

International Conference on the Deep Carbon  
Cycle

# Micro-XANES Study of the Oxidation state of Chromium in Natural Ferropericlase Inclusions

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# Redox condition of the Earth's interior

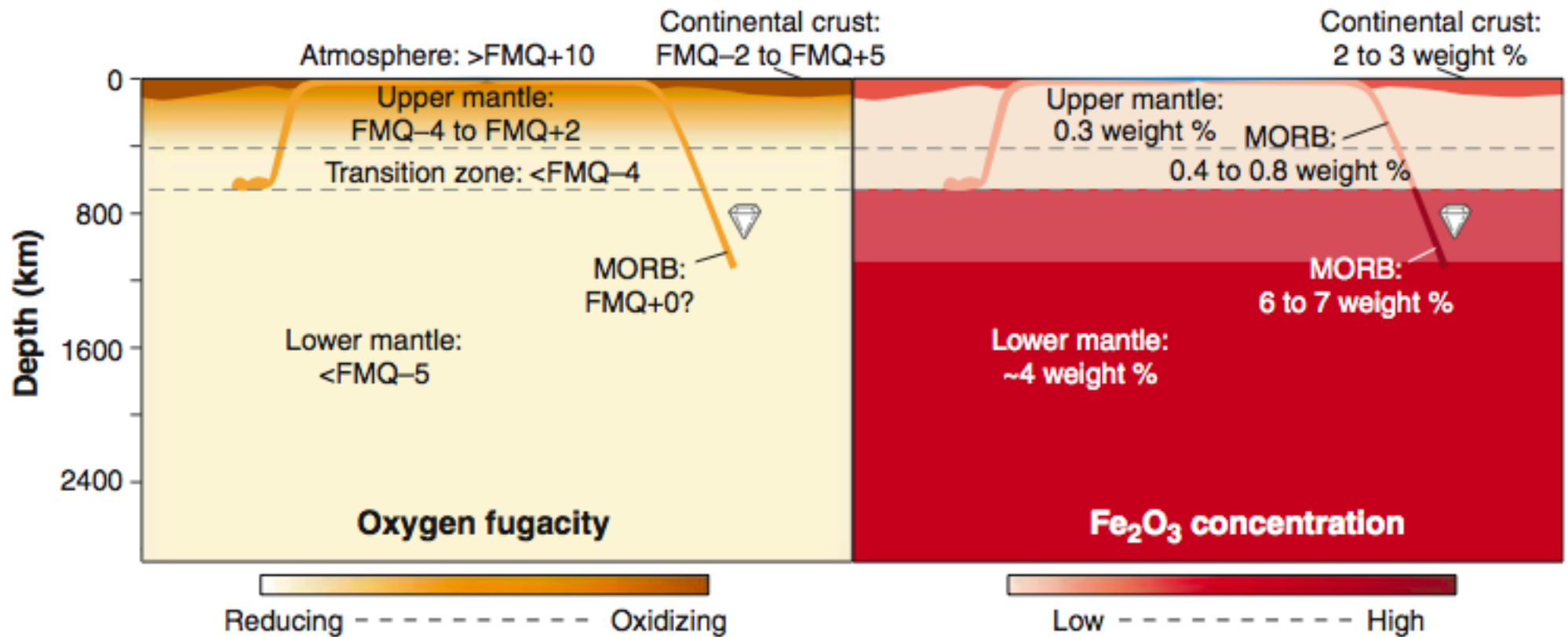
Redox condition of the earth's interior influences various properties such as ...

- Phase relationship
- Water content
- Elastic property
- Electrical conductivity
- **Carbon cycles**

The valence of iron in mantle-derived minerals has been investigated in order to determine the redox condition of the earth's interior (e.g., Luth et al., 1990).

$\text{Fe}^{3+}/\sum\text{Fe}$  of lower mantle?

