

A micro-Raman and synchrotron radiation XANES study of coordination mode for iron in black coral

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Abstract

- Iron is a biolimiting nutrient in most of the surface ocean, especially in the high nutrient and low Chla (HNLC) regions. To date, lack of environmental Fe proxy with high resolution limits the understanding of iron cycle in ocean. Coordination mode of Fe in potential archives is foundation in establishment of Fe proxy profiles.
- In the present work, in situ micro-Raman and synchrotron radiation XANES were applied to investigate the coordination mode between Fe and organic skeleton of black coral (*Antipatharia*). The Raman peaks of Fe-O complexes (531 cm^{-1} , 589 cm^{-1} , 638 cm^{-1}) in black coral skeleton were proved by treatment with ethylene diamine tetraacetic acid (EDTA) and FeCl_3 solutions.
- Moreover, X-ray absorption near edge spectroscopy (XANES) of Fe k-edge was applied, showing that tris-DOPA-Fe complex is the main existing form of Fe in black coral, followed by bis-DOPA-Fe complex. This coordination structure provides black coral with high accumulation of Fe in ambient environment. Hence the Fe incorporated in black coral skeleton would be proportional to the ambient seawater Fe concentration as well as variations in ocean primary productivity.
- Our work initially demonstrates the coordination mode of Fe in black coral and further presents the feasibility of black coral as environmental Fe proxy.

Materials and methods

Sample collection: One living black coral sample, which was afterwards identified as of *Cirrhopathes spp.*, was collected from Luhuitou Reef in Sanya Bay, south of Hainan Island (SY-1), at the depth of 9 m, in April 2012.

Raman microspectroscopy: Three coral spices were prepared for the Raman spectroscopy. Two coral slices was soaked in a mixed solution of 200 mM EDTA and 10 mM Tris with stirring for 18 h at pH 4.7. After sufficient reaction, coral slices were rinsed in the ultrasonic bath using Milli-Q water for 10 min. One slice was then put into a 1 mM solution of FeCl_3 and soaked for 1 h and rinsed slightly using stream of Milli-Q water.

XANES spectroscopy: XANES analyses were conducted at Beamline 15U1, Shanghai Synchrotron Radiation Facility (SSRF). The coral samples were powdered to reduce the influence of orientation and inhomogeneity.

Calculation of XANES for several suspected structure: All the Density Functional Theory (DFT) calculations were carried out using the Gaussian09 software package. The contribution of different Fe coordination structures was calculated using LCF method implemented in the software package ATHENA.

