

INAA applied to the multielemental characterization of a sedimentary column: a contribution to oceanographic studies

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Abstract The environmental changes that occurred in different periods can be identified through the increase or decrease of the concentrations of metals and other substances throughout sediment cores. The purpose of this study was to determine Al, As, Ba, Br, Cs, Eu, K, La, Mn, Sb, Sc, Sm, Th, Ti, U and V in a sediment core collected from São Paulo State South Seashore. Instrumental neutron activation analysis followed by gamma-ray spectrometry was the analytical method used. Results showed an abrupt decrease in the concentration of all elements in the 132–134 cm layer depth. This finding indicates an impact of anthropic activity.

Keywords INAA · Sedimentary column · Trace elements

Introduction

The knowledge of the total concentration of inorganic constituents in sedimentary columns is an important parameter for oceanographic studies. The environmental changes that occurred in different periods can be identified through the increase or decrease of metals and other substances throughout the sediment cores [1].

Several elements are considered paleoclimatic proxies. For example, Shigemitsu et al. [2] estimated the content of eolian dust in the sediments and its percentage in the whole detritus from levels of Al, Sc, La, Yb and Th, which are used to calculate the excess of Ba and U. The excess

amount of Ba and U indicated that biological production was lower in glacial periods than in interglacial ones.

On the other hand, some elements are used for dating rocks or sediments. Suguio et al. [3], through use of thermoluminescence and K, Th, and U contents obtained the ages of eight samples from Comprida Island, which corroborate the Pleistocene age assumed during mapping surveys of these deposits.

In view of this, the objective of this study was to evaluate the performance of instrumental neutron activation analysis (INAA) followed by gamma-ray spectrometry [4] to determine Al, As, Ba, Br, Cs, Eu, K, La, Mn, Sb, Sc, Sm, Th, Ti, U and V in a sediment core, collected from São Paulo State South Seashore.

Experimental

Collection and treatment of samples

A sedimentary core was collected from São Paulo State South Seashore, over 200 cm deep, using a “liner” of PVC previously treated to avoid contaminating the sediment with impurities. The material used in this study was provided by the Oceanographic Institute of the São Paulo University. According to Mahiques et al. [5] the average sedimentation rate for this core is 0.887 ± 0.166 cm year⁻¹, representing a time interval of 177 ± 33 years for the sequence sampled.

The column (200 cm deep) was brought to the laboratory of Oceanographic Institute, São Paulo University—USP, and it was divided into pieces of 2 cm each, resulting in 100 samples. From this total 20 samples (one every 10 cm) were selected for this study. Each sample was lyophilized for removal of all moisture and then pulverized. Subsamples of approximately 1 g were sent to the

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Table 1 Elemental concentrations in the sedimentary column (mg kg^{-1}), as a function of depth, with its combined uncertainty (%), in parentheses

