In situ x-ray scattering studies from interfaces of solid and supercritical CO_2 and water

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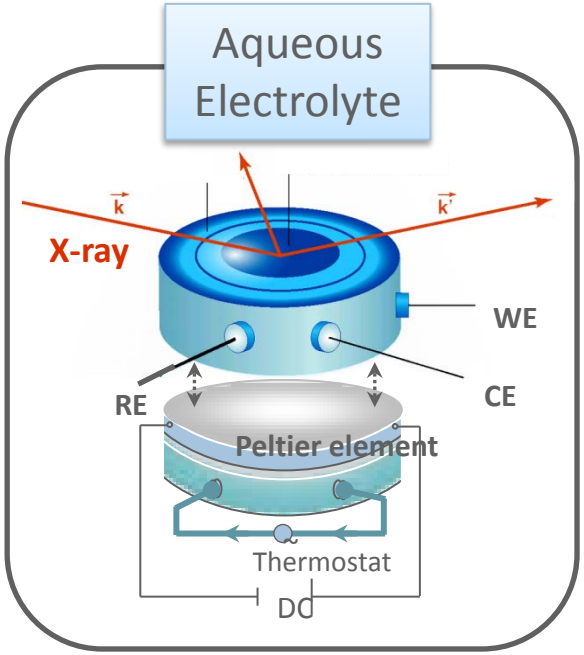
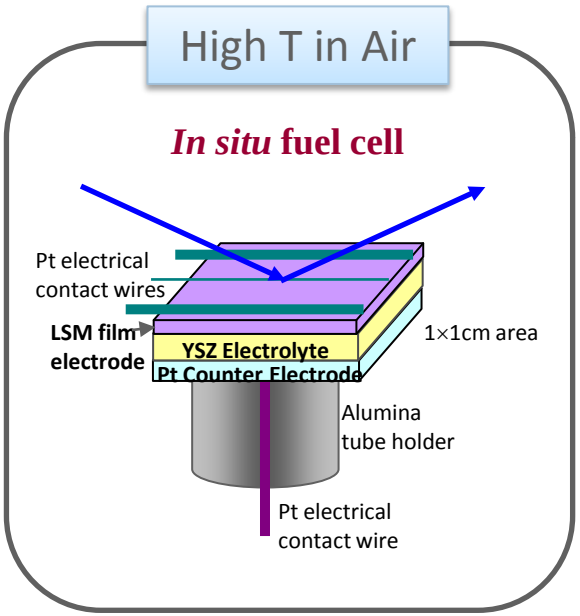
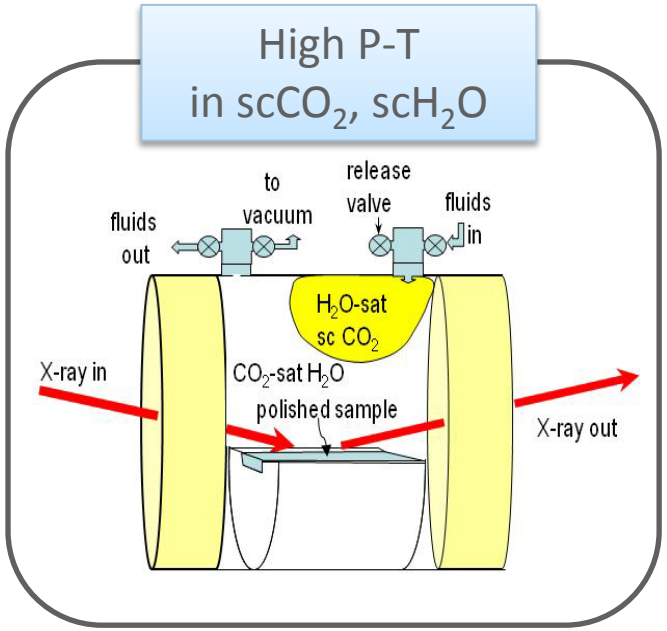
Outline

- Introduction
  - Transmission geometry
  - Electrochemical corrosion of copper
- Corrosion of Ni and SS in supercritical water
- Mineral dissolution in CO_2-H_2O binary fluid
  - Enhanced Geothermal System
  - Quartz surfaces
  - Feldspar (Orthoclase) surfaces
  - Mica

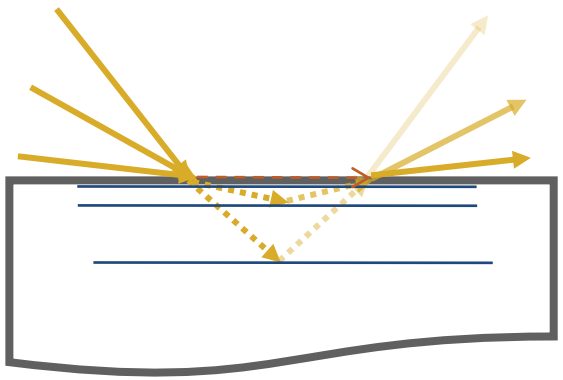
In situ X-ray studies of interfaces in extreme environments

