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In situ chemical speciation of iron in estuarine sediments using XANES spectroscopy with partial least-squares regression

Akihito Kuno,^{a*} Motoyuki Matsuo^a and Chiya Numako^b

^a*Graduate School of Arts and Sciences, The University of Tokyo, 3-8-1 Komaba, Meguro, Tokyo 153-8902, Japan,*

^b*Faculty of Integrated Arts and Sciences, The University of Tokushima, 1-1 Minami-josanjima, Tokushima 770-8502, Japan.*

Email: akuno3@dolphin.c.u-tokyo.ac.jp

X-ray absorption near-edge structure (XANES) spectroscopy has been applied to the quantitative determination of iron species in estuarine sediments. Mixtures of pyrite, olivine, and goethite were prepared as model mixtures containing ferrous sulfides, ferrous silicates, and ferric oxides and/or hydroxides, respectively. For resolving XANES spectra of these mixtures and quantifying the Fe-bearing minerals, partial least-squares (PLS) regression has been employed. The obtained PLS regression gave sufficient precision and this technique was applied to the XANES spectra of estuarine sediments collected from the Tama River in Tokyo, Japan. The relative abundances of iron species thus determined were consistent with the Mössbauer spectroscopic results.

Keywords: XANES; PLS; estuarine sediment; iron; quantitative speciation.

1. Introduction

Chemical speciation of elements in environmental samples is of great importance because the environmental behaviour of an element highly depends on its chemical form. The most commonly employed methods for estimating oxidation states and phase associations of elements in solid environmental samples have involved serial chemical extraction followed by assignment of the extracted fractions to operationally defined chemical forms. These indirect methods suffer from significant variabilities introduced by system specificity and also by the uncertainty surrounding chemical species transformations that may be induced during extraction (Bertsch *et al.*, 1997). From this point of view, non-destructive methods such as XANES spectroscopy have an essential advantage in chemical speciation. However, XANES spectra of different species often have severe overlap in the whole spectral region. So far, quantitative methods using XANES for the determination of oxidation states have been developed for several elements (Schulze & Bertsch, 1995). In this study, partial least-squares (PLS) regression is employed to resolve XANES spectra of mixtures and quantify the species therein.

PLS regression is a multivariate analysis, which has been applied to multi-component determination using spectroscopic methods such as infrared spectroscopy, spectrophotometry, *etc.*

(Otto & Wegscheider, 1985; Kelly *et al.*, 1989). Generally, a spectrum is a series of numbers. In particular, a usual XANES spectrum is a series of more than hundred numbers. The basic idea is to predict relative abundances of species in a mixture by the series of numbers constituting its XANES spectra. However, ordinary least-squares regression does not work for this purpose because the independent variables are too many. To avoid this difficulty, PLS regression is performed by decomposing both the independent and dependent variables into latent variables. Basically, with increasing number of latent variables, the difference between predicted values and actual ones become smaller but overfitting is more likely to occur. Therefore, validation with test samples is necessary to search for the appropriate number of latent variables. PLS regression is preferable to principal component analysis (PCA) or factor analysis (FA) because latent variables are computed both to model independent variables and to correlate with dependent variables in PLS regression while latent variables are computed only to model independent variables in PCA or FA (Lindberg *et al.*, 1983). Because of the quality of the calibration models produced, PLS regression has come to dominate the practice of multivariate calibration (Lavine, 1998). That is the reason why we use PLS regression for the quantitative speciation by XANES spectroscopy.

To the best of our knowledge, this is the first time that PLS regression has been applied to the interpretation of XANES spectra. At first, the availability of PLS regression is checked for mixtures containing known amounts of Fe-bearing minerals. Then its application is extended to the speciation of iron in the sediments collected from the Tama River estuary in Tokyo, Japan. The vertical distribution of iron species in the sediments are thus investigated and compared with that determined by ⁵⁷Fe Mössbauer spectroscopy.