# Redox condition of the earth's interior



Frost et al., (2004)  
McCammon et al., (2005)

$\text{Fe}^{3+} / \text{Fe}^{2+}$  ratios in the lower mantle are higher than those in the upper mantle.

# Valence state of Cr and redox condition

Cr : +2, +3, and +6

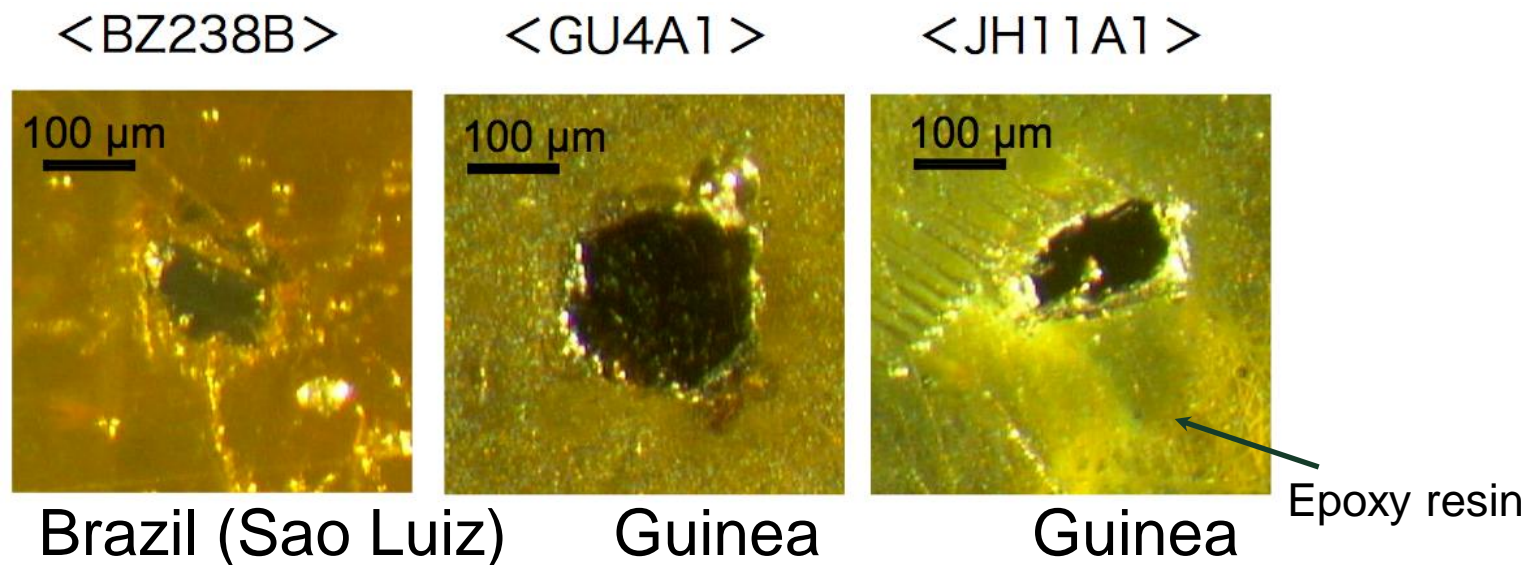
- Chromium is mostly found as  $\text{Cr}^{3+}$  and  $\text{Cr}^{6+}$  ions in terrestrial minerals.
- Minerals formed under extremely reduced conditions can contain  $\text{Cr}^{2+}$  in their structure. (e.g. lunar olivine, (Sutton et al., 1993))

Valence states of Cr have possibility to change with redox condition.

- During cooling from high temperature, the reaction( $\text{Cr}^{2+} + \text{Fe}^{3+} \rightarrow \text{Cr}^{3+} + \text{Fe}^{2+}$ ) will occur in ferropericlase. But if there was insufficient  $\text{Fe}^{3+}$ ,  $\text{Cr}^{2+}$  occurring under low oxygen fugacity could be retained. (Eeckhout et al. 2007)

The presence of  $\text{Cr}^{2+}$  in a mineral could be an indicator of the reduced environment.

