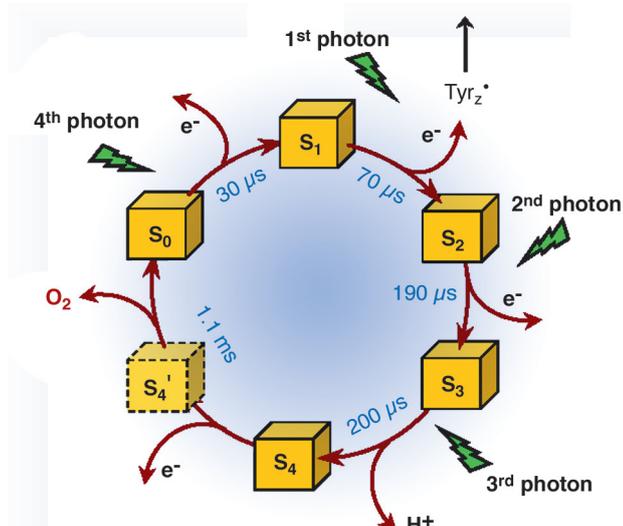


The third Laser flash induced the  $S_3$  to  $S_0$  transition. An absorption increase due to Mn reduction by the substrate water upon  $O_2$  formation was observed. The absorption increase was preceded by a lag phase of about 250  $\mu\text{s}$  duration (Figure 2a). This lag phase suggested a kinetically resolvable intermediate. However, a minor fraction of PSII that undergoes the  $S_2 \rightarrow S_3$  transition on the third flash (due to PSII which did not turn over on the first laser-flash) might mimic a delay phase in the  $S_3 \Rightarrow S_0$  transition. A time-resolved XAS experiment at 6556 eV clarified the situation since no change in the X-ray absorption is observed for  $S_2 \rightarrow S_3$  at this energy. A sizable lag phase still was present (Figure 1b), proving the existence of a kinetically resolvable intermediate. The intermediate is formed prior to the Mn-reducing/ $O_2$ -forming step and thus represents the long-searched-for  $S_4$ -state.



**Fig. 2:** Extension of the classical S-state cycle of photosynthetic oxygen evolution. The half-times of the S-transitions were determined by the X-ray experiment at the Mn K-edge. Existence and formation rate of the  $S_4$  state have been uncovered in the present investigation.  $S_4$  is not formed by electron transfer to  $\text{Tyr}_Z^\bullet$ , but by a deprotonation reaction and represents the starting point for O-O bond formation.  $S_4'$  denotes a hypothetical intermediate where four electrons have been extracted from the Mn complex, but  $O_2$  has not been formed.

Further characterisation of the intermediate enabled us to identify the chemical nature of the  $S_4$ -state. We propose a 'proton-first' reaction sequence on the oxygen-evolving transition, where the  $\text{Tyr}_Z^\bullet$  radical induces, likely electrostatically, the deprotonation reaction which is a prerequisite to the subsequent electron transfer from the manganese/water complex to  $\text{Tyr}_Z^\bullet$ . Our identification of the  $S_4$  state will spur further investigations on this key step in photosynthetic water oxidation. It leads to an extension of the classical S-state cycle because the deprotonation must be followed by electron transfer to  $\text{Tyr}_Z^\bullet$ , this implying an  $S_4'$ -state

(Figure 2). The described progress was facilitated by a novel time-resolved X-ray experiment. This represents another step forward towards a structural biologist's dream: watching biological function in real time.

#### Acknowledgements

We thank Drs. T. Neisius, S. Eeckhout, and P. Glatzel (all ESRF) for excellent support and P. Loja (our group) for her important contributions to XAS data collection. Financial support by the Deutsche Forschungsgemeinschaft (SFB 498, projects C6 and C8) and the Bundesministerium für Bildung und Forschung (grant 05KS1KEA/6) is gratefully acknowledged.

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#### Principle Publication and Authors:

M. Haumann, P. Liebisch, C. Müller, M. Barra, M. Grabolle, H. Dau, *Science*, published on 11. Nov. 2005. Freie Universität Berlin, FB Physik (Germany)

### Iron Oxidation State in Impact Glass by High-resolution XANES Spectroscopy: Implications on the Formation Conditions

An impact event occurring at the limit between the Cretaceous and Tertiary (K/T) ages resulted in the formation of a ~ 180 km wide impact crater and possibly triggered the K/T mass extinction event. The impact event distributed a huge mass of ejecta material worldwide, including impact glass spherules resulting from the quenching of molten target rock. While most of the glassy spherules worldwide are almost completely recrystallised, fresh unaltered impact glass can be recovered at few sites, e.g., at Beloc, Haiti and Mimbral, Mexico. Three glass varieties have been found so far at Haiti: black, yellow, and HSiK impact glass. Black impact spherules consist of silicate glass of andesitic composition (63 wt%  $\text{SiO}_2$ , 7 wt% CaO), whereas the much rarer yellow variety consists of silicate glass (49 wt%  $\text{SiO}_2$ ) with high Ca (about 25 wt% CaO) and S contents (0.5 to 2 wt% S). The HSiK glass is represented by a single sample with very high Si content (86 wt%  $\text{SiO}_2$ ) and especially low Ca content (0.38 wt% CaO). Although several studies on the chemical and isotopic composition of these impact glasses exist, almost no studies on the Fe coordination number and oxidation state have been reported. Such studies are however of uttermost importance to reconstruct the oxygen fugacity conditions prevailing during impact melt formation.

