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Gradient of heavy elements in the ocean sediments from the Gulf of Tehuantepec

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With the scope of determining the concentrations of heavy elements in regard to the ocean's depth in the Gulf of Tehuantepec, several samples were analyzed by using PIXE. The gradients of the concentrations of the elements found, are presented.

Keywords: PIXE analysis; ocean sediments; heavy elements; contamination.

Usando la técnica PIXE se analizaron muestras de sedimento marino del Golfo de Tehuantepec para determinar las concentraciones de elementos pesados respecto a la profundidad. Se presentan los gradientes de las concentraciones medidas.

Descriptores: Análisis PIXE; sedimentos marinos; medio ambiente; contaminación; elementos pesados.

PACS: 92.20.Vu; 92.20.Wx; 32.30.Rj; 78.70.En

1. Introduction

An accelerator of particles produces ion beams of kinetic energy $E \pm \Delta E$ that give origin to different interactions when impacting on a material, always dependent on the particle's energy, and with a different probability of occurrence for each interaction (cross section). Some of the events are: inelastic and elastic collisions with the atomic nuclei and collisions with the electrons. These last ones produce ionization, leaving vacancies in the electronic layers. When the vacancies are filled, X-rays of characteristic energies of each chemical element (characteristic X rays) are emitted, Fig. 1. This method of production of characteristic X-rays is known as PIXE (Particle Induced X-Ray Emission). PIXE technique is suitable to identify elements with $Z \geq 13$, in concentrations of some parts per million, ppm (typically, 50 ppm).

In previous works [1-2], the results of monitoring the presence of heavy metals in the environment by analysis of the concentrations in materials exposed to the contamination have been shown. In this work, the preliminary results of a study focused on the evaluation of the changes in the concentrations of heavy elements accumulated in the sedimentary column of the Gulf of Tehuantepec, are presented. The

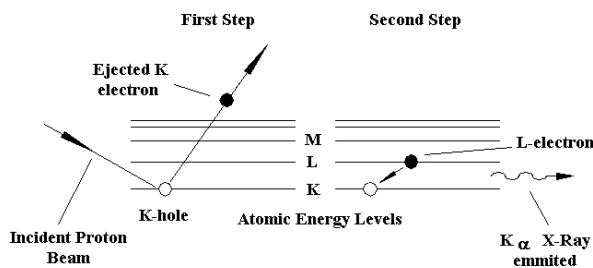


FIGURE 1. Proton induced X-ray emission.

concentrations were measured by PIXE at the EN Tandem Accelerator facility of the ININ, schematically depicted in Fig. 2.

2. Experiment

The nucleus used in this study was gathered in the Gulf of Tehuantepec, on October 11 of 2004, in station 21 of the cruise TEHUA II whose coordinates are $15^{\circ} 59.987'N$ and $94^{\circ} 48.469'W$, ranging to a depth of 66.7 m. The sediment was extracted with a box compactor type Reineck, and by using a 7 cm diameter PVC tube it, manually, gathered a nucleus 18 cm long, which was sliced in contiguous sections of 0.3 cm of thickness in the first 10 cm of depth, and in sections of 1 cm until the end. The samples were weighted, frozen, lyophilized, and weighted again, to calculate the content of humidity.

Each powdered sample was mixed with 1000 ± 10 ppm of Se, to have an internal standard, and by using an aggluti-

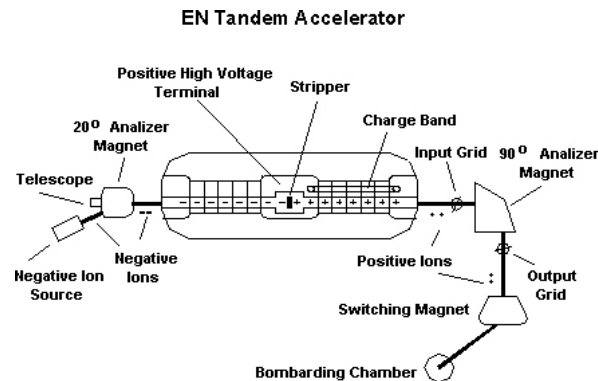


FIGURE 2. EN Tandem Accelerator.

nant, the target pills were manufactured. The samples were placed inside a camera with a residual pressure of 5×10^{-5} torr, and bombarded with 3 MeV protons until an accumulated electric charge Q of $2.4 \mu\text{C}$ was reached (Q is proportional to the number of incident protons). A Si(Li) type detector, placed at 135° in relation to the incident beam direction, was used, as shown in Fig. 3.

