MONITORING THE EFFECTS OF X-RAY-INDUCED RADIOLYSIS ON HIGH TEMPERATURE FERROUS CHLORIDE SOLUTIONS USING ENERGY DISPERSIVE XANES

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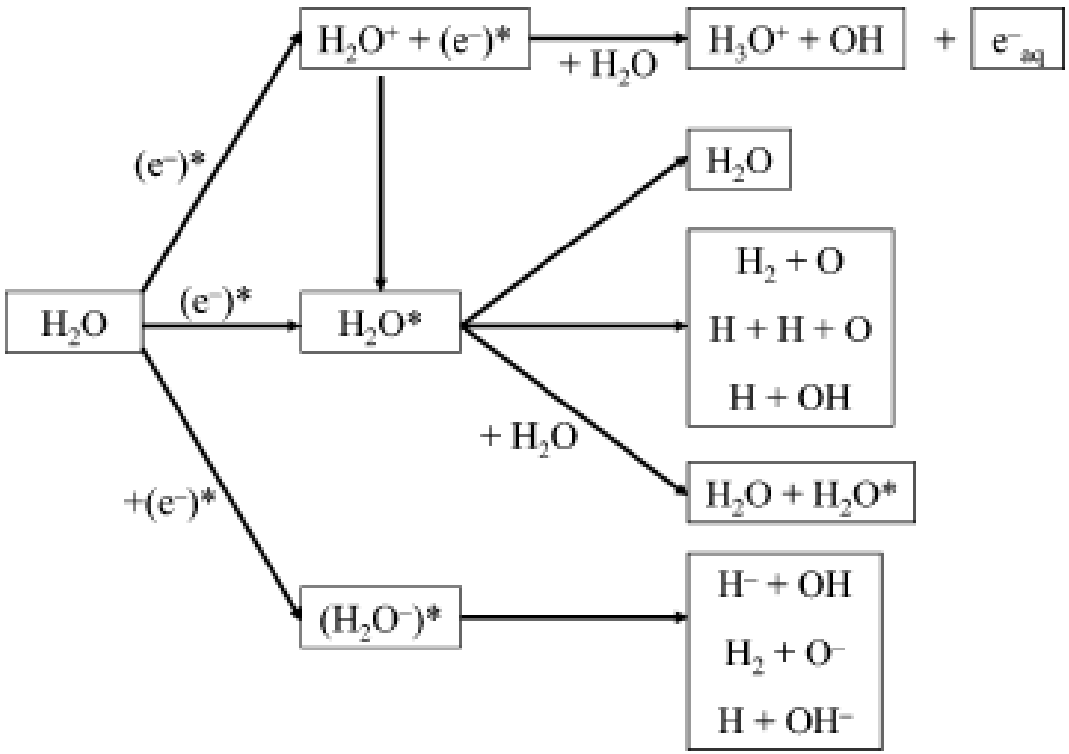
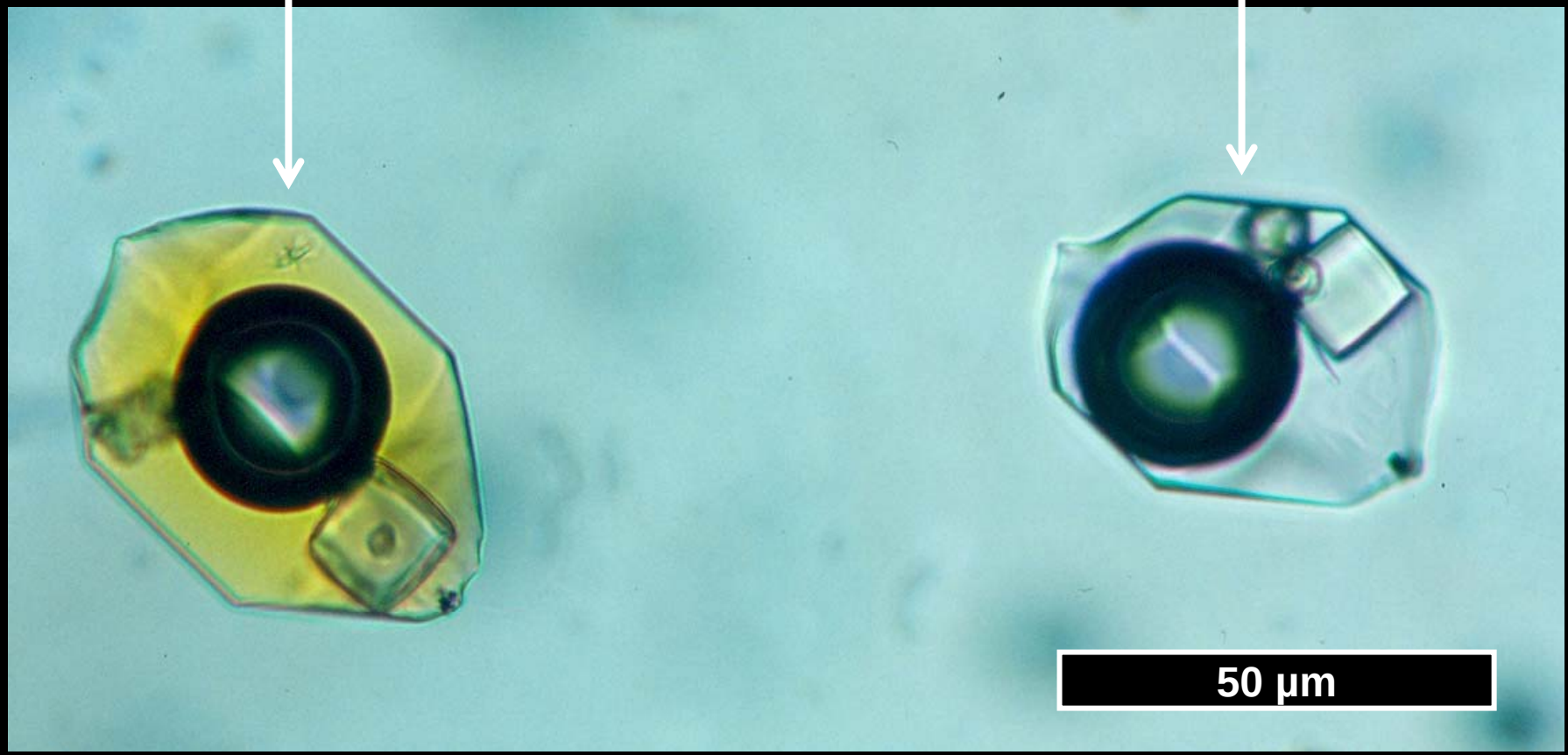
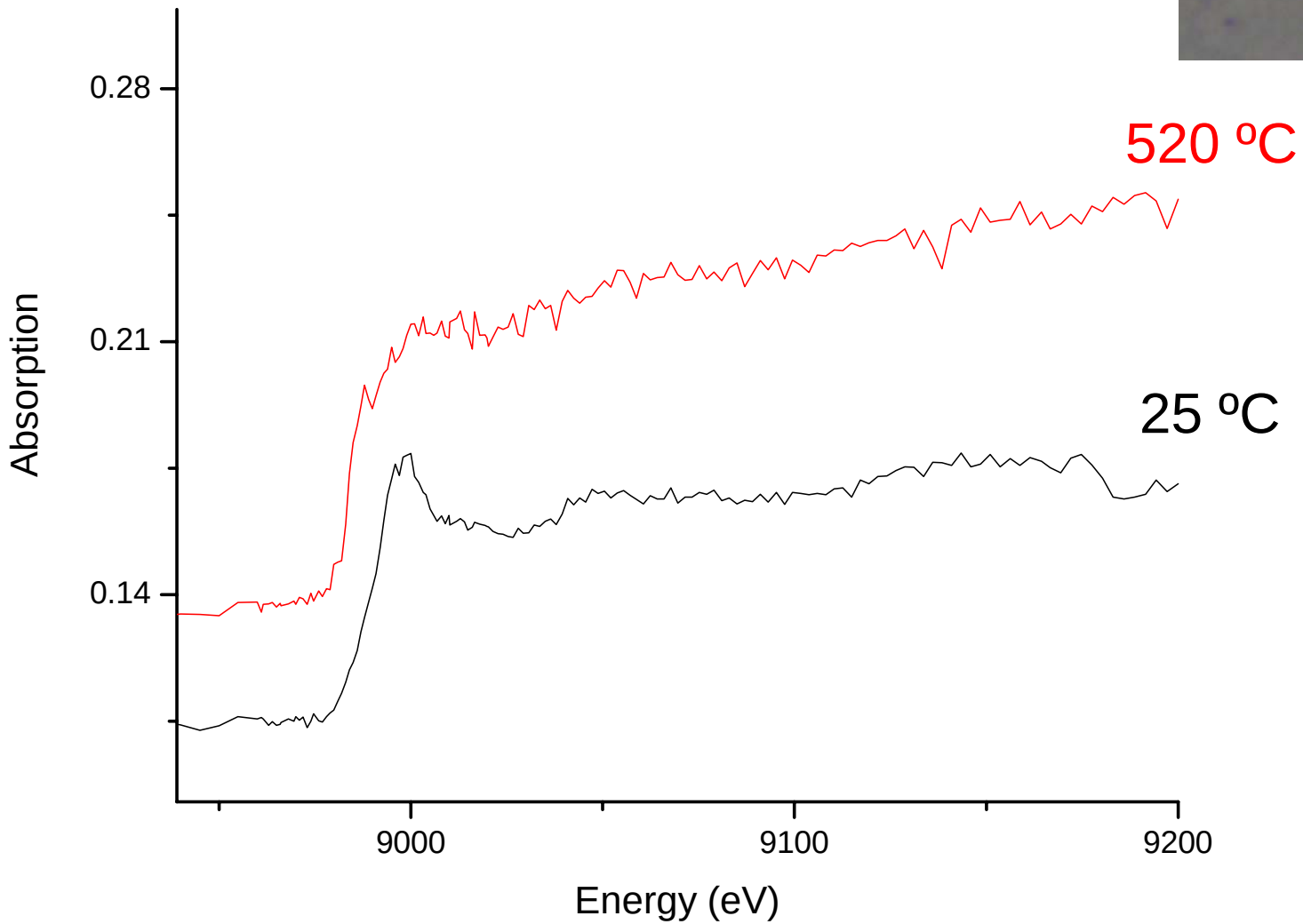
Initial processes in the decomposition of water by ionizing radiation.