# Samples : natural ferropericlase

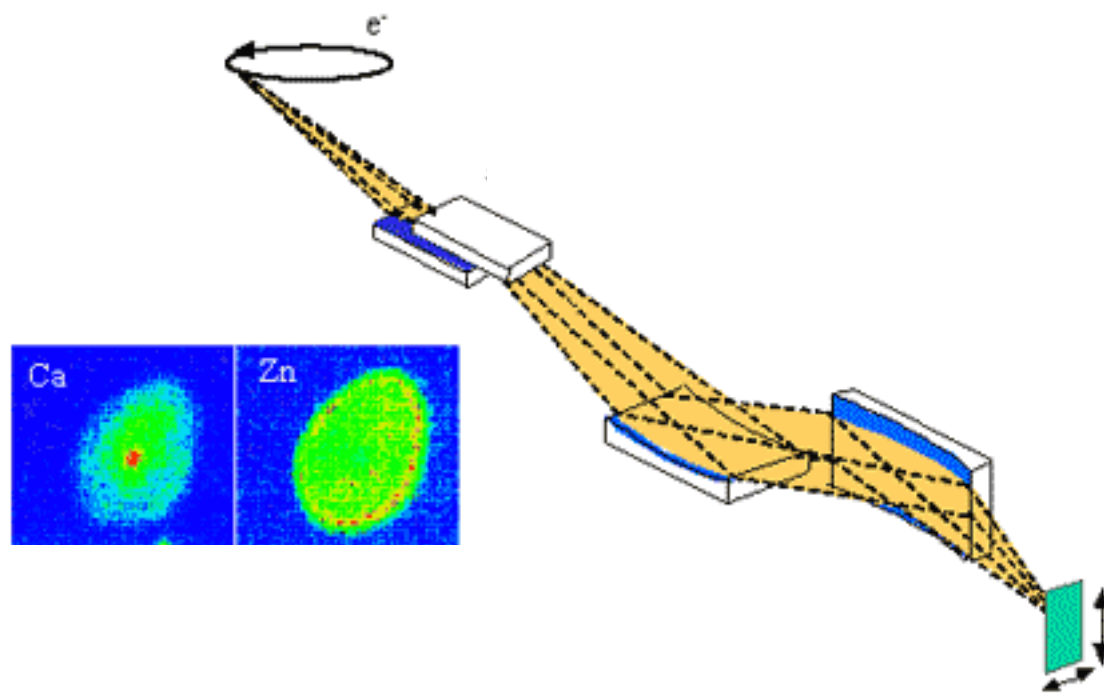


- The ferropericlase specimens used in this study were present as **inclusions in diamonds**.
- These ferropericlase inclusions were described as the **lower mantle origin** (Harte et al., 1999).
- All the ferropericlase specimens were extracted by crushing diamonds, mounted in epoxy resin, and polished for measurement.

