Nuclear Instruments and Methods in Physics Research B 267 (2009) 2229–2232

Contents lists available at ScienceDirect

Nuclear Instruments and Methods in Physics Research B

journal homepage: www.elsevier.com/locate/nimb

Investigation of impact materials from the Barringer Meteor Crater by micro-XANES and micro-PIXE techniques

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ARTICLE INFO

Available online 12 March 2009

PACS:
91.67.Gn
91.65.Sn
29.30.Kv
78.70.En

Keywords:
Meteoritic impact
Micro-PIXE
Micro-XANES

ABSTRACT

Impact materials from the Barringer Meteor Crater were examined by combined micro-X-ray absorption near edge structure (micro-XANES) and micro-particle induced X-ray emission (micro-PIXE) methods. Efforts were focussed on the complex characterization of their iron-rich inclusions. The lateral distribution of elements as well as the oxidation state of iron was determined. The study demonstrates the capabilities of chemical speciation screening based on energy selective micro-XRF maps in geology. With the help of this method zero-valent (metallic) and three-valent iron were excluded in the studied specimens without performing XANES in every pixel.

1. Introduction

Impact craters are formed when a large meteoroid (asteroid or comet) crashes into a planetary body. Up to date less than 200 impact sites have been confirmed on the Earth. They provide extraterrestrial material for mineralogical, geochemical and cosmochemical studies.

Barringer Meteorite Crater, also known as Meteor Crater or Canyon Diablo Crater, in Northern Central Arizona was the first recognized impact crater on Earth. It is a bowl-shaped depression 180 m deep and about 1200 m in diameter encompassed by a rim that rises 30–60 m above the surrounding plain [1]. The age of the crater has been determined by thermoluminescence techniques as 49,000 ± 3000 years [2].

The meteorite that created the crater had a surface-impact velocity of about 12 km/s only [3]. This explains the puzzling fact that the crater does not contain large volumes of melted rock. A small portion of the incoming iron asteroid survived in the form of solid fragments, these are the Canyon Diablo meteorites. Most of the asteroid material melted by the shock and were either deposited as metallic spherules or, predominantly, dispersed. Materials collected from a well-known impact area may provide clues for the recognition of suspected impact events. Therefore, the thorough characterization of samples from the Barringer Meteorite Crater is desirable.

During our previous investigations, impact material from the Barringer Crater was examined with various analytical techniques [4–6]. These efforts were dedicated to the study of the elemental composition of S–Fe–Ni systems (inclusions) within the samples but the characterization of their chemical state was missing. However, by combining micro-X-ray absorption near edge structure (micro-XANES) and micro-particle induced X-ray emission (PIXE) both the distribution of the elements and their oxidation state can be determined. In this work, we investigated the oxidation state of iron besides elemental analysis for more complex characterization of iron-rich inclusions using synchrotron radiation and nuclear microprobe.

2. Materials and methods

2.1. Samples

Samples were collected at the Barringer Meteor Crater. Iron-rich specimens were selected with an electromagnetic separator. These were microobjects of a few 100-μm in size. They were embedded in artificial resin and polished to get a flat surface. Five iron containing materials served as standards with known oxidation state. These were pellets containing finely grained hematite, chromite,

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doi:10.1016/j.nimb.2009.03.016

pyrrhotite and magnetite, homogenized in boron nitride matrix, and a pure iron foil.

2.2. Measurements using synchrotron radiation

The measurements were conducted on the "LUCIA" (Line for Ultimate Characterization by Imaging and Absorption) beamline installed at the Swiss Light Source synchrotron in the Paul Scherrer Institute, Villigen, Switzerland. The LUCIA beamline is dedicated to micro-spectroscopy performing chemical speciation by micro-X-ray absorption spectroscopy (micro-XAS) and elemental mapping by X-ray micro-fluorescence (micro-XRF), covering the 0.8–8 keV energy domain. For detailed description of the LUCIA beamline see Flank et al. [7]. In our case, the $V \times H$ spot size was $4 \times 10\ \mu m^2$. XAS spectra were collected in transmission mode for the iron foil using a photo-diode positioned behind the sample. All the other samples were measured in fluorescence mode with a mono-element energy dispersive silicon drift diode. Measurements were performed at the Fe K-edge in the energy range of 7.0–7.2 keV, with 0.3 eV steps in the near-edge region and with 1 eV steps before and 2 eV steps after the near-edge region. Collection time was set to 2 s/step. Three scans were collected and merged for each sample. Spectra were evaluated using the ATHENA software [8]. Micro-XRF maps were recorded at 7117, 7124, 7125.8 and 7193 eV photon energies, moving the sample on an $x - y$ translation stage with 4 μm horizontal and 10 μm vertical step size. Acquisition time in each spot was 1.1 s.

2.3. Measurement using ion beam microprobe

PIXE measurements for elemental concentrations and distributions were performed as described in a separate paper of this volume [9]. For the detailed description of the ion microprobe in ATOMKI, Debrecen, and the data evaluation software packages see [10,11].

