

Yellow impact glass from the K/T boundary at Beloc (Haiti): XANES determination of the Fe oxidation state and implications for formation conditions

Gabriele GIULI^{1*}, Sigrid Griet EECKHOUT², Christian KOEBERL³, Giovanni PRATESI^{4, 5},
and Eleonora PARIS¹

¹Dipartimento di Scienze della Terra, Università di Camerino, Via Gentile III da Varano, 62032 Camerino, Italy

²European Synchrotron Radiation Facility, 6 rue Jules Horowitz, BP 220, 38043 Grenoble, France

³Center for Earth Sciences, University of Vienna, Althanstrasse 14, A-1090 Vienna, Austria

⁴Museo di Storia Naturale, Sezione di Mineralogia e Litologia, Università di Firenze, Via G. la Pira 4, 50121 Firenze, Italy

⁵Museo di Scienze Planetarie della Provincia di Prato, Prato, Italy

*Corresponding author. E-mail: gabriele.giuli@unicam.it

(Received 20 June 2007; revision accepted 04 December 2007)

Abstract—We determined the iron oxidation state and coordination number in five samples of yellow impact glass from the Cretaceous-Tertiary (K/T) boundary section at Beloc, Haiti, which formed as the result of impact melting during the Chicxulub impact event. The samples were analyzed by Fe K-edge XANES spectroscopy and the results were compared with published data on eight black impact glasses and one high Si-K impact spherule from the same impact layer. The pre-edge peak of our high-resolution XANES spectra displays evident variations indicative of significant changes in the Fe oxidation state, spanning a wide range from about 75 to 100 mole% Fe³⁺. Yellow K/T glasses have significantly higher Fe³⁺/(Fe²⁺ + Fe³⁺) ratios compared to black K/T impact glasses (from 20 to 75 mole% Fe³⁺) and high Si-K glass (20 mole% Fe³⁺). In particular, all the pre-edge peak data on these three types of impact glasses plot between two mixing lines joining a point calculated as the mean of a group of tektites studied so far (consisting of [⁴]Fe²⁺ and [⁵]Fe²⁺) to [⁴]Fe³⁺ and [⁵]Fe³⁺, respectively. Thus, the XANES spectra of the yellow K/T glasses can be interpreted as a mixture of [⁴]Fe²⁺, [⁵]Fe²⁺, [⁴]Fe³⁺, and [⁵]Fe³⁺.

Our observations can be explained by a very large range of oxygen fugacity conditions during melt formation. Furthermore, there is a clear positive relationship between the Fe³⁺/(Fe²⁺ + Fe³⁺) ratio and the Ca content of these glasses, suggesting that the Fe oxidation state was influenced by the relative contribution of Ca-sulfate- and Ca-carbonate-bearing sedimentary rocks at the impact site.

INTRODUCTION

The presence of relict impact glass within the K/T boundary layer has been well documented by a number of authors. In particular, fresh impact glass found at the K/T boundary of Beloc (Haiti) and displaying a variety of chemical compositions with very different Si and Ca contents has been often referred as belonging to two main groups of glasses: black impact glasses, the most common, and yellow impact glasses. Sigurdsson et al. (1991a, b), Izett (1991), and Kring and Boynton (1991) described the presence of relict glass within alteration spherules (that are otherwise very common at numerous K/T boundary locations) from the K/T boundary at Beloc, Haiti, and interpreted the material as impact glass. These black and yellow impact glasses display compositions similar to those of the upper continental crust

(Izett 1991; Sigurdsson et al. 1991a, b; Koeberl and Sigurdsson 1992; Bohor and Glass 1995). The yellow glasses are rich in Ca (~25 wt% CaO), S (~0.6 wt% SO₃), and Sr, which is most likely the result of a carbonate and/or anhydrite contributions (Izett 1991; Sigurdsson et al. 1991b). Sigurdsson et al. (1992) have shown, from comparison with experimental glasses, that the Haitian glasses have been quenched from temperatures much higher than those of typical volcanic processes. All available evidence supports an impact, not volcanic, origin for these glasses.

A detailed geochemical study by Koeberl and Sigurdsson (1992) provided not only detailed geochemical arguments for the impact origin of these glasses, but also demonstrated the existence of rare inhomogeneous glasses with lechatelierite and other mineral inclusions, which are typical for an origin by impact. Blum and Chamberlain (1992) obtained oxygen

Table 1. Major element compositions (in wt%) of yellow impact glasses from Beloc (Haiti).