2. Experimental

Pyrite (FeS₂), olivine ((Fe,Mg)₂SiO₄), and goethite (α-FeOOH) were selected as model components in order to obtain results comparable with Mössbauer spectroscopic results. By applying Mössbauer spectroscopy to the Tama River estuarine sediments collected previously, 4 iron components were separated according to the valence, spin state, and magnetism (Kuno *et al.*, 1998; Matsuo *et al.*, 1996). The diamagnetic low-spin ferrous component was attributable to pyrite, and therefore, pyrite was selected as a model mineral in the present study. The paramagnetic high-spin ferrous component was attributable to ferrous silicates. The possibility that other high-spin ferrous compounds exist in the samples could not be excluded, but ferrous silicates were dominant compared to them according to its Mössbauer parameter (König & Hollatz, 1990). Although Fe-bearing clay minerals such as chlorite are common among ferrous silicates in sediments, olivine was selected as the second model mineral in this study because it does not contain ferric component and is a relatively stable ferrous silicate. The paramagnetic high-spin ferric component was ascribable to various ferric compounds including amorphous ferric hydroxides. The magnetically ordered component mainly consisted of ferric oxide and/or hydroxide. Goethite was selected as the third model mineral corresponding to the ferric components, which contributes to the paramagnetic high-spin ferric or magnetically ordered components in Mössbauer spectra. For these reasons, mixtures of pyrite, olivine, and goethite were prepared as model mixtures containing ferrous sulfides, ferrous silicates, and ferric oxides/hydroxides, respectively, which approximates the Tama River estuarine sediments.

Thirteen mixtures containing these three minerals at different ratios in the range of 0% to 100% were prepared for calibration and 6 mixtures for test. Pyrite and olivine were prepared from natural minerals and their iron contents were determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES) after decomposition. Goethite was prepared from highly pure reagent. Each mineral was ground into fine powder, mixed with one another, diluted with boron nitride, and made into a pellet.

A vertical sediment core of approximately 50 cm in length was collected from an estuarine area of the Tama River on November 6, 1997. The upper portion (< 20 cm) of the core was composed of brown, sandy sediment, and the lower portion (> 20 cm) of black clay-like sediment. The collected sediment core was cut into 3-cm long sediments immediately after sampling, and porewater was extracted by a pressure filtration technique (5 atm, N₂). In order to avoid air oxidation, the pressure-filtered sediments were packed in oxygen-impenetrable bags with nitrogen gas. Elemental analysis and Mössbauer spectroscopic investigation were also conducted for these sediments in the same manner as our former works (Kuno *et al.*, 1997; Kuno *et al.*, 1998). The Fe content of the sediments was *ca.* 3 wt%.

The Fe K-edge spectra of all the samples were measured in a fluorescence mode using a Si(111) double-crystal monochromator and a Lytle-type detector (Lytle *et al.*, 1984) at BL-7C, Photon Factory, KEK, Japan. The spectra of the sediments were measured in the *in situ* mode without sample dilution. Transmission mode is not available for these *in situ* samples because these samples often cannot be made to have appropriate thickness (Waldo *et al.*, 1991). In order to minimize self-absorption effect, the area density of iron in the mixture pellets was adjusted to almost the same as that in the sediment samples, which was *ca.* 5 mg cm⁻² and not so different among samples. The XANES spectra measured over a 150-eV energy range at about 1-eV step increments were normalized by following treatments. First, a background spectrum was calculated by Victoreen's equation (Victoreen, 1948) and subtracted from the raw data. After extracting the data of the XANES region, the minimum value in the XANES region was subtracted from all the data and finally all the data were divided by the maximum value in the XANES region. A XANES spectrum thus normalized consisted of 174-point data.

For 13 mixtures in the calibration set, PLS model was constructed using these spectrum data as 174 independent variables and the relative abundances of pyrite, olivine, and goethite as 3 dependent variables. The XANES spectrum data ranging between 0 and 1 by normalization and the relative abundances ranging between 0 and 1 were subjected to the PLS algorithm (Lindberg *et al.*, 1983), although the relative abundances are shown in percentage for plain presentation in this paper. The standard error and square of correlation coefficient, R^2 , of calibration were calculated for 13 mixtures in the calibration set. The standard error and R^2 of prediction were calculated for 6 mixtures in the test set that was not used to construct the calibration model.

3. Results and discussion

The normalized XANES spectra of the model components, *i.e.* pyrite, olivine, and goethite, are shown in Fig. 1, where severe spectral overlap is observed. To make the difference clear, XANES spectra over a 20-eV energy range around the edge are shown. It can be seen that the energy of absorption edge of pyrite is significantly different from that of olivine even though both are ferrous compounds, which means that the type of ligating atoms

Table 1

Results of PLS regression for mixtures of pyrite, olivine, and goethite.

