X-ray Diffraction and Instrumental Neutron Activation Analysis applied to Environmental Studies

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- **Soil pollution is one of the most serious problems in the world, with long term consequences on human life. In recent years, with the rapid development of industry, various dangerous pollutants such as heavy metals have been released in soils around industrial areas.**
- **Heavy metals and some trace elements are biologically toxic and can affect the human health due to their accumulation and persistence in the compartments of the food chain.**
- **It is very important to investigate and monitor soil contamination for economic sustainable development and people's health.**

➢ **Environmental studies (control and monitoring) requires reliable and effective analytical techniques for widely different concentration ranges**
➢ **Important to assess - Elemental contents in soils, sediments, lichens, mosses, bulk deposition and airborne particulate matter…**

Instrumental Neutron Activation Analysis (INAA)

INAA is a simultaneous irradiation comparison between standard and studied samples in a nuclear reactor.

Sampling/laboratory protocols and INAA

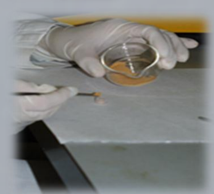
Soils - The whole-rock portion of the samples is the <2 mm fraction (dry sieving).

About 100 gr of the whole rock sample is dried at 30ºC and ground in agate mortars into a fine powder

The powder samples and standard are then dried in an oven at 110ºC for 24 h and stored in a desiccator for 2 hours

Sediment and soil (GSS-4 and GSD-9) from the Institute of Geophysical and Geochemical Exploration from the People's Republic of China are used as standards.

The samples and standards are prepared by weighing 200-300 mg of powder into cleaned high-density polyethylene vials



Each dried sample are irradiated together with standards for 1.5 min or 6h in the core grid of the Portuguese Research Reactor according to the semi-period of elements

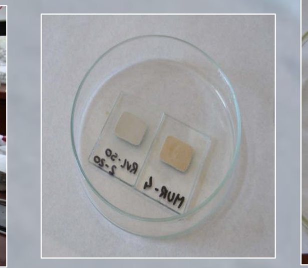
Nuclear reactor core

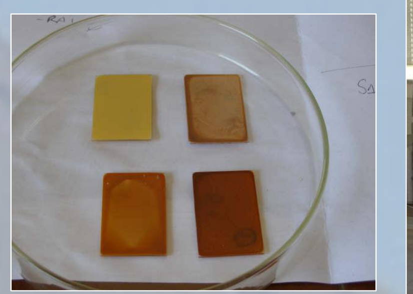
The Portuguese research reactor (RPI) is an open-core pool-type reactor, with a maximum power of 1 MWth.

X-ray diffraction (XRD)

X-ray diffraction (XRD) is a rapid analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions.

Sample preparation and XRD





-The analyzed material is finely ground, homogenized, and average bulk composition is determined.

- Powder non-oriented aggregates for the whole rock and size fractions (Φ≥ 125 µm, 63-125 µm, 20-63 µm, 2-20 µm and Φ <2 µm).

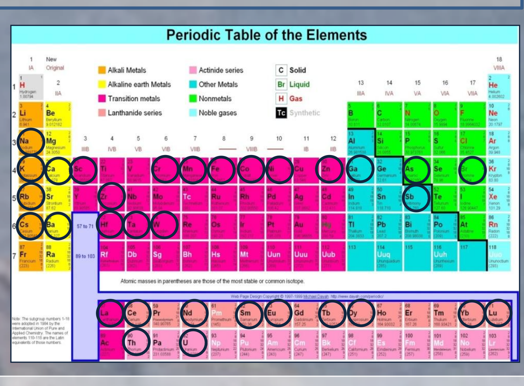
- Samples are scanned at a rate of 1º2θ/min from 2º to 70º2θ.

-Oriented aggregates (normal, glycolated and heated at 550ºC) for the < 2 µm fraction are scanned at a rate of 1º2θ/min from 2º to 30º2θ

Equipment: Philips Pro-Analytical diffractometer with CuKα radiation.

Strengths of INAA

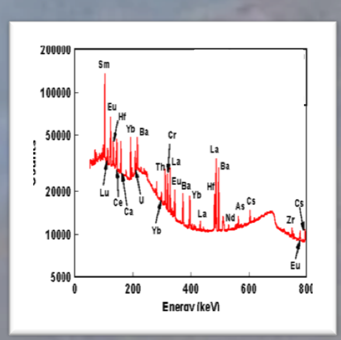
❖**Can analyze a large number of elements simultaneously**
❖**Very low detection limits for many elements**
❖**Small sample sizes (1—200 mg)**
❖**No chemical preparation**



Limitations of INAA

There are very few limitations: the major limitation is the number of elements that can be analyzed by this technique. Several elements of geological interest, such as Nb, Y and some transition metals, are better determined by other analytical methods.