Sample Oxide	Be4a	Be4b	Be4c	Be4e	Be4f
SiO ₂	46.50	51.40	48.55	47.18	48.81
TiO ₂	0.58	0.49	0.62	0.49	0.60
Al ₂ O ₃	12.58	13.25	13.15	12.71	13.31
FeO	5.17	5.00	5.02	4.77	5.06
MnO	0.26	0.13	0.12	0.14	0.14
MgO	4.59	4.46	4.21	4.61	4.67
CaO	26.83	21.84	23.19	26.67	24.62
Na ₂ O	2.05	2.31	2.54	2.26	2.34
K ₂ O	0.78	0.92	0.75	0.55	0.66
P ₂ O ₅	0.00	0.00	0.00	0.00	0.00
SO ₃	0.09	0.11	0.41	0.86	0.58
Total	99.43	99.91	98.55	100.22	100.79

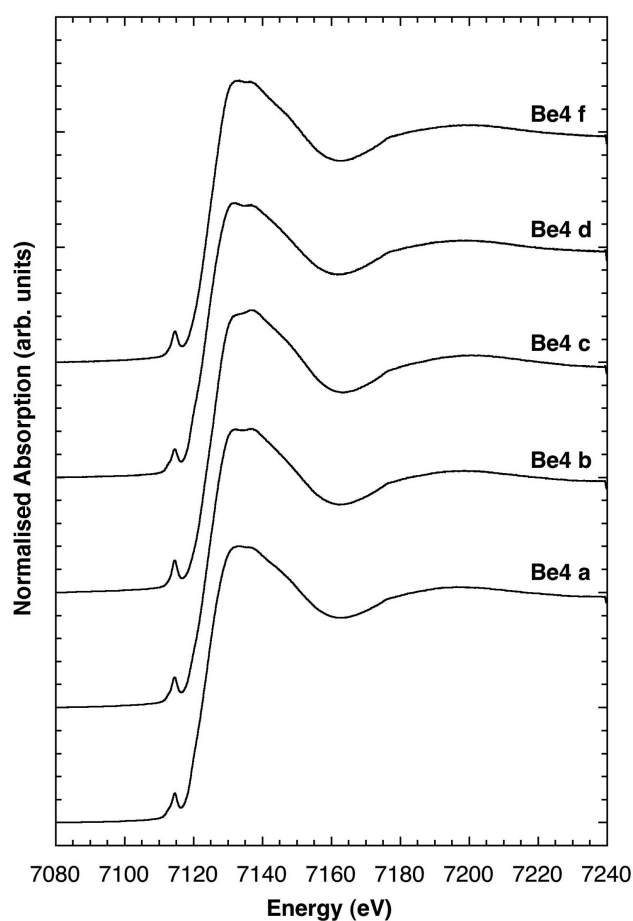


Fig. 1. Experimental Fe K-edge XANES spectra of the K/T yellow glass spherules. The spectra have been normalized setting the step height to one.

isotope data on Haitian glasses that specifically rule out a volcanic origin of these glasses. Blum et al. (1993) and Premo and Izett (1992) confirmed this result from Rb-Sr and Sm-Nd isotopic data, showing that the Haitian glasses are mixtures of silicate rocks of upper crustal composition with a high CaO-endmember (e.g., limestone). Chaussidon et al. (1996) have