The detection system was calibrated with the energies of the X rays from an Am241 source. Sample No. 8 spectrum is shown in Fig. 4.

3. Results and discussion

The data was analyzed with GUPIX program, described in [1] and [2]. Doping each sample with Se as an internal standard allowed to decrease the error in the electric charge measured, as well as the one introduced by changes in the geometry of the experiment each time a new sample was placed as a target. In the calculations, it was considered that Si, Cl, K and Ca made up chemical compounds with C and O. Some of

the concentrations obtained, expressed in $\text{mg}\cdot\text{g}^{-1}$ (1×10^{-3} ppm), are presented in Table I, where the first column indicates the sample number, and the second one, the depth in cm.

The average error pertaining to the concentration of each element are listed in Table II. They are the quadratic one obtained from the statistical and fitting errors.

The concentrations profiles of some elements are shown in Fig. 5.

The profiles show very high and considerable variations in concentrations of metals with regard to the depth. Elements like S and Zn show small concentrations toward the surface, probably as a consequence of the co-precipitation of compounds like Zn sulfides, which are formed in sub-oxic and anoxic conditions typical of the studied area (area of minimum oxygen of the Gulf of Tehuantepec). Elements Si and

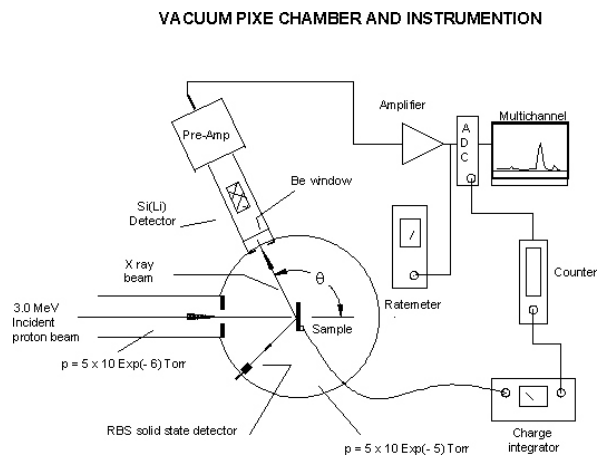


FIGURE 3. Irradiation chamber and PIXE instrumentation.

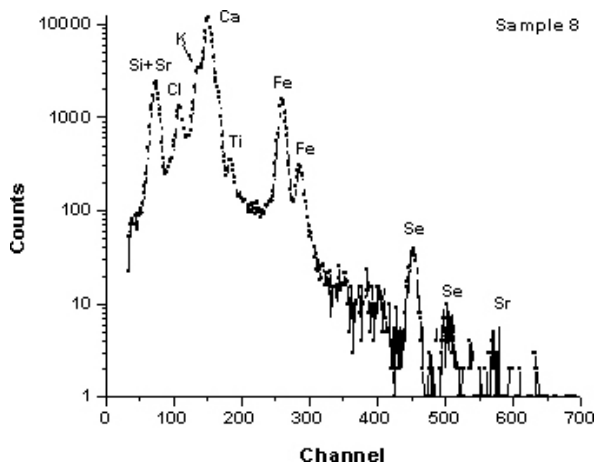


FIGURE 4. Sample 8 X-ray spectrum.

TABLE I. Concentrations (mg g^{-1}) in función of depth (cm).