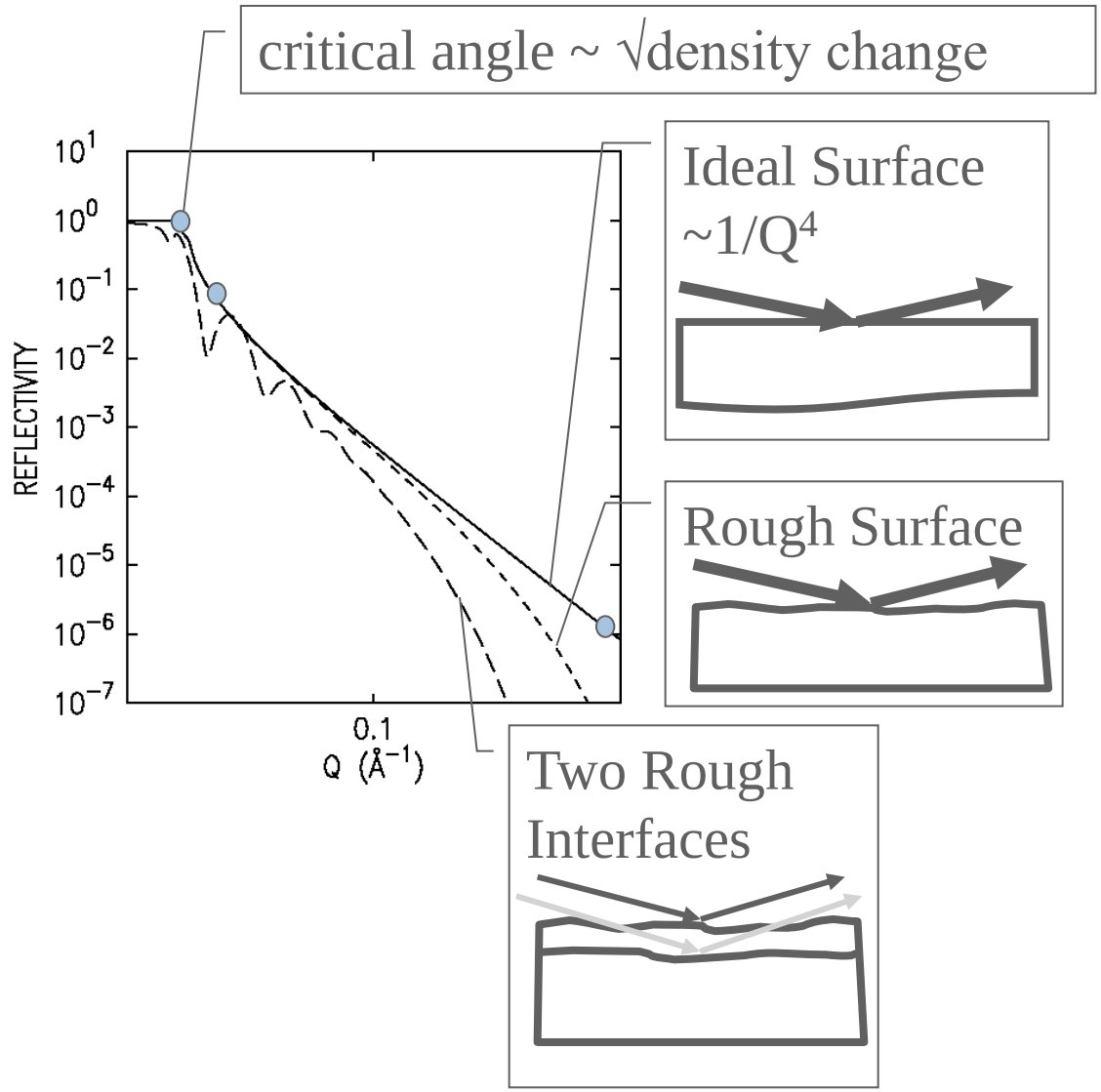






X-ray Reflectivity

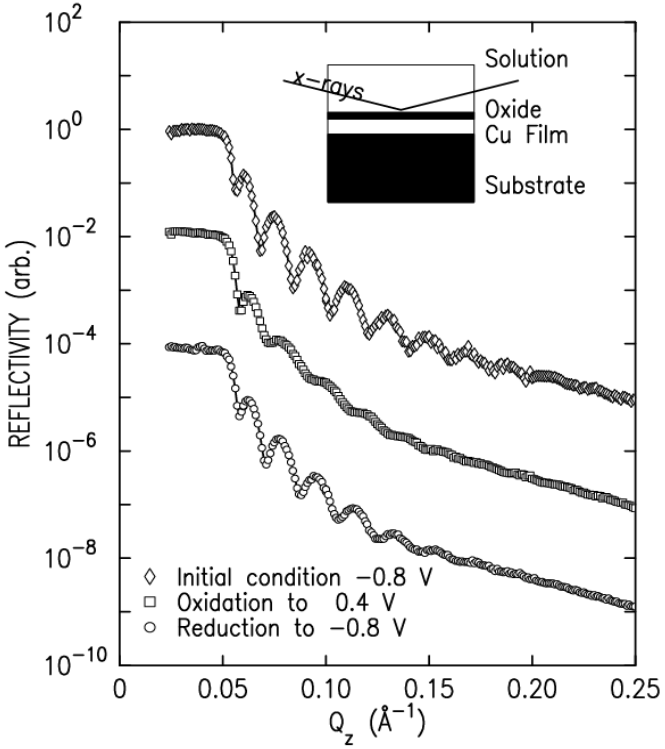




In Situ X-ray techniques in transmission

- Specular and off-specular x-ray reflectivity
- Glancing-angle reflection: depth-sensitive diffraction

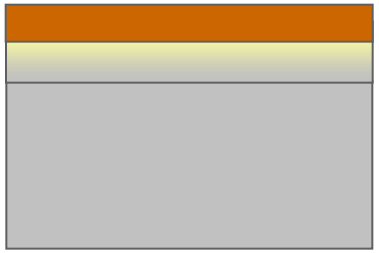
- X-rays reflect and refract as ordinary light does
- X-rays reflects/refracts when interfacial density changes
- The reflections from interfaces interfere to modulate the reflectivity curve otherwise smooth and monotonic
- In the example, the oscillation period represents (inversely) the oxide thickness and the overall variation signifies interfacial details



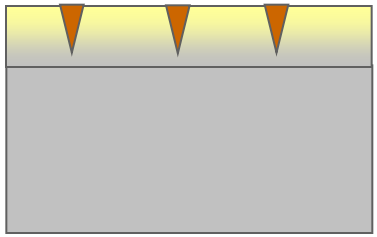
Corrosion Phenomena

- General corrosion
  - Instability of the oxide (passivation) film
- Pitting corrosion
  - local instability of the oxide film
- Intergranular corrosion
  - corrosion along grain boundaries
- Stress corrosion cracking
  - corrosion due to both chemical and mechanical influences

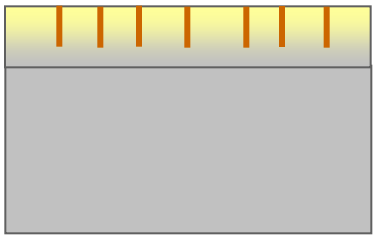
Need to monitor morphological and surface phase changes during the initial stages of corrosion.