Depth (cm)	Al	As	Ba	Br	Cs	Eu
2–4	81455 (3.5)	7.9 (5.8)	495 (12.9)	25.3 (5.1)	6.8 (7.5)	1.56 (11.9)
12–14	73291 (3.0)	6.2 (7.1)	515 (13.6)	23.3 (5.3)	5.3 (9.6)	1.20 (12.5)
22–24	63706 (2.8)	6.7 (6.9)	634 (11.4)	15.9 (5.7)	4.7 (8.7)	1.19 (13.1)
32–34	84608 (3.2)	5.7 (7.4)	698 (11.2)	10.9 (6.7)	7.4 (7.0)	1.57 (12.6)
42–44	104506 (3.4)	4.5 (6.9)	742 (11.0)	9.7 (6.3)	7.6 (6.8)	1.54 (12.3)
52–54	91852 (3.3)	5.7 (7.4)	660 (11.9)	11.6 (6.3)	8.7 (7.1)	1.54 (12.3)
62–64	86437 (3.6)	7.9 (5.8)	932 (12.5)	13.4 (5.7)	9.3 (6.7)	1.84 (12.2)
72–74	90602 (3.1)	7.0 (5.9)	784 (16.6)	9.5 (6.4)	9.5 (7.6)	1.22 (12.9)
82–84	75186 (4.0)	6.6 (6.0)	867 (15.1)	10.0 (6.2)	8.3 (7.4)	1.75 (12.1)
92–94	98375 (3.2)	6.3 (6.1)	686 (24.0)	11.5 (5.6)	8.3 (7.4)	1.39 (12.3)
102–104	106023 (3.3)	6.4 (6.1)	607 (11.5)	9.2 (5.6)	7.8 (5.4)	1.63 (11.4)
112–114	93799 (3.8)	6.7 (5.4)	402 (13.2)	9.5 (4.8)	9.2 (5.7)	1.88 (11.3)
122–124	81420 (3.4)	14.0 (5.4)	472 (14.5)	31.6 (4.3)	8.8 (4.9)	1.49 (11.4)
132–134	23844 (3.4)	3.7 (5.9)	201 (22.8)	6.5 (4.7)	1.9 (5.5)	0.44 (11.0)
142–144	17670 (3.9)	3.2 (6.1)	242 (11.9)	7.0 (5.6)	1.8 (5.8)	0.40 (12.5)
152–154	12919 (2.9)	1.6 (8.1)	182 (11.2)	2.7 (5.4)	0.8 (12.6)	0.21 (13.8)
162–164	35272 (3.1)	6.8 (6.0)	280 (11.4)	11.8 (4.9)	3.2 (9.5)	0.64 (13.7)
172–174	18358 (3.1)	2.3 (6.8)	211 (23.2)	3.6 (6.6)	0.8 (12.6)	0.29 (12.1)
182–184	24173 (3.0)	3.8 (5.8)	263 (27.1)	5.2 (5.3)	2.2 (9.2)	0.53 (12.5)
192–194	27468 (3.1)	4.1 (5.7)	277 (30.9)	3.8 (6.4)	1.4 (7.3)	0.36 (13.0)

Table 2 Elemental concentrations in the sedimentary column (mg kg^{-1}), as a function of depth, with its combined uncertainty (%), in parentheses

Depth (cm)	K	La	Mn	Rb	Sb	Sc
2–4	16196 (3.4)	54.4 (12.1)	726 (3.9)	81 (10.1)	0.73 (11.9)	15.74 (1.2)
12–14	15141 (3.6)	44.9 (12.1)	609 (3.9)	75 (10.9)	0.52 (20.5)	12.34 (1.2)
22–24	14373 (3.6)	42.6 (12.1)	511 (3.4)	63 (11.3)	1.11 (12.9)	10.97 (1.2)
32–34	17190 (3.6)	52.2 (12.1)	521 (3.9)	79 (10.3)	0.31 (29.9)	14.05 (1.2)
42–44	16164 (3.5)	51.3 (12.1)	626 (3.9)	83 (9.8)	0.48 (18.1)	13.97 (1.2)
52–54	16935 (3.5)	52.9 (12.1)	553 (4.0)	84 (9.7)	0.57 (18.9)	14.47 (1.2)
62–64	18396 (3.3)	57.7 (12.1)	873 (3.4)	86 (10.7)	0.24 (42.5)	16.51 (1.2)
72–74	15809 (3.3)	47.9 (12.1)	804 (3.4)	75 (10.9)	0.71 (17.0)	14.30 (1.2)
82–84	17589 (3.3)	53.7 (12.1)	714 (3.6)	94 (9.8)	0.41 (23.1)	15.98 (1.2)
92–94	15739 (3.3)	53.1 (12.1)	570 (4.2)	81 (10.0)	0.66 (35.6)	14.51 (1.2)
102–104	16712 (3.3)	60.5 (12.1)	546 (4.0)	92 (8.9)	0.60 (15.1)	13.90 (1.1)
112–114	17341 (3.3)	60.7 (12.1)	456 (4.0)	86 (8.4)	0.56 (12.9)	14.25 (1.1)
122–124	15102 (3.7)	50.3 (12.1)	499 (3.7)	94 (7.7)	0.64 (13.0)	13.60 (1.1)
132–134	7891 (3.2)	12.5 (12.1)	163 (3.8)	27 (11.3)	0.15 (27.6)	2.99 (1.1)
142–144	7129 (3.3)	11.7 (12.1)	123 (4.1)	26 (11.7)	0.14 (29.4)	2.78 (1.2)
152–154	4887 (3.2)	6.8 (12.2)	70 (4.4)	18 (11.3)	0.13 (16.9)	1.22 (1.3)
162–164	9808 (3.3)	21.3 (12.1)	219 (3.8)	38 (10.7)	0.24 (26.0)	5.64 (1.2)
172–174	6523 (3.3)	8.3 (12.2)	90 (4.7)	21 (9.7)	0.08 (38.2)	1.45 (1.2)
182–184	8494 (3.3)	15.7 (12.1)	123 (4.1)	28 (7.4)	0.08 (38.2)	3.43 (1.2)
192–194	7406 (3.3)	11.2 (12.1)	144 (3.9)	27 (7.7)	0.11 (37.1)	2.40 (1.2)