INAA Counting rooms



A sample is subjected to a neutron flux and radioactive nuclides are produced. As these radioactive nuclides decay, they emit gamma rays whose energies are characteristic for each nuclide. Comparison of the intensity of these gamma rays with those emitted by a standard permit a quantitative measure of the concentrations of the various nuclides. Gamma spectrometry is used for the determination of several elements contents present in the sample.

Elements routinely analyzed in environmental and geological samples at IST/ITN: Na_2O, K_2O, MnO, Fe_2O_3T, Sc, Cr, Co, Zn, Ga, As, Br, Rb, Zr, Sb, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Dy, Yb, Lu, Hf, Ta, W, Th and U

Environmental and Geological Applications of Instrumental Neutron Activation Analysis and X- ray diffraction

Chemical composition / Geochemistry

- Separation of samples into chemical groups environmentally meaningful and sufficient to:
(a) distinguish among different pollution sources;
(b) trace the routes and the extent of pollution in sediments/soils/...;
(c) define the least affected areas representing the geochemical background.

-Application of a normalization procedure in determining regional geochemical baselines:

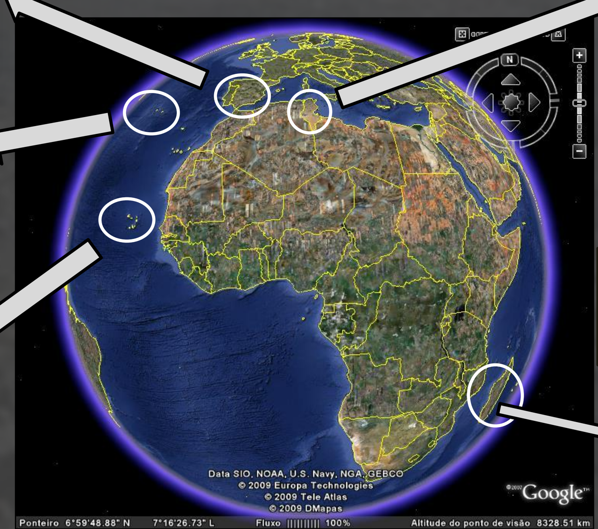
Enrichment factors

For the estimation of anthropogenic inputs, it is more useful to calculate the degree of enrichment of an element by dividing its ratio to the normalizing element by the same ratio found in the chosen baseline to yield a non dimensional enrichment factor (EF):

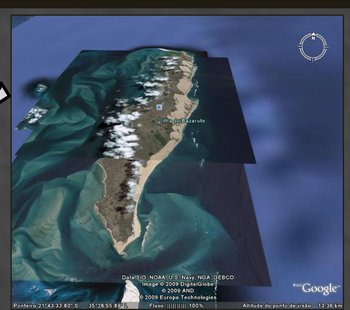
$$EF p(X/Y)_{sample}/(X/Y)_{baseline}$$

where X is the concentration of the potentially enriched element and Y is the concentration of the proxy element.
A value of unity denotes no enrichment or depletion relative to the baseline.

Natural background / evaluation of anthropogenic inputs



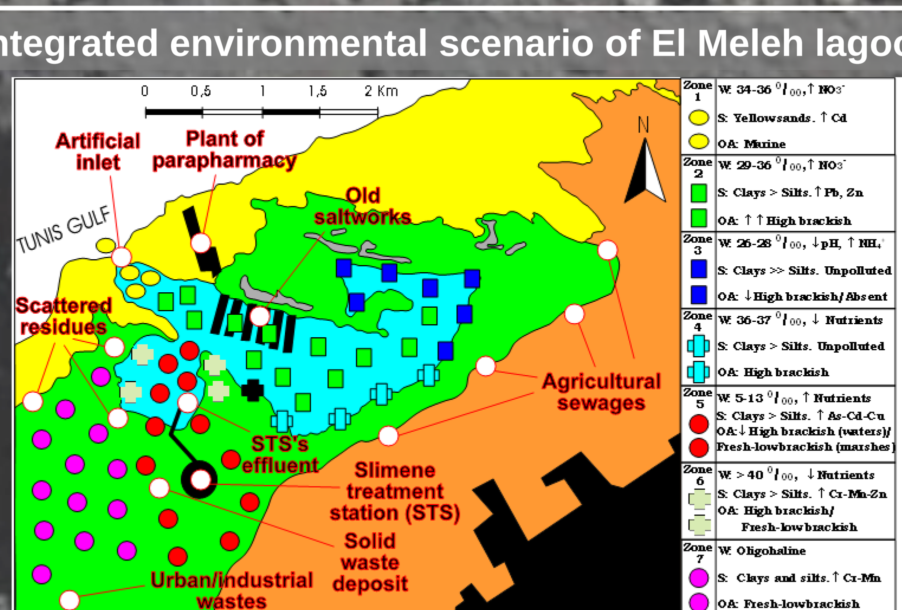
Paleoenvironmental reconstruction
Long-term environmental change of climate and shoreline