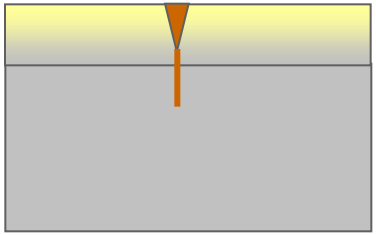
general corrosion



pitting corrosion

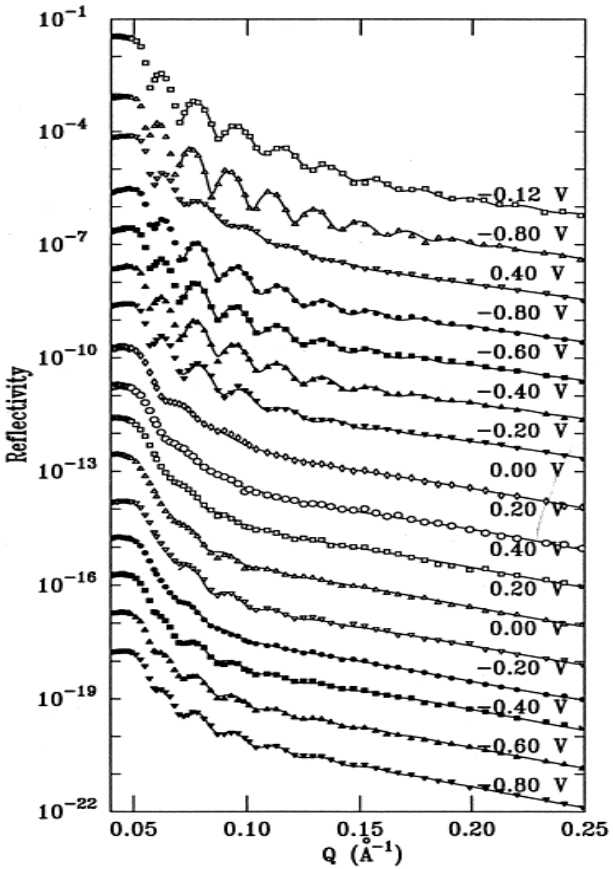


intergranular corrosion



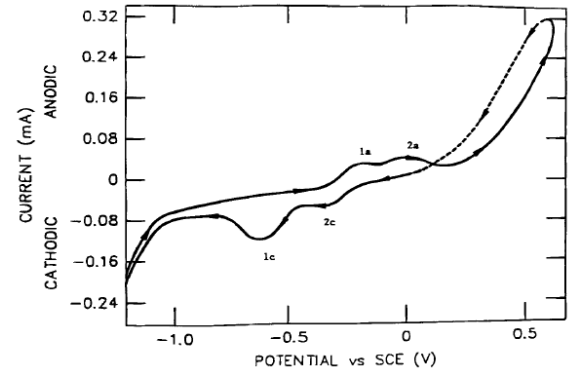
stress corrosion cracking

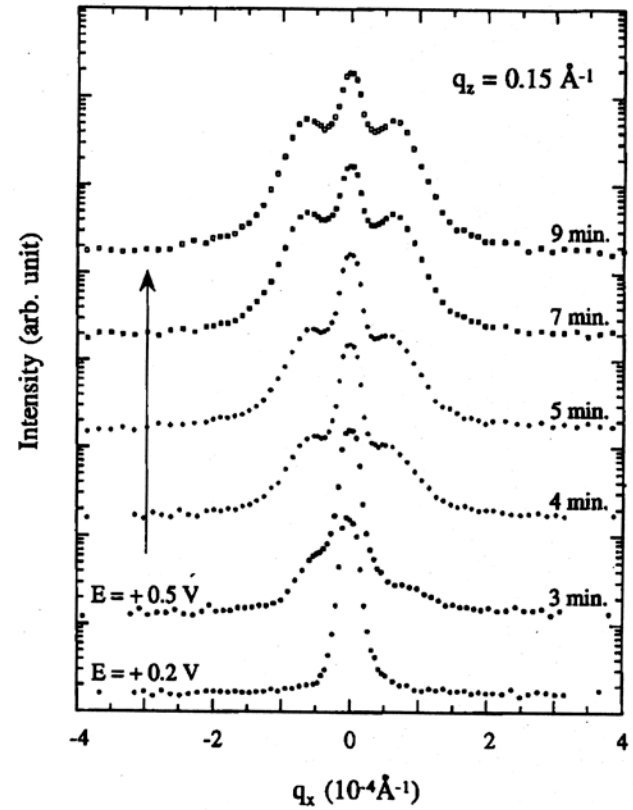
Specific Phenomena to be Studied



PRB 45 11288 (1992)

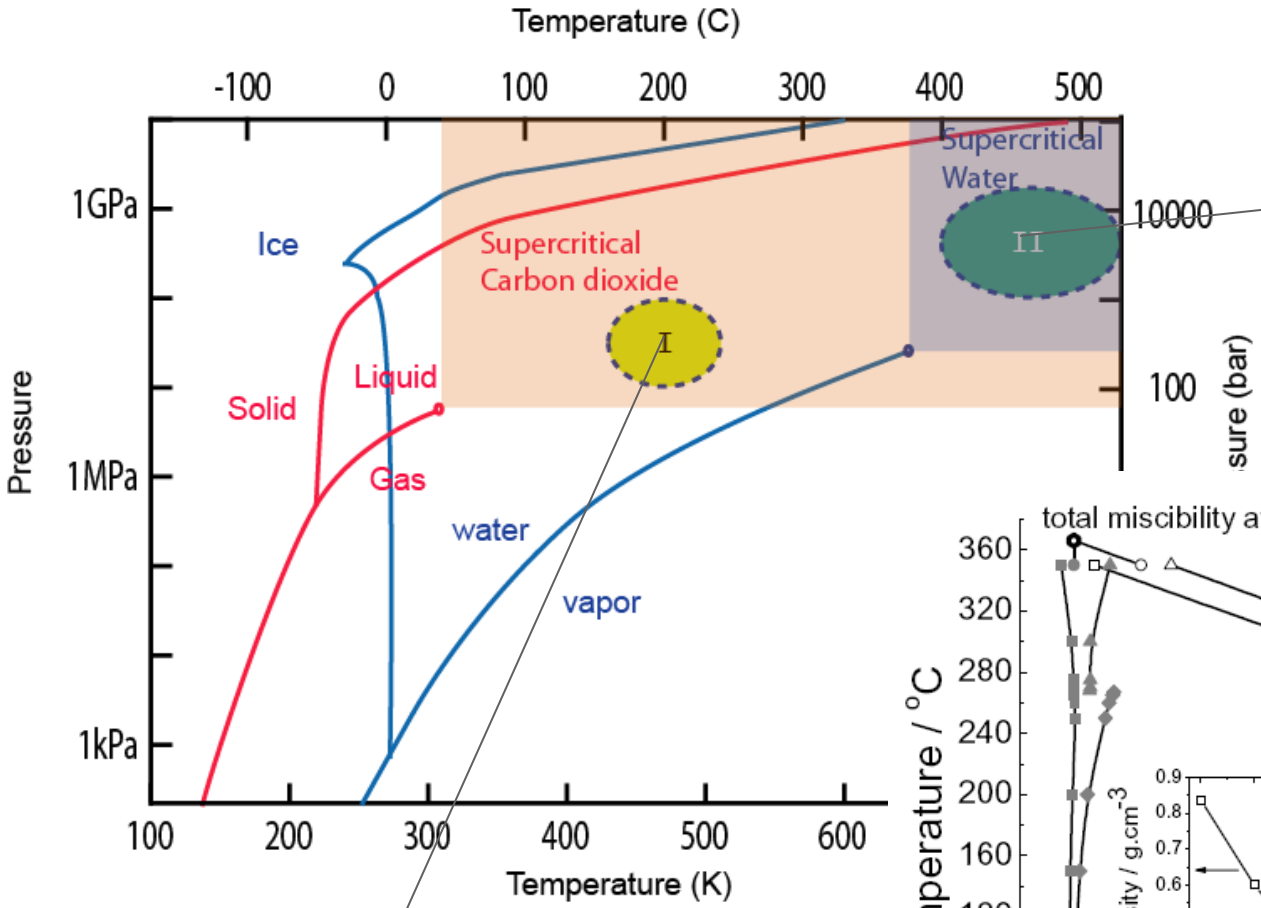
- Specular reflectivity for density profile normal to the interface
- Off-speciular glancing-angle diffraction for in-plane structure





Y. P. Feng, et. al., *Physica* **B221** (1996) 251.

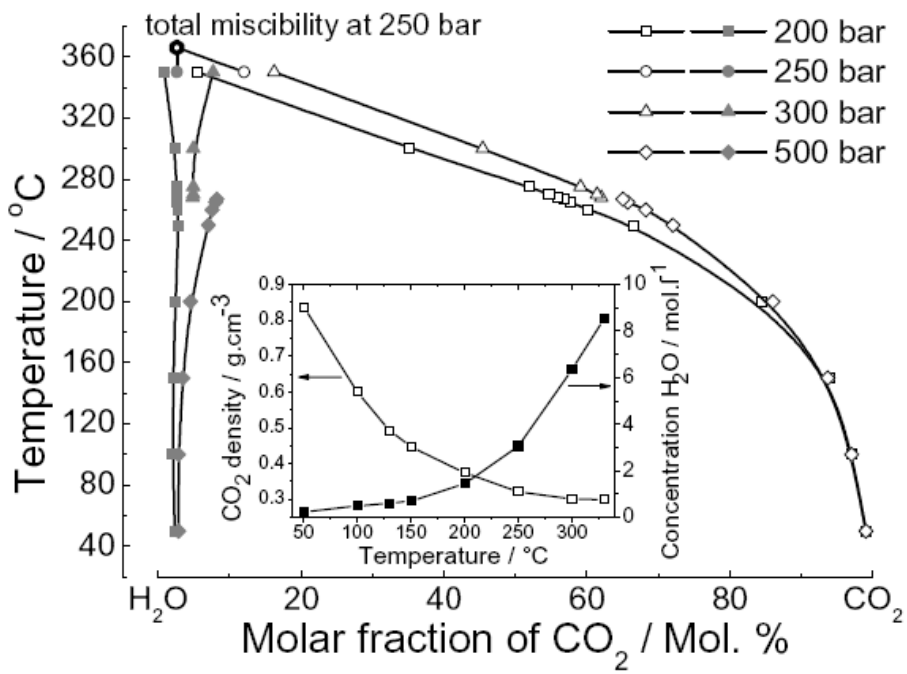
Synchrotron X-ray Study of binary fluids – Mineral Interfaces Important to Geothermal applications