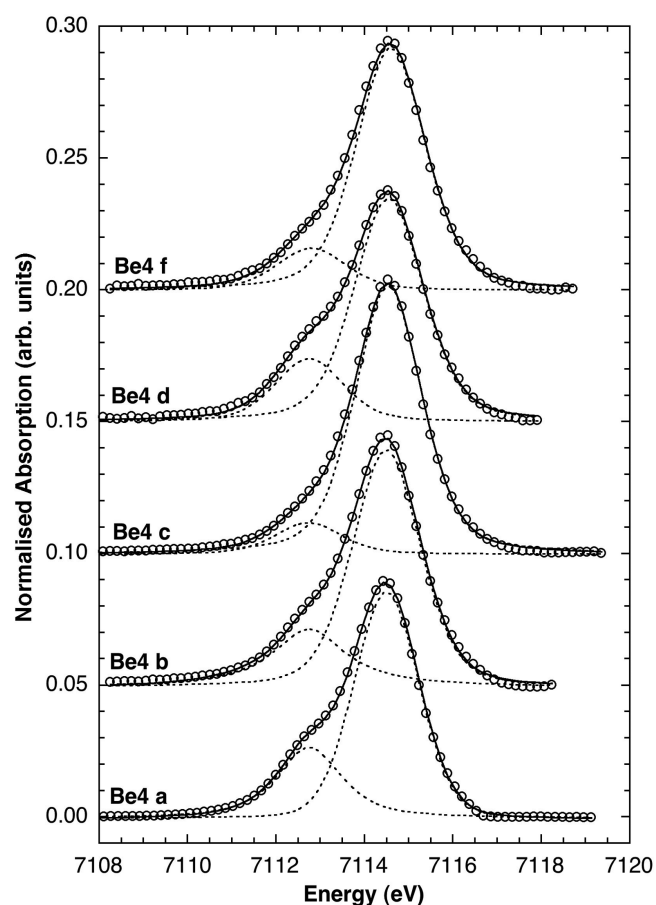


Fig. 2. Background subtracted pre-edge peaks of the K/T yellow glass spherules (empty circles). Also the single pseudo-Voigt components (dotted lines) used in the fit and their sums (solid lines) are shown.

shown that the sulfur in the yellow glasses occurs in the form of sulfate, which is not compatible with a volcanic source. Koeberl (1992) measured the water content in glasses from Haiti and found a range of 0.013 to 0.021 wt% H₂O, which is further evidence for an origin by impact, as impact glasses are extremely dry. Osmium isotopic analyses by Koeberl et al.

Table 2. Pre-edge peak features of the Fe K-edge XANES spectra.

Sample name	Centroid (eV) ^a	Integrated intensity	Fit agreement index (%)
Siderite	7112.80	0.054	99.84
Kirschsteinite	7113.00	0.062	99.83
Grandierite	7113.00	0.101	99.32
Staurolite	7113.00	0.218	99.88
Fe-akermanite	7112.90	0.283	99.84
Andradite	7114.40	0.107	99.93
Aegirine	7114.51	0.103	99.97
Yoderite	7114.30	0.169	99.91
Yellow glass			
Be4a	7114.05	0.211	99.98
Be4b	7114.10	0.233	99.95
Be4c	7114.40	0.235	99.97
Be4d	7114.15	0.233	99.95
Be4f	7114.35	0.232	99.94
Black glass			
H1 ^b	7113.9	0.202	99.97
H2 ^b	7113.4	0.169	99.98
H3 ^b	7113.3	0.153	99.95
H4 ^b	7113.4	0.138	99.96
H5 ^b	7113.8	0.179	99.97
H6 ^b	7114.0	0.182	99.97
H7 ^b	7113.7	0.171	99.98
H8 ^b	7113.2	0.142	99.97
H10 ^b	7113.8	0.182	99.98

^aPrecision and accuracy of the pre-edge peak centroid energy are ± 0.05 and 0.1 eV, respectively.

^bData on black glasses and high Si-K spherule (H8) from Giuli et al. (2005).

(1994) showed evidence for the presence of a small meteoritic component in the Haitian glasses. Furthermore, high-precision age determinations on the Haitian glasses have shown that the materials have an age indistinguishable from that of the K/T boundary, at 65 Ma (e.g., Izett 1991; Swisher et al. 1992). Glasses with similar properties have later been recovered from some K/T boundary locations in Mexico (e.g., Mimbral) as well (e.g., Smit et al. 1992; Premo et al. 1995).

Giuli et al. (2005) studied the oxidation state of the black glass from Haiti and found more oxidized compositions (with $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratios ranging from 20 to 75%) than what is known for “normal” tektites. So far the only study of the oxidation state of the yellow glasses was published by Oskarsson et al. (1996): on the basis of Mössbauer spectroscopy data on two spherules, they concluded that the $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio for black glasses and yellow glasses amounted to 40% and 74%, respectively. From this they inferred that yellow glasses were affected by a larger contribution from marine sediments that were incorporated during melting. In the present study, we used XANES to determine the oxidation state and coordination number of Fe for samples previously analyzed by Koeberl and Sigurdsson (1992).