# Micro-XANES Measurement

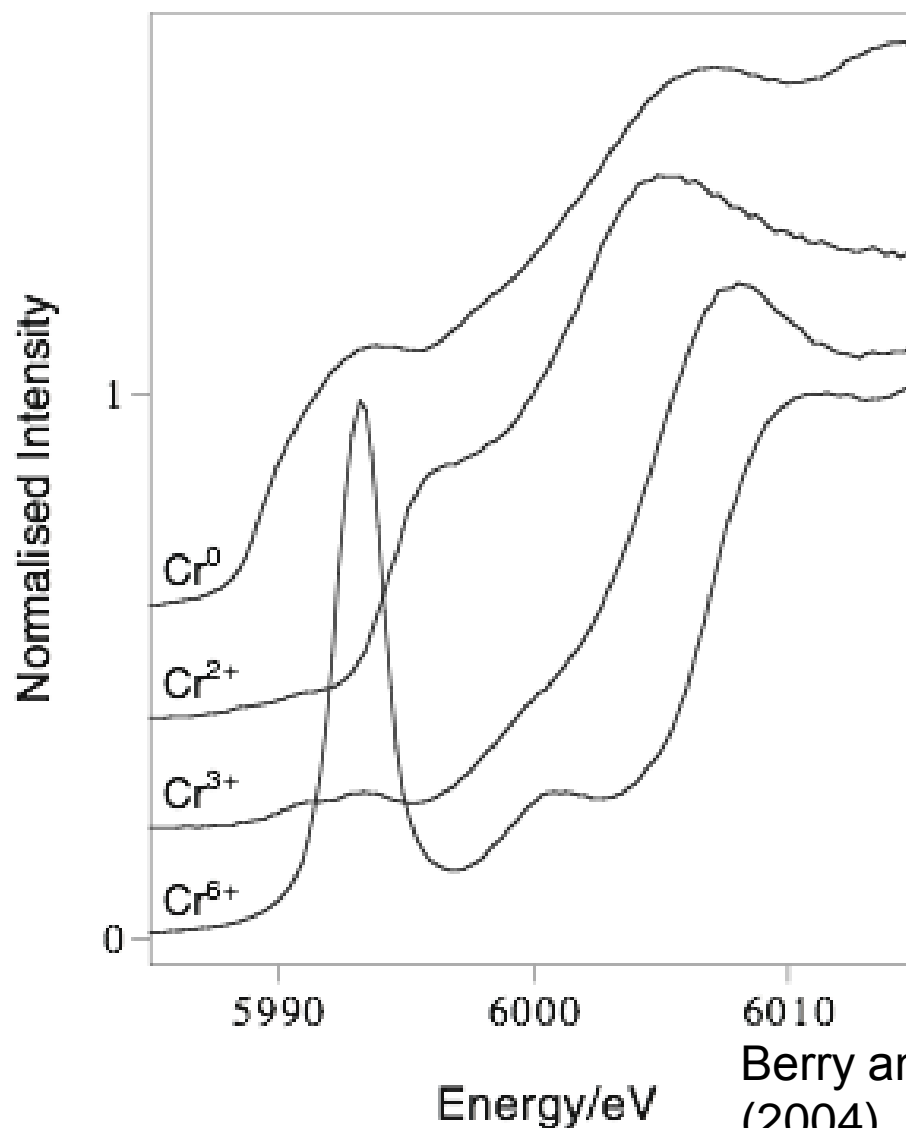
High Energy Accelerator Research Organization (KEK), Japan  
Photon Factory

Beamline 4A (designed for micro-beam X-ray fluorescence analysis)



# X-ray absorption near-edge structure

- XANES is region of x-ray absorption spectrum within  $\sim 50\text{eV}$  of the absorption edge.
- XANES depends on a **coordination environment** and **valence state**.
- Chromium *K*-edge shows significant edge shifts with oxidation state.



