

Synchrotron-Based X-Ray Absorption Spectroscopy for the Study of Geological Materials

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Received June 18, 2019; revised July 17, 2019; accepted July 17, 2019

Abstract—X-ray absorption spectroscopy (XAS) is a new highly effective nondestructive technique for diagnostics of the local atomic and electronic structure of materials, including those that do not have long-range order in their atomic arrangement. In particular, X-ray absorption near edge structure (XANES) spectroscopy makes it possible to identify materials, to assess the oxidation states of atoms, and to find the parameters of the full 3D local structure around absorbing atoms with a high degree of accuracy, up to 1 pm for bond lengths and several degrees for bond angles. This review describes the current state and capabilities of XAS spectroscopy and, in particular, XANES in studying terrestrial and extraterrestrial natural materials. Modern synchrotron centers allow the acquisition of XAS spectra of materials with high energy and time resolutions, with microfocusing and nanofocusing, and spectral measurements under real conditions (for example, directly under high pressures and temperatures). These broad possibilities make X-ray absorption spectroscopy a unique highly effective technique for the diagnostics of geological materials.

Keywords: X-ray absorption spectroscopy, XANES spectroscopy, synchrotron radiation, local atomic and electronic structure, geological materials, tektites, impact glasses, meteorites

DOI: 10.1134/S1027451020020111

INTRODUCTION

X-ray absorption spectroscopy (XAS) is a unique modern highly effective method for studying materials in the condensed state [1–5]. XAS makes it possible to determine the parameters of the local atomic structure and electronic subsystem of materials with high accuracy. This method is local and element-selective and has advantages over other analytical techniques, for example, X-ray diffraction (XRD) because it does not require long-range order in terms of the atomic arrangement and is applicable at a low concentration (~1%) of atoms in a sample. Of importance is the fact that XAS is a nondestructive method. These advantages are especially valuable in studying geological materials, because XAS can be used for diagnostics of the atomic and electronic structure of natural glasses, impact rocks, minerals with defect/impurity atoms, and microscale and nanoscale inclusions in minerals and extraterrestrial natural objects (for example, meteorites). XAS, however, is still not widely used to study geological materials because of insufficient data on its capabilities, the relative difficulty in interpreting experimental data, and the limited availability of unique experimental facilities for measurements (third generation synchrotron centers) despite its obvious advantages. The aim of this work is to acquaint the scientific community with the physical foundations of

XAS, its variants, its unique capabilities, and to give an overview of the current state of this method for studying terrestrial and extraterrestrial natural materials.

When X-ray radiation interacts with a substance, some part of this radiation is absorbed. The X-ray absorption coefficient μ is used to quantify the processes of X-ray absorption. This coefficient describes a decrease in the intensity of an X-ray beam depending on the sample depth x [2, 3, 6]:

$$I_x = I_0 e^{-\mu x}, \quad (1)$$

where I_0 is the intensity of X-ray radiation incident on a sample and I_x is the intensity of X-ray radiation at depth x .

The absorption coefficient increases sharply during interaction between a substance and X-ray radiation at a quantum energy equal to the minimum energy required to remove an electron from a certain electron shell (level-ionization energy): an absorption edge is observed. Each absorption edge is due to a certain type of atom in the substance and quantum-mechanical transition of an electron from low energy levels to free or unoccupied continuous levels. The energies of the absorption edges are characteristic of a certain type of atom absorbing X-ray radiation and correspond to the bond energies of electrons at the K , L , M , etc. shells of the absorbing atom. The systematics of absorption

edges implies that they are denoted in order of increasing energy (K , L_1 , L_2 , L_3 , M_1 , etc.), which corresponds to the excitation of an electron from the $1s$, $2s$, $2p_{1/2}$, $2p_{3/2}$, $3s$, etc. orbitals (states). Indeed, the K edge indicates that the $1s$ inner level is ionized due to an electronic transition. The systematics of X-ray absorption spectra is given in [7]. An excited electron is a photoelectron: it has sufficient kinetic energy and can freely move in a substance and scatter at surrounding atoms.

When the materials are studied, the X-ray absorption fine structure (XAFS), which includes the oscillatory absorption coefficient of X-ray radiation at energies above the absorption edge, is analyzed. The X-ray absorption fine structure is due to interference of a photoelectron wave outgoing from the absorbing atom with those scattered at atoms surrounding the absorbing atom. XAFS may be conditionally divided into two regions corresponding to different behaviors of photoelectrons with different energies during scattering. These regions are X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS). The EXAFS region corresponds to that from ~ 30 – 50 to ~ 1000 eV beyond the absorption edge, and single-photoelectron-scattering processes at surrounding atoms make the main contribution to this region. The analysis of EXAFS spectra, therefore, makes it possible to obtain detailed information on the coordination numbers and bond lengths in the nearest environment of absorbing atoms, but not on the bond angles. The XANES region, which covers the spectral region up to ~ 30 – 50 eV beyond the absorption edge, is much more interesting, and multiple-photoelectron-scattering processes make the main contribution to form this region. As a result, the analysis of XANES spectra makes it possible to obtain unique information about the full geometry of materials: the three-dimensional local atomic structure around absorbing atoms, including both bond lengths and bond angles [8]. The way to extract structural information from analysis of the XANES region, however, is indirect, therefore, until recently EXAFS spectroscopy was more widely used in studying materials because of the complexity of interpreting XANES spectra. Successful theoretical methods for analyzing XANES spectra [9, 10], however, contributed to an increase in those choosing this method for studying the structure of materials. Currently, experimental equipment for recording XANES spectra and theoretical methods for their analysis makes it possible to obtain information on the local atomic structure around absorbing-type atoms with the highest accuracy: up to 1 pm for bond lengths and several degrees for bond angles. Besides atomic structure, XANES spectroscopy allows study of the electron subsystem of materials, in particular, analysis of the density of unoccupied electronic states near the bottom of the conduction band and assessment of the oxidation states of atoms.