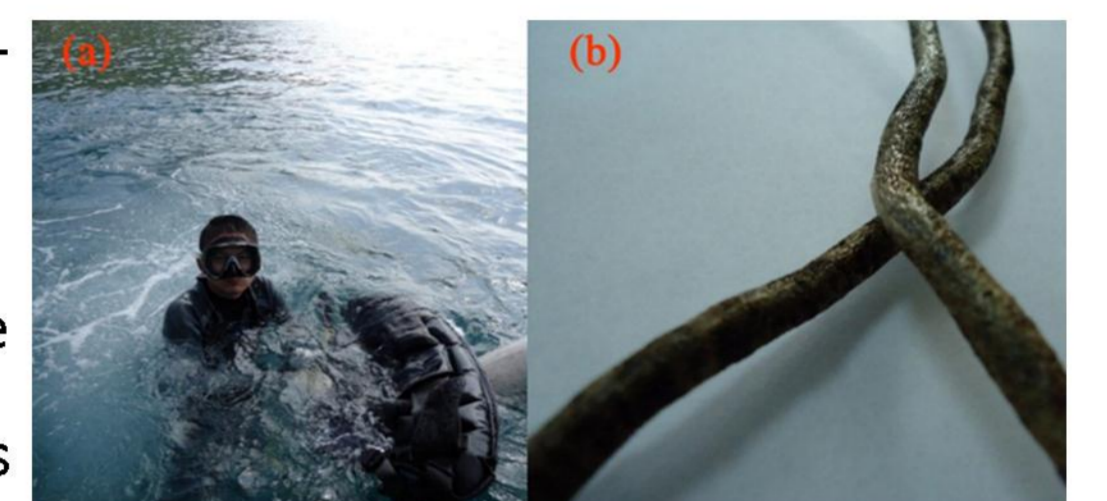


Fig. 1 (a) Coral collection by diver; (b) living black corals collected

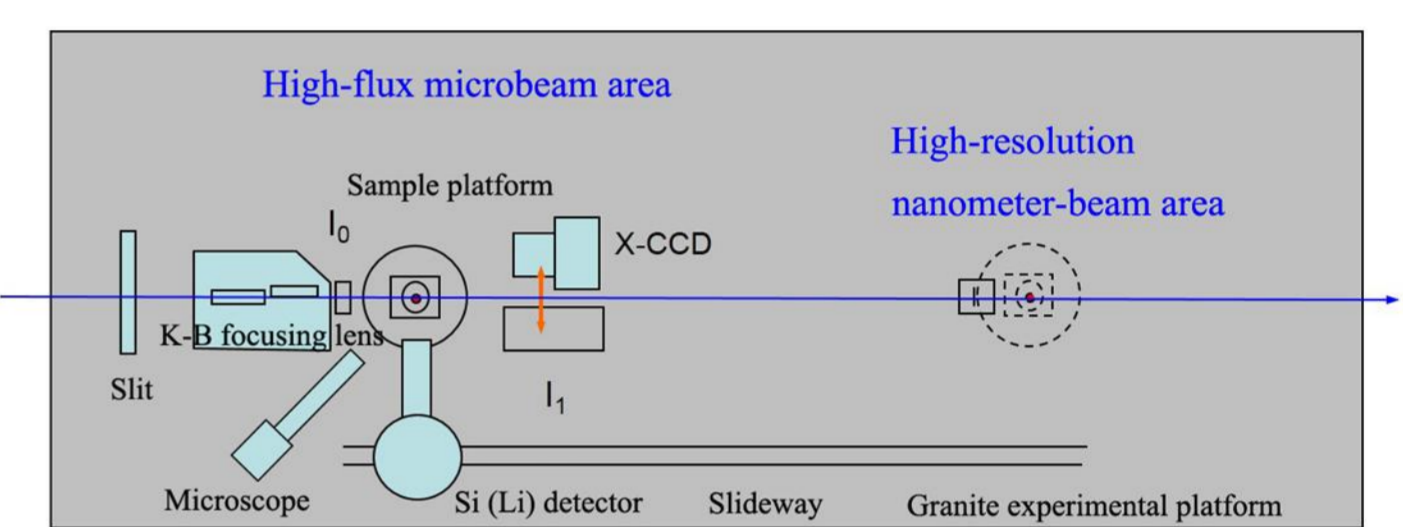


Fig. 2 Experimental platform of beamline 15U1

Results and discussion

- Identification of the iron peaks in Raman spectra:** The results of Raman microspectroscopy demonstrated that the skeleton of black coral was mainly composed of organic matters (Fig. 3). For the native sample, the highest peak located in 531 cm^{-1} , 589 cm^{-1} , 638 cm^{-1} was assigned to bidentate chelation of Fe(III) by the phenolic oxygens of 3,4-dihydroxyphenylalanine (DOPA), which is formed as a post-translational modification of tyrosine. The simultaneous disappearance and recovery located at 531 cm^{-1} , 589 cm^{-1} and 638 cm^{-1} prove that all those three peaks are assigned to bidentate chelation of Fe(III) by the phenolic oxygens of DOPA (Fig. 4).

