



	<b>Experiment title:</b> <b>A XANES approach to the colouring of geomaterials by iron</b>	<b>Experiment number:</b> EC 87
<b>Beamline:</b> ID-21	<b>Date of experiment:</b> from: December 1, 2006                      to: December 5, 2006	<b>Date of report:</b> 06.03.2007
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr. Jean Susini & Dr. Emilie Chalmin	<i>Received at ESRF:</i>
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## Report:

The purpose of the experiment was to assess the electronic state of iron in geomaterials (essentially pure minerals) with varied colourings always due to the presence of this element: red, yellow, ochre, brown, green, blue, violet, white and even grey-to-black with metallic lustre.

Fe K-edge XANES spectra were therefore collected from *oxide-hydroxide ochres* – *goethite*,  $\alpha$ -FeO(OH), *lepidocrocite*,  $\gamma$ -FeO(OH), *hematite*,  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, *siderite*, Fe CO<sub>3</sub> – as well as from reddish pre-soils or *regoliths*, *olivine*, (Mg,Fe)<sub>2</sub>Si O<sub>4</sub>, always in octahedral coordination.

Depending on the crystal structure, Fe<sup>2+</sup> ↔ Fe<sup>3+</sup> *intervalence charge transfer transitions* (IVCT) may account for complete opacity as occurs for *magnetite*, Fe<sub>3</sub>O<sub>4</sub>, in which the valence electrons of cations are delocalised to such an extent that the range of charge transfer energies extends through the whole visible region of the electromagnetic spectrum. Accordingly, the colour of *vivianite*, Fe<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·8H<sub>2</sub>O, *changes from white to blue by the action of sunlight*.

Irradiated samples were mainly small mineral fragments; only a few samples were milled and the powder spread over kapton for irradiation.

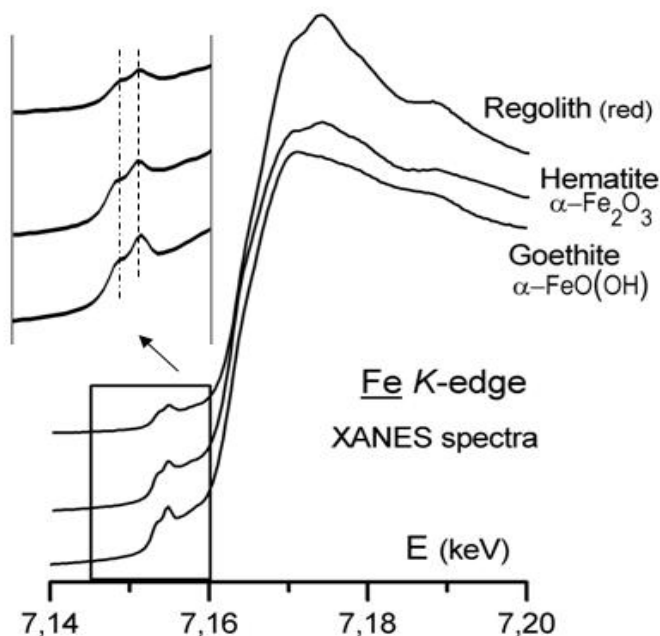
**Fe K-edge** (7.05-7.35 keV) was scanned for the model minerals and also for some iron sulphates – mostly brownish (e.g., the jarosites) –, including the green pigment called “vitriol” – the mineral melanterite, Fe(SO<sub>4</sub>)·7H<sub>2</sub>O.

As a preliminary approach to the study of sulphur in sulphates, the **S K-edge** spectrum (2.44 to 2.56 keV) was also scanned from these and from some whitish sulphate minerals.

**XANES spectra** were collected in fluorescence yield (FY) and total electron yield (TEY) modes. Various points were irradiated in each sample and about ten scans were performed per point. From a total of about 2500 registered scans, 400 spectra were obtained.

Figures 1 and 2 illustrate the good quality of pre-edge details in the Fe K-edge XANES spectra collected from differently coloured Fe-O minerals and from the iron phosphate used as blue pigment (vivianite).

**Fig. 1**



**Fig. 2**

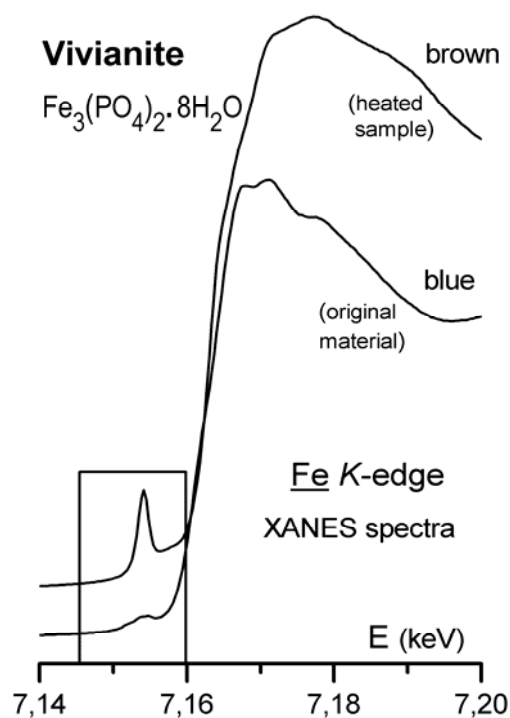
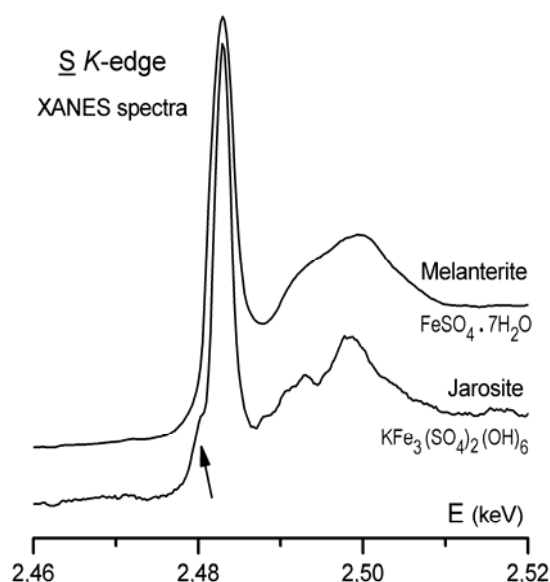


Figure 3 emphasizes small differences noticed in the  $\underline{\text{S}}$  K-edge XANES spectra collected from two natural sulphates with distinct crystal structures – jarosite, trigonal, and melanterite, monoclinic – namely, a detail preceding the white line.

**Fig. 3**



A preliminary appraisal of  $\underline{\text{S}}$  K-edge in BETESPT (bis-tri-ethyl-oxy-silyl-propyl-tetrasulphide) thin films deposited over an aluminum alloy and treated with cerium nitrate was attempted (6 XANES spectra).

To complete spectroscopic data on calcium in high-lead glazes,  $\underline{\text{Ca}}$  K-edge XANES spectra were collected from 6 tile glaze samples plus 3 model minerals (fluorite, calcite and gypsum); the results will be presented at the forthcoming European Materials Research Society (EMSR) Spring Meeting to be held in Strasbourg.