XAS as an analytical method of the structure of materials appeared in the 1970s after the publication of Sayers, Stern, and Little's pioneering work [11], which showed that the interference structure of an EXAFS spectrum may be used to obtain quantitative information about the local atomic structure around absorbing atoms. Laboratory spectrometers, however, do not provide the recording of high resolution X-ray absorption spectra because of the low intensity of X-ray radiation and, as a result, do not always allow structural information about materials to be obtained with high accuracy based on their analysis. XAS spectroscopy was developed due to high-intensity synchrotron-radiation sources [12], which make it possible to acquire X-ray absorption spectra with a high energy resolution. XAS spectra, for example, can be obtained in the structural materials science end-station [13] at the National Research Center "Kurchatov Institute" (Moscow, Russia). ESRF (Grenoble, France), DESY (Hamburg, Germany), BESSY (Berlin, Germany), SLS (Villeggen, Switzerland), Diamond (Oxfordshire, UK), ELETTRA (Trieste, Italy), SOLEIL (Paris, France), MAX IV (Lund, Sweden), and ALBA (Barcelona, Spain) are powerful European centers for synchrotron radiation. When conventional X-ray absorption spectra are recorded at synchrotron centers, the diameter of the X-ray beam on a sample is usually from tenths of a millimeter to several millimeters to give an integrated signal from a given region of the sample. A breakthrough was recently made in the study of complex materials due to specialized stations at advanced synchrotron centers, and it has become possible to perform X-ray absorption experiments not only with high energies, but also with a high spatial resolution, i.e., with microfocusing and even nanofocusing. The Scanning X-ray Microscopy (SXM) end-station of the ID21 beamline [14] at the European Synchrotron Radiation Facility (ESRF), for example, allows point micro-XANES analysis and radiation can be focused to a spot on a sample up to $0.3 \mu\text{m}$ (ver.) \times $0.7 \mu\text{m}$ (hor.) [14]. This makes it possible to extract structural information from a given small spatial region, which is especially important for Earth sciences (for example, to study heterogeneous minerals).

This review discusses the current state and capabilities of X-ray spectral techniques on synchrotron radiation sources with particular attention focused on XANES spectroscopy and its capabilities in studying terrestrial and extraterrestrial natural materials.

DATA ON GEOLOGICAL MATERIALS FROM XAS

Identification of Materials and the Fingerprint Method

Conventionally, XAS may be used in Earth sciences to identify materials based on the "fingerprint" method [15]. X-ray absorption spectra are due to the local atomic and electronic structures of a sample and

is a unique characteristic of the material studied. A person can be identified via comparison of their fingerprints with those available in a database; similarly, an unknown material may also be identified from comparison of its X-ray absorption spectrum with those of well-known substances, i.e., reference samples. In other words, the “fingerprint” method allows material to be identified through the comparison of its experimental X-ray absorption spectrum with those of reference samples that have a well-known local atomic structure. If there are no comparison samples nor their X-ray absorption spectra, it is possible to identify a material via comparison of its experimental spectrum with theoretical spectra calculated for several structural models.

A garnet taken from magnetite-garnet placers of modern deposits of the Taman Peninsula, for example, was analyzed [16]. Minerals, whose structure and composition act as indicators of thermodynamic parameters of the mineral-formation environment, are actively studied to reconstruct geological processes in the Earth’s crust and upper mantle. Garnets, a group of minerals bound by isomorphic substitutions and whose general formula is $A_3B_2(SiO_4)_3$ (where $A = Mg^{2+}, Fe^{2+}, Ca^{2+}, Mn^{2+},$ and Y^{2+} and $B = Al^{3+}, Fe^{3+}, Cr^{3+}, V^{3+}, Mn^{3+}, Ti^{4+},$ and Zr^{4+}), are also assigned to these minerals. Preliminary X-ray fluorescence analysis (XRF) revealed that there is a significant amount of iron in the garnet samples from placers of the Taman Peninsula. As a result, the XANES spectrum was recorded at the next stage beyond the K -edge of iron of the sample. A comparison of the experimental FeK -XANES spectrum of the garnet sample with the theoretical spectra calculated for iron-containing end-members of the isomorphic garnet series (almandine $Fe_3^{2+}Al_2(SiO_4)_3$ and andradite $Ca_3Fe_2^{3+}(SiO_4)_3$) showed that the garnet from modern placers of the Taman Peninsula contains mainly the almandine component.

When samples are analyzed via the fingerprint method, an important point is the availability of a high-quality experimental library of spectra of standards (comparison samples) to identify the materials and to quantitatively find the component fractions in complex mixtures with XAS. As a result, works devoted to the accumulation of X-ray absorption spectra for standards to analyze materials are especially important.

XAS and the fingerprint method are used to analyze complex natural systems (for example, soils and deposits). At the same time, the identification of a specific mineral or amorphous substance in a heterogeneous system is important. The FeK -XANES spectra were recorded for 27 common Fe-containing reference compounds, including sulfides, carbonates, phosphates, oxides, oxyhydroxides, and phyllosilicates [17]. The effectiveness of the XANES and EXAFS methods to identify a specific iron-containing

mineral (or class of minerals) in soils or sediments is analyzed. The calibration curves were obtained for mixtures of sulfide and nonsulfide (phyllosilicate-oxide) components of iron binary and ternary mineral mixtures (at 5% of the total Fe amount) in a quartz matrix to simulate natural deposits besides the analysis of XANES and EXAFS spectra [17].

The MgK -XANES spectra were recorded and analyzed for some Mg-containing geological materials (silicate and carbonate minerals, sediments, and rocks) [18]. The authors showed that the fine structure of the XANES spectra of various Mg-containing model compounds is significantly different, making it possible to use the “fingerprint” method to identify various magnesium geological materials. The authors recorded the BaL_3 edge X-ray absorption spectra for barium carbonates (witherite, alstonite, and baritocalcite), barium hydroxides (VI), barium sulfate (VI), and Ba-containing organic compounds for further use as structural standards in the analysis of biominerals (celestite, aragonite, and calcite) [19]. The NaK -XANES spectra of various minerals and glasses having a different structure, environment, and sodium coordination were recorded and thoroughly analyzed [20]. They showed that the analysis of the NaK -XANES spectra is an effective tool to determine the coordination of Na in important minerals and glasses. The XANES spectra of crystal reference samples are used as “fingerprints” in the interpretation of the NaK -XANES spectra of silicate and borate glasses. If necessary, the XANES spectra behind the FeK edge of some model Fe-containing compounds can be found, for example, in [21].

Oxidation State Estimation

As mentioned above, X-ray absorption near-edge structure spectroscopy can be used to study the electronic structure of geological materials, in particular, to analyze the densities of electronic states near the bottom of the conduction band of compounds [22, 23]. The oxidation state of atoms, however, is widely assessed with XANES spectroscopy to study terrestrial and extraterrestrial natural materials. It is possible to determine the oxidation state of atoms with XANES spectroscopy via analysis of the exact position of the X-ray absorption edge (a chemical shift). When a substance interacts with X-ray radiation, a core level is ionized. The X-ray absorption spectrum shows that the absorption coefficient increases sharply: there is an absorption edge. The energies of the X-ray absorption spectra edges have strictly defined values, being a unique parameter of materials. If the oxidation state of an atom in a material changes, the energy of the X-ray absorption edge changes due to the fact that the effective charge on the atom changes and the energy of the core levels shifts. This effect is used to assess the unknown oxidation state of atoms. The desired oxidation state of an element may be estimated through

comparison of the position of the absorption edge in a material (with an unknown oxidation state of the chemical element of interest) and in reference samples (with well-known oxidation states of atoms). Indeed, the method described above was successfully used to find the oxidation state of lanthanides in lanthanide-containing silicates [24, 25], promising from the point of view of determining the natural conditions of mineral formation. The determination of the oxidation state of atoms from the position of the absorption edge, however, can lead to incorrect conclusions in some cases. It was shown, for example, that the position of the edge may be different for the same oxidation state of atoms, because the position of the FeK-edge of X-ray absorption spectrum is influenced by the structure of the material [26]. A similar situation was also observed during the analysis of CrK-XANES spectra (Fig. 1 in [27]).