No.	Depth (cm)	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Zn	Se	Sr	Hg
1	0.6	62	1	5	5	23	.4			4	.03	1	.1	
2	0.9	115	1	7	7	30	.5			4	.06	1	.2	
3	1.2	97	2	7	7	31	2			4	.05	1	.1	
4	1.5	73	.7	4	7	17	.3			3		1	.2	
5	1.8	192	2	15	17	49	2			8	.06	1	.5	
10	3.3	134	2	5	9	49	.3			4	.04	1	.3	
11	3.6	58	3	17	6	24	.4			6	.1	1	.2	
12	3.9	110	3	16	12	36	2	.2	.1	9		1	.1	
13	4.2	63	1	5	4	21	.4	.08	.09	4	.03	1	.1	
14	4.5	195	1	5	8	40	.6			5	.07	1	.3	
15	4.8	146	4	10	11	56	1			9	.09	1	.4	.2
21	6.9	131	5	17	12	49	.7			8	.1	1	.4	.2
22	7.2	75	3	11	6	26	.4	.04	.06	4	.07	1	.2	
23	7.8	51	5	31	5	31	.7		.1	7	.07	1	.2	
24	8.1	112	5	23	11	54	.8		.1	9	.09	1	.2	
25	8.4	85	3	17	8	37	.7		.1	6	.09	1	.2	
31	10.2	47	2	9	5	40	.5	.4	.1	7	.06	1	.2	
32	11.2	57	2	5	4	25	.3	.2	.06	5	.04	1	.1	
33	12.2	44	3	7	5	28	.6	.03	.07	5	.1	1	.2	
34	13.2	54	4	6	6	46	1	.04	.1	8	.08	1	.3	
35	14.2	98	4	5	5	34	.6		.06	5	.08	1	.1	
36	15.2	40	2	4	4	27	1	.03	.06	6	.05	1	.1	
37	16.2	154	4	6	10	41	.7	.1	.05	9	.05	1	.4	
38	17.2	79	3	4	5	38	.7	.02	.1	5	0.5	1	.2	
39	18.2	87	2	2	5	29	.4	.02	.05	4	.04	1	.1	

TABLE II. Average errors in the concentrations.

Element	Si	S	Cl	K	Ca	Ti	Cr	Mn	Fe	Zn	Ge	Se	Sr	Hg
Error %	5	11	5	5	5	7	42	32	5	30	61	8	36	64