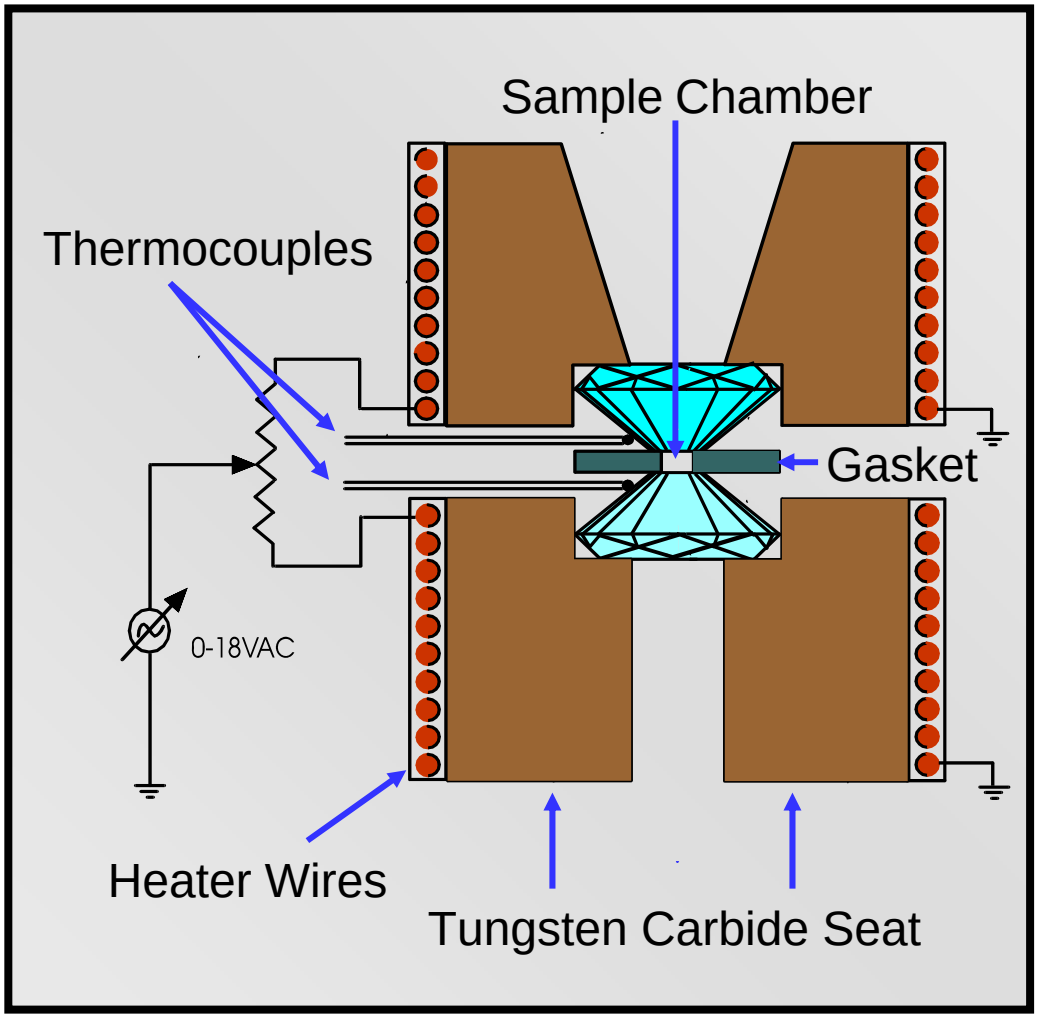

Exposed to synchrotron x-rays
~ 1 x 10^5 photons/s at 230 mA
for a few seconds.
Neighboring inclusion not
exposed to the x-ray beam.
50 µm

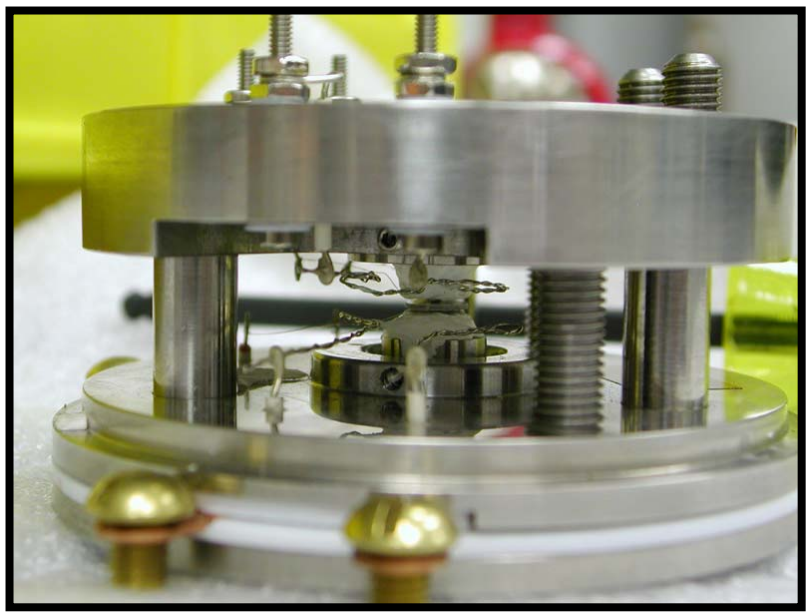
Cu K-edge X-ray Absorption Spectra
Synthetic Fluid Inclusion