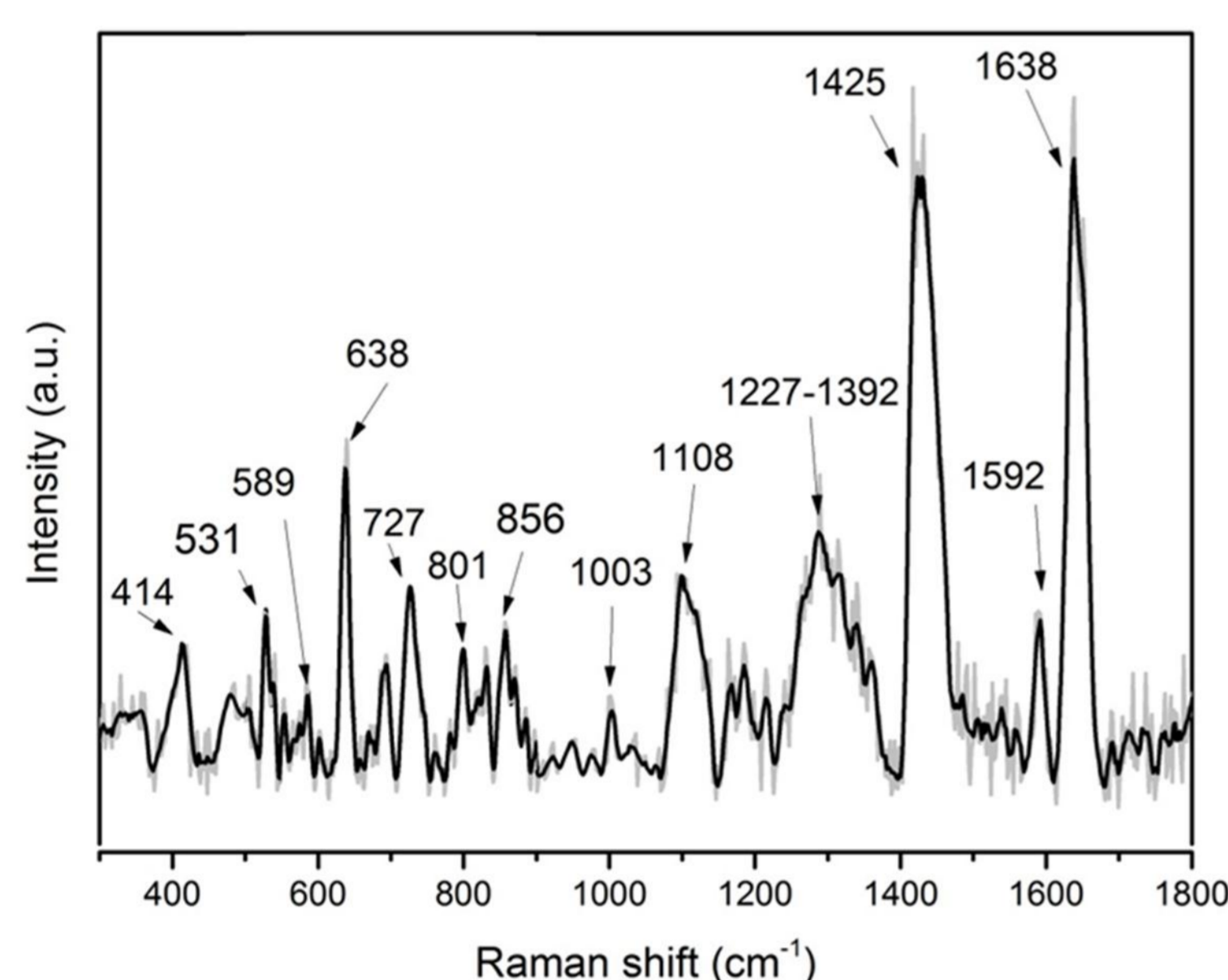


Fig. 3 Raman characteristic spectrum of black coral (sample SY-1) skeleton: Measured line (gray); Fourier filtering line (black)