2.4. Chemical speciation screening

X-ray absorption fine structure refers to the modulation of the X-ray absorption of an atom near and above the core-level binding energies. X-ray absorption depends on the oxidation state and the coordination chemistry of the atom and also on its immediate neighbours, therefore, the fine structure of the absorption spectra may differ remarkably for the same atom in different compounds. This variability provides a tool to differentiate among oxidation states, mineral phases, or molecular species. The X-ray absorption spectrum is usually divided into two regions: X-ray absorption near edge spectroscopy (XANES) from around −10 eV below and to ~30 eV above the main edge and extended X-ray absorption fine structure spectroscopy (EXAFS) from 30 eV to as much as 1000 eV above the edge. XANES is very sensitive to the oxidation state thus we examined this region of the absorption spectra to determine the oxidation state of iron in our samples.

Fig. 1 shows the Fe K-edge XANES spectra for three iron reference compounds: iron metal, chromite and hematite. Iron metal corresponds to the 0, chromite to the 2^+ and hematite to the 3^+ oxidation state. The most obvious feature is the shift of the edge position towards higher energies with increasing oxidation state. We exploited this feature for an overall characterization of the samples, namely chemical speciation mapping was applied following the method described in Grolimund et al. [12]. X-ray fluorescence maps were recorded at four different excitation energies, 7117, 7124, 7125.8 and 7193 eV, reflecting the differences of the spectra. Iron(0) absorption is significantly higher at the lowest excitation energy (7117 eV) than Fe(II) and Fe(III) absorption. On the other hand, Fe(III) iron exhibits low absorbance at the two medium energies (i.e. 7124 and 7125.8 eV) compared to Fe(0) and Fe(II). At higher energies differences in the chemical and physical states do not play a significant role so the right end of the spectra is used for normalization. In our experiment the following conditions would be valid for a predominantly zero-valent area: the ratio of the absorption measured at 7117 and 7193 eV is above 0.2 while the ratio of the absorption measured at 7125.8 and 7193 eV is between 0.7 and 0.9. An area, mainly containing Fe(III), would produce a ratio of the absorptions at 7124 and 7193 eV below 0.4 and a ratio at 7125.8 and 7193 eV between 0.2 and 0.5. This screening allows an estimation of the dominant oxidation states for the whole sample. Obviously, this method is more powerful if only a limited number of potential compounds can occur in the sample. In this case, measuring all the necessary reference compounds and selecting carefully the excitation energies for the fluorescence maps we can obtain the distribution of the compounds.

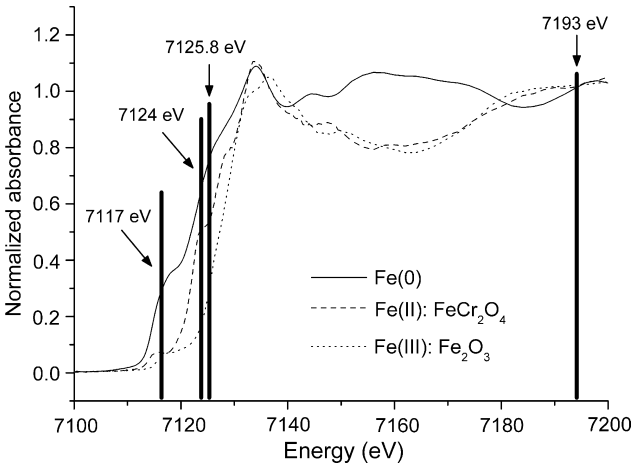

Fig. 1. XANES spectra of elemental Fe^0 (solid line), $Fe^{II}Cr_2O_4$ (dashed line) and $Fe^{III}_2O_3$ (dotted line). Arrows indicates the excitation energies for chemical speciation screening.

2.5. Pre-edge peak position

To corroborate the chemical speciation map results and to obtain more specific information, XANES measurements were performed in selected spots of the samples. A special attention has been devoted to the pre-edge peak, since this region could provide valuable information about the degree of iron oxidation [13,14]. The position of the pre-edge peak, as well as that of the edge, for an iron(III) compound is shifted towards higher energy compared to the iron(II) state. For a constant coordination number, the shift of the pre-edge peak can be considered as a linear function of the Fe(III)/ΣFe ratio with a good approximation [13]. Modulations in this linearity occur when varying simultaneously oxidation state and coordination number [14]. After determining the position of the pre-edge peaks for reference materials with known oxidation state, a calibration curve can be plotted to determine the Fe(III)/ΣFe ratio in unknown samples (Fig. 2). In our case, chromite served as a reference material for the pure 2^+ and hematite to the pure 3^+ oxidation state and magnetite for a mixed, Fe(III)/ΣFe = 0.69, state.

3. Results and discussion

Chemical speciation screening was applied on four iron rich samples. The weakening of the X-ray fluorescence signal by lowering the excitation energy around the absorption edge is demonstrated in Fig. 3. Systematic calculations of the appropriate yield ratios pixel by pixel, as described in the Section 2, showed no