As a result, there is a sufficient number of works devoted to the search for methods of extracting data on the oxidation state of chemical elements in geological materials and their comparative analysis. Researchers have determined the oxidation state of Fe in natural materials in particular. Iron is one of the most abundant elements on Earth, having a variable degree of oxidation and occurring in minerals and melts in both Fe²⁺ and Fe³⁺ states. The Fe³⁺/ΣFe ratio in geological samples can be used as an indicator of redox conditions (or the oxygen fugacity, f_{O_2}), under which a mineral or melt is formed. Estimation of the Fe³⁺/ΣFe ratio in natural materials, therefore, plays an important role.

It was found that an effective method is the analysis of the pre-edge feature to determine the oxidation state of atoms in various geological materials. Wilke's et al. pioneering work is significant from the point of view of estimation of the oxidation state of iron from analysis of a pre-edge feature of XANES spectra [21]. FeK-XANES spectra were measured for Fe²⁺ and Fe³⁺-containing model crystal compounds to find a correlation between the pre-edge features of the spectrum and the oxidation state and local coordination of iron atoms [21]. The model compounds were 30 natural minerals and synthetic samples with an iron coordination from 4 to 12 O atoms for Fe²⁺ and from 4 to 6 O atoms for Fe³⁺. They found that the most useful characteristics of the pre-edge features of FeK-XANES spectra in determining the oxidation state and coordination numbers of iron were the position of a pre-edge centroid and its integrated intensity. The difference between the positions of the centroids for Fe²⁺ and Fe³⁺ were 1.4 ± 0.1 eV.

They showed, therefore, that the position of a pre-edge feature can be used to estimate the average oxidation state of iron in materials studied. The smallest normalized intensity of the pre-edge and its integrated intensity were observed for the most centrosymmetric positions of iron. A study of the pre-edge features of the X-ray absorption spectra of mechanical-phase

mixtures containing different contents of Fe²⁺ and Fe³⁺ suggests that the position and intensity of the pre-edge features for these mixtures can vary completely nonlinearly depending on the average oxidation state of iron. There were, however, distinct relationships between the position of the pre-edge feature and the intensity of the pre-edge region depending on the coordination of Fe²⁺ and Fe³⁺. If there are reference compounds with a known geometry (iron coordination) for each oxidation state of iron (Fe²⁺ and Fe³⁺), analysis of the relationship between the position of a centroid and the integrated intensity of a pre-edge feature of the XANES spectra, therefore, allows estimation of the unknown oxidation state of iron in a sample studied. In other words, comparison of the positions of the pre-edge intensity–pre-edge energy relationship plot for materials (with unknown oxidation states and Fe coordination numbers) and reference samples (with well-known oxidation states and Fe coordination numbers) makes it possible to find the desired oxidation states and coordination numbers of iron in the materials studied. Indeed, analysis of the pre-edge feature of the X-ray absorption spectra was used to assess the Fe³⁺/Fe²⁺ ratio in 12 minerals (magnetite, vesuvianite, franklinite, rhodonite, etc.) containing variable/unknown values of Fe²⁺/Fe³⁺ [21].

Berry et al. analyzed the oxidation state of Fe and simulated the calibration curves from the analysis of XANES spectra to find Fe³⁺/ΣFe in various natural materials [28–31]. At the same time, they evaluated various parameters of the X-ray absorption spectrum associated with the pre-edge feature, absorption edge, and, in some cases, post-edge features to find the oxidation state of iron. Calibration curves, for example, were constructed from analysis of the various alternative parameters of a XANES spectrum (pre-edge feature and absorption edge) to estimate the oxidation state of iron in silicate glasses [28]. They showed that the energy of the centroid of the $1s \rightarrow 3d$ pre-edge feature has a linear correlation with the oxidation state. In addition, they found that the environment and coordination of iron potentially influence all calibration methods. As a result, it is undesirable to use minerals as reference samples in assessing the oxidation state of silicate glasses. Nevertheless, it has been shown that the Fe³⁺/ΣFe ratios in silicate glasses can be extracted from XANES spectra with an accuracy comparable to Mössbauer spectroscopy data from empirical calibration curves obtained on compositionally similar standards. Such compositionally selected standards were used to estimate the oxidation state of iron in inclusions of melts [29].

Calibration curves obtained from the analysis of XANES spectroscopy data to assess the oxidation state of iron in mantle garnets were constructed [30]. Solid solutions of various garnets, in which the Fe³⁺/ΣFe ratio was estimated from Mössbauer spectroscopy data and systematically varied from 0 to 1, were synthe-

sized. A search for the relationship between the features of the absorption spectra and the oxidation state of iron in the samples showed that the pre-edge feature of the XANES spectra, which is usually used to analyze the oxidation state of geological materials [21], is almost insensitive to changes in $\text{Fe}^{3+}/\Sigma\text{Fe}$ in the case of garnets. The best parameter to predict the oxidation state of garnets was the position of the X-ray absorption edge at the point, where the normalized intensity is 0.9. In the case of mantle garnets, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio strongly correlates with that of the intensities of the post-edge features at 7138.4 and 7161.7 eV. XANES spectroscopy at the *K*-edge of iron was used to construct highly precise calibration curves to find the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in natural basalt and rhyolite glasses [31].

It can be concluded, therefore, that XANES spectroscopy makes it possible to extract data on the oxidation state of elements in geological materials with a high accuracy, but it requires the right choice of compositionally selected standards and accuracy in obtaining and analyzing data. The accuracy of estimation the oxidation state from XANES spectra is similar to that from Mössbauer-spectroscopy data. The high acquisition rate of X-ray absorption spectra in modern synchrotron centers and relative simplicity during the preparation of samples for measurements, however, are undoubted advantages of the method. Another great advantage of the method is the possibility of using microfocusing of the X-ray beam, which can be achieved in advanced synchrotron centers. This makes it possible to sequentially determine the oxidation state in small spatial regions and to obtain distribution maps of the oxidation state of a chemical element in a test sample.

