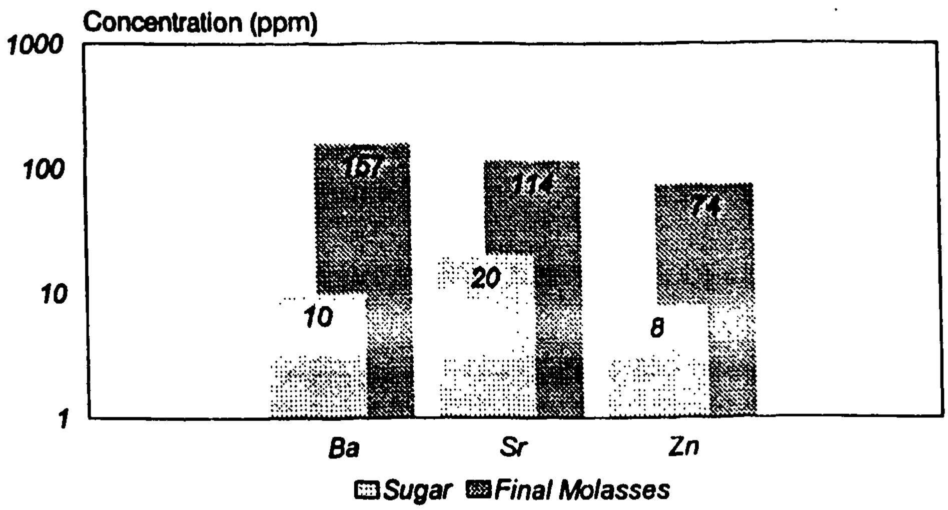

Figure 3.- Concentration values of Ba. Sr and Zn determinated in Cuban sugar and final molasses.

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