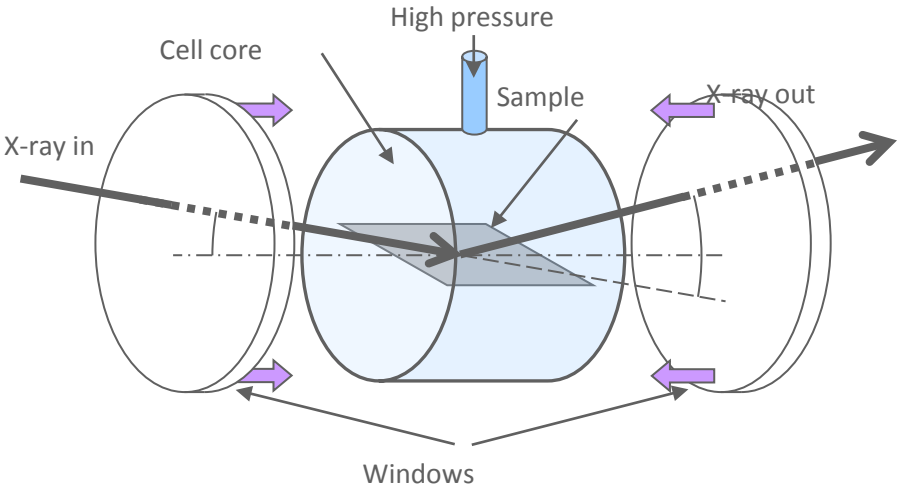
Power plants region

Geothermal region

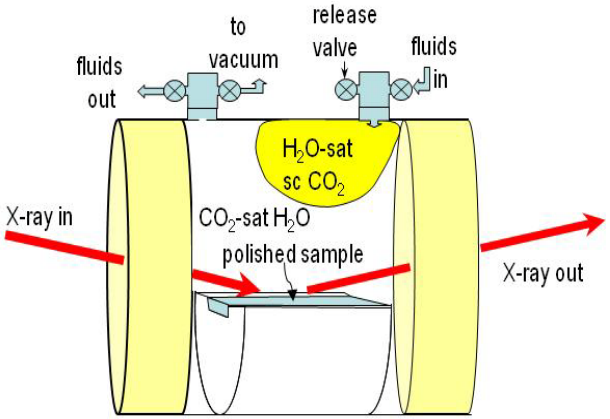
Tassing et al. 2005

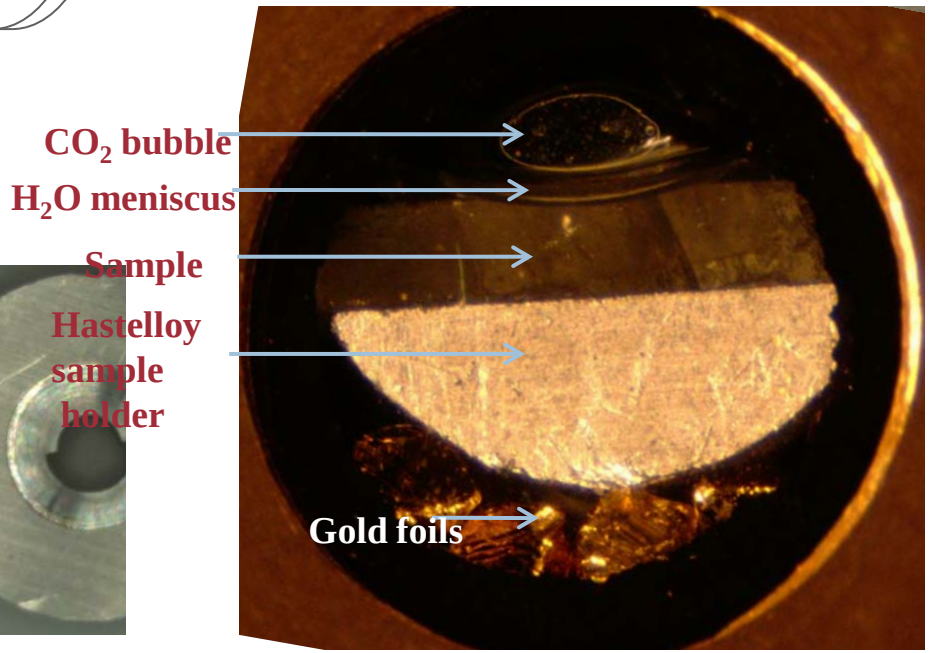


X-ray cell for in situ study of binary fluids – solid Interfaces



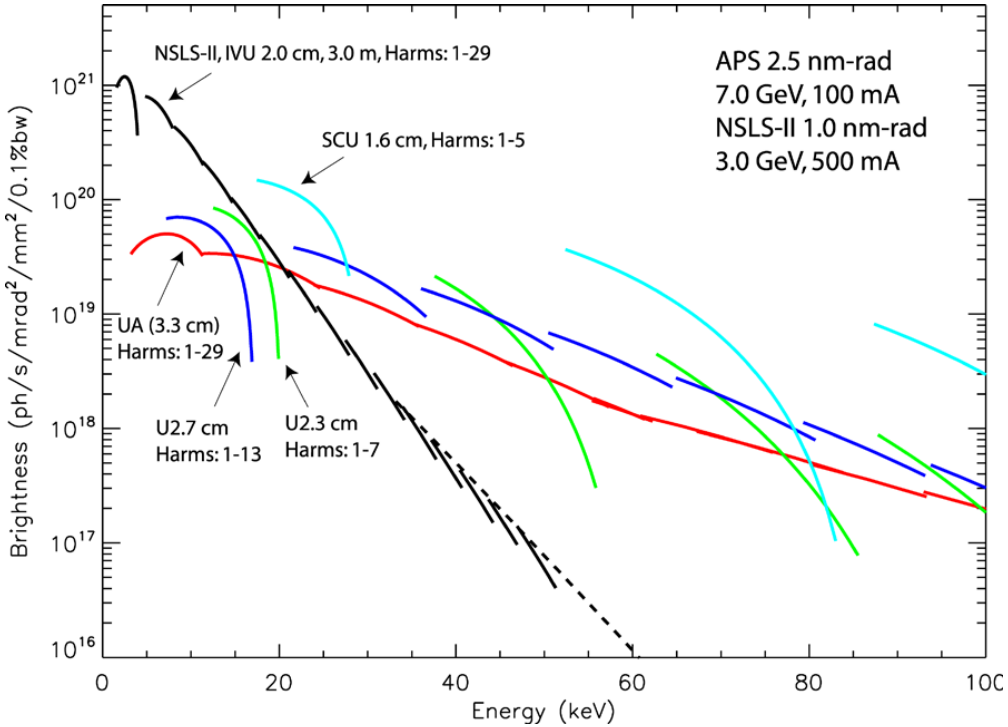
Diefenbacher, McKelvy, Chizmeshya, Wolf
Rev. Sci. Instrum. **76**, 015103 (2005);