Determination of the Local Atomic Structure Parameters

Analysis of the X-ray absorption spectra makes it possible to determine not only the features of the local electronic structure, but also the parameters of the local atomic structure. EXAFS spectroscopy, as discussed above, provides information on the coordination numbers and bond lengths around absorbing atoms; it is relatively simple to interpret the data. On the other hand, XANES spectroscopy is more informative for obtaining data on the atomic structure, because it allows estimation of not only the coordination numbers and bond lengths, but also the bond angles to obtain information about the full 3D geometry around certain absorbing atoms. XANES spectroscopy is also useful for finding the atomic positions and local structure around defect positions and impurity atoms in geological materials. It should be noted, however, that the extraction of structural information from XANES experimental spectra is indirect, relatively complex, and requires computer simulation of the structure and theoretical analysis of the X-ray absorption spectra. As a result, the procedure to analyze the experimental XANES spectra to find the

parameters of the structure around the studied type of atoms is as follows. Probable models of a structure are constructed at the first stage. The constructed structural models are also optimized at this stage within density functional theory (DFT) [32–34]. The structure may be optimized, for example, within DFT with the ADF program [35], BAND software or DFT approach in the approximation of pseudopotentials with the VASP program code [36, 37]. Theoretical XANES spectra are then calculated for the structural models obtained. XANES spectra may be calculated, for example, with the full multiple scattering theory within the muffin-tin approximation for a potential shape realized in the FEFF9 program code [38, 39], with the FDMNES code based on the full-potential finite difference method [40, 41], and other program codes depending on the structural features of the compound studied. Then the experimental spectrum is compared with the theoretical those calculated for structural models, and a probable structural model is deduced. The structural parameters of the most probable structural model can be further refined. The advanced approach facilitates, simplifies, and accelerates significantly the extraction process of quantitative data from XANES spectra. This approach implies that relatively small changes in the structural parameters do not significantly change the shape of the XANES spectra, so that spectral interpolation schemes can be used for calculations as functions of the structural parameters [42]. This multidimensional interpolation of XANES spectra as a function of the structural parameters was implemented in the FitIt program code [43] and made it possible to significantly decrease the computational complexity to find the parameters of the local atomic structure of materials.

The local atomic structure around the titanium positions in Ti-containing forsterite was recently analyzed based on XANES spectroscopy. Forsterite (Mg_2SiO_4) is the end member of the olivine group $(\text{Mg,Fe})_2[\text{SiO}_4]$ and may include some trace elements, including titanium. Olivine is a mineral widely distributed in Earth's mantle. It was shown that OH groups bind to Ti atoms in the upper mantle; therefore, determination of the titanium positions was important to understand the water-accumulation processes in olivine and Earth's mantle as a whole. The DFT SIESTA code [44] made it possible to simulate the probable structural models of Ti-containing forsterite [45]. Then the X-ray absorption spectra at the *K*-edge of titanium were calculated for the following structural models with the full-potential finite difference method (FDMNES code): Ti in the substitution position of Si atoms, Ti in the substitution position of Mg atoms, 50% of Ti atoms are in the substitution positions of Si atoms, and 50% of Ti atoms are in the substitution positions of Mg atoms. Comparison of the experimental Ti*K*-XANES spectrum with the theoretical one calculated for the structural models showed that the model of the substitution of silicon positions by tita-

nium atoms is the most probable model of a Ti-bearing forsterite structure [46].

The local atomic structure around the Ti positions of hibonite ($\text{CaAl}_{12}\text{O}_{19}$), a mineral found in Ca-Al-rich inclusions of chondrite meteorites, was studied [47, 48]. Possible potential of Ti-bearing hibonite was discussed to assess the oxygen fugacity $f\text{O}_2$ [48]. Hibonite has a complex structure, in which Ca is 12 coordinated, whereas Al is distributed over five M positions [47, 48]. The analysis of computer simulation and XANES spectroscopy data showed that at low Ti concentrations, the most probable structure is that Ti is located at five coordinated M2 positions, whereas the clustered Ti model at six coordinated M4 positions is the most probable model of the hibonite structure containing a high concentration of titanium.

XANES spectroscopy, however, is still not used widely enough to analyze the atomic structure around impurity atoms and defect positions in geological materials in comparison with studies of the electronic subsystem of materials despite its great potential and high accuracy for obtaining structural information (up to 1 pm for bond lengths for materials without long-range order in atomic ordering).

CURRENT STUDIES OF GEOLOGICAL MATERIALS WITH X-RAY SPECTRAL TECHNIQUES

Modern X-ray Spectral Methods for Studying Geological Materials

The current studies of geological materials involve both the improvement of existing methods to obtain data on geological materials and the development of new X-ray spectral research methods.

As already mentioned above, a breakthrough recently occurred in the possibilities of studying heterogeneous materials due to the introduction of specialized stations at some advanced synchrotron centers. It became possible to perform experiments based on X-ray techniques, such as XRD, X-ray fluorescence analysis (XRF), XANES, and EXAFS with microfocusing and even nanofocusing [49] or techniques with a *high spatial resolution*. Studies based on X-ray techniques with microfocusing and nanofocusing allow the extraction of information from a small spatial region, which is especially important in the case of heterogeneous minerals. Micro X-ray absorption near-edge structure (micro-XANES) spectroscopy was recently used to study geological materials [50–60]. A significant number of studies based on micro-XANES [52, 53] have been performed at the scanning X-ray microscopy (SXM) end-station of the ID21 beamline of the ESRF synchrotron center (Grenoble, France), which makes it possible to focus an X-ray spot on a sample up to a spot of size $0.3\ \mu\text{m}$ (ver.) \times $0.7\ \mu\text{m}$ (hor.). The environment of sulfur and iron in natural compounds (sulfides, sulfates, and silicate basalt

glasses), which likely have different oxidation states of sulfur and iron, for example, was studied with XANES spectroscopy [52]. The size of inclusions of natural glasses found in volcanic minerals is from a few micrometers to several tenths of micrometers, which made it necessary to use the micro-XANES method. Micro-XANES spectra were measured at the *K* edges of iron and sulfur of olivine glass inclusions at the ID21 beamline of the ESRF synchrotron center. The authors showed that micro-XANES makes it possible to quantify the oxidation states of sulfur and iron through the combination of high energy and spatial resolution. The oxidation states of sulfur (S^{2-} , S^{4-} , and possibly S^{6-}) were identified in the inclusions of basalt glass in olivine grains. A method was proposed for calibration of the amount of Fe^{3+} in basalt glasses, for which the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio varies from 0.05 to 0.48. As already discussed above, determination of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in geological samples is of particular interest, because it can be used, for example, as an indicator of oxygen fugacity ($f\text{O}_2$), at which a mineral appeared. As a result, the oxidation state of Fe in zoned garnet and omphacite single crystals was studied [49]. The micro-XANES method was used; measurements were performed on the ID22 beamline of the ESRF synchrotron center and the size of the X-ray spot on the sample was $1.7 \times 5.3\ \mu\text{m}$. The amount of Fe^{3+} in garnet was found with spatial resolution via analysis of the pre-edge feature and the energy position of the X-ray absorption edge at a ~ 0.9 -normalized intensity. They showed that the second approach to finding the oxidation state provides the best results during studies of small spatial variations in the oxidation state of iron in garnet. Indeed, accurate quantitative analysis of the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio of zoned garnet microcrystals performed with high spatial resolution showed that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio gradually changes from 0.00 at the edge of the garnet microcrystal to 0.09 at its center. The influence of X-ray polarization on the parameters of the micro-XANES spectra was discussed in the case of non-cubic omphacite microcrystals. Micro-XANES, therefore, is important for studying complex samples because it provides an unprecedented description of heterogeneous geological materials. The micro-XANES technique is especially important for study meteorite samples, which are also inhomogeneous [61, 62].