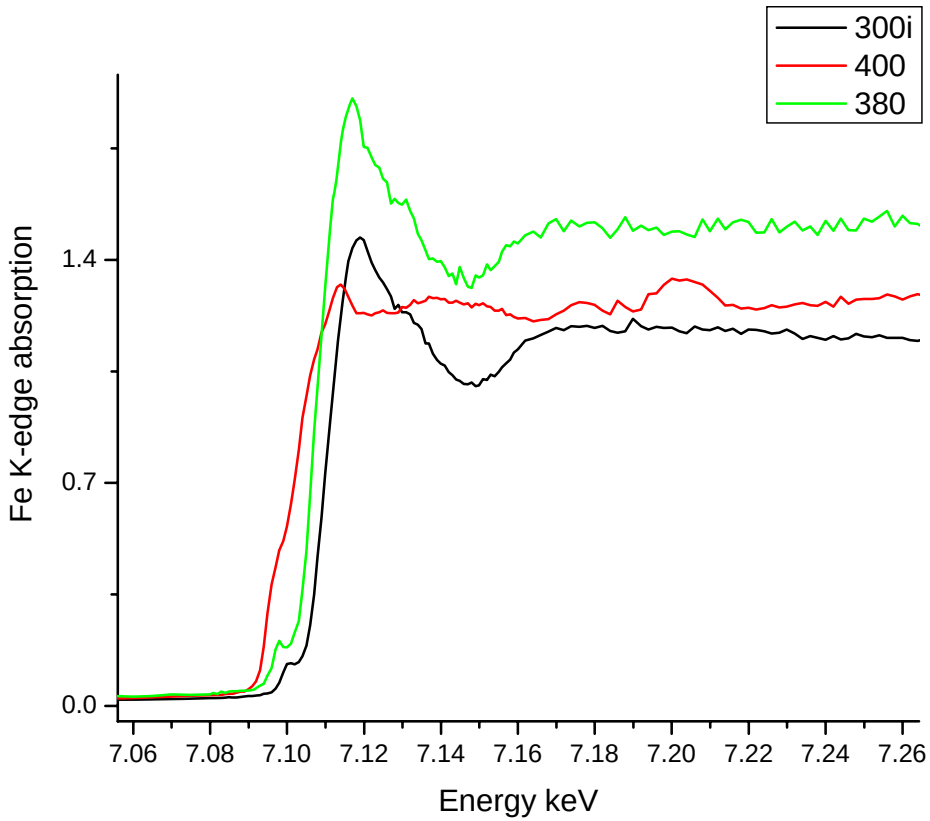
Pt, Mo, Ni-Cr, Heater wires
1/8 carat diamonds, 3 mm table face,
1 mm culet face
Re gasket 0.05 - 0.125 mm thick, 0.3 – 0.5 mm ID

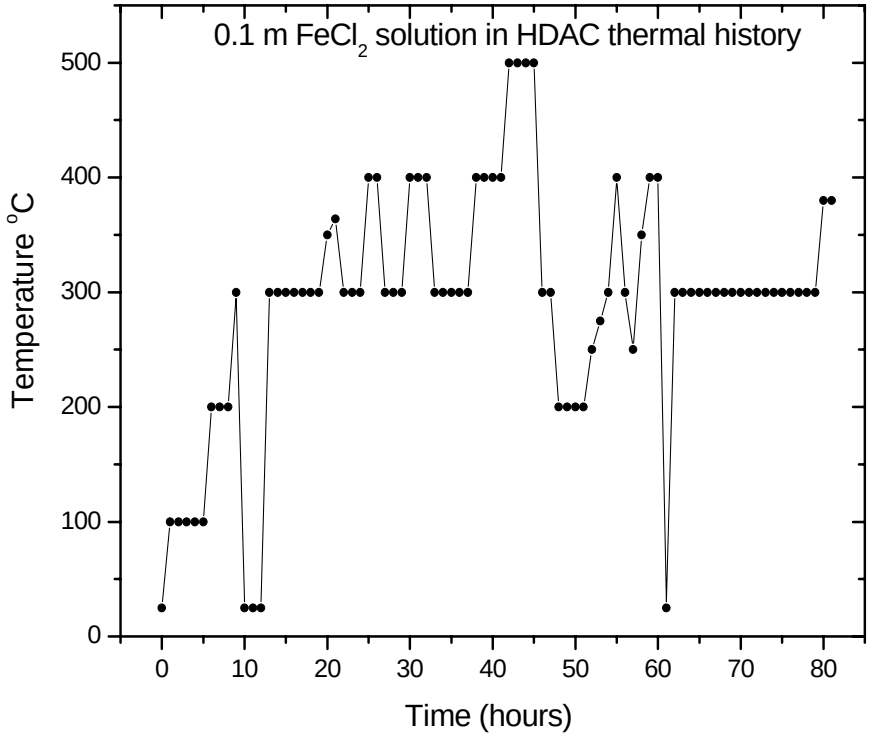
Temperature measurements are calibrated by observing the melting of NaCl, CsCl, $NaNO_3$ and the alpha-beta phase transition of quartz



