EXAFS and XANES characterization of sedimentary iron in the Gulf of Trieste (N. Adriatic)

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XANES and EXAFS results from the sediments in the Gulf of Trieste show that Fe is principally bounded to oxygen throughout the sediment profile. Goethite is found to be the dominant crystalline structure. From this we conclude that even with high rates of sulfate reduction, dissolved sulfide will not accumulate in sediment pore waters forming pyrite when iron oxides are present. The released dissolved sulfide in pore water diffuses upwards and becomes oxidized at the sediment-water interface.

Keywords: marine sediments, Fe XANES, Fe EXAFS, iron oxides.

In marine sediments iron is mainly present in the form of amorphous iron oxyhydroxides and various iron oxides. Fe can act as an electron acceptor in the microbial degradation of sedimentary organic matter in anoxic sediments (Froelich *et al.*, 1979). Besides, in dissimilatory reduction iron oxides are also reduced by organic acids (Luther *et al.*, 1992) and by other electron acceptors (i.e. sulfides) forming pyrite.

In order to decode the complex role of iron during early diagenesis in coastal marine sediments in the Gulf of Trieste (N. Adriatic), we studied iron local environment in iron-containing sedimentary phases with XANES and EXAFS. Waters overlying these bioturbated sediments are often oxygen depleted in late summer and occasionally become anoxic due to strong vertical temperature and salinity gradients.

Sediment cores (approx. 6 cm dia.) were taken by SCUBA at station F (45° 32′ 43″ N, 13° 33′ 13″ W) in the central part of the Gulf of Trieste. Sediment was extruded and sectioned in 1, 2 or 4 cm intervals in an N_2-filled glove bag. Sediment samples (Fe-0, Fe-8, and Fe-17, taken at different depths) were prepared by freeze drying and gentle grinding. XANES and EXAFS spectra at the Fe K-edge were measured at the EXAFS II station in HASYLAB at DESY (Hamburg, Germany). Synchrotron radiation from the DORIS storage was focused by an Au-coated mirror on a Si(111) double-crystal monochromator with 1.5 eV resolution at 7 keV. Harmonics were effectively eliminated by a plane Ni coated mirror and by detuning the monochromator crystal using a stabilisation feedback control. Powdered samples were prepared on multiple layers of adhesive tape. A Fe K-edge jump of only about 0.1 was obtained at the total absorption thickness of ~1.5 due to the low concentration of Fe in the sediment. Reference spectra were taken on empty tapes. Exact

energy calibration is established with the simultaneous absorption measurements on the Fe metal foil.

Bulk sediment chemical analysis, visual examination and mineralogy of the sediment indicate that the sediment in profile is practically uniform. With scanning electron microscope we observed that Fe minerals are dispersed on the surface of the sediment and bound to the surface of layered silicates.

Normalised Fe K-edge XANES spectra of the sediment samples are shown in Fig. 1, together with the spectra of reference samples of Fe_2O_3, and Fe metal. The K-shell contribution is obtained by removing the extrapolated pre-edge (-250 .. -50 eV) trend. Zero of the energy scale is taken at the first inflection point in the Fe metal spectrum at 7112 eV, which marks the 1s ionisation threshold in the Fe metal. The Fe XANES spectra of the three sediment samples at the different depth exhibit identical edge structure, indicating that the local environment of Fe atoms should be the same in all three samples.
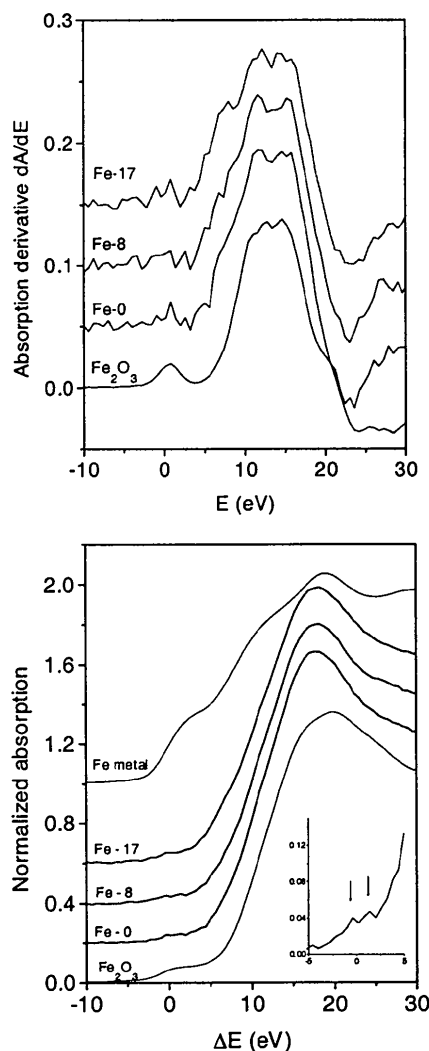

Figure 1
Derivative and normalised Fe K-edge absorption spectra displaced vertically, for the sediment and reference samples. Energy scale is relative to the Fe K-edge in Fe metal (7112 eV). The average of the three spectra measured in sediment in the energy region of the pre-edge resonances (indicated by arrows) is shown in the inset.

