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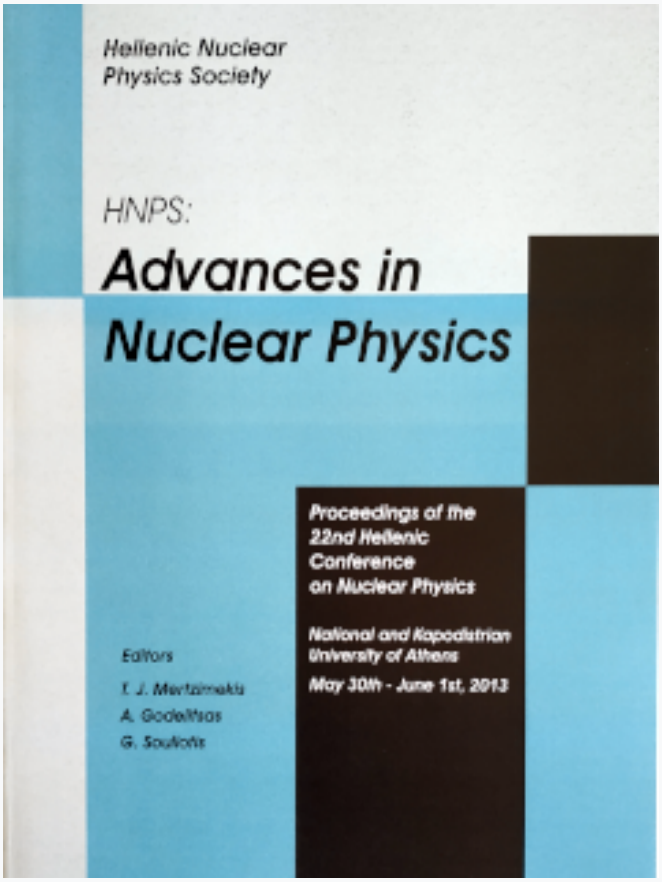

Using synchrotron radiation to study iron phases in Saharan dust samples from Athens skies

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Using synchrotron radiation to study iron phases in Saharan dust samples from Athens skies

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Abstract

The Sahara desert is the largest source of dust in the world. Saharan dust is characterized by great complexity, composed mainly of mixtures of mineral phases (amorphous or crystalline, with particle sizes of the order of μm or even nm). The presence of amorphous components makes it difficult to detect their structure. For this purpose the spectroscopic technique of X–ray absorption fine structure μ–XAFS combined to ultrabright synchrotron SR microbeams is suitable. SR's main advantage is the recording of spectra in a very short time. In this paper we focus on the study of forms of iron deposited on southeast Mediterranean Sea and mainland of Greece by the waves of Saharan dust. Data collection was carried out at the premises of ANKA (KIT, Germany) on the beamline SUL–X of the environmental research laboratory with advanced X–ray spectroscopic techniques, μ–XRF, μ–XRD and μ–XAFS. Results from the measurements and the simulated spectrum are presented.

Keywords: synchrotron, Saharan dust, microbeam

1. Introduction & Motivation

At least 2.4 million tons of dust are transferred every year from Sahara desert to the Mediterranean Sea. It is estimated that some of the paleosoils in Attica have been formed over time due to the repeated deposition of dust from the African desert. The clouds of Saharan dust enliven a variety of ecosystems with the deposition of nutrients. A characteristic example is iron, which is contained in the dust. Iron helps in fertilization of soils, plant growth and is one of the key factors of enrichment in nutrients, as is necessary for the phytoplankton. Iron is the fourth element in abundance in Earths crust and the second most abundant metal. It appears in a variety of minerals, including sulphides, oxides, hydroxides and hydroxide anion complex types.

The purpose of this work is to assess whether the iron in Saharan dust is associated with hematite [1] or ferrihydrite/hematite/goethite [2] or clay minerals [3].

2. Theoretical Background

EXAFS (Extended X-ray Absorption Fine Structure) and XANES (X-Ray Absorption Near Edge structure) are regions of the spectrum obtained from XAS (X-ray Absorption Spectroscopy).

EXAFS: corresponds to the oscillating part of the spectrum to the right of the absorption edge (appearing as a sudden, sharp peak), starting at roughly 50 eV and extending to about 1000 eV above the edge.Through mathematical analysis of this region, one can obtain local structural information for the atom in question.

XANES: the absorption edge corresponding to the liberation of a core electron from an element will exhibit several identifiable features which change depending on the chemical environment of the element being probed.The study and modelling of the characteristics of near-edge features helps answer questions

about the oxidation state, coordination, and spin state of the probed element. The EXAFS equation (contributor function) is the following:

$$\chi(k) = \sum_j \frac{N_j S_0^2 f_j(k) e^{-2R_j/\lambda(k)} e^{-2k^2\sigma_j^2}}{kR_j^2} \sin\left(2kR_j + \delta_j(k)\right) \quad (1)$$