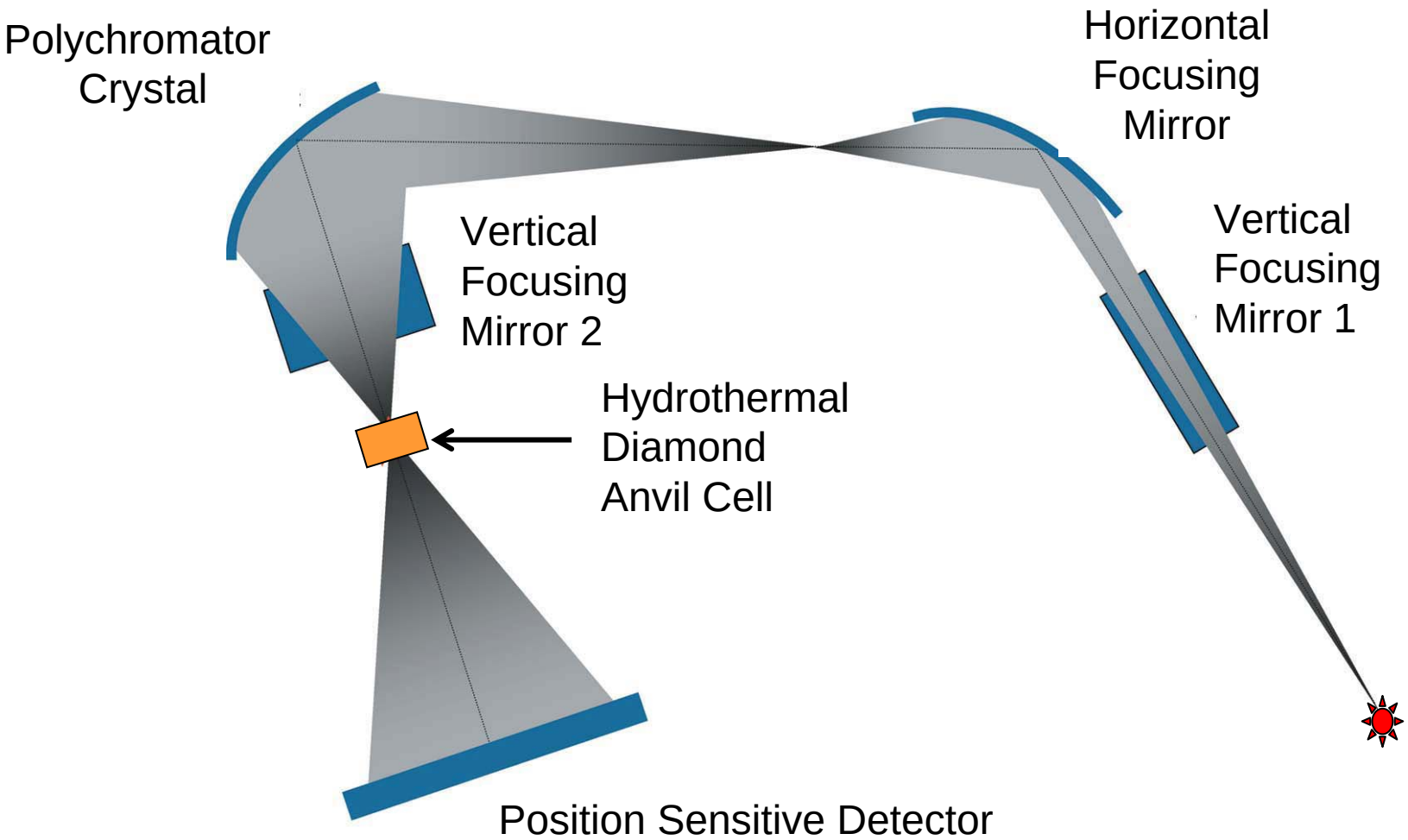


$FeCl_2$ Aqueous Solution in Hydrothermal Diamond Anvil Cell

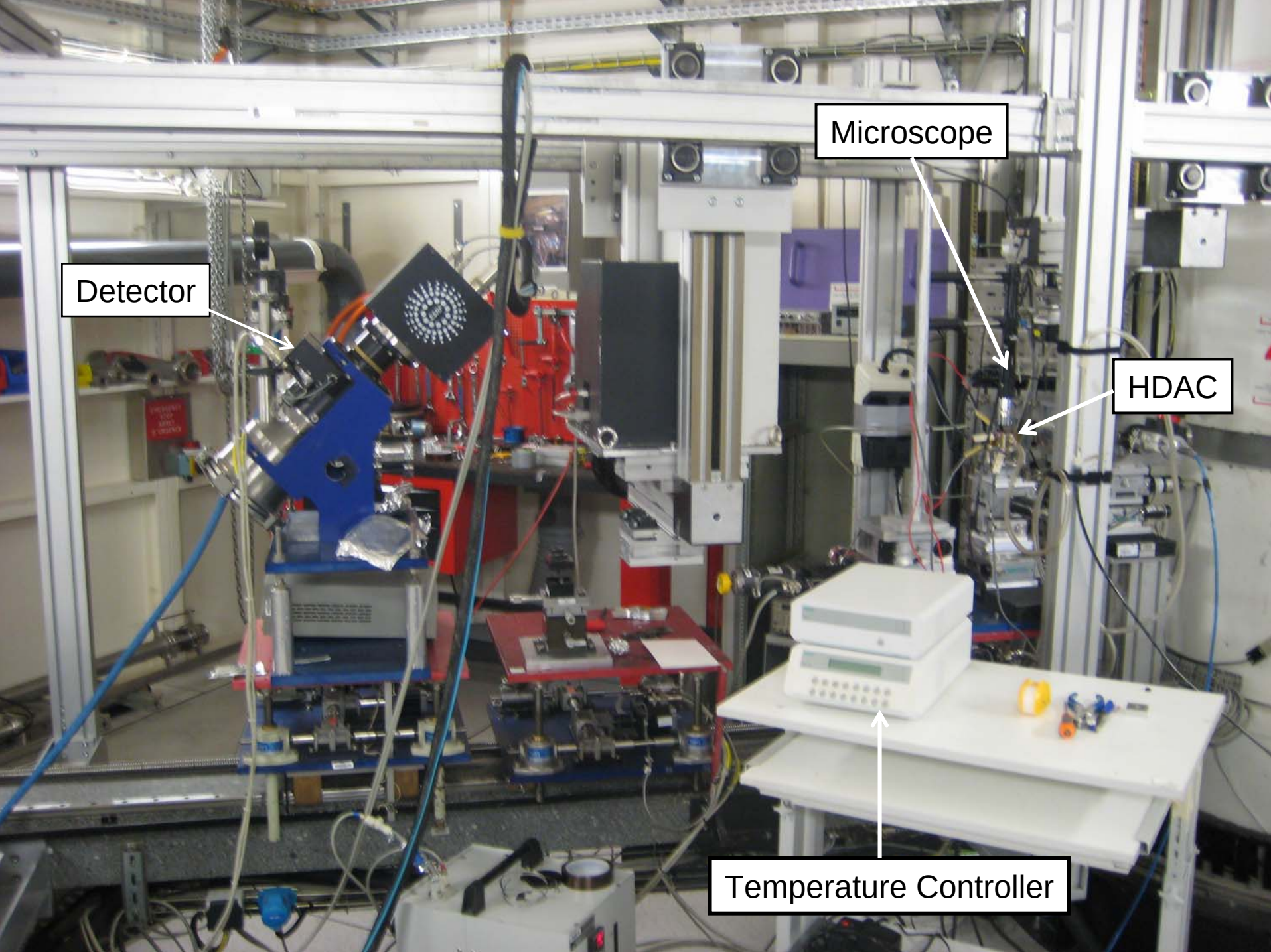


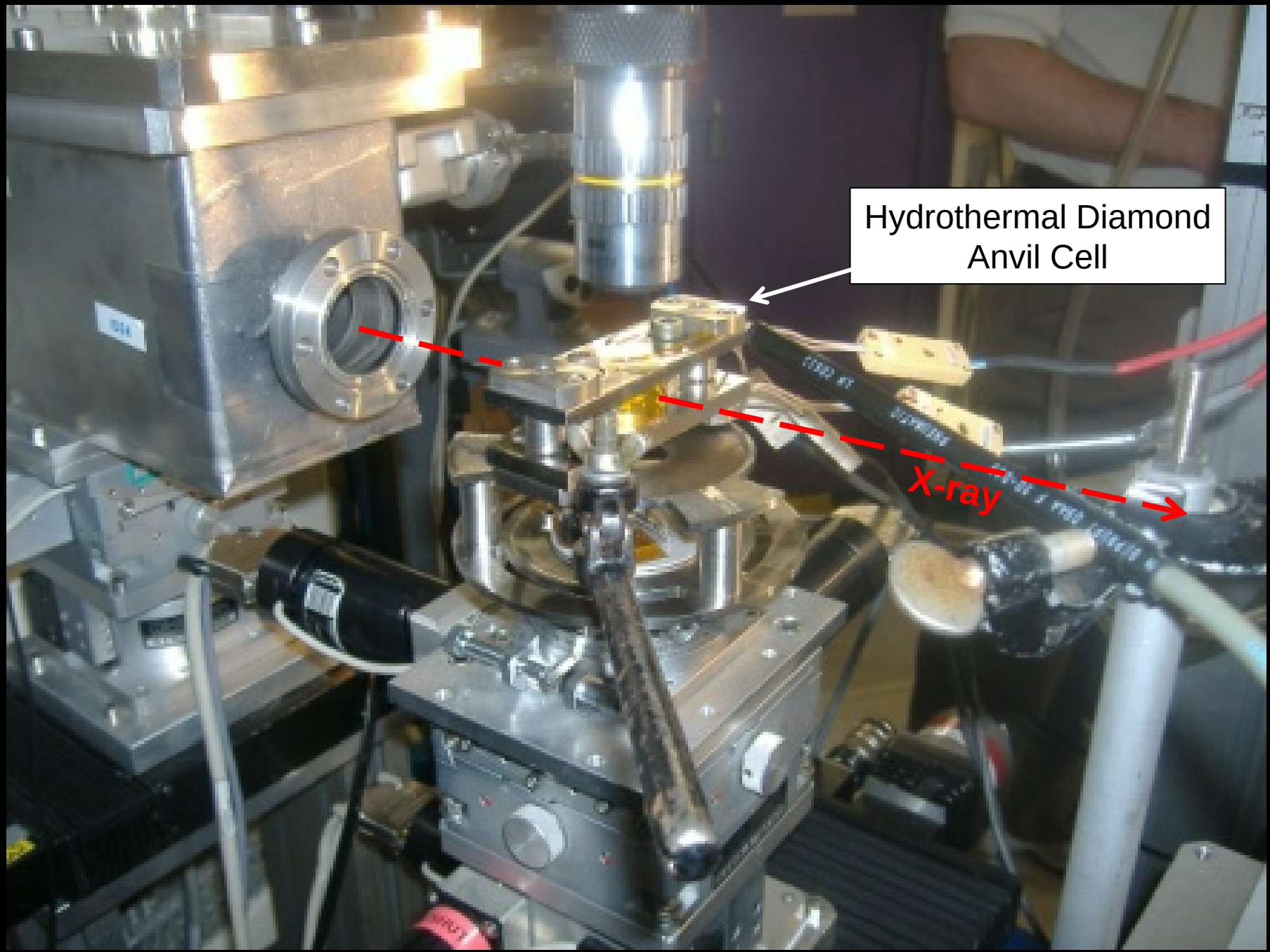


Optical Layout Beamline ID24
