

Investigation of Atmospheric Aerosol by Means of X-Ray Diffraction and X-Ray Absorption Spectroscopy Using the Synchrotron Radiation

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Abstract

The spectra of aerosol samples collected near the Lake Baikal are investigated with the help of synchrotron radiation (SR). It is demonstrated that it is possible to determine the phase composition of real atmospheric aerosol and the oxidation degree of 3d-elements in them by means of XANES and X-ray diffraction using SR.

INTRODUCTION

Investigations of atmospheric aerosol are mainly aimed at the determination of their elemental composition [1–3]. In addition, sorption of organic substances on the aerosol surface is considered [4–6]. However, an essential problem is the determination of phase composition of aerosol and oxidation degree of the atoms of transition elements in it. Knowing the oxidation degree of transition metals helps getting additional information concerning the hazardous character of these aerosol samples, as well as their reactivity. For example, nickel as a metal is much more dangerous carcinogenic agent than divalent nickel [7]. In addition, the possibility of catalytic and photocatalytic reactions to occur on the aerosol surface leading to new dangerous compounds is considered during the recent years [8–10]. In these processes, the major activity is also exhibited by the transition metal ions; their ability to photoabsorption and their catalytic activity depend on their oxidation degree and phase state.

The problem of using the standard methods of X-ray diffraction to investigate atmospheric aerosol is linked with small sample mass (usually several tens milligrams). In addition, the sample is spread over rather large area of a Whatman-type filter. Investigation of such samples by standard procedures is difficult because of the lack of sensitivity. For the recent 10 years, the number of works determining the phase composition of atmospheric aerosol by means of X-ray diffraction is very small [12]. The problem can be solved by performing investigations using the synchrotron radiation (SR). The use of SR allows one to elevate the sensitivity of measurements to a level sufficient for the investigation of atmospheric aerosol samples, due to higher intensity of X-ray radiation and to the possibility of conducting measurements in a regime close to the sliding incidence mode, because the SR beam is strongly collimated. The beam deviation along vertical direction is about 10^{-4} rad.

The procedure of determining oxidation degree of an element using the shape and position of the edge of its X-ray absorption spect-

rum (XANES spectroscopy) has been widely used in mineralogy during the recent years [13]. In order to record XANES spectra, it is necessary to have 1–2 mg of an element under investigation on the irradiated area of the sample. Because of this, both the total amount of the aerosol collected at the filter and the content of an element of interest are important. As a rule, such a determination of the oxidation degree can be performed for heavy elements starting from titanium. The possibility to determine oxidation degree of heavy elements in atmospheric aerosol with low content of these elements requires verification.

The determination of the charge state within the XANES method is performed according to the position of the edge of absorption in *K* or *L* absorption spectra (photoionization of *1s* and *2p* levels, respectively), which shifts towards higher energy with the increase in effective charge on an atom. The determination of oxidation degree of a series of elements is possible using a structure that appears near the edge because of the *1s*–*3d* transitions which are prohibited according to selection rules. These elements include iron, titanium vanadium.

In the present investigation, an attempt is made to check whether it is possible to determine phase composition and oxidation degree of some heavy metals in aerosol samples of non-anthropogenic origin from the Lake Baikal region.

EXPERIMENTAL

The samples collected near Lake Baikal in January and February 1998 at the station situated in Irkutsk, and at the mountain atmospheric station of Mondy were investigated. Aerosol was collected with a Whatman-type paper filters by pumping the air through them for 1 day (the samples of the Irkutsk series) and for 5 days (for Mondy-15 sample). No selection of aerosol according to the particle size was performed. Characteristic particle size was 0.1–2 μm . The samples were stored in polyethylene bags to exclude contamination. The samples in their

initial form, *i. e.* without additional treatment, were used in all the measurements. Filter pieces with an area of about 2 cm^2 were used for measurements.

