Detection and Identification of Fe-Bearing Minerals in Pelagic Limestone: Micro-XANES/XAFS and Fluorescence Imaging

Y. Guyodo,[1] J. E.T. Channell,[1] M. Davidson,[2] A. Mikhailova,[3] H. Tostmann,[4] M. Newville,[4] R. Duran[5]
[1] *Dept. of Geological Sciences, University of Florida, Gainesville, FL, U.S.A.*
[2] *Microfabritech, University of Florida, Gainesville, FL, U.S.A.*
[3] *Biomedical Engineering Program, University of Florida, Gainesville, FL, U.S.A.*
[4] *Advanced Photon Source, Argonne National Laboratory, Argonne, IL, U.S.A.*
[5] *Chemistry Department, University of Florida, Gainesville, FL, U.S.A.*

Introduction

In the earth sciences, studies of ancient climates and environments require precise correlation of globally distributed records and absolute timing of processes that took place millions of years ago. As many sediments (and igneous rocks) become magnetized in the ambient field at the time they are formed, the natural remanent magnetization (NRM) reflects past variations of the geomagnetic field vector.[1] The record of the ancient geomagnetic field in sediments and rocks is central to the generation of geologic time scales because the geomagnetic (dipole) field varies on a global scale. Reversals in geomagnetic polarity have occurred aperiodically throughout geologic time, providing a means of global correlation. A finer-scale correlation between reversals can be achieved by monitoring geomagnetic paleointensity proxies.

Magnetization (NRM) in sediments and rocks is usually carried by micron-scale grains of iron oxide or iron sulfide. The most important magnetic mineral is magnetite (Fe_3O_4), and micron-scale grains of this mineral carry a permanent (hard and stable) magnetization at room temperature. Larger magnetite grains (>100 microns) are less important carriers of NRM, as they carry a soft (nonpermanent) magnetization. Information about the average magnetic mineralogy and magnetic grain size of geologic samples is routinely provided by "rock magnetic" studies. The origin of the magnetite grains (biogenic or detrital) is usually unclear, and their association with the nonmagnetic fraction of the sediment is usually poorly known.

To understand the origin and role of these particles in the magnetization process, it is crucial to examine their occurrence in their natural setting rather than in magnetic extracts. Unfortunately, because of the scarcity and small size of these particles, *in situ* detection and imaging with electron microscopy or magnetic force microscopy is almost impossible. This dilemma motivated us to use the highly sensitive x-ray fluorescence mapping techniques available at Sectors 10 (MR-CAT) and 13 (GSE-CARS) of the Advanced Photon Source (APS), to locate Fe-bearing minerals present in pelagic limestone samples. The fluorescence maps are being used to study the distribution of magnetic grains, determine their composition, estimate their grain size for comparison with estimates based on magnetic parameters, and determine their relationship to the nonmagnetic matrix.

Methods and Materials

The x-ray undulator beams at Sectors 10 and 13 have been used to provide area scans of thin polished sections of Cretaceous (~120 Myrs old) limestone from the Maiolica Formation (Italy).[1] The intensity of fluorescence was measured while scanning the x-ray energy at the Fe absorption edge (~7112 eV). The intensity was recorded as a function of the location of the beam on the sample surface, with step/beam sizes ranging between ~100 µm (at Sector 10, using the unfocused beam) and ~4 µm (at Sector 13, using the focused beam). This provided fluorescence maps representing variations of Fe concentration in the sample. Previous study of the limestone magnetic properties indicated the presence of fine-particle magnetite dispersed in a Fe-poor calcium carbonate matrix.[1] Therefore, isolated Fe anomalies on the fluorescence map should be associated with particular Fe-bearing grains. Discrimination of the diverse mineral phases was determined by acquisition of micron-scale x-ray absorption near-edge structure (micro-XANES) from individual grains and comparison to standard XANES. XAFS data were also collected, background corrected, and then compared with theoretical models for particular mineral compositions. The standard XANES were obtained from powders of inorganic and bacterial magnetite (Fe_3O_4), titanomagnetite ($Fe_{2.4}Ti_{0.6}O_4$), hematite (α-Fe_2O_3), maghemite (γ-Fe_2O_3), goethite (α-FeOOH), and pyrite (FeS_2). The XANES patterns obtained for magnetite, hematite, and pyrite were compatible with previously published data.[2,3]

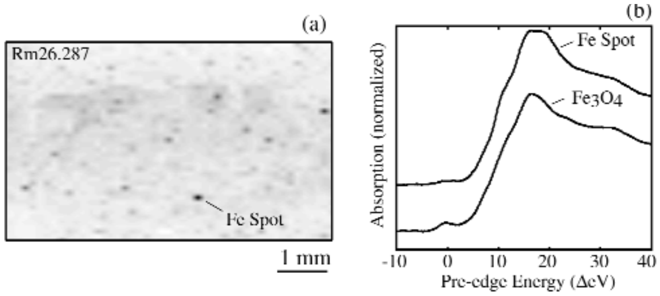

FIG. 1. (a) Fluorescence map obtained at Sector 10 with a beam size of ~100 µm. Dark spots are regions with higher fluorescence at the Fe absorption edge and correspond to the location of Fe-bearing minerals in the sample. (b) Micro-XANES obtained on the Fe anomaly marked in (a), compared to the standard XANES of magnetite.