In situ X-ray absorption spectroscopy (during real processes) is extremely important for Earth sciences. The in situ recording of spectra makes it possible to study changes in the electronic structure and atomic structure of materials, for example, directly under high temperatures and pressures. Indeed, geophysically important systems, such as Fe-containing oxides and silicates, including $(\text{Mg}_{0.88}, \text{Fe}_{0.12})\text{SiO}$ and $(\text{Mg}_{0.86}, \text{Fe}_{0.14})(\text{Si}_{0.98}, \text{Al}_{0.02})\text{O}_3$ perovskites together with $(\text{Mg}_{0.80}, \text{Fe}_{0.20})$ ferropericlases, were studied based on the analysis of FeK-XANES spectra at room temperature directly under high pressures of up to 85 GPa

[63]. The structure of a hydrated La^{3+} ion in an aqueous solution was studied with X-ray absorption spectroscopy within the temperature range from 25 to 300°C and pressures up to 1600 bar [64]. The design of a furnace to record XANES spectra at a controllable oxygen fugacities and temperature up to 1773 K is described [65]; it was used to find the oxidation state of Cr in basaltic silicate melts. Some elements (for example, Zr and Hf) are important geochemical indicators of processes occurring in the interior of the Earth. Aqueous fluids play an important role in the transfer of heat and matter in these systems. The concentrations and complex formation of Zr and Hf in these fluids under high pressure and temperature conditions, however, are predominantly unknown. The high-resolution ZrK-XANES and Hf L_3 -XANES spectra of aqueous fluids were obtained in situ under high pressures and temperatures to find the specific structure and coordination of Zr and Hf atoms in these systems [66].

The geological materials were in situ studied in combination with the micro-XANES technique in a number of works [67, 68]. An estimation of the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in magmas before eruption remains an interesting problem. To solve this, the oxidation states of iron in peralkaline rhyolite glasses/melts were estimated based on micro-XANES spectroscopy at high temperature (from 800 to 20°C) [67]. Iron is also the main aqueous solute under various hydrothermal conditions; however, issues regarding the solubility and speciation of iron under hydrothermal conditions remain debatable. The solubility and speciation of iron in fluids buffered by various mineral complexes were studied during in situ hydrothermal a diamond anvil cell experiments at hydrothermal temperatures and pressures using micro-XRF, micro-XANES, and Raman spectroscopies [68].

Another feature of X-ray absorption spectroscopy on the latest generation synchrotron sources is the possibility of in situ experiments with a *high time resolution*, up to ~ 100 ps. These capabilities of the method, however, are more important not in Earth sciences, but in the study of structural changes during different fast processes (for example, during chemical reactions). Fortunately, modern X-ray free electron lasers, in particular, the European XFEL [69] make it possible to study fast processes with a time resolution up to ~ 100 fs.

Modern mega-class research facilities allow the recording of X-ray absorption spectra with a high-energy resolution. It is important to acquire XANES spectra with a high-energy resolution in the pre-edge spectral region for the qualitative analysis of atomic oxidation states [70]. A high-energy resolution is especially important for recording the spectra of heavy elements. The X-ray absorption spectra recorded via conventional methods (for example, the total electron yield or TEY) are broadened, almost have no spectral

features, and thus are not informative from the point of structural data because of the large widths of the core levels of heavy chemical elements. The HERFD (high-energy resolution fluorescence detected) XAS method available in modern synchrotron centers for recording XAS spectra in the high-energy resolution mode [71, 72] allows studies beyond the limitations associated with the large widths of the core levels of heavy elements and recording of the more detailed fine structure of X-ray absorption spectra. As a result, this provides more accurate information about the local structure around heavy elements in materials. The study of geological materials by the HERFD-XAS is described, for example, in [73–75]. Indeed, the local atomic and electronic structures of iron in high-temperature hydrothermal fluids were studied with HERFD-XAS spectroscopy combined with ab initio molecular-dynamics calculations and Monte Carlo methods [75].

Conventionally, XAS and X-ray emission spectroscopy were considered as independent processes, which was because of experimental limitations that allowed the recording of these spectra only separately. Technical improvement of synchrotron facilities led to a new X-ray spectroscopy method—resonant inelastic X-ray scattering (RIXS) [76, 77], in which X-ray absorption and X-ray emission are combined in a two-photon process. RIXS, during which an electron from the valence band fills a core vacancy, is also called resonant X-ray emission. RIXS spectroscopy can be used to study the dispersion of energy bands in crystals, the electronic structure, and assessment of the band gap in materials. When primary synchrotron radiation is used, which is variable in energy, it becomes possible to separate the features of emission spectra due to the various nonequivalent atoms of a chemical element. Two-dimensional RIXS maps become more widespread, in which the energy of X-ray radiation incident on a sample is plotted along the horizontal axis, and the energy difference between the absorbed and emitted photons (energy transfer) is along the vertical axis. Two-dimensional RIXS cards and HERFD-XAS spectra, for example, can be recorded on the ID26 undulator beamline of the ESRF synchrotron center. XAS and RIXS spectra in the soft X-ray region can be measured on the ID32 beamline of ESRF [78]. The RIXS method is widely used in materials sciences, but less in Earth sciences [79]. Arsenic is a toxic element present in various contaminated surface media. In natural environments, data on its chemical speciation and oxidation state is crucial to understand its mobility, bioavailability, and toxicity for ecosystems. The local environment of As in sulfide minerals was studied with RIXS, HERFD-XANES spectroscopies, and the ab initio calculations of XANES spectra [79]. The authors showed that the position of the fluorescence maximum on RIXS map can be used as a “fingerprint” of the local As environment.