Energy Dispersive X-ray Absorption Spectroscopy

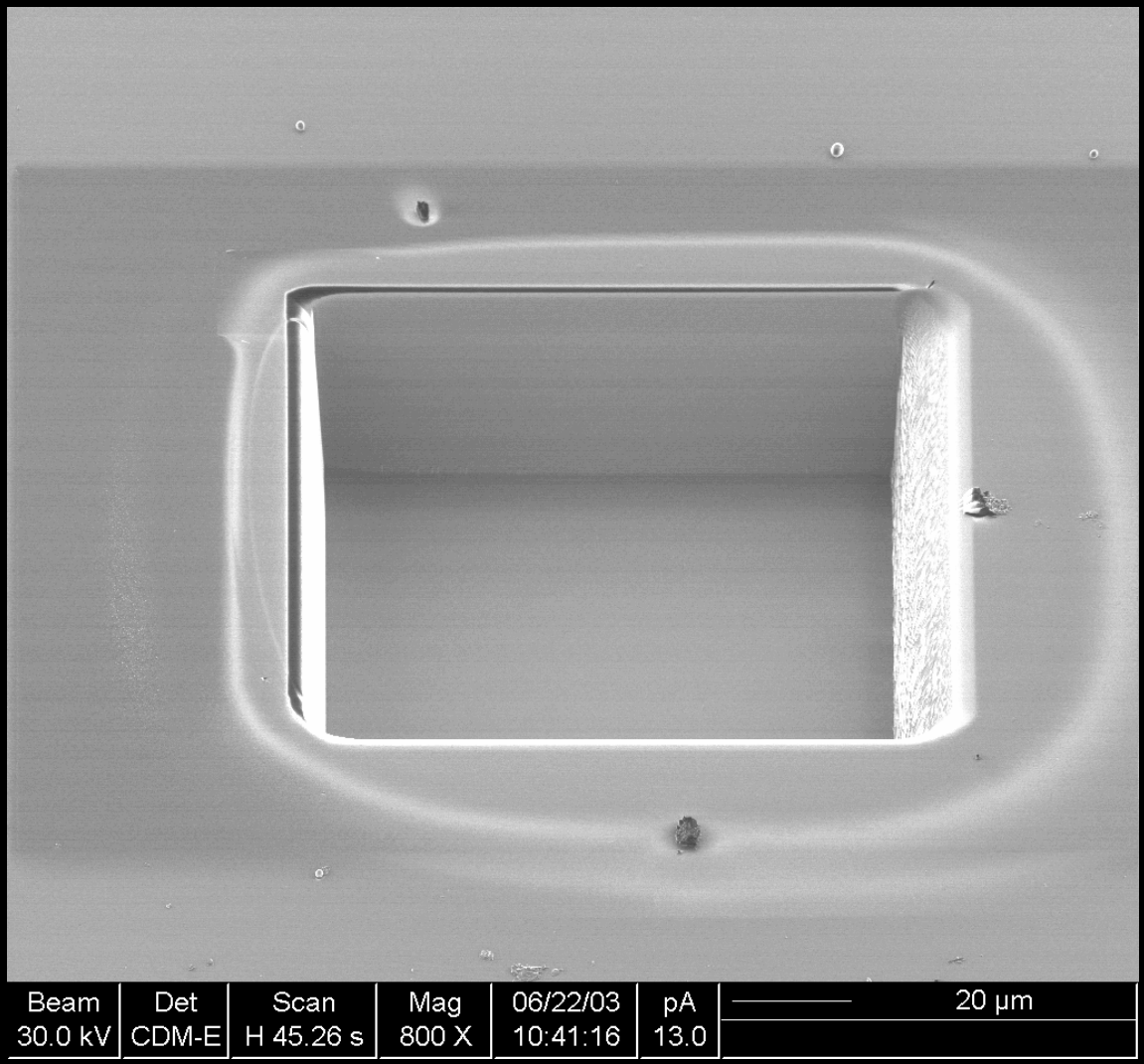


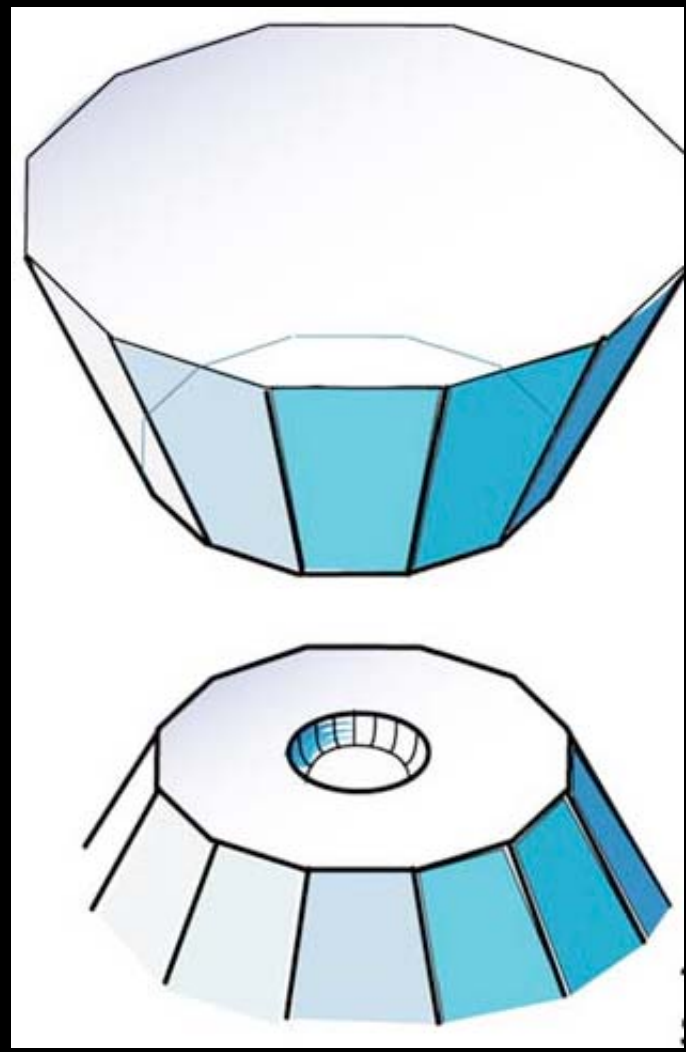
A source with a large divergence is used to maximize the footprint of the synchrotron beam on the polychromator crystal.