Table 3 Elemental concentrations in the sedimentary column (mg kg^{-1}), as a function of depth, with its combined uncertainty (%), in parentheses

Depth (cm)	Sm	Th	Ti	U	V
2–4	7.7 (5.5)	14.6 (4.5)	4947 (10.9)	2.7 (24.5)	94 (12.5)
12–14	6.4 (5.5)	8.9 (4.6)	3988 (12.0)	2.3 (32.2)	68 (12.4)
22–24	6.3 (5.5)	10.7 (4.4)	4521 (11.2)	2.9 (29.5)	61 (12.0)
32–34	7.5 (5.5)	13.3 (4.6)	4748 (11.9)	2.8 (30.4)	81 (12.4)
42–44	7.5 (5.5)	13.6 (4.6)	6518 (9.5)	3.2 (27.1)	82 (12.4)
52–54	7.6 (5.5)	13.7 (4.6)	5595 (10.5)	4.0 (24.8)	73 (12.9)
62–64	8.4 (5.5)	15.6 (4.4)	5447 (13.7)	4.5 (22.5)	79 (16.1)
72–74	4.7 (5.7)	13.3 (4.6)	6370 (10.3)	4.6 (22.6)	70 (12.3)
82–84	8.0 (5.4)	15.6 (4.4)	4803 (12.9)	3.0 (28.6)	55 (17.7)
92–94	7.6 (5.5)	13.7 (4.6)	4844 (9.4)	4.2 (23.8)	102 (11.6)
102–104	9.0 (5.4)	13.7 (4.6)	6835 (12.5)	5.3 (18.3)	122 (12.4)
112–114	9.8 (5.4)	13.1 (4.3)	6304 (10.8)	5.0 (17.4)	71 (10.9)
122–124	8.0 (5.4)	11.7 (4.3)	5294 (10.7)	4.6 (18.4)	110 (11.9)
132–134	2.1 (7.1)	3.5 (4.9)	1463 (18.1)	1.0 (32.8)	23 (16.4)
142–144	2.1 (7.1)	2.9 (5.3)	732 (26.7)	2.7 (21.2)	13 (12.6)
152–154	1.1 (10.5)	1.8 (6.8)	357 (28.6)	0.8 (27.1)	7 (17.4)
162–164	3.6 (6.0)	5.2 (4.4)	2490 (11.6)	3.8 (21.2)	25 (18.9)
172–174	1.5 (8.5)	2.2 (6.1)	905 (23.9)	2.4 (23.3)	15 (16.7)
182–184	2.5 (6.6)	4.4 (4.6)	1808 (14.4)	1.0 (41.3)	22 (13.5)
192–194	1.8 (7.7)	2.6 (5.5)	1465 (17.5)	1.5 (28.6)	19 (14.5)

Neutron Activation Analysis Laboratory (IPEN—CNEN/SP) for multielemental analysis.

For irradiation, aliquots of sediments (40 mg) were transferred to polyethylene bags, which had been previously cleaned by leaching with a diluted HNO_3 (1:5) and purified water.

Preparation of standards

Certified standard solutions (Spex Certiprep) of Al, As, Ba, Br, Cs, Eu, K, La, Mn, Sb, Sc, Sm, Ti, Th, U and V were used to prepare elemental synthetic standards. Aliquots (50–100 μL) were pipetted on to small sheets of analytical filter paper (Whatman No. 42) for irradiation. After drying, these filter papers were placed into polyethylene bags.