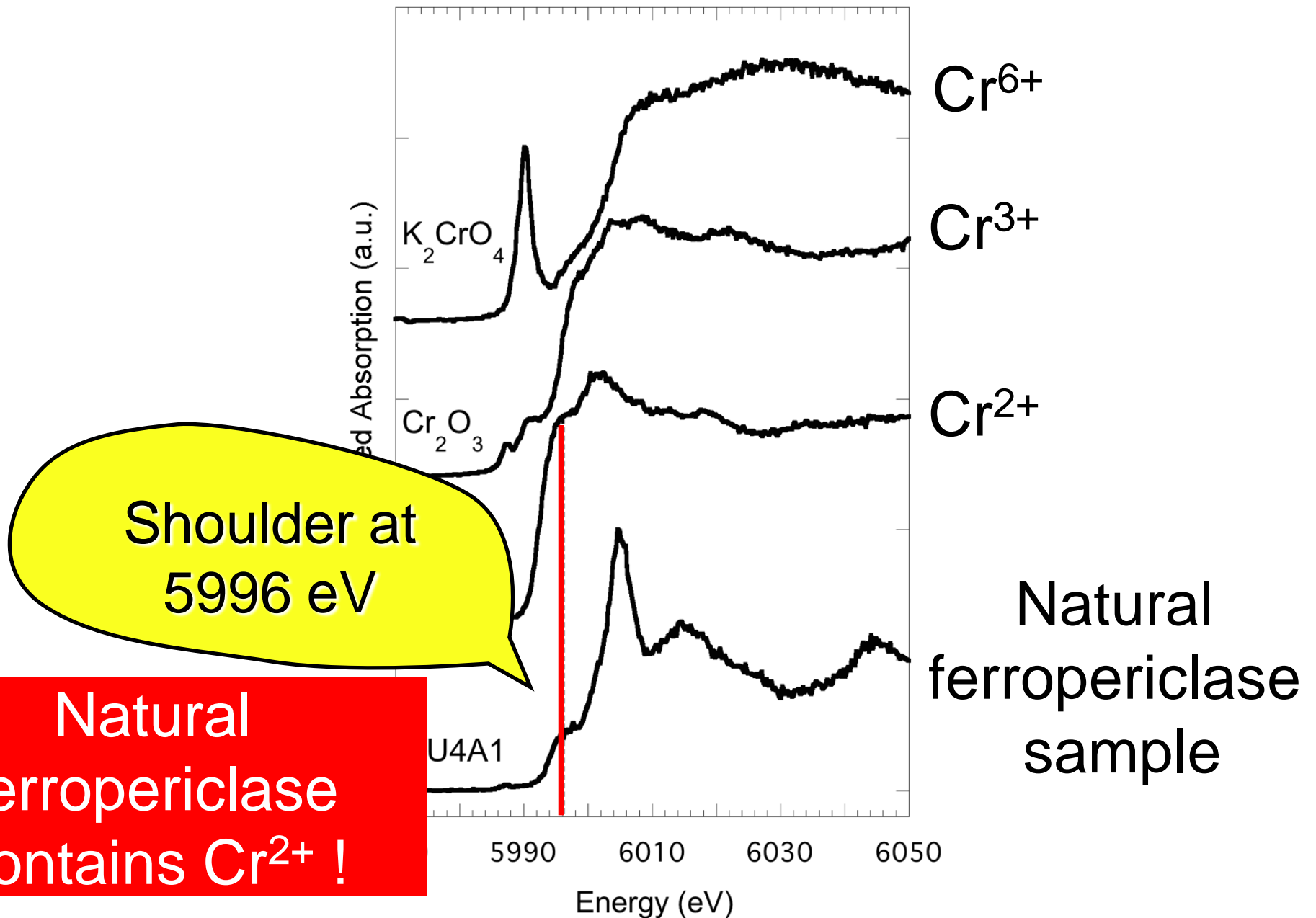
Cr<sup>0</sup>: Stainless steel

Cr<sup>2+</sup>: AD glass quenched at  $\log fO_2 = -14$

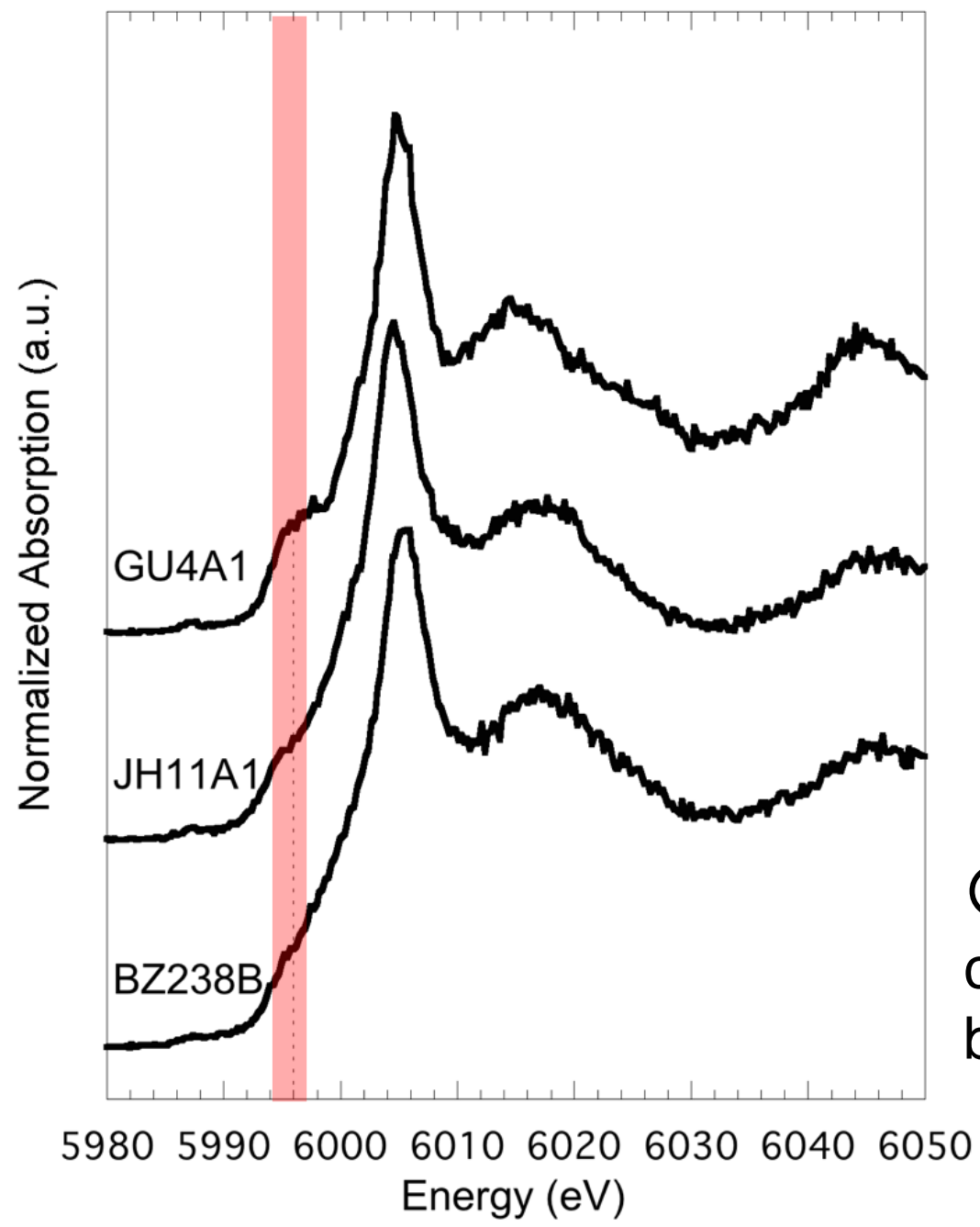
Cr<sup>3+</sup>: AD glass quenched at  $\log fO_2 = -2$

Cr<sup>6+</sup>:  $K_2CrO_4$

# Cr K-edge XANES spectra



# Results: Cr K-edge XANES spectra



○ The valence state of Cr changes considerably between different samples.

# Conclusions

- ✓ Chromium K-edge X-ray absorption near-edge structure (XANES) spectra were recorded on Cr-bearing ferropicriolase inclusions in natural diamonds obtained from the lower mantle.
- ✓ The obtained spectra revealed that a considerable amount of Cr<sup>2+</sup> was present in the studied samples and the results are consistent with the reduced condition of the lower mantle. The concentrations of Cr<sup>2+</sup> varied in the range of 4 to 15%.
- ✓ The valence state of Cr is a promising indicator of the chemical environment in the lower mantle.