Microscope
Detector
HDAC
Temperature Controller


Hydrothermal Diamond Anvil Cell
X-ray

Recess in Lower Diamond Anvil





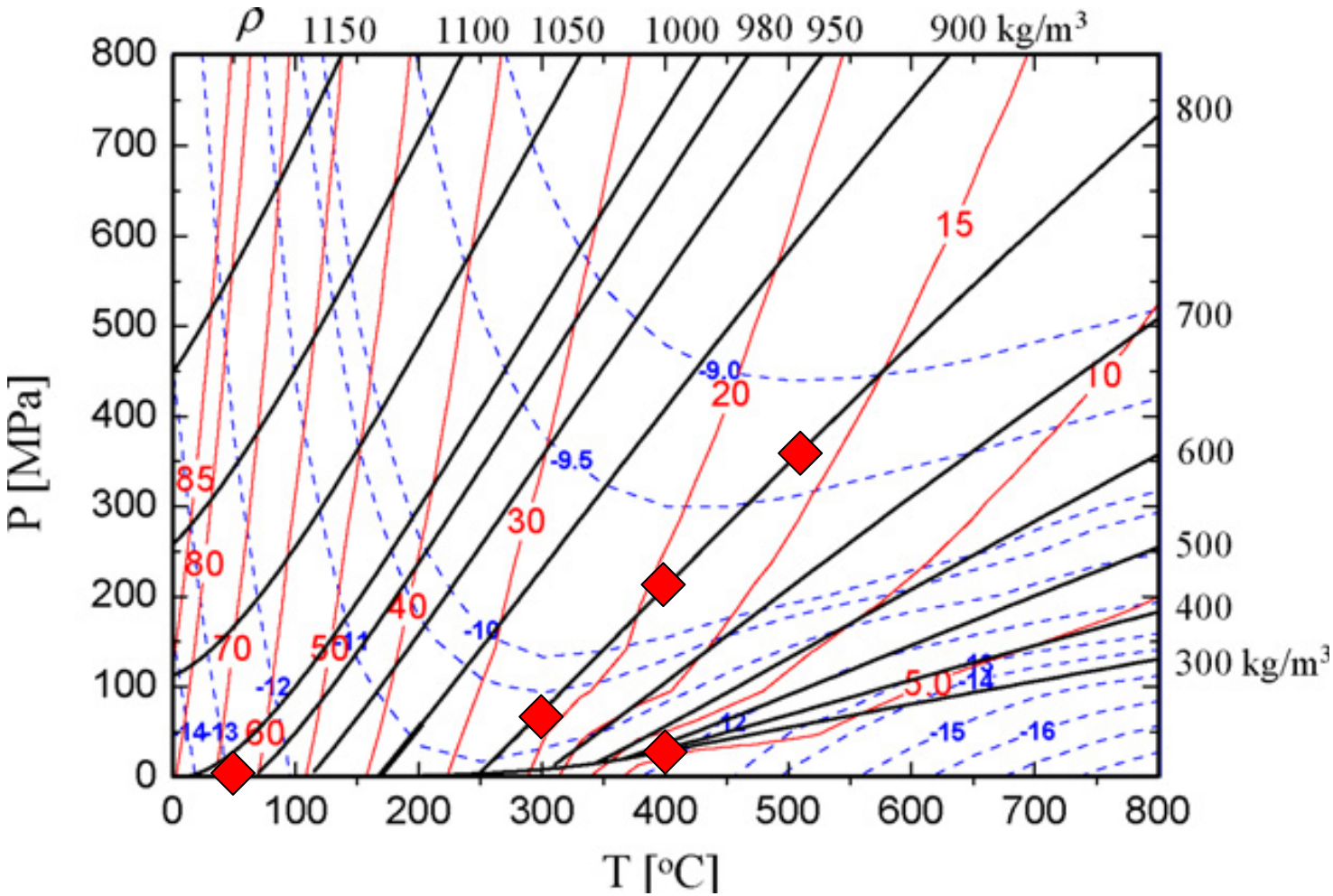
Solution in HDAC

- 0.69 *m* and 0.4 *m* ferrous chloride solution loaded in an Ar atmosphere.

- Temperature of L-V homogenization

  251 ºC (ρ = 0.87 g/cm^3)

  400 ºC (ρ = 0.5 g/cm^3)