Irradiation and counting

Irradiations were carried out at the IEA-R1 nuclear research reactor. The thermal neutron flux utilized ranged from 1 to $4 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. Two types of irradiation were carried out at the IEA-R1 nuclear research reactor. First, the sample and standards of the elements Al, Ba, Mn, Ti, and V were irradiated together in a nylon container for 12 s. After a decay time of 2 min the ^{28}Al , ^{51}Ti and ^{52}V

were measured in the sample and in the standards. ^{139}Ba and ^{56}Mn were measured after 90 min of decay time. In the second irradiation, the sample and standards (As, Cs, Eu, K, La, Sb, Sc, Sm, Th and U) were irradiated together in an aluminum container for 4 h. The ^{76}As , ^{42}K , ^{140}La , ^{122}Sb , ^{153}Sm and ^{239}Np ($^{239}\text{U} \rightarrow ^{239}\text{Np}$) were measured after 3 days of decay time, while ^{134}Cs , ^{152}Eu , ^{46}Sc , and ^{233}Pa ($^{233}\text{Th} \rightarrow ^{233}\text{Pa}$) were measured after, at least, 7 days of decay time.

The equipment used to measure the gamma-radiation was a Canberra model GX2020 hyperpure Ge detector, coupled to a model 1510 Integrated Signal Processor and MCA System 100, both from Canberra. The detector used had a resolution (FWHM) of 0.9 keV for 122 keV gamma rays of ^{57}Co and 1.9 keV for 1332 keV gamma-ray of ^{60}Co .

In addition, analysis of the certified reference material IAEA Soil-7 was also carried out. The relative error between the arithmetic mean of three determinations and the certified/reference values were taken as the uncertainty of the method.

Results and discussion

Elemental concentrations determined in the sedimentary column are shown in Tables 1, 2 and 3. Each value is the result of one determination with its combined uncertainty in percentage. The combined uncertainty takes into consideration the uncertainty of the method (as described in the “Experimental”) and the counting statistics of the measurement.

The variation of the uncertainty in the results of Sb, U, Ti and Ba were more affected by uncertainty of counting statistics due to the following factors: (a) low sensitivity of the method for these elements; (b) low concentration in the sample, especially for Sb; (c) different time of measurement.

Advantages and drawbacks of methods are indeed dependent on the nature of the material analyzed and on the elements to be determined. INAA is specifically suited for analysis of solid samples, since sediment samples are difficult to dissolve. When sample dissolution is required, analyte losses due to incomplete dissolution or volatilization (e.g. of As, Br, Sb) are possible. In addition, the risk of contamination of the sample from the vials, reagents and water is possible. For INAA, a quantity of about 40 mg of sediment is sufficient. This fact is relevant since the sample of sediment cores could be also used for biological and chemical analyses that requires a large amount of material.

In Fig. 1 the element concentrations from Tables 1, 2 and 3 are plotted as a function of the depths. In this figure, an abrupt decrease in the concentration of all elements was observed from layer 132–134 cm downwards. This result