We examined the iron local environment in a suite of impact glasses (Figure 1) from the Cretaceous-Tertiary (K/T) boundary section at Beloc spanning the widest possible variety of glasses (9 black impact glasses, 5 yellow impact glasses, and the only HSiK impact glass available so far) by Fe K-edge high-resolution X-ray Absorption Near Edge Structure (XANES) spectroscopy at the ID26 beamline. The very high intensity and collimation of the X-ray beam allowed us to collect data on glass samples as small as 100 micrometres. The pre-edge peaks of our XANES spectra (Figure 2) display noticeable variations which are indicative of significant changes in the Fe oxidation state, spanning a wide range from about 20 to 100 mol% trivalent Fe. All data plot along a trend, falling between two mixing lines joining a point calculated as the mean of a group of tektites studied so far (consisting of 4- and 5- coordinated Fe<sup>2+</sup>) to [4]Fe<sup>3+</sup> and [5]Fe<sup>3+</sup>, respectively. Thus, the XANES spectra can be interpreted as a mixture of [4]Fe<sup>2+</sup>, [5]Fe<sup>2+</sup>, [4]Fe<sup>3+</sup> and [5]Fe<sup>3+</sup>. There is no evidence for six-fold coordinated Fe; however, its presence in small amounts cannot be excluded from XANES data alone. Our observations are explained by a very large variety of oxygen fugacity conditions prevailing during melt formation. Furthermore, there is a clear positive relationship between the Fe<sup>3+</sup>/(Fe<sup>2+</sup> + Fe<sup>3+</sup>) ratio and the Ca content of the studied glasses, suggesting that the Fe oxidation state was affected by the variable contribution of the Ca-sulphate bearing sedimentary rocks overlying the target rock at the impact site.

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#### Principal publication and authors:

G. Giuli (a), S.G. Eeckhout (b), E. Paris (a), C. Koeberl (c), and G. Pratesi (d) (2006) (in preparation).

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Fig. 1: Microphotograph of black impact glass spherules.

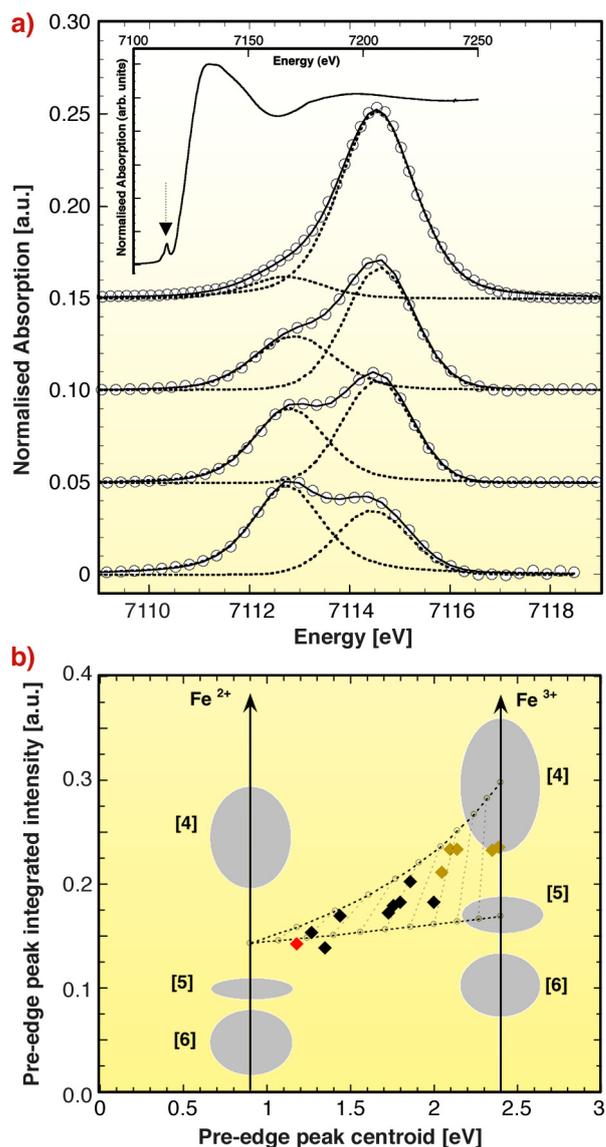


Fig. 2: a) Pre-edge peaks of Fe K-edge XANES spectra of impact glasses from the K/T boundary layer. The calcium concentration in the samples increases from bottom to top spectra. The experimental data (empty circles) are shown along with the fitted components (dashed line) and their sum (solid line). In the inset the XANES spectrum of a sample is shown. The arrow points to the pre-edge region. b) Plot of the pre-edge peak integrated intensity vs. centroid energy (zero refers to the edge energy of metallic iron). Diamond symbols refer to the samples studied here (black, yellow and red for black, yellow and HSiK spherules respectively). The shaded ellipses indicate the field of data occupied by Fe model compounds of known oxidation state and coordination number (Giuli *et al.*, 2005). Also shown are the mixing lines (dashed lines + circles) between [4]Fe<sup>3+</sup> or [5]Fe<sup>3+</sup> and Fe<sup>2+</sup> in a mixture of 4- and 5-fold coordinated sites.