Calibration mixture no.	Relative abundance (%)					
	Pyrite		Olivine		Goethite	
	Actual	Calc'd	Actual	Calc'd	Actual	Calc'd
1	0.0	-0.5	0.0	0.2	100.0	100.2
2	0.0	0.1	100.0	98.8	0.0	1.0
3	100.0	99.1	0.0	-0.5	0.0	1.4
4	0.0	0.1	49.9	51.2	50.1	48.7
5	50.0	53.6	0.0	0.9	50.0	45.5
6	47.3	47.0	52.7	54.6	0.0	-1.6
7	29.7	30.8	37.6	35.3	32.7	33.9
8	25.3	25.5	25.4	24.1	49.3	50.4
9	28.2	31.0	46.8	45.6	25.1	23.4
10	46.8	47.3	28.1	26.1	25.2	26.6
11	30.1	29.6	34.2	34.0	35.7	36.5
12	36.7	34.4	42.6	46.0	20.7	19.6
13	40.4	36.3	16.3	17.3	43.3	46.4
Std error of calibration	1.9		1.6		1.9	
R^2 of calibration	0.995		0.996		0.995	
Test mixture no.	Actual	Calc'd	Actual	Calc'd	Actual	Calc'd
1	19.1	20.2	35.5	36.3	45.4	43.5
2	22.7	22.4	44.9	45.5	32.3	32.1
3	35.2	35.8	15.6	12.5	49.2	51.7
4	30.5	32.4	45.7	45.3	23.8	22.2
5	48.4	46.3	20.4	20.4	31.1	33.3
6	45.8	44.6	29.9	30.4	24.3	25.1
Std error of prediction	1.4		1.4		1.7	
R^2 of prediction	0.984		0.986		0.969	

has much influence on the Fe-XANES spectral features as well as the oxidation state.

The appropriate number of latent variables in PLS regression was determined by constructing PLS models with different numbers of latent variables and then comparing the prediction errors from the independent test set. The standard error of calibration decreased with increasing number of latent variables while the standard error of prediction reached a minimum at 5 latent variables. Consequently, we decided that the best number of latent variables is 5 in this case. The results of PLS regression with 5 latent variables are shown in Table 1. The actual and calculated relative abundances of each mineral for 13 mixtures in the calibration set agreed well in the whole ratio range of 0% to 100% and resulted in the high R^2 of calibration. For 6 mixtures in the test set, the R^2 of prediction are sufficiently high and the standard errors of prediction are low enough, which means that PLS regression can resolve XANES spectra and quantify the Fe-bearing minerals for mixtures of pyrite, olivine, and goethite.

The spectra of the sediments at different depths are also shown as solid curves in Fig. 1. They slightly shifted to lower energy side with increasing depth, which corresponds to the fact that the deeper sediments were in more reduced condition. By applying the PLS model obtained for mixtures of pyrite, olivine, and goethite to these spectra, the relative abundances of pyrite-

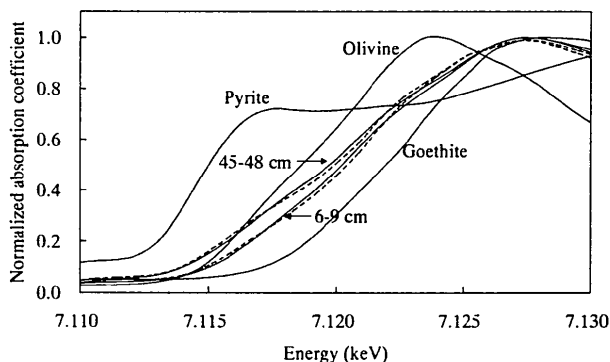


Figure 1

Normalized Fe K-XANES spectra of the model components and the sediments at different depths (dashed curves are the fits for the sediments).