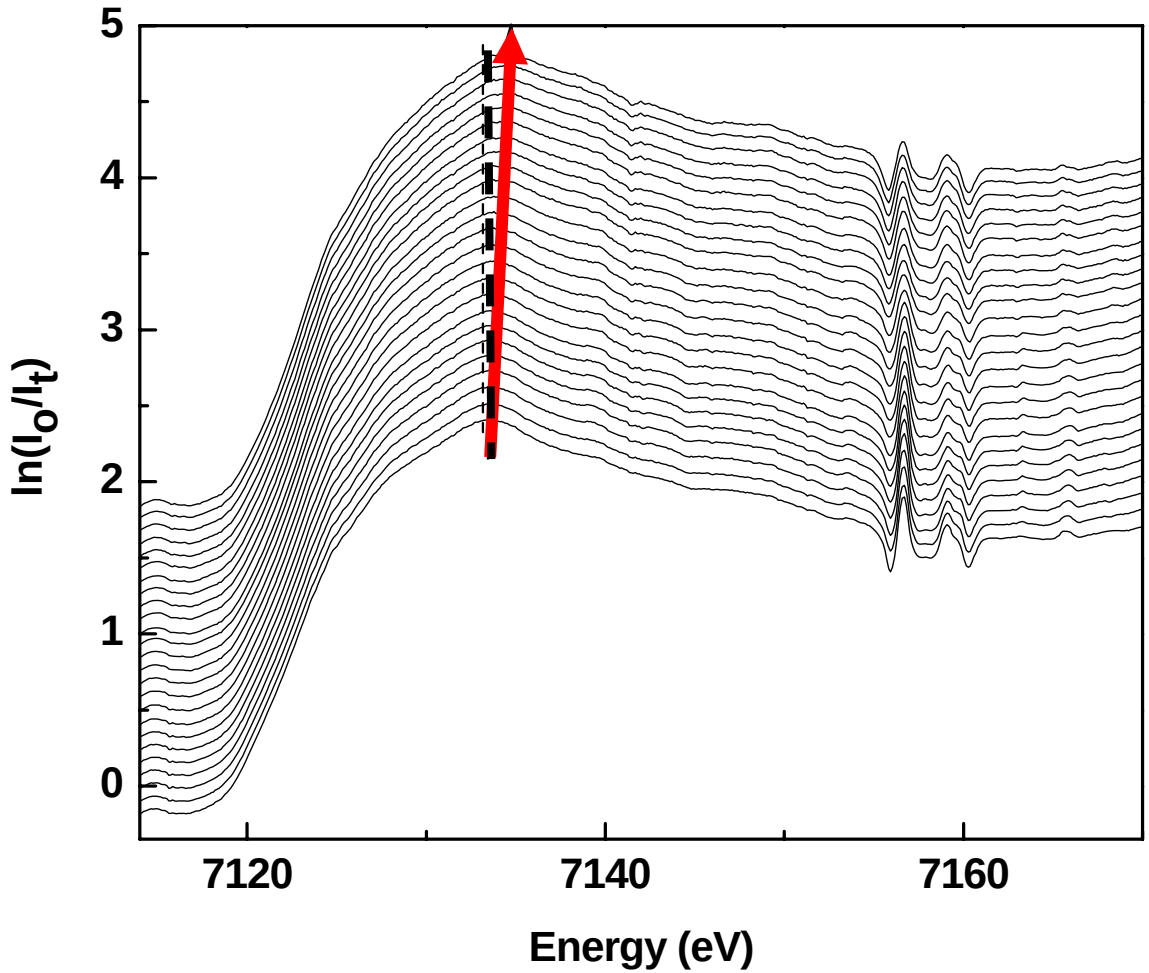


Pressure–temperature diagram of water showing isochores (heavy black lines) convenient for DAC along with contours of dielectric constant (red thin lines) and base 10 logarithm of the ion product (blue dashed line).

XANES Acquisition

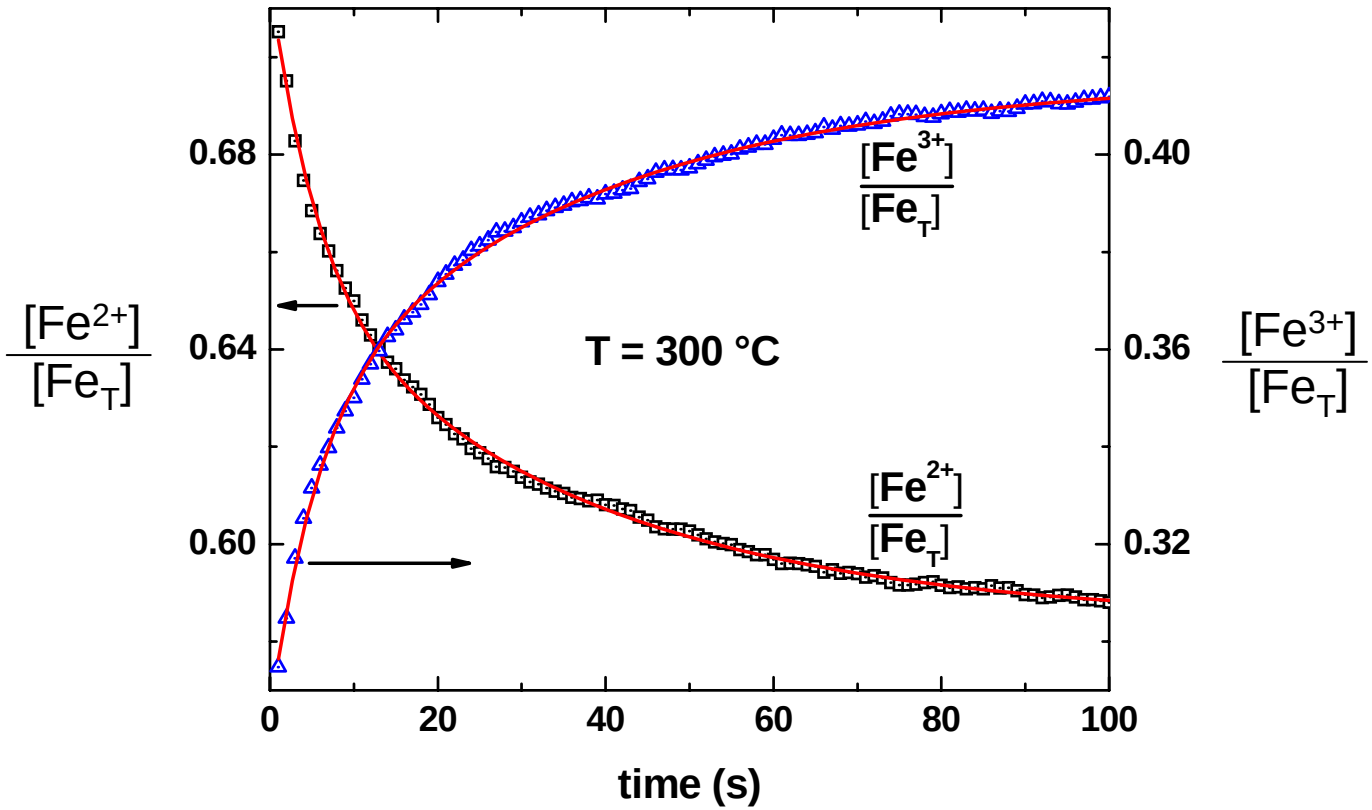
- Each spectrum was collected in 1 or 100 seconds
- Up to 100 time-resolved spectra were measured from the solutions at 300, 400 and 500 °C
- Energies ranged from 7.07 to 7.29 keV,
- Incident flux of ~1 x 10^{13} photons/s
- Beam spot size on sample = 5 x 7 µm

XANES data indicating a positive shift in the Fe *K*-edge energy with irradiation time at 300 ºC



The Fe *K*-edge energy (Eo) was determined by fitting Lorentzian peak-curves to the primary peak shape of the derivative of each XANES spectrum.

Normalized $[Fe^{2+}]$ and $[Fe^{3+}]$ concentrations versus time, measured from the 0.69 *m* Fe (II)Cl_2 aqueous solution at 300°C.