One of the varieties of XAS, which is currently being intensively developed, is X-ray magnetic circular dichroism (XMCD) spectroscopy [80, 81]. This method involves measurement of the difference in the absorption of left-polarized and right-polarized X-rays by a sample. XMCD spectroscopy is used to study magnetic materials, namely their magnetic structure. Sum rules [80, 81] make it possible to obtain quantitative information on the distribution of orbital and spin moments on atoms from XMCD spectra. The possibilities of XMCD spectroscopy were discussed to obtain quantitative information on the occupation of positions in ferrimagnetic and ferromagnetic minerals [82–85]. XMCD spectroscopy was used to study the occupation of cation positions in spinel ferrites [82–85].

Methods for obtaining information about the local atomic and electronic structure with conventional X-ray absorption spectroscopy are also being improved together with new X-ray spectral techniques. Considering that natural terrestrial and extra-terrestrial objects are mainly complex systems, often consisting of several phases, including amorphous ones, the analysis of such complex and multicomponent systems often requires the simultaneous and complementary consideration of spectral data of various ranges, including pre-edge, XANES, and EXAFS. Complementary techniques were recently used to study the electronic structure, in particular, the oxidation state of atoms, in complex geological compounds [86–89].

A new microscale oxybarometer for basalt glasses of the Solar System based on the analysis of vanadium X-ray absorption near-edge structure (XANES) was described [86]. Vanadium is unique among the other numerous elements in siliceous materials because it can potentially exist in nature in four valence states: V^{2+} , V^{3+} , V^{4+} , and V^{5+} . As a result, a vanadium redox system can be effectively used as a reliable oxybarometer. In other words, the oxygen fugacity fO_2 is proposed to be assessed from analysis of the oxidation state of vanadium. The method involves analysis of the intensity of the pre-edge features of the micro-XANES spectra. The micro-VK-XANES and EXAFS spectra were recorded. Calibration curves showing the relationship between fO_2 and the intensity of the pre-edge feature of the XANES spectrum for synthetic-glass standards obtained at known fO_2 and temperature were then plotted. These curves were used to analyze fO_2 in lunar, Martian, and terrestrial glasses.

A method of assessing fO_2 for basalt glasses from the oxidation state of vanadium based on the analysis of micro XANES spectra was developed [87]. Previous calibration curves for basalt glasses [86] provided a relationship between the oxidation state of vanadium or the oxygen fugacity and the pre-edge feature of VK-XANES spectra. The previous model [86], however, did not use data from entire XANES spectrum, which can also provide information on the chemical state of vanadium depending on fO_2 . A multivariate analysis

was proposed [87], which has significant prospects for developing calibration models, in which the full range of XANES spectra is used. New calibration models are proposed for prediction of the fO_2 equilibrium value in basalt glasses developed with the Lasso method (least absolute shrinkage and selection operator) to assess the linear regression coefficients. The calibration curves were tested on a set of natural glasses from a basalt ridge in the middle of the ocean and Kilauea volcano.

Analysis of the pre-edge feature [86] and the entire XANES spectrum [87], therefore, should be combined to reliably find the oxidation state of vanadium in basalt glasses.

A multivariate analysis of synchrotron micro-XANES spectra is described to find the oxidation state of iron in amphiboles [88]. Amphiboles are needlelike silicates and aluminosilicates; their crystal structure includes various isomorphic substitutions. There are many minerals, which occupy an intermediate position in composition between the end-members of the family. A calibration set based on the analysis of micro X-ray absorption spectra of amphibole single crystals with polarization of the X-ray beam along the main optical directions (X, Y, Z) has been developed. The following seven different methods were used to predict the amount of Fe^{3+} : (i) the centroid position of the normalized pre-edge feature, (ii) the energy of the main absorption edge, (iii) the ratio of the spectral intensities at two energies, (iv) the slope of the first derivative, (v and vi) partial least squares method with variable and constant number of components, and (vii) the Lasso method. The last three complex multidimensional analysis methods for predicting $Fe^{3+}/\Sigma Fe$ exhibited significant improvements in accuracy compared to the first methods mentioned. Multivariate approaches show that for amphiboles, the region of the main edge of the X-ray absorption spectrum and the EXAFS region contain important features to predict the oxidation state of iron.

It was shown that use of the full region of the X-ray absorption spectrum, from the pre-edge to the EXAFS region, combined with multivariate-analysis methods provides more accurate results in assessing the oxidation state of iron in silicate glasses [89]. The Lasso method for estimating the coefficients of the linear regression model leads to an accuracy of $\pm 3.6\%$ in the case of the full spectral region. This method can be used for a wide range of glass compositions.

These examples [86–89] showed that three regions of the X-ray absorption spectrum (pre-edge, XANES, and EXAFS regions) should be combined for the quantitative analysis of complex natural materials.

Modern synchrotron centers make it possible to record the X-ray absorption spectra of materials with a high energy and time resolution, microfocusing and nanofocusing, with different polarization of the X-ray beam, and under real conditions (for example, under

high pressures and temperatures). Such broad possibilities and a combination of spectral techniques to extract more complete information make X-ray absorption spectroscopy a truly unique and highly effective tool for studying geological materials.

X-ray Absorption Spectroscopy for Studying Some Natural Materials

As mentioned above, X-ray absorption spectroscopy, being a local, nondestructive, and element selective method, is well suitable for studying systems without long-range order in the arrangement of atoms and inhomogeneous multicomponent systems. In this section, we consider the current state of studies based on the X-ray absorption spectroscopy of complex natural materials, such as tektites, impactites, and meteorites.

Tektites and impactites being rocks of shock genesis are interesting geological objects that attract the considerable interest of researchers.

Tektites are natural silicate glasses scattered in long fields for thousands of square kilometers [90]. There are four main fields of tektite dispersion: Central European, Australasian, North American, and Ivory Coast. The tektites differ from other natural glasses in form, petrography, and chemistry. In shape and structure, there are splash-form, flanged (button-like), and layered (Muong Nong-type tektites (the latter named after the city of Muong Nong in Laos, where they were described for the first time). The body size of tektites can vary from several tens of centimeters to millimeters or less (microtektites). Microtektites have a shape similar to splash-form tektites, but their size is less than 1 mm. Tektites are relatively homogeneous and their composition is similar to those of the upper rocks of the Earth crust. The chemical composition of tektites includes significant amounts of silicon dioxide (68–82%), a high amount of alumina, low amount of water, and microcavities filled with a mixture of some gases (carbon dioxide, hydrogen, methane, and noble gases). It is generally accepted that tektites appear due to high-speed ejecta at the early stages of the formation of impact craters [91], which arise due to collisions of asteroids with the Earth. On the other hand, it was suggested that large aerial bursts caused by extraterrestrial bodies, such as comets and asteroids, can explain the formation of a tektite field in Indochina without an associated impact crater [92].