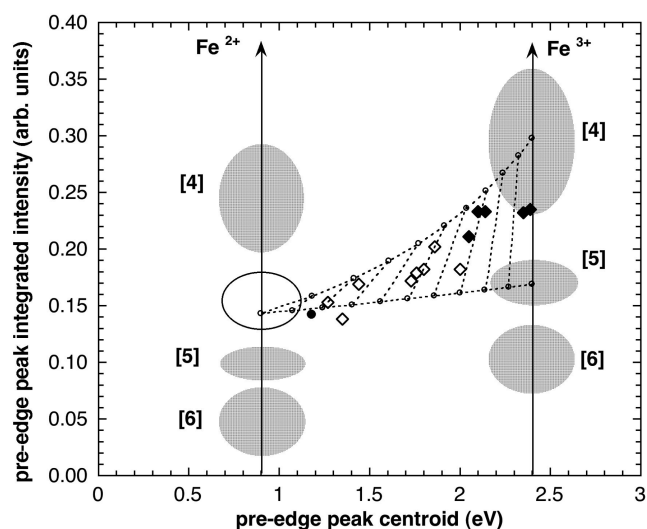


Fig. 3. Plot of the pre-edge peak integrated intensity versus centroid energy. Solid diamonds refer to the K/T yellow glasses studied here, whereas open diamonds and the solid circle refer to black glass spherules and high Si-K spherule, respectively (Giuli et al. 2005). The unshaded open ellipse on the left side indicates the field of data occupied by all splash-form tektites analyzed so far (Giuli et al. 2002; and Giuli et al., unpublished data). Also shown are the mixing lines (dashed lines + circles) between $^{[4]}\text{Fe}^{3+}$ or $^{[5]}\text{Fe}^{3+}$ and the mean of about 30 tektites analyzed (see text).

SAMPLES AND EXPERIMENTAL METHODS

The samples studied have been collected from the K/T boundary layer outcrops along the Jacmel highway in the Beloc region (Haiti) (see Sigurdsson et al. [1991a, b] and Koeberl and Sigurdsson [1992] for details). The glass is usually altered to smectite spherules; however, relict glass can occur in the spherule interior. After careful separation from the smectite matrix, the glass spherules have been immersed in a diluted HCl aqueous solution for 5 min and cleaned by an ultrasonic bath to wash away the smectite exterior. The cleaned glass chips were embedded in bee wax, gently abraded and subsequently polished to expose the unaltered interior. The glass spherules examined are all of the yellow glass type, with diameters in the 200–800 μm range. No microcrystals or residual smectite were found after optical microscopic examination. In electron microscopic images the samples appear uniform.

The samples were then embedded in epoxy resin and polished for microprobe analyses. Chemical compositions were obtained using a JEOL JXA 8600 electron microprobe at the University of Florence operating at 15 kV acceleration voltage and 10 nA sample current, with the electron beam defocused to a radius of 20 μm to avoid losses of volatile elements. The following standards were used: albite for Si and Na, anorthite for Al, ilmenite for Fe and Ti, bustamite for Mn, diopside for Ca, olivine for Mg, sanidine for K. Data were corrected according to the method of Bence and Albee (1968). Tabulated data are averages of 6 individual analyses (Table 1).

The standards used for XANES measurements are a staurolite from Canton Ticino (Switzerland) and a synthetic Fe-akermanite for Fe²⁺ in tetrahedral coordination, a grandidierite from Madagascar for Fe²⁺ in trigonal bipyramidal coordination, a synthetic kirschsteinite and a siderite from Erzberg (Austria) for Fe²⁺ in octahedral coordination, a natural andradite from Italy, and a natural aegirine from Malawi for Fe³⁺ in octahedral coordination, and a natural yoderite from Mautia Hills (Tanzania) for Fe³⁺ in 5-fold coordination. The natural standards were separated by hand picking from thumb-sized crystals choosing the clearest portions to avoid impurities. All the standards were checked for purity by both optical microscopy and X-ray diffraction.

Model compounds for XAS measurement were prepared by smearing finely ground powder on a kapton tape, whereas the K/T glass spherule samples were prepared as microprobe mounts. The flat surface was placed at 45° from the X-ray beam directed towards the fluorescence detector. Fe K-edge XANES spectra were recorded at room temperature at the ESRF on the undulator beamline ID26 (Gauthier et al. 1999; Solé et al. 1999) operating at 6 GeV in four bunch mode for samples one to five, and in 2 × 1/3 filling for samples six to ten. A fixed-exit Si(220) double-crystal monochromator was used, providing an energy resolution of ~0.4 eV at the Fe K-edge. However, the main limitation for energy resolution is the finite core-hole width of the absorbing element (~1.15 eV at the Fe K-edge; Krause and Oliver [1979]), resulting in a convoluted energy resolution (FWHM) of ~1.4 eV. The energy was calibrated by defining the first derivative peak of a metallic Fe reference foil to be at 7112.0 eV. Two Si mirrors were used for the harmonics rejection of the incident X-ray beam. Beam dimension at the sample was 200 × 100 μm. Before each measurement, care was taken in sample centering, so as to have the beam pointing at the sample geometric center. XANES data were recorded in quick-scan mode by simultaneously scanning the monochromator angle and the undulator gap with a typical energy step of 0.25 eV and counting 20 ms per point. Each scan took 30 s and an average of 15 spectra was taken per sample. The spectra were acquired in fluorescence mode, using a Si photo diode and I₀ was monitored by measuring the fluorescence signal of a titanium foil using a Si photo diode. The sample was positioned at 90° with respect to the beam and the detector at 45° with respect to the sample.