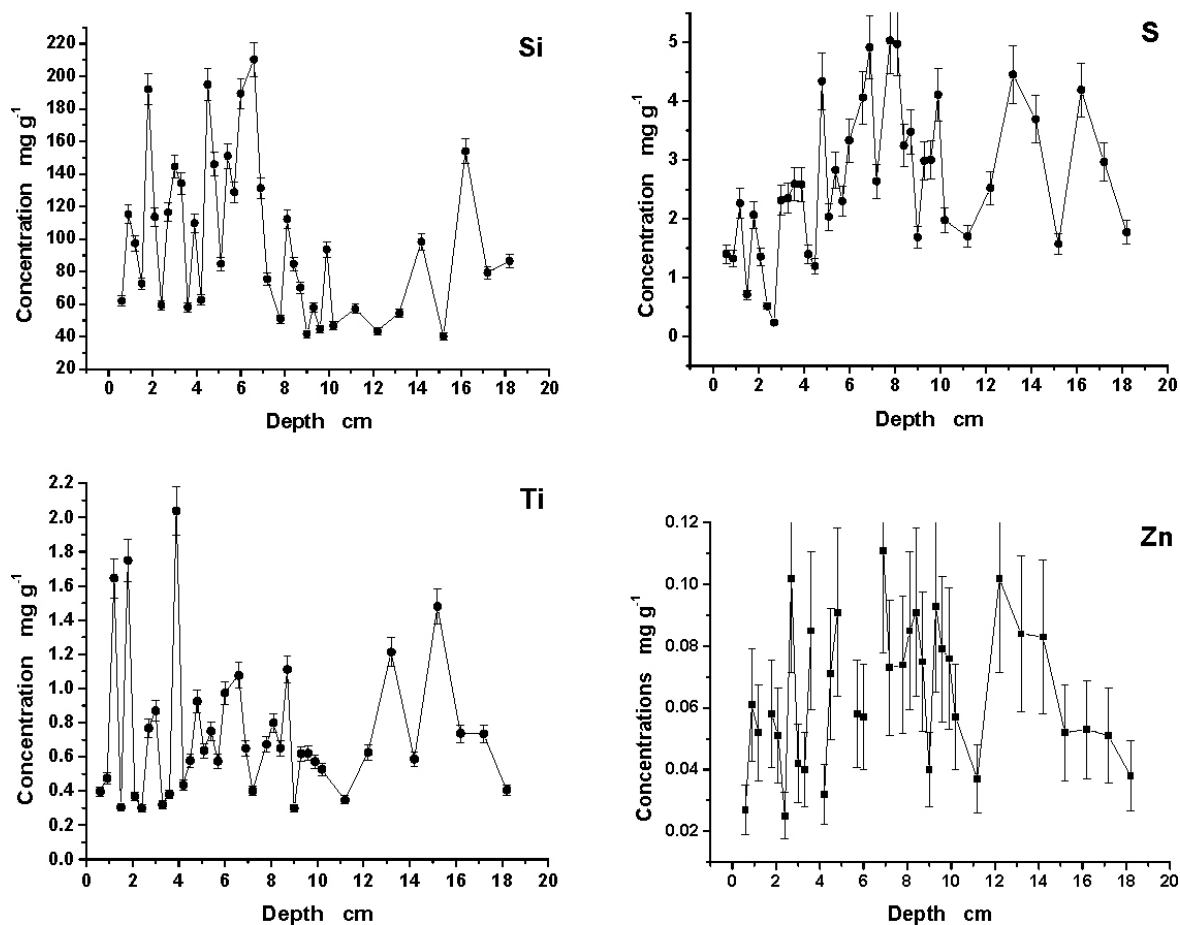
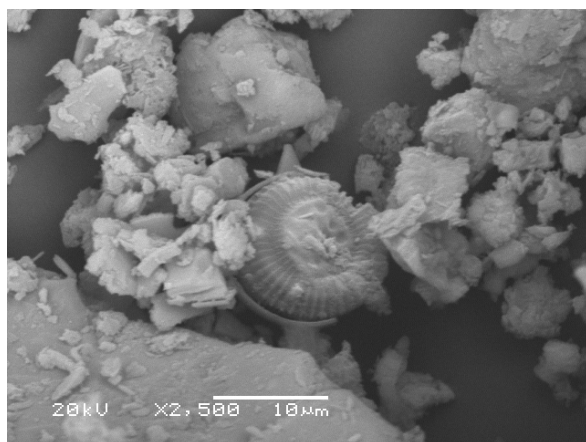


FIGURE 5. Concentrations profiles for some elements.

FIGURE 6. Silicated head *Cyclotella striata*.

Ti show high concentrations toward the surface, maybe as consequence of a bigger detritus distribution of continental origin, as well as a bigger abundance of residuals of phytoplanktonic organisms like radiolarian, and some foraminiferal species that have silicated heads (Fig. 6). The high concentrations of Ca are owed to the accumulation of

organisms with carbonated structures (CaCO_3). In regards to the concentrations of Ge and Hg, it is difficult to determine any change. Se standard exhibits constant concentration, like it should be.

4. Conclusions

Thirty-nine samples of a sedimentary nucleus of marine origin were analyzed by using PIXE, with the purpose of determining concentration changes of elements accumulated in the sedimentary column that could result from the industrial activities that are carried out in the coastal area next to the studied area. Highly variable concentrations of Ti, Cr, Mn, Zn, and Hg were determined and, in some samples, traces of V, Co, Ni, Cu and As are also present. The obtained results show very high concentrations for most of the elements; however, to be able to evaluate the real enrichment of these elements it is necessary to normalize the measured concentrations with reference elements, like Al and Li, and to take in account other variables, as the content of organic matter and the distribution of grain size. This task will be carried out in a later stage.

1. J.A. Aspiazu F. *et al.*, *International Journal of PIXE* **12** (2002) 225.
2. J. López M., J.J. Ramírez Torres, J.A. Aspiazu F., P. Villaseñor S., L. Cervantes N., *V Simposio de Contaminación Atmosférica*, El Colegio Nacional, México, D. F. (2005) 233.