Geochemical Atlas

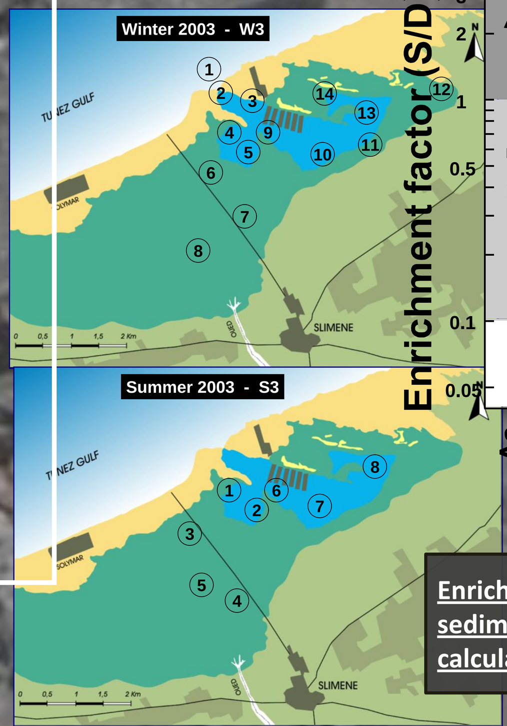
Anthropogenic Inputs – Environmental Study El Meleh Lagoon, Tunisia

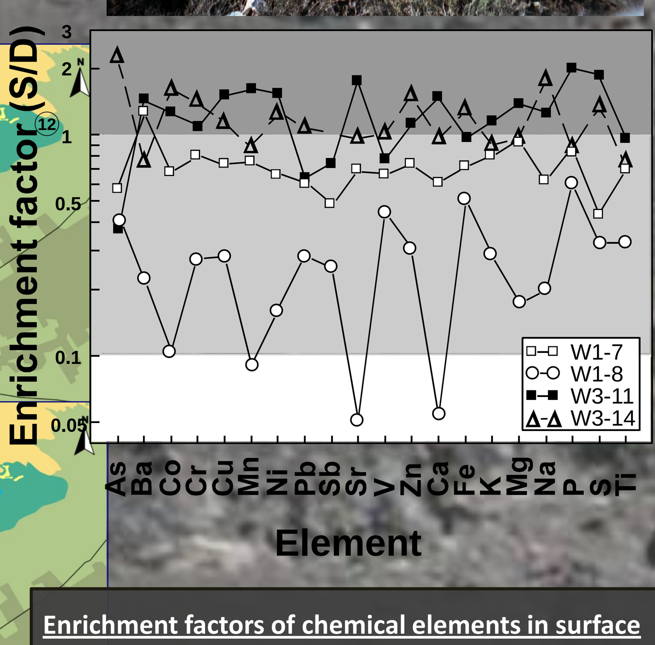
Integrated environmental scenario of El Meleh lagoon



W: waters; S: sediments; OA: ostracode assemblage

Sediment sampling location





Enrichment factors of chemical elements in surface sediments compared to respective deeper levels, calculated relatively to Al.

Mineralogical composition

- **Complement geochemical data**
- **Paleoreconstruction studies**
- **Clay-mineral environmental relationships**
- **The harmful effects of some minerals on human health have been recognized for centuries**
  - Minerals may cause damage when inhaled, and rarely by ingestion, or penetration into the skin

Determining the types of minerals is important because:
(1) many minerals are known to accumulate in lung tissue and adversely affect health (for example: quartz, mica, gypsum, apatite, talc, rutile, pyroxene, feldspar, numerous clay and zeolite minerals, and numerous serpentine and amphibole minerals, some of which are commonly referred to as 'asbestos')
(2) some minerals are highly chemically reactive and can pose increased risk because known carcinogens may be absorbed onto them or they may be bioreactive

This work was supported by the FCT funded project PTDC/AAC-AMB/121375/2010 - VADOSE