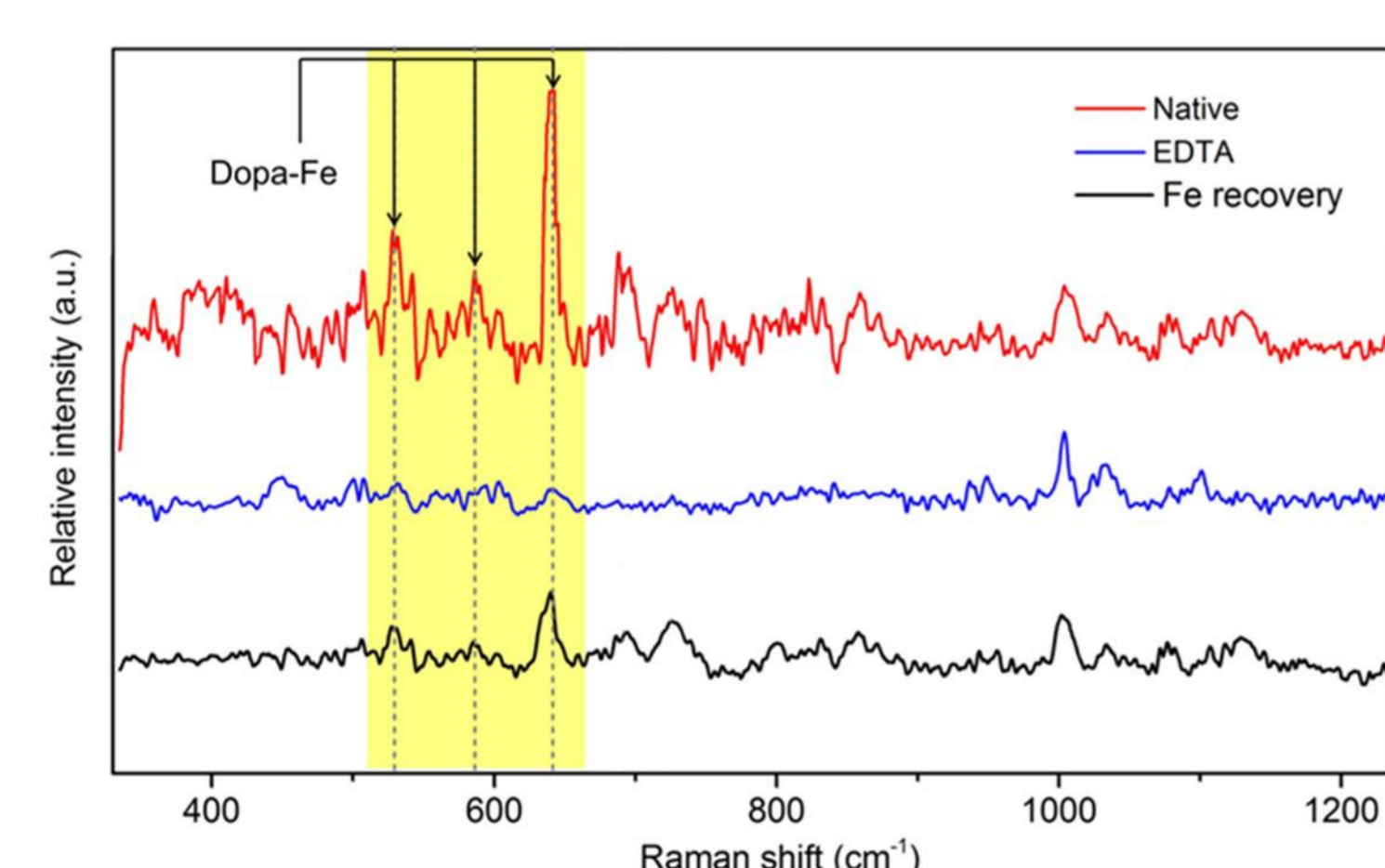


Fig. 4 Raman spectra of sample SY-1 under different experimental conditions (a. native slice; b. EDTA-treated slice; c. FeCl_3 -recovered slice)

- Coordination mode between Fe and black coral skeleton:** His-Fe spectrum differs with the coral sample. The characteristic peaks poorly matched, indicating the inexistence of this mode. Both normalized and first differential spectra of tris-DOPA-Fe and bis-DOPA-Fe are in good accordance with coral sample, including the characteristic peak location and relative peak height, especially for the tris-DOPA-Fe (Fig. 5). This result indicates the existence of these two modes in black coral, and the dominant composition of tris-DOPA-Fe.