The elemental composition of the samples was determined by means of the secondary ion mass spectrometry (SIMS) with the MS-7201 instrument according to the procedure described in [14]. The samples were etched by argon ion beam of the energy of 4 keV. The data shown in Table 1 correspond to the depth of 40 nm. The features and the possibilities of the analysis of atmospheric aerosol samples from the Lake Baikal region by means of SIMS are described in detail in [15].

The diffraction data were obtained in the Siberian SR Centre at the Station of Precise diffractometry of polycrystals (SR bunker of the VEPP-3 electron accumulator, SR outlet channel No. 2). Electron energy in the accumulator was 2 GeV; mean current was 80 mA. The SR beam was monochromatized by a split Si(111) monochromator crystal. Radiation wavelength was 0.154 nm. Thanks to high natural collimation of the SR in the vertical plane and the use of plain perfect analyzer crystal Ge(111), high spatial resolution is achieved in the diffracted beam. Unlike the standard regime θ – 2θ , the sample was kept immobile during measurements, thus providing maximal sensitivity.

Since, according to the data shown in Table 1, among heavy metals, only titanium and iron are present in the aerosol samples under investigation, titanium concentration being very small, we investigated the state of iron. The XANES spectra for the *K*-edge of iron absorption were recorded at the EXAFS Spectroscopy Station of the Siberian SR Centre in the VEPP-3 accumulator of 2 GeV and mean current 80 mA. The SR was monochromatized with a split single-block monochromatizing crystal Si(111). The spectra were recorded in the fluorescence regime. A photoelectron multiplier with scintillator operating in the current mode was used as a detector. The samples were placed with respect to the SR beam so that a maximal area could be irradiated. No filters of the (Z-1) type were used.

TABLE 1

Atomic fraction of cations in atmospheric aerosol sampled near Lake Baikal in January–February 1998 (according to the SIMS data), %

Station	Sample No. (collection dates)	Na	Mg	Al	Si	K	Ca	Ti	Fe
Irkutsk	1 (22–23.01.98)	3.5	2.3	9.4	61.0	2.0	15.5	1.5	4.6
	2 (28–29.01.98)	6.6	3.8	9.6	54.5	1.3	23.2	1.1	1.9
	3 (26–28.02.98)	18.8	3.7	31.1	35.2	2.6	6.9	0.4	1.1
	4 (25–26.02.98)	11.1	1.9	10.8	59.4	2.2	11.0	0.8	2.7
	5 (24–25.02.98)	6.4	3.8	21.2	62.0	0.1	2.5	0.6	3.6
	6 (22–23.02.98)	10.1	2.8	14.6	49.3	4.1	14.1	0.5	4.4
Mondy	15 (01–05.10.98)	4.8	2.0	7.9	29.1	2.0	36.7	–	17.6

RESULTS AND DISCUSSION

The diffraction patterns of all the samples of the Irkutsk series were measured. Any reflections except those related to the filter material were found to be almost completely absent from the diffraction patterns. In some cases, only one reflection of a foreign phase is exhibited; however, it seems impossible to identify a phase using only one reflection. In addition, there is no correlation of the intensity of this reflection with sampling time and site or duration of filtering. The interplane spacing for the discovered reflection is 3.3460(6) Å. Its intensity varies within the range 0.0 to 0.7 % of the intensity of reflection from the material (Fig. 1).

The absence of noticeable reflections from the aerosol matter in the diffraction patterns is likely to be caused by the fact that for the aerosol particles with a size of 0.1–2 μm, coherent lengths are substantially smaller. Thus, the aerosol matter is close to the X-ray amor-

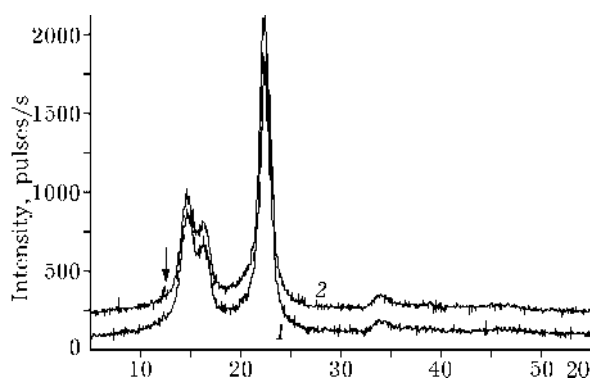


Fig. 1. X-ray diffraction patterns of the filter (1) and Irkutsk-2 sample (2). Arrow indicates peaks from aerosol.