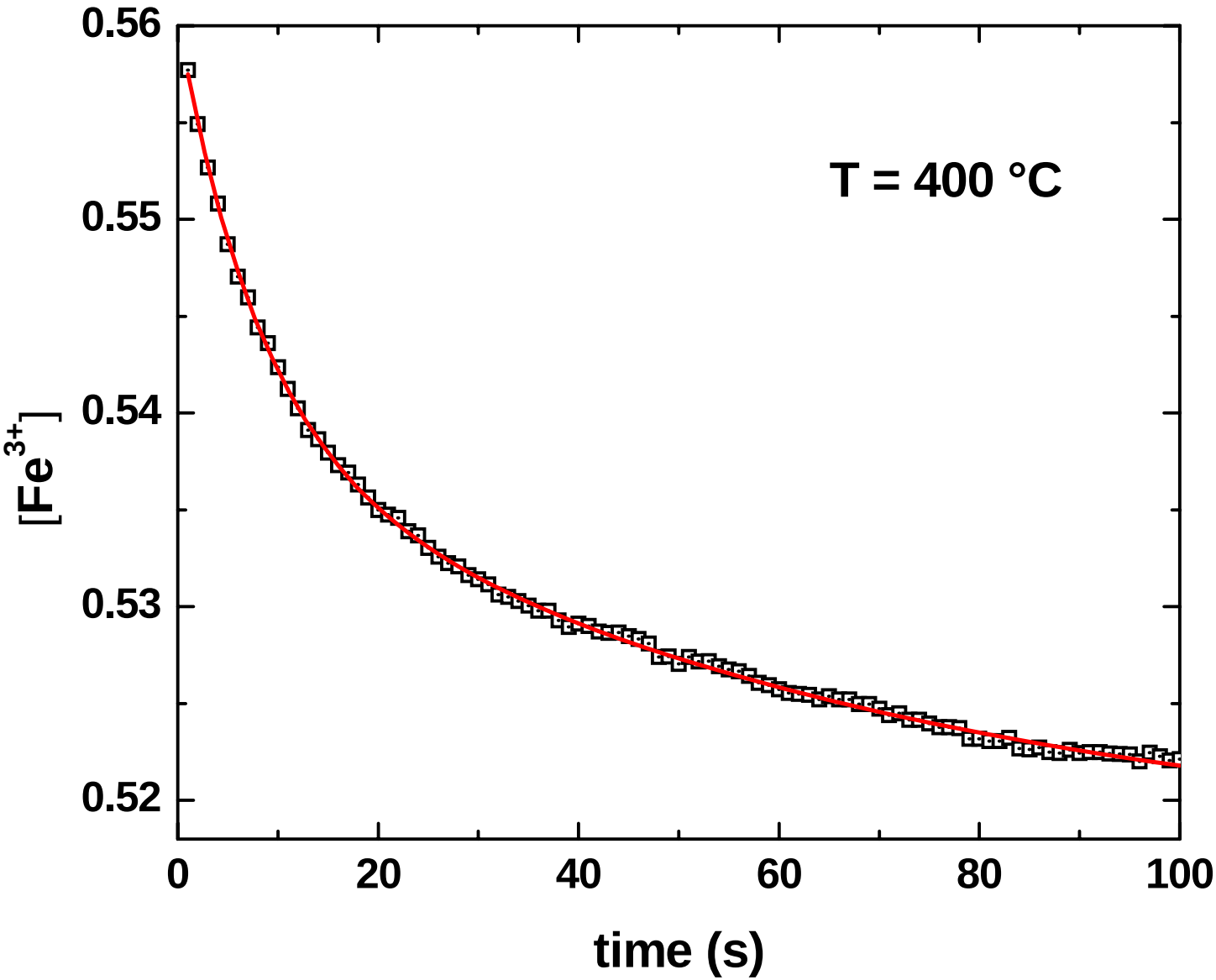
$E_o = xE_o^{2+} + yE_o^{3+}$, where E_o^{2+} and E_o^{3+} are Fe *K*-edge energies of Fe^{2+} and Fe^{3+} species, respectively. $x = [Fe^{2+}]/[Fe_T]$ and $y = [Fe^{3+}]/[Fe_T]$

Using $x + y = 1$, we have:

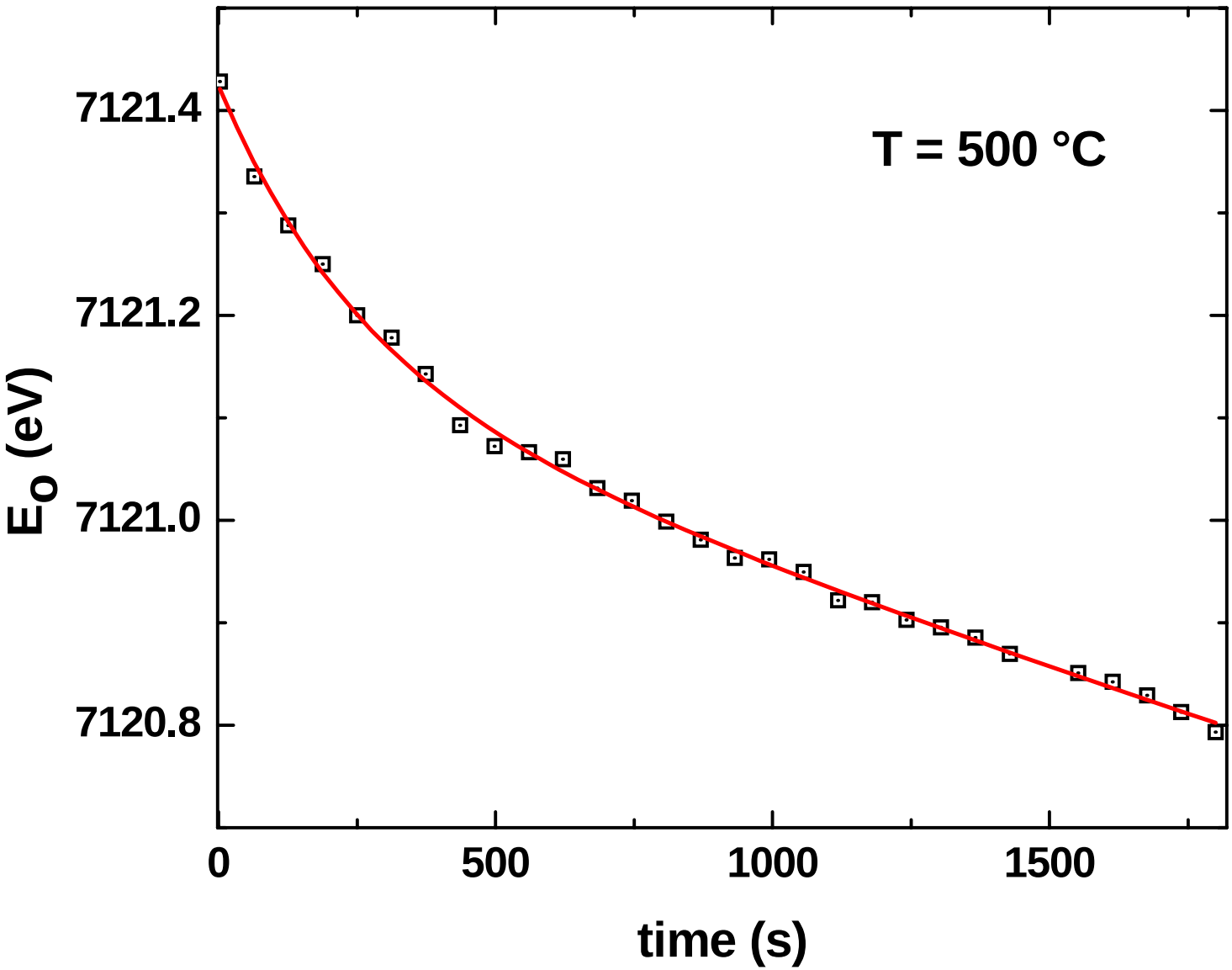
$$[Fe^{2+}] = [Fe_T](E_o^{3+} - E_o)/(E_o^{3+} - E_o^{2+}) \text{ and}$$

$$[Fe^{3+}] = [Fe_T](E_o - E_o^{2+})/(E_o^{3+} - E_o^{2+})$$

[Fe $^{3+}$] as a function of irradiation time at 1 s resolution measured from the 0.69 *m* Fe (II)Cl_2 aqueous solution at 400ºC



The Fe *K*-edge energy E_o versus time at 60 s resolution, measured from the 0.69 *m* Fe (II)Cl_2 aqueous solution at 500 °C



The time-resolved Eo data was fit using second-order exponential decay curves.

Temperature (°C) of Solution	k'_1 (s^{-1})	k'_2 (s^{-1})	Reaction During Irradiation
300	0.029 ±0.001	0.18 ±0.01	oxidation
400	0.015±0.001	0.127 ±0.006	reduction
500	0.008 ±0.242	0.4 ±2.0	reduction

The kinetic rate constants determined from fitting of the data using an equation of the general form $y = y_o + A_1 e^{-k1t} + A_2 e^{-k2t}$

Conclusions

- ED-XAS data show that radiolysis reactions result in oxidation at 300 °C and reduction of iron species at 400 to 500 °C in aqueous fluids.

- Fitting of the time-resolved Fe *K*-edge energy (*Eo*) data allows for the determination of kinetic rate constants for reactions involving the Fe^{2+} and Fe^{3+} species.

- Energy dispersive x-ray absorption spectroscopy opens new opportunities to predict the kinetics of reactions between transition metals and water under conditions of extreme temperature, pressure and radiation.