DATA REDUCTION

Experimental XANES spectra were reduced by background subtraction with a linear function and then normalized for atomic absorption on the average absorption coefficient of the spectral region from 7150 to 7300 eV. The threshold energy was taken as the first maximum of the first derivative of the spectra. Pre-edge peak analysis was carried out following the same procedure reported in Wilke et al.

(2001) and Giuli et al. (2002, 2003). The pre-edge peak was fitted by a sum of pseudo-Voigt function and the integrated intensities along with centroid energies were compared with those of the model compounds analyzed here and others in the literature (Wilke et al. 2001; Farges 2001) in order to extract information on Fe oxidation state and coordination number in the glasses studied.

RESULTS

XANES spectra of the 5 K/T yellow impact-glass spherules samples are shown in Fig. 1. The XANES spectra of all the K/T impact glass samples display very broad features as expected from their amorphous nature. Clear differences can be noted in the energy region below 7120 eV, called the pre-edge region. The peak located in the pre-edge region (the pre-edge peak) is the most useful feature to discriminate the oxidation state and co-ordination number of Fe (Fig. 2). This peak represents an *1s-3d* like transition and is thus dipole-forbidden, but becomes partially allowed by mixing of the *d*-states of the transition metal with the *p*-states of the surrounding oxygen atoms. Its energy position depends mainly on the mean Fe oxidation state, gradually increasing from Fe²⁺ to Fe³⁺, while its intensity depends on the geometry around Fe (Calas and Petiau 1983; Brown et al. 1995; Wilke et al. 2001), so that it will be virtually zero in the case of regular octahedral symmetry around the absorber, whereas it will reach its maximum in the case of tetrahedral coordination. For these characteristics of the XANES spectra, we analyzed model compounds chosen to represent a variety of oxidation states (from Fe²⁺ to Fe³⁺) and coordination numbers (from 4 to 6). Figure 2 displays how the pre-edge peak varies in the K/T impact glass samples, and also shows the results of the pre-edge peak deconvolution into single pseudo-Voigt components each of which represent an electronic transition from the *1s* level to different *3d* levels (see Wilke et al. 2001; Giuli et al. 2002).

The pre-edge peaks of almost all the samples display two components. By extracting the pre-edge peak centroid and the integrated intensities (given in Table 2), these data can be compared with those of the model compounds with known Fe oxidation state and coordination number (Wilke et al. 2001; Farges 2001; Giuli et al. 2002, 2003) in order to evaluate the contribution of the different Fe oxidation states and coordination numbers in our samples.

All the pre-edge peak data (integrated intensity versus centroid energy) are plotted in Fig. 3, where also the data of model compounds from the literature are shown. It can be noticed that all samples, including our earlier data on black spherules and the high Si-K spherule (Giuli et al. 2005), plot along a well-defined trend. All the samples can be bracketed between the two mixing lines shown in the figures: the mixing lines are calculated from a point representative of divalent Fe in a mixture of five-fold and four-fold coordinated sites (which is taken as the mean of more than 20 tektites from the

we found no correlation between Fe oxidation state and chemical or structural parameters (i.e., alkali, alkali ratio, and polymerization) possibly related to glass alteration. Moreover, the water content of the yellow glass samples from the same outcrop is very low, at about 20 ppm (Koeberl 1992). We thus suggest that the glasses studied are pristine, and that the Fe oxidation state is indicative of a range of oxygen fugacities during the formation of the glass.

Acknowledgments—We acknowledge the European Synchrotron Radiation Facility for provision of beamtime. We would like to thank the ID26 staff (ESRF) for assistance. C. K. is supported by the Austrian Science Foundation (grant P18862-N10).

Editorial Handling—Dr. John Spray

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