LCF was performed on the spectra of tris-DOPA-Fe and bis-DOPA-Fe to fit with our coral sample showing that the tris-DOPA-Fe fraction of 78.7% and 21.3% for bis-DOPA-Fe, which coincides with our suspect.

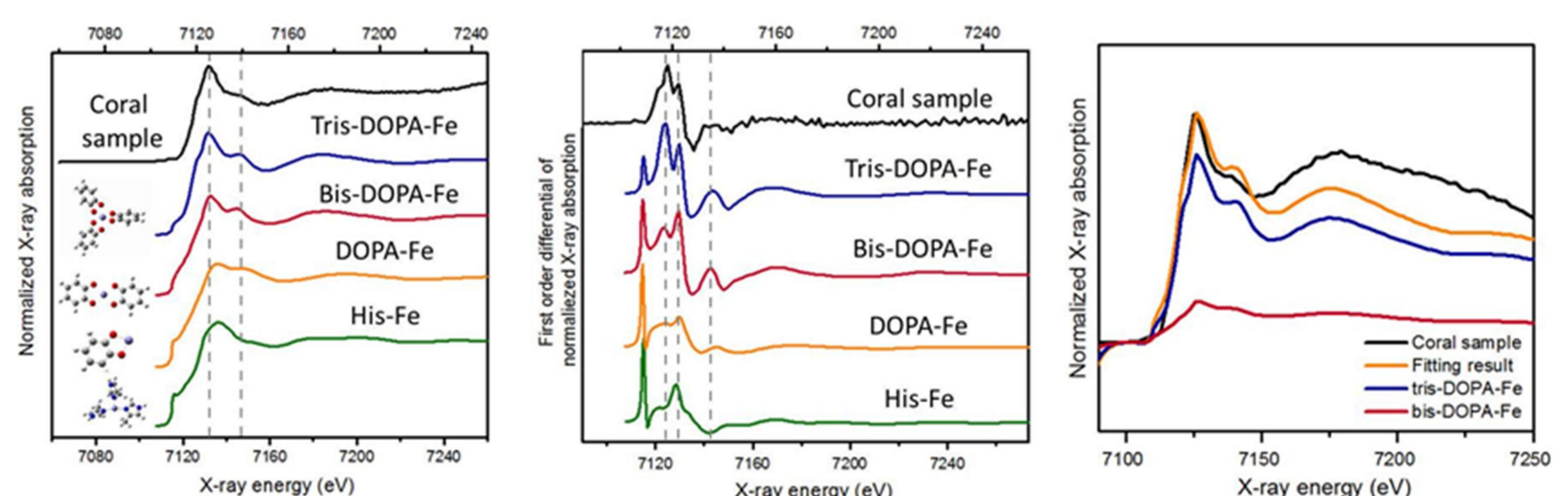


Fig. 5 A: normalized Fe K-edge XANES spectrum of coral sample and calculated XANES spectra of potential structures; B: First differential of normalized X-ray absorption of Fe in black coral skeleton and calculated XANES spectra of potential coordination structures of Fe; C: LCF result of XANES spectra.

Conclusions

- Using in situ Raman microspectroscopy, combined with the chemical treatment with EDTA and FeCl_3 solutions, Fe(III) is found to exist in the form of Fe-DOPA complexes in black coral skeleton. Furthermore, preponderant existence of tris-catecholate Fe-DOPA coordination mode is confirmed using Gauss computation and XANES spectroscopy.
- Fe ions are incorporated into the coral skeleton in response to environmental conditions. Our results indicate that black coral may be one of the powerful biodeposition materials to reconstruct paleoceanographic conditions across a wide depth and geographic range, especially for trace metals such as Fe proxies.

References

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