Table 1

FEFF model parameters for the goethite crystal structure for the first and second shell of neighbours. Elements are labelled according to their distances from the central Fe atom in the crystal structure (Szytula *et al.*, 1968). Uncertainty of the last digit is given in the parentheses.

Neighbor element	ΔR/R	σ^2 (Å^2)
O1..O6	-0.017(3)	0.003(1)
Fe1..Fe4, O7	0.02(1)	0.007(2)

The energy position of the edge is correlated with the valence state of the atom in the sample: with increasing oxidation state the edge is shifted to higher energies (Wong *et al.*, 1984). Energy shifts of the Fe K-edge of all three samples, taken at the edge inflection point (Fig. 1), coincide with the energy position of the Fe K-edge in the reference Fe_2O_3 sample, indicating that average valence state of iron in the sediments is Fe^{3+}. The two pre-edge resonances, separated by about 2 eV, are characteristic for octahedral co-ordinated Fe atoms (Petiau & Calas, 1983).

Fe K edge EXAFS spectra of the sediment samples have been analyzed with the University of Washington analysis programs using FEFF6 code for ab-initio calculation of scattering paths (Stern *et al.*, 1995, Rehr *et al.*, 1992). No significant difference could be found between the spectra of the three sediment samples.
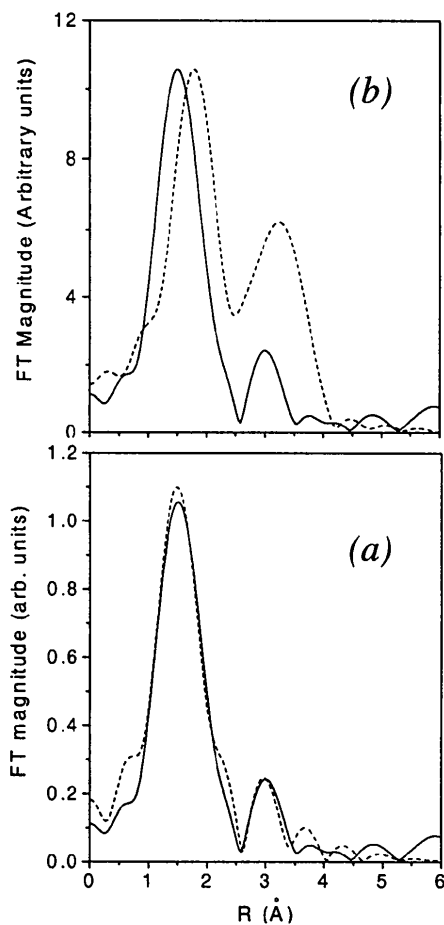
Figure 2
Fourier transform of k^2 weighted Fe-8 EXAFS spectrum in the k range from 4 to 9 Å^{-1} (solid line); (dashed line): *(a)* goethite model; *(b)* pyrite model.
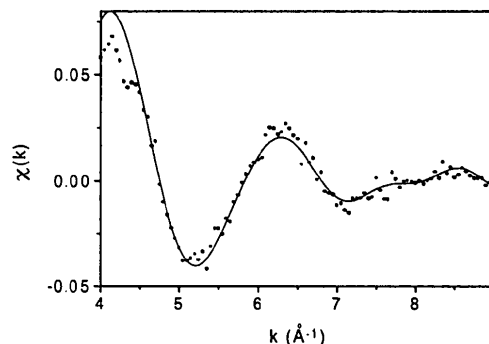
Figure 3
EXAFS spectrum of Fe-8 sample (dots) and goethite model in the R range of 1Å – 3.4 Å (solid line).

A FEFF model based on the goethite crystal structure (Szytula *et al.*, 1968) is found to describe satisfactorily the measured EXAFS spectra. In spite of rather low signal to noise ratio, a very good fit was found in the R region from 1.1 Å to 3.4 Å in the Fourier transform, using all single and multiple scattering paths of the lattice within this range (Fig. 2a and 3). Small distortions of the model lattice are allowed by varying the four FEFF model parameters in Table 1.

Iron atoms are therefore surrounded by a distorted octahedron of six oxygens. In the second shell contributions of six Fe atoms and one oxygen are confirmed. Contributions of more distant shells cannot be distinguished from the noise. An alternative FEFF model based on the pyrite crystal structure (Brostigen & Kjekshus, 1969) cannot describe the experimental spectrum (Fig. 2b).

In conclusion, XANES and EXAFS results from the sediments in the Gulf of Trieste show that Fe is principally bound to oxygen throughout the sediment profile. Goethite is found to be the dominant crystalline structure. From this we conclude that even with high rates of sulfate reduction, dissolved sulfide will not accumulate in sediment pore waters forming pyrite when iron oxides are present. The released dissolved sulfide in pore waters diffuses upwards and becomes oxidized at the sediment-water interface.

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