Results and Discussion

Figure 1a represents an example of an iron fluorescence map established for one of the limestone samples (Rm26.287), with a spot size of ~100 µm. Isolated regions of higher Fe content (dark spots) appear scattered over the entire surface of the sample, suggesting a random distribution of Fe-bearing minerals in sample Rm26.287. Figure 1b shows an example of a micro-XANES performed on one of these anomalies, which was identified as magnetite (Fe_3O_4).

Given the size of the x-ray beam, the information provided by the map and the XANES on this specific iron anomaly is averaged over a 100 x 100 μm2 square of the sample surface. Therefore, the fluorescence signal could have been emitted either by a single grain or by a cluster of smaller particles. Nevertheless, the fact that the micro-XANES was uniquely correlatable to the magnetite standard suggests uniform composition in the region.

Figure 2a shows a fluorescence map obtained at Sector 13 from another sample (AC5.46). In this experiment, the focused beam (~4 μm) was used to improve the discrimination of close-by individual grains with (possibly) different mineralogies. The map reveals the presence of a grain with dimensions ~10 x 20 μm^2, and a much smaller spot (at the bottom) with a diameter of less than ~4 mm. The micro-XANES obtained on the major Fe anomaly was easily correlated to the standard curve of FeS_2 (pyrite) (Fig. 2b). The smaller grain was attributed to a composition intermediate between Fe_3O_4, and $Fe_{2.4}Ti_{0.6}O_4$, although the micro-XANES was noisier than for the larger grain.

Other Fe anomalies on these and other fluorescence maps (from different samples from the same pelagic limestone formation) yield micro-XANES that have been compared with XANES from standards. Grains of magnetite, titanomagnetite, hematite, and pyrite have been tentatively identified based on these comparisons.

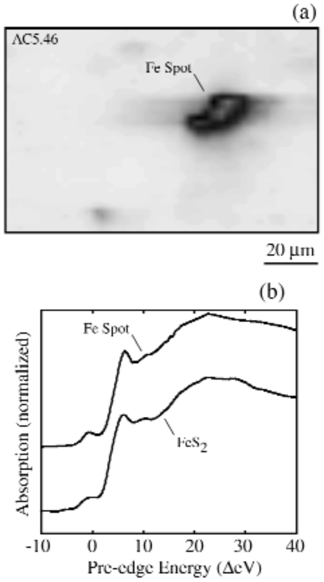

FIG. 2. (a) Fluorescence map obtained at Sector 13 with a beam size of ~4 μm. Dark spots correspond to the location of Fe-bearing minerals in the sample. (b) Micro-XANES obtained on the Fe anomaly marked in (a), compared to the standard XANES of pyrite.

Conclusion

Fluorescence maps representing the micron-scale distribution of Fe-bearing minerals in a Fe-poor calcium carbonate matrix have been obtained at Sectors 10 and 13 of the APS. Micro-XANES and XAFS generated for those anomalies at the Fe absorption edge allowed discrimination among mineral phases. The method should lead to a new understanding of the composition, grain size, and distribution of Fe minerals contributing to the magnetic properties of natural sediments. The fluorescence maps also aid in the localization of the magnetic grains by conventional microscopy techniques. We expect these initial results to lead to a new understanding of the origin of naturally occurring magnetic grains and the process of magnetization in sediments and sedimentary rocks. These are important challenges in view of the role of sediment magnetization in the generation of time scales for geologic dating.

Acknowledgments

Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38, the Materials Research Collaborative Access Team, and the GeoSoilEnviro Consortium for Advanced Radiation Sources. This work has been supported by the University of Florida Opportunity Fund from the Office of Research, Technology, and General Education. The standard samples of titanomagnetite and bacterial magnetite were kindly provided by Bruce Moskowitz and Richard Frankel, respectively.

References

[1] J.E.T. Channell and C. McCabe, J. Geophys. Res. **99**, 4613-4623 (1994).

[2] G. Drager, R. Frahm, G. Materlik, and O. Brummer, Phys. Stat. Sol. (b) **146**, 287-294 (1988).

[3] S. Bajt, S.R. Sutton, and J.S. Delaney, Geochim. Cosmochim. Acta **58**, 5209-5214 (1994).