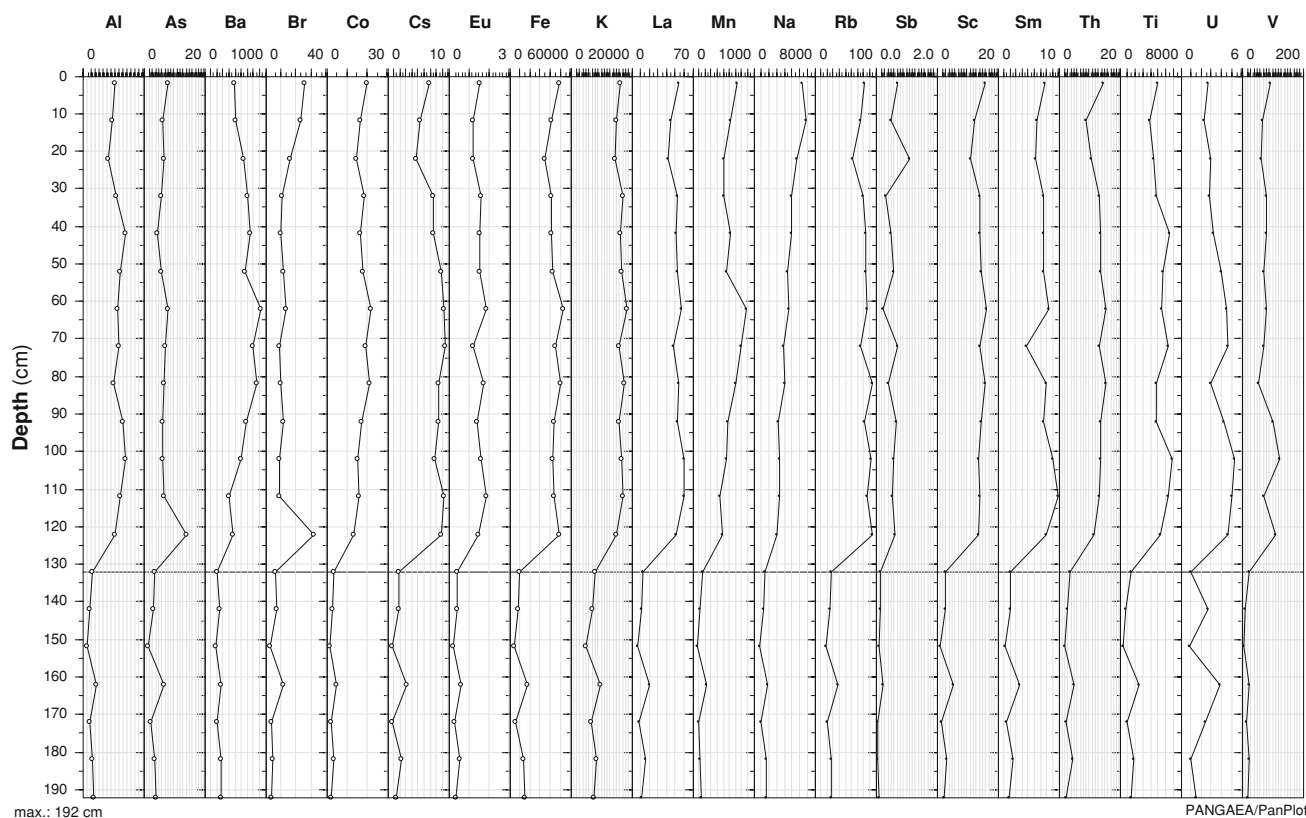


Fig. 1 Elemental concentrations (mg kg^{-1}) in the sedimentary column as a function of the depths

may be regarded as evidence of the impact of anthropic activities that started from the period of formation of the layer at 132–134 cm. This result may have been influenced by the opening of the Valo Grande Channel [6], in 1852, built at the North region of the Iguape Estuarine System to be possible the transport of rice through this region where the core was collected.

Conclusion

INAA was a suitable method for multielemental determinations in sediment cores. Results obtained suggest further application of this technique in oceanography studies.

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References

1. Förstner U (1989) Contaminated sediments: lectures on environmental aspects of particle-associated chemicals in aquatic systems. Lecture Notes in Earth Sciences, vol 21. Springer, Berlin, p 157
2. Shigemitsu M, Narita H, Watanabe YW, Harada N, Tsunogai S (2007) *Mar Chem* 106:442
3. Suguio K, Tatumi SH, Kowata EA, Munita CS, Paiva RP (2003) Upper Pleistocene deposits of the Comprida Island (São Paulo State) dated by thermoluminescence methods. *Ann Braz Acad Sci* 75–1:91
4. de Soete D, Gijbels R, Hoste J (1972) Neutron activation analysis. Wiley, New York
5. de Mahiques MM, Burone L, Capellari B, Figueira RCL Anthropogenic influences in a lagoonal environment: a multiproxy approach at Valo Grande mouth, Cananéia-Iguape system (SE Brazil). *J Braz Oceanogr* (paper submitted)—personal communication
6. Nascimento Jr DR, Giannini PCF, Tanaka APB, Guedes CCF (2008) Mudanças morfológicas da extremidade NE da Ilha Comprida (SP) nos últimos Dois Séculos. *Geologia USP: Série Científica* 8-1:25, see <http://geologiausp.igc.usp.br>.