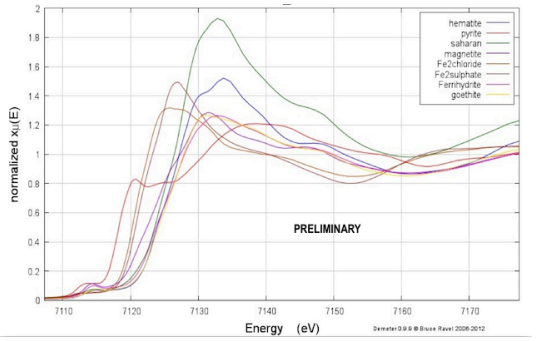
3. Experimental Method

The Saharan dust sample 1 was collected after filtering the rain water precipitated during an intense red rain event over Athens megacity. A part close to one quarter of the filter area containing the sample was first examined with scanning electron microscopy (SEM) and optical microscopy to determine the bulk features and record the coordinates of the Fe microparticles positions. It was subsequently placed on the aluminum holder using Kapton tape before being mounted to the scattering chamber.The sample was irradiated with ultra-bright, micro-focused X–ray beams provided by the SUL–X wiggler and monochromator. Iron's K absorption edge is equal to 7112 eV. Around that energy value μ–XAFS spectroscopies (μ–XANES and μ–EXAFS) were applied. The scattered X–rays were detected by a number of radiation detectors (ionization chambers). In addition to the sample, a few reference materials were irradiated for comparison: *hematite* (Fe_2O_3), *pyrite* (FeS_2), *magnetite* (Fe_3O_4), *Fe(III) chloride* ($FeCl_2$), *Fe(III) sulphate* ($FeSO_4$), *ferrihydrite* ($Fe_2O_3{\cdot}0.5H_2O$) and *goethite* (α-FeOOH).

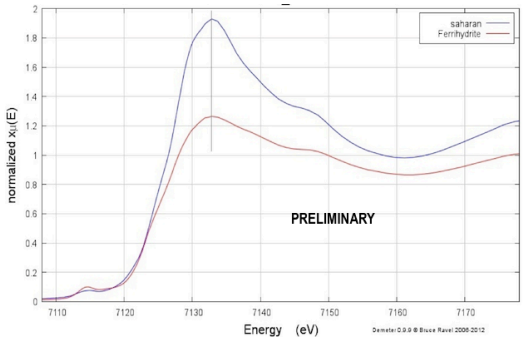
Figure 1: A map of sampling locations

4. Results and Discussion

The μ–XANES spectra of the sample were compared to the corresponding spectra of the reference materials (Fig. 2a). Detailed examination showed that iron is contained in the dust as Fe(III) in a form analogous to the structure of the mineral ferrihydrite (Fig. 2b), which was used as reference material for the simulation of the Fe K–edge (7112 eV) spectrum of Saharan dust.



(a) The Saharan dust sample compared to reference materials: hematite, pyrite, magnetite, Fe(III) chloride, Fe(III) sulphate, ferrihydrite and goethite.



(b) The Saharan dust sample compared to reference material: ferrihydrite

Figure 2: The μ–XANES spectra comparison between the Saharan dust sample and the reference materials collected at the Fe K absorption edge

A subsequent study using the μ–EXAFS technique was undertaken. The μ–EXAFS data analysis showed that for the first group of neighbours Fe–O, the average O center is situated at a distance of R = 2.019 Å from

the central Fe atom, in very good agreement with data existing in bibliography for the structure of ferrihydrite (Fig. 3).

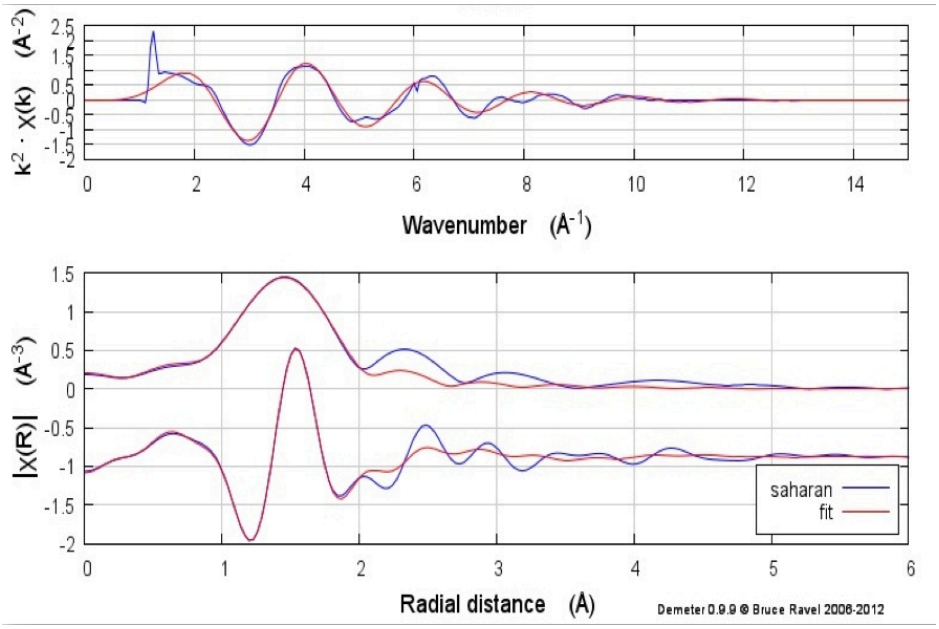


Figure 3: The simulated μ–EXAFS spectrum of Saharan dust in k and R space.

References

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