phous state, which causes broadening of the diffraction maxima. Along with small amount of the substance on filters, the particles with small coherent lengths (less than 100 Å) give weak broad reflections with intensities below the sensitivity of the diffractometer.

The samples for which the measurements of the XANES spectra of *K*-edge of iron absorption have been performed are listed in Table 1. It should be noted that the sensitivity turned out to be insufficient for the major part of samples to record XANES spectra suitable for analysis. This caused high level of noise in XANES spectrum, which did not allow to perform the analysis of the shape of adsorption edge. A typical example of such a spectrum with high level of noise is shown in Fig. 2. One can see that the noise is high-frequency and causes blurring of line shape. Because of this, here we report only the results of investigation of samples containing the maximal amount of iron. These samples are Irkutsk-1 and Irkutsk-6. The oxides α -Fe₂O₃, γ -Fe₂O₃ and a sample of ground (sand) collected at the depth of 3 m were used as reference samples. It should be noted that we did not manage to obtain satisfactory XANES spectra for the aerosol sample collected at the mountain station, in spite of high content of iron atoms (see Table 1), because the sample mass was very small.

When determining the degree of iron oxidation using the *K* absorption spectrum, two parameters were taken into account: the position of inflection at the edge of adsorption (ionization potential), and the position of the

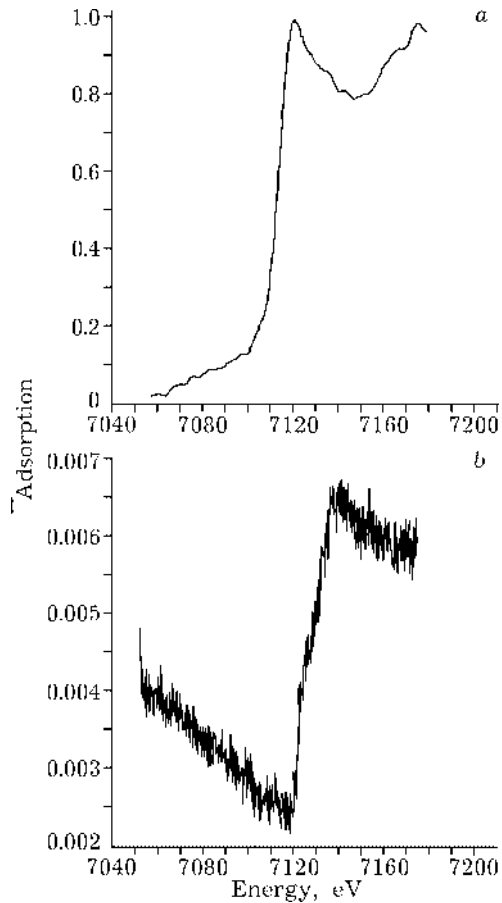


Fig. 2. XANES absorption spectra of the Irkutsk-6 (a) and Mondy-15 (b) samples. Absorption is given in absolute units.

edge maximum. The latter arises because of the removal of prohibition for electron transitions from $1s$ to vacant $3d$ levels in the case of asymmetry of the oxygen atoms surrounding the iron ion. The XANES spectra of the samples of $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3$ are shown in Fig. 3. The latter sample has spinel structure and Fe^{2+} ions with tetrahedral surroundings. One can see that the spectrum of the sample containing divalent iron ions ($\gamma\text{-Fe}_2\text{O}_3$) has lower ionization potential. The position of the edge maximum for this sample is also shifted to smaller energies. This is fully consistent with the literature data [16]. In addition, the intensity of the edge maximum depends on the extent of the distortion of surroundings. In the works dealing with the investigation of the status of iron in minerals [17, 18] It is demonstrated that the intensity of the edge maximum is decreased substantially in these materials. This is linked with the fact that the major part of