One of the features of crater-forming processes is also the formation of impact glasses or impactites due to the melting of target rocks after impact interaction. The impactites have a more complex history of their formation and are due to the melting of various rocks located at different depths in Earth's crust.

As already mentioned, various tektites and impact glasses appear from various target rocks and under different conditions. It is known that environmental parameters, such as pressure (P) and temperature (T),

significantly influence the structure of glasses during their formation (for example, the coordination number of cations) [93–96]. Previously, the relationship between the formation conditions and the local atomic structure around the positions of aluminum and titanium in natural glasses was widely studied [97–100]. Iron is also a fairly common element in natural glasses, which can also act as a potentially useful “probe” to obtain information on the formation conditions (P , T , and fO_2) of tektites and impactites. Indeed, the authors discussed that the redox state of iron in melts depends on P , T , fO_2 , and the composition of the melt [101]. The influence of the P – T – fO_2 parameters on the Fe^{3+}/Fe^{2+} ratio in impact melts was discussed as well [102]. Determination of the oxidation state of iron in tektites and impact glasses, therefore, is important from the point of view of subsequent determination of the conditions of their formation and a relationship between different rocks.

The oxidation state of various chemical elements in geological materials, as discussed above, can be effectively assessed from the analysis of X-ray absorption spectra. X-ray absorption spectroscopy was used to analyze the oxidation state and local-structure features around the positions of aluminum [100], calcium [103], titanium [104, 105], and zirconium [106] in tektites and natural glasses. The oxidation state and local atomic structure around the positions of iron in various tektites and impact glasses were studied as well [90, 107, 115].

Indeed, the oxidation states, coordination numbers (the number of nearest neighbors) of iron, and the Fe–O average interatomic distances were determined for three tektites (moldavite and two australasian tektites) and some impact glasses from analysis of the pre-edge feature of the FeK-XANES spectra and FeK-EXAFS data [107]. The authors showed that the average oxidation state of iron for tektites is 2+, whereas it varies in a wider range for impact glasses; the average coordination number for tektites is 4.5, whereas it is from 4 to 6 for various impact glasses. The oxidation states and coordination numbers of iron in Libyan desert glass, a mysterious glass found in the Libyan desert in western Egypt, were assessed from the analysis of FeK-XANES spectra; the authors concluded that Libyan desert glass is an impact glass and not a tektite-like one [108]. The local atomic and electronic structure of iron in impact glasses at the Cretaceous-Tertiary boundary (Haiti) were studied with XANES spectroscopy [109, 110]. X-ray absorption spectroscopy was used to find the oxidation state and iron coordination of six tektites belonging to the North American field of tektites (four bediasites and two georgiites) and a tektite from the 612 deep-sea drilling project also belonging to the North American field [111]. The oxidation states of iron in silicate glasses formed during the first atomic-bomb explosion at the Trinity test site (New Mexico) and tektites from the

Ivory Coast were also analyzed with XANES spectroscopy [112]. The local atomic and electronic structure of iron in the tektites (indoshinite, phillipinite, australite, bediasite, and moldavite) from six fields of tektites and some impact and non-impact glasses were studied with XANES and EXAFS spectroscopies [113]. In this case, the oxidation states of iron were found both from analysis of the pre-edge feature of the XANES spectra and assessment of the position of the X-ray absorption edge. The authors also published a calibration curve to analyze the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio (x) by the position of the absorption edge of the FeK-XANES spectrum (y), which can be expressed through the equation $y = 4.084x + 7117.299$ [113]. As mentioned above, the study of microtektites, whose size is less than 1 mm, is also of interest. X-ray spectral analysis of the oxidation state of iron of microtektites from Antarctica of the Australasian field was performed [114]; the authors showed that the $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio in the samples is less than 0.1 and is comparable with that for most tektites and microtektites of the Australasian field. At the same time, analysis of the X-ray absorption spectra indicated that the $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio of the microtektites from the North American tektite field varies widely from 0.02 to 0.61 [115] and, consequently, they are more oxidized than tektites. Impact glasses from the Zhamanshin impact crater (Kazakhstan)—irghisites, and silica-rich and silica-poor zhamanshinites—were recently studied via the XANES and EXAFS methods [90]. The oxidation states of Fe were $\sim +2.2$ and $\sim +2.3$ in the irghisites and silica-rich zhamanshinite, respectively. The highest oxidation state of Fe was observed for the silica-poor zhamanshinite samples, $+2.3$, $+2.6$, and $+2.8$.

Studies [90, 107–115] based on the analysis of X-ray absorption spectra showed that iron in tektites from various tektite fields has an oxidation state of approximately Fe^{2+} distributed over four or five coordinated positions. In impact glasses, it is from Fe^{2+} to Fe^{3+} , and the coordination numbers are from 4 to 6. It should be noted that the oxidation states of iron obtained from the analysis of XANES spectra are in agreement with the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in tektites and impactites from various tektite fields obtained with various non-X-ray spectral methods and described in [102]. Indeed, the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in tektites [102] varies approximately within 0.02–0.12 (Fig. 1 in [102]), which is significantly lower than that of their parent rocks (>0.2 – 0.25), whereas the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio in impact glasses is much higher (Fig. 2 in [102]) than in tektites. In general, studies [107–115] on the role of iron in tektites and impactites showed that X-ray absorption spectroscopy (in particular, XANES) is an effective method for determining the features of local electronic and atomic structure in materials without long-range order in the atomic arrangement, in natural glasses. There are, however, some discussion points. The study of the tektites (moldavites, australites, phil-

lipinites, and indoshinites) with Mössbauer spectroscopy [116], for example, showed that the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in these samples is within 0.05–0.15 and Fe is distributed in five or six coordinated positions. It is not, however, consistent with the XAS data [113] for the tektites (australite, moldavite, indoshinite, phillipinite, and bediasite), in which Fe is distributed over four or five coordinated positions. As a result, a systematic study of the role of iron, its oxidation state, and local environment in tektites and impact glasses remains an actual task.

Meteorites are interesting extraterrestrial natural objects. They are the most important source of information about the early stages of the evolution of the Solar System. Being a carrier of cosmic stellar dust, meteorites are also potentially useful not only in the study of interplanetary matter of the Solar System, but also comets and matter brought from other stellar systems. A number of techniques are widely used to characterize various meteorites. XRF [117] or micro-XRF analysis [118], for example, are used to analyze the elemental composition of meteorites; the distribution maps of elements in the samples are constructed [119]. Mössbauer spectroscopy is used to determine the iron-containing phases in meteorites and to assess the oxidation state of iron [120, 121]. Phase analysis is performed based on XRD [122, 123] or micro-XRD [124]. IR spectroscopy is less used to study insoluble organic matter extracted from meteorites [125] and to assess changes in them due to impact [126]. Modern nondestructive methods used to study extraterrestrial bodies are reviewed in [127]. Various types of meteorites were studied: for example, ordinary chondrites [128, 129], achondrites [130], carbonaceous chondrites [131, 132], and Martian and lunar meteorites [133, 134]. Recently, X-ray absorption spectroscopy was also used to study meteorites. Being a local, non-destructive, and element-selective research method, XAS is well suited to studying the local atomic and electronic structures of amorphous sections of meteorites and to analyzing organic inclusions of meteorites. X-ray absorption spectra, for example, were recorded at the *K* edges of Ca [135], Ti [135], and Fe [135–140] and the *L* edges of transition metals (Fe, Si, V, Cr, Mn, Cu [141–143], and Os [144]) to study meteorites. X-ray absorption spectra at the *K* edges of light elements, such as C [145–148], S [149–151], and N [148], are analyzed.