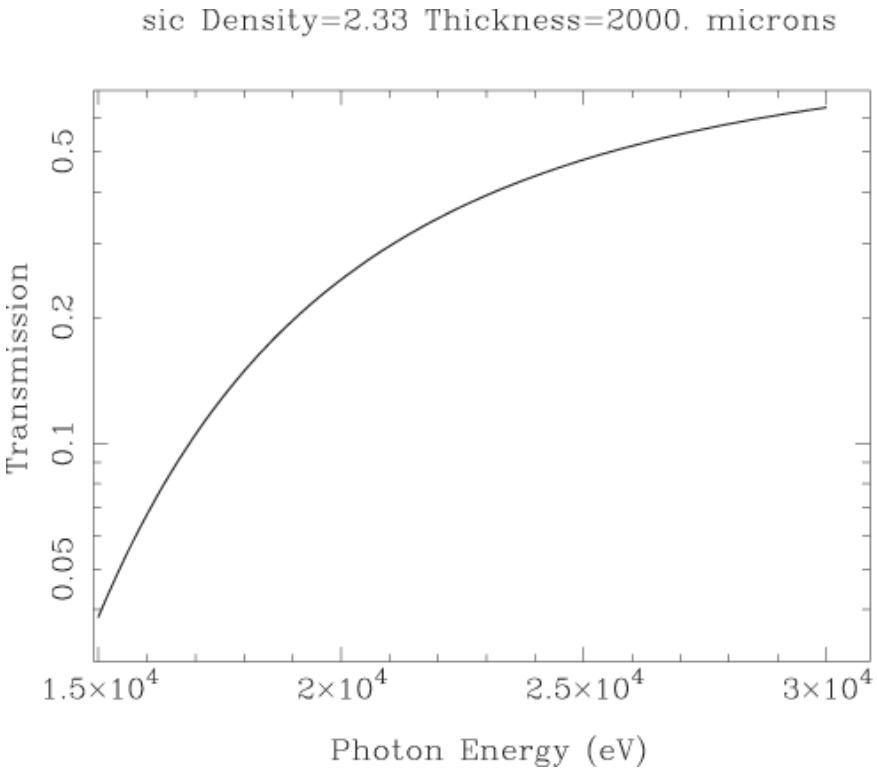


Sample mounting in the micro reactor and status after experiment

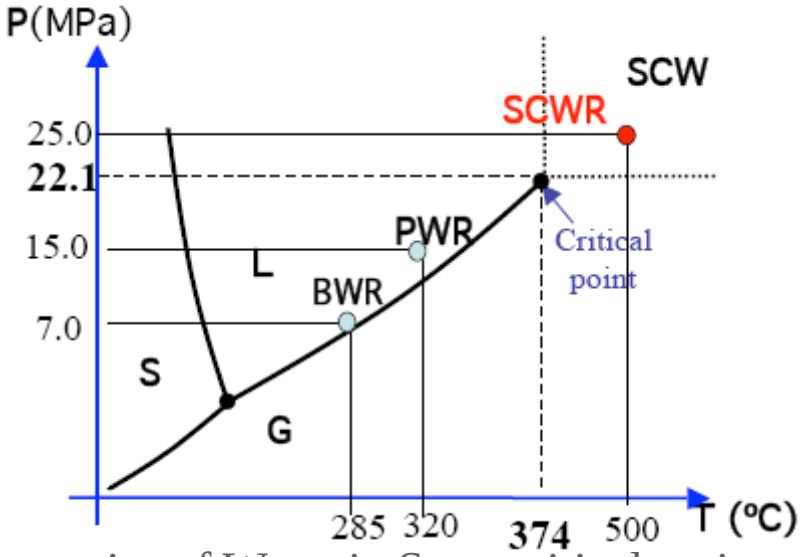
X-ray transmission through the moissanite windows



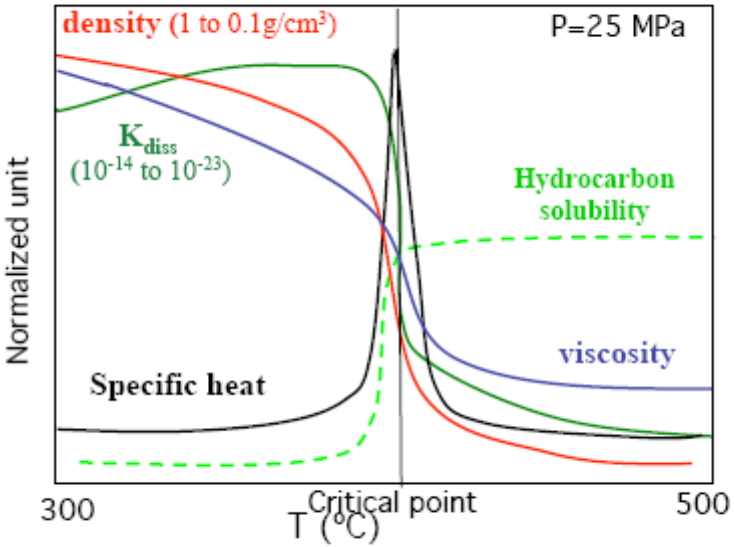
BrightnessTuningCurves_NSLSII_vs_APS.pdf



Interfaces under Supercritical Water



Properties of Water in Supercritical region



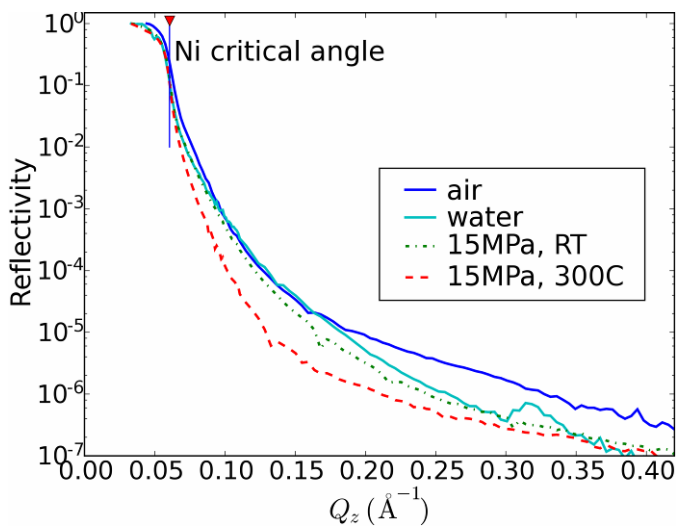
G. S. Was, *SCWR Review Workshop*, Albany NY, 03/2006