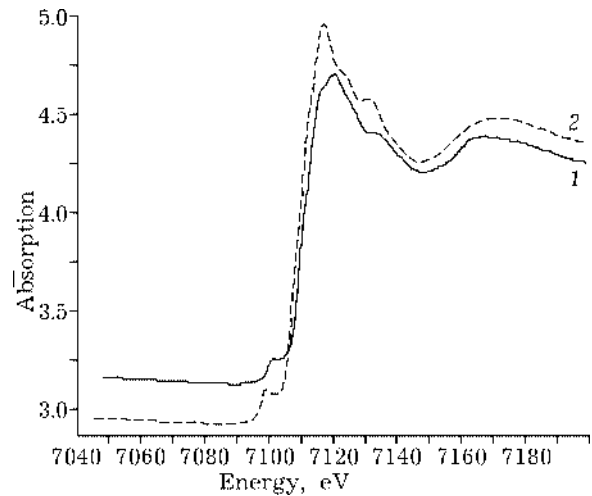


Fig. 3. XANES spectra of the K-edge of absorption of iron for $\alpha\text{-Fe}_2\text{O}_3$ (1) and $\gamma\text{-Fe}_2\text{O}_3$ (2).

iron ions in silicate compounds is isolated; hence, the number of Fe–O–Fe bonds is small, which causes decrease in the extent of distortion of the oxygen surroundings of the iron ion. This effect is clearly observed in Fig. 4 if we compare the intensity of the edge maximum in iron oxide (curve 1) and in the sand sample (curve 2). It should be stressed that the edge maxima are absent also from the spectra of the aerosols: Irkutsk-1 and Irkutsk-6 (curves 3 and 4 in Fig. 4). This allows us to state that iron ions are also present in these samples in the isolated form. Coincidence of the inflections at the edges of absorption in the spectra of all the samples (see Fig. 4) allows us assum-

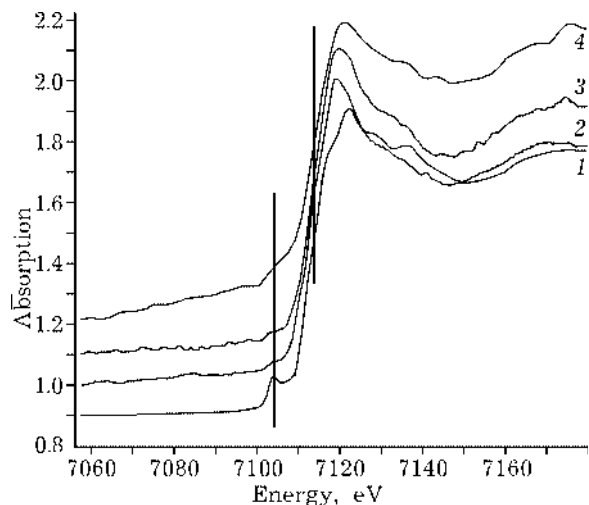


Fig. 4. XANES spectra of the K-edge of absorption of iron for $\alpha\text{-Fe}_2\text{O}_3$ (1), model sand sample (2), and aerosols Irkutsk-1 (3) and Irkutsk-6 (4).

ing that iron is present in these samples in the oxidation state +3.

CONCLUSIONS

Comparison of the spectra of aerosols Irkutsk-1 and Irkutsk-6 with the spectra of model compounds allows concluding that iron is present in these samples in the oxidation state +3 and most likely in the form of isolated ions in the surroundings close to octahedron. Thus, we have demonstrated that it is possible to determine phase state and oxidation state of iron in atmospheric aerosol of the Lake Baikal region with the help of XANES and X-ray diffraction involving SR.

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