Considering that meteorite samples are chemically inhomogeneous materials, micro-XAS techniques [151–153] have an advantage in determining the features of their electronic or atomic structures.

The X-ray absorption spectra of an organic component of a matrix can be analyzed at the edges of light elements, such as C, N, and O [145–148, 151, 154]. The similarities and differences of an organic compound of the 81P/Wild2 comet collected by the NASA Stardust spacecraft, interplanetary dust particles, and

carbonaceous meteorites, for example, were analyzed [151]. Carbon XANES spectra acquired using a Scanning X-ray transmission microscope (SXTM) at the National Synchrotron Light Source (United States) were analyzed. The C-XANES spectra of seven particles of a compound isolated from five different tracks of the 81P/Wild2 comet were analyzed in comparison with those of a database of thirty-four interplanetary dust particles (IDPs) and several carbonaceous meteorites. They showed that the C-XANES spectra and the size distribution of the carbonaceous compound in the particles of the 81P/Wild2 comet are not identical to those of IDPs or meteorites, but the C-XANES spectra of cometary particles are more similar to those of IDPs than carbon meteorites. The particles of the 81P/Wild2 comet, IDPs, and meteorites contain amorphous carbon, but the spectra of the particles of the 81P/Wild2 comet contain components that are much more aliphatic than IDPs or meteorite organics.

The oxidation state of iron attracts attention during the study of meteorites because the physicochemical processes of meteorite formation (thermal metamorphism and hydration) influence the oxidation-state value. It is known that in newly formed meteorites, iron can exist as Fe^0 in Fe-Ni metal, Fe^{2+} in silicates and sulfides, and Fe^{3+} in phyllosilicates and magnetite. Fe^0 and Fe^{2+} are transformed into Fe^{3+} crystalline phases during oxidation over time [138]. The oxidation state of iron in the meteorites was studied from analysis of the X-ray absorption spectra of iron [135–140].

The authors used XANES spectroscopy at the FeK edge to assess the $\text{Fe}^{3+}/\text{Fe}_{\text{total}}$ ratio in 90 chondrites belonging to six different species. FeK-XANES spectra were also recorded for 10 terrestrial samples with a well-known oxidation state used as reference samples [138].

The oxidation state of iron in the Jiddat Al Harasis055 ordinary chondrite was assessed from analysis of the pre-edge feature and the position of the X-ray absorption edge [140].

The local atomic and electronic structures of the meteorite fusion crusts were studied with XANES and EXAFS spectroscopies at the CaK, TiK, and FeK edges [135]. The meteorite fusion crust is due to melting under extremely high temperature and a large temperature gradient, when the meteorite enters the atmosphere. The study [135] showed that the meteorite crust has a unique local structure, which differs from that of tektites. The high $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio in the meteorite crust indicates that the crusts appear under atmospheric oxidation conditions. The authors concluded that the meteorite fusion crust have a unique local structure due to the fact that they underwent extremely high temperatures and short quenching times. It has been shown that X-ray absorption spectroscopy is effective tool to distinguish the meteorites fusion crusts and natural glasses [135].

The Northwest Africa (NWA) 8114 Martian meteorite was studied, which makes it possible to study the

thermal history of Martian regolith and to study surface processes and existed environmental conditions near the impact crater on Mars [136]. Grains of pyroxenes and iron oxides were studied via transmission and scanning electron microscopies, IR spectroscopy, XRF, XRD, and micro-XANES spectroscopy. Analysis of the micro FeK-XANES spectra revealed that there are oxidation processes and that the $\text{Fe}^{3+}/\Sigma\text{Fe}$ ratio is up to 25%. In addition to point measurements, FeK-XANES maps were obtained for several areas to visually demonstrate the change in the oxidation state of iron. The authors concluded that the fragments, which were predominantly pyroxene, were converted at high temperature to iron oxide and a K-containing glassy feldspar with a porous texture.

Some works, in which XANES spectroscopy was used to study the structural features of meteorites, are reviewed in [8].

In general, analysis of the works [8, 135–154] shows that X-ray absorption spectroscopy, in particular, XANES and micro-XANES spectroscopy, is a valuable and effective method for studying the local electronic and atomic structures of meteorites influenced by the conditions of their formation, although it is currently not widely used. Considering that meteorites are complex, researchers usually combine X-ray absorption spectroscopy with other methods, such as XRF, micro-XRF, XRD, IR, and Mössbauer spectroscopies for the most complete and comprehensive characterization of meteorite samples.

CONCLUSIONS

In summary, it has been shown that X-ray absorption spectroscopy, in particular, X-ray absorption near-edge spectroscopy (XANES), is a nondestructive, element-selective, and local method to study materials without long-range order in the arrangement of atoms. XANES makes it possible to find the oxidation state of atoms and the features of the 3D local atomic structure around the absorbing atoms with a high degree of accuracy, up to 1 pm for bond lengths and several degrees for bond angles. Synchrotron radiation allows the measurement of X-ray absorption spectra with a high energy resolution, with micro- and nanofocusing of the X-ray beam and the acquisition of spectra under real conditions, for example, directly under high pressures and temperatures. Such wide possibilities and a high accuracy in obtaining structural information make X-ray absorption spectroscopy a unique and highly effective tool for diagnostics of the local electronic and atomic structures of terrestrial and extraterrestrial natural objects, including minerals with defect/impurity atoms, microscale and nanoscale inclusions, natural glasses, impact rocks, and meteorites.

ACKNOWLEDGMENTS

I am grateful to L. V. Guda, A. A. Guda, A. V. Soldatov, D. D. Badyukov, A. Berry, A. L. Trigub, M. I. Mazuritskiy, S. P. Kubrin, G. E. Yalovega, and Yu. V. Popov for collaboration in studying the terrestrial and extraterrestrial natural materials.

FUNDING

This work was financially supported by the Russian Ministry of Education and Science (no. 16.3871.2017/4.6).

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Translated by A. Tulyabaev