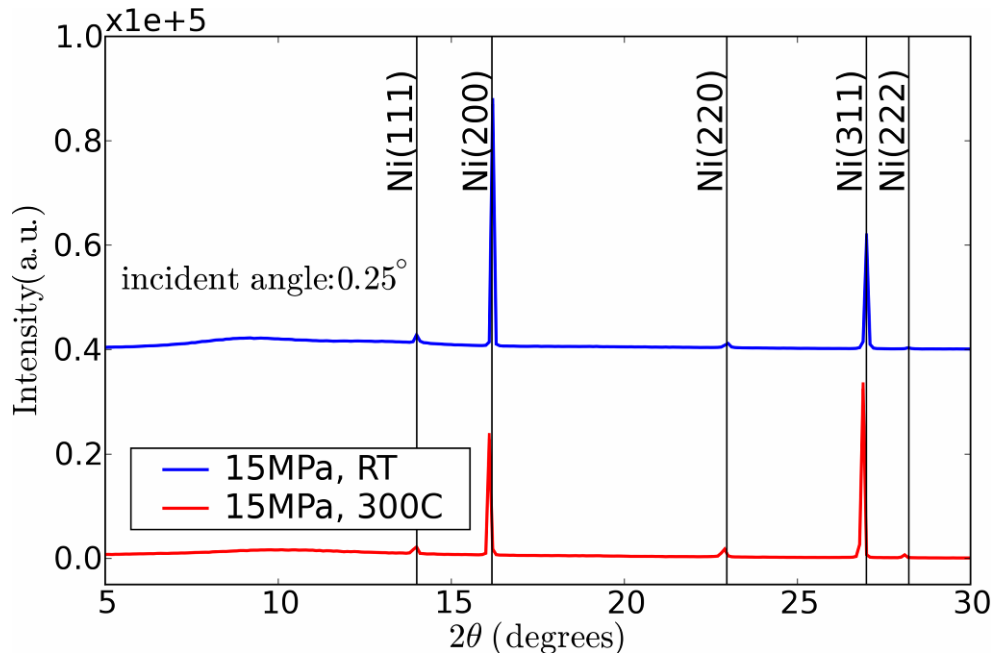
- Properties of water are highly tunable near the critical point.
- Supercritical-water cooled power plants.
  - higher thermal efficiency
  - only works with single phase (plant simplification possible)
  - materials constraints due to operation at 500°C, 25MPa (~250 atm)

How does water at high pressure, high temperature affect the corrosion behavior of alloys?

Ni alloy results

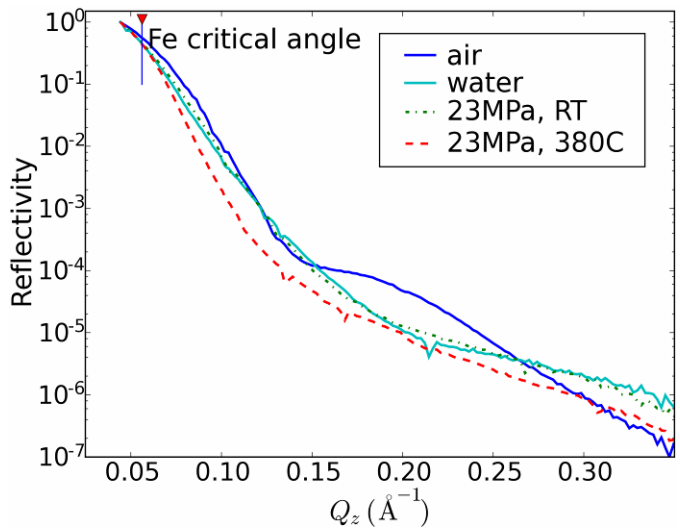
- Ni alloy was mechanically polished and shows a well defined critical angle.
- Reflectivity changes with the introduction of water in the cell.
- The films seem to be conformally rough. (no increase in roughness with the formation of film.
- Powder diffraction – textured alloy. No new peaks form. Nickle hydride film?

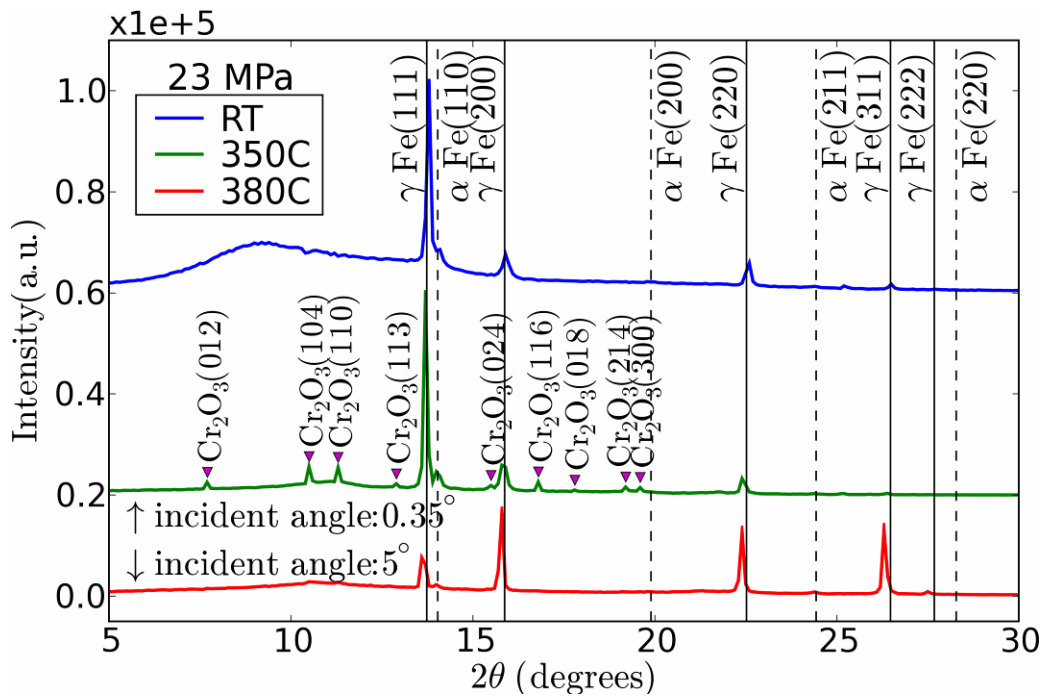




SS304 results

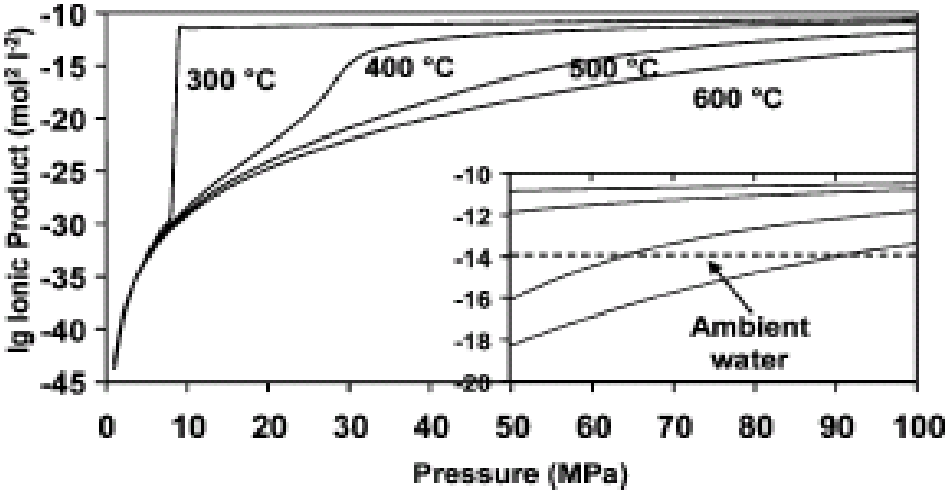
- Commercial mirror finish SS304 does not give a well defined critical angle.
- No increase in roughness with the formation of film.
- Powder diffraction is mostly from austenite iron. Formation of Cr_2O_3 was observed on the surface at subcritical temperature.



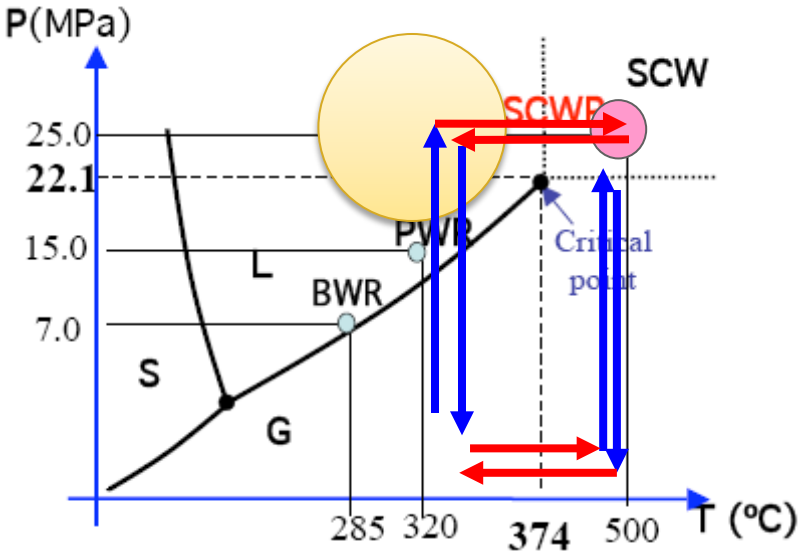


Corrosivity of pressurized water

- At high pressure water has the highest ionic product at low temperature
- This corroborates our observation of corrosion products a subcritical water
- Experimental path to supercritical water is important.

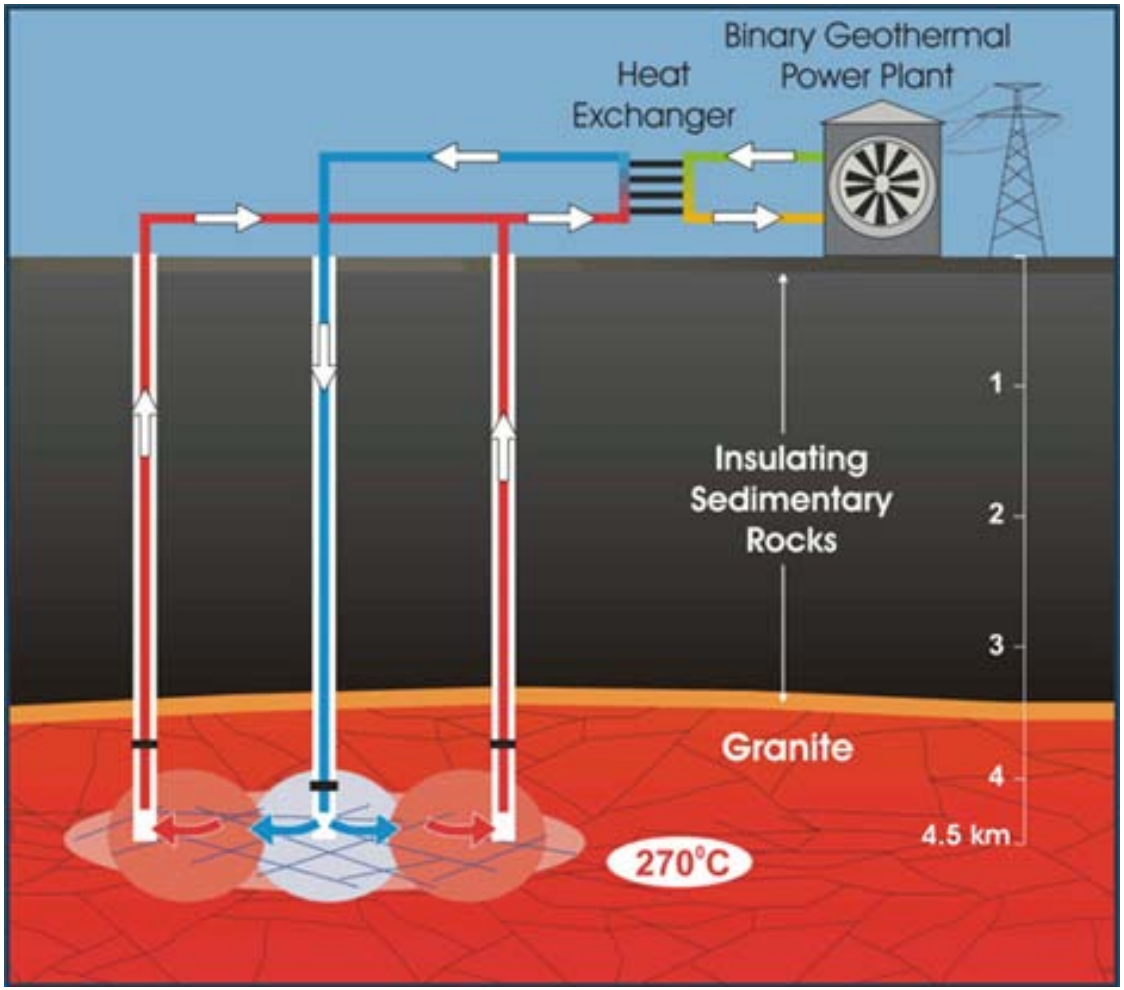


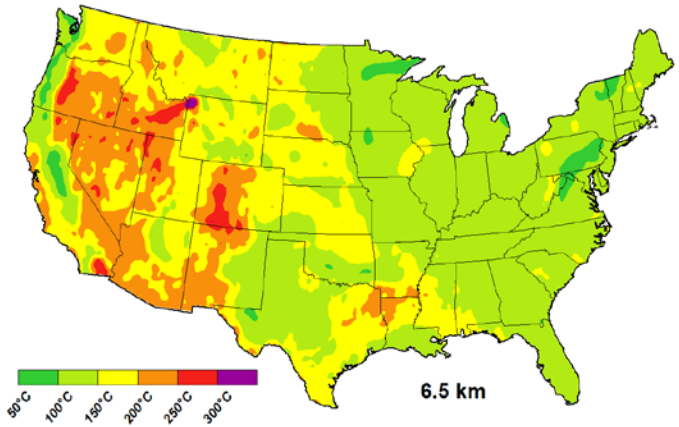
Ionic product of high-temperature water and steam at different temperatures versus pressure.

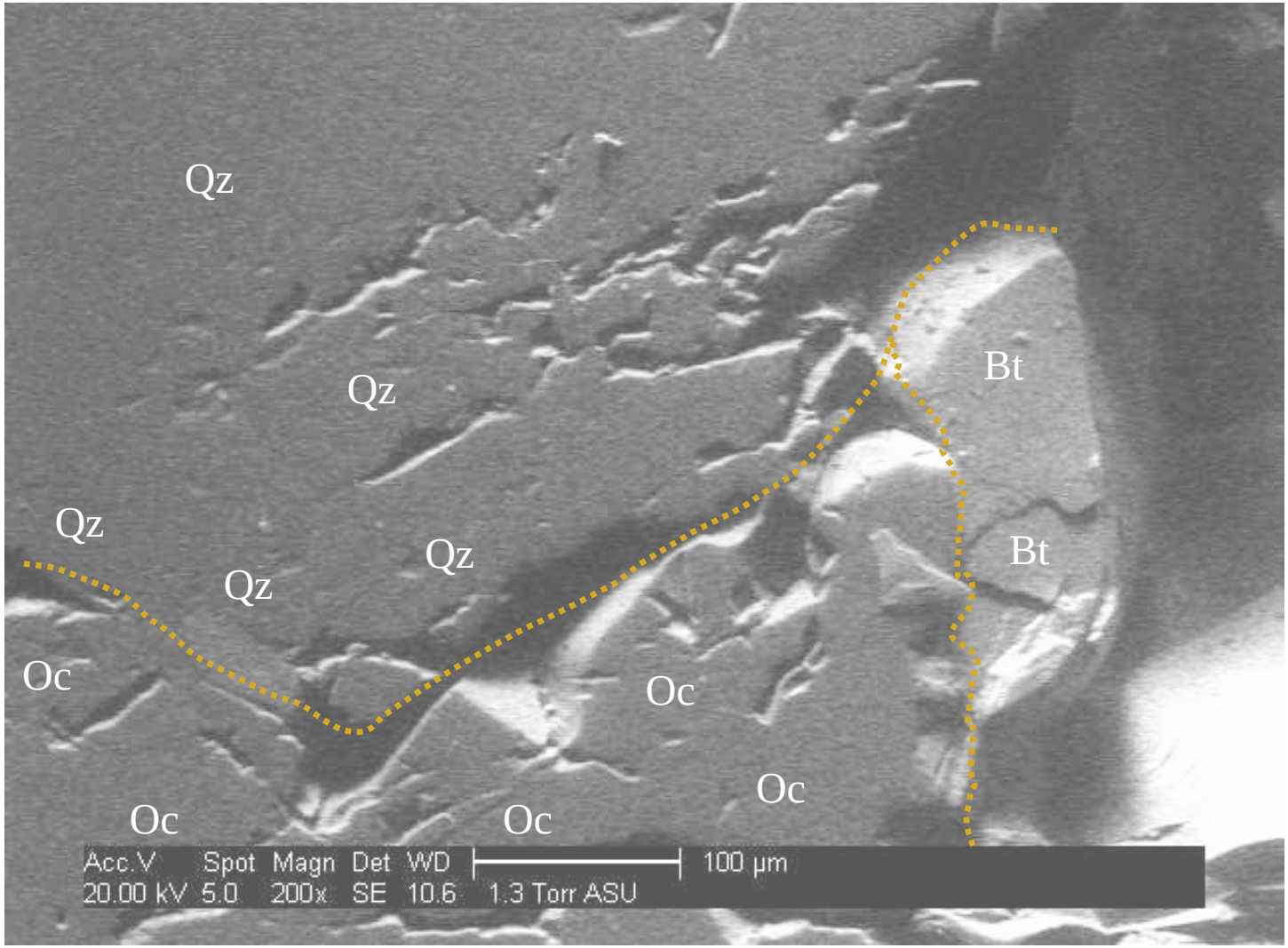


ENHANCED Geothermal System

- Major CO_2 offsets
- CO_2 sequestration while generating power
- Significant improvements in efficiency
- Reductions in cost to less than half cost with current technology



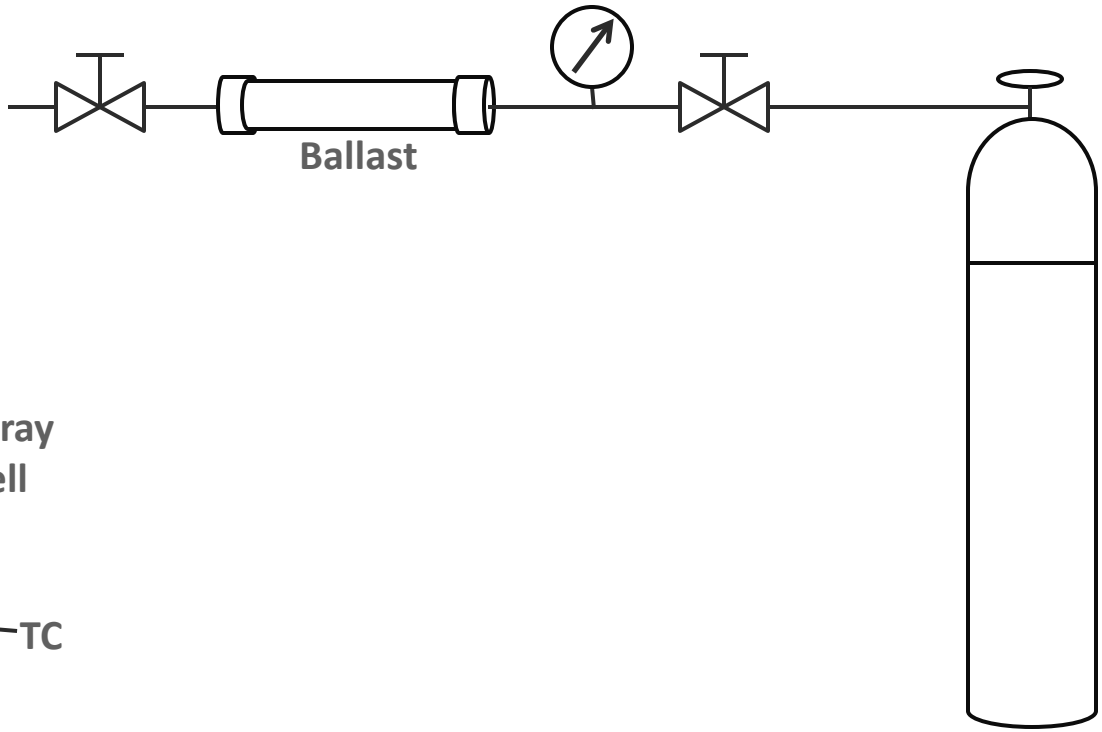


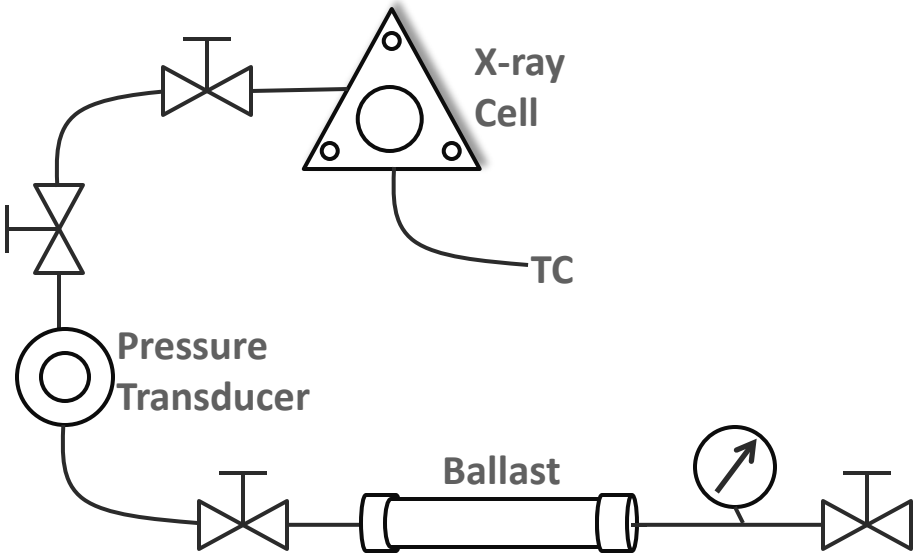


Secondary electron image taken, with ESEM, for a polished section of a granite sample showing the three mineral components: quartz (Qz), orthoclase (Oc) and biotite (Bt). Notice that grain boundaries are not always resolved

Experimental Setup