olivine-, and goethite-like components in the sediments were determined. The dashed curves in Fig. 1 are the fitted curves by the PLS model and agree well with the spectra of the sediments. The standard deviation of residuals in the fits of spectra was less than 0.013 for all the sediment samples, which confirms that the selection of model components was justifiable (Lindberg *et al.*, 1983). The closed symbols in Fig. 2 shows the depth profile of iron components thus determined. In this case, the relative distribution approximately corresponds to the absolute distribution of these components because the total amount of iron in the sediments did not show substantial variance vertically. The pyrite-like component increases with increasing depth, accompanied by a slight decrease in the olivine- and goethite-like components. In order to clarify what errors or ambiguities are introduced by assuming model components, the authors measured the XANES spectra of other iron compounds than those in model mixtures and subjected their spectra to the PLS model calibrated for the model mixtures. Each iron compound approximately contributed to the component that was similar in oxidation state and ligating atom, and it was found that the approximation by model mixtures was justifiable when the model components were dominant in analyzed samples (Kuno & Matsuo, 1999). Since the oxidation state and the type of ligating atoms have much influence on the Fe-XANES spectral features (Bajt *et al.*, 1994; Westre *et al.*, 1997), pyrite-, olivine-, and goethite-like components could be considered as S-ligating ferrous component, O-ligating ferrous component, and O-ligating ferric component, respectively.

The Mössbauer spectra of the sediments were almost the same as those of the sediments collected previously that were reported by Kuno *et al.* (1998), and above-mentioned 4 iron components were separated as well. A detailed discussion on the Mössbauer results of the Tama River estuarine sediments can be found in the reference. The relative abundances of these components were determined with an error of less than 2% by curve fitting of the Mössbauer spectra. The depth profile of iron components thus determined is shown as open symbols in Fig. 2, which is quite similar to that determined by XANES spectroscopy combined with PLS regression. The diamagnetic low-spin ferrous component, *i.e.* pyrite, increases and the other components decreases with increasing depth. A detailed comparison reveals that the goethite-like component is smaller and the olivine-like component is larger in the XANES results than in the Mössbauer results. This is probably because the magnetically ordered

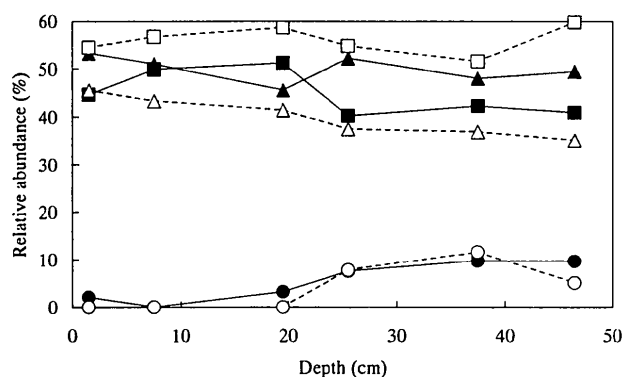


Figure 2
Depth profile of iron components in the sediment core determined by XANES spectroscopy combined with PLS regression (closed symbols) and by Mössbauer spectroscopy (open symbols): ●, pyrite-like component; ▲, olivine-like component; ■, goethite-like component; ○, diamagnetic low-spin Fe(II); △, paramagnetic high-spin Fe(II); □, paramagnetic Fe(III) & magnetically ordered Fe.

component partly includes ferrous components that should have corresponded to the olivine-like component.

As a whole, it is noteworthy that these two totally different methods resulted in a good agreement. In conclusion, XANES spectroscopy combined with PLS regression has been successfully applied to the quantitative speciation of iron in estuarine sediments. Among quantitative methods using XANES for speciation, PLS regression has the advantage of wide availability; it can be applied to any elements and any mixtures, no matter how many components they consist of, if appropriate model mixtures are selected. In particular, PLS regression can separate 3 or more components, unlike other quantitative methods using one variable such as edge energy or intensity at a specific energy. PLS regression can properly use the information from the whole region of spectra and the composition of calibration mixtures. For these reasons, XANES spectroscopy combined with PLS regression can be a promising tool for non-destructive speciation of a wide variety of environmental samples. Basically, environmental samples are mixtures of various species. Mixtures containing all possible compounds are ideal but preparation of mixtures containing such many compounds is impossible. Since this study focused on comparison with Mössbauer results, mixtures of pyrite, olivine, and goethite were selected as a model that approximates iron components in the sediments and reasonable results were obtained. Both the Mössbauer results and the well-fitted spectra in the regression confirmed that the selection of model components in this study was justifiable. In further study, however, it should be investigated how the calculated results depend on the selection of model components. Once model components are selected, results of PLS regression are uniquely deduced if the number of latent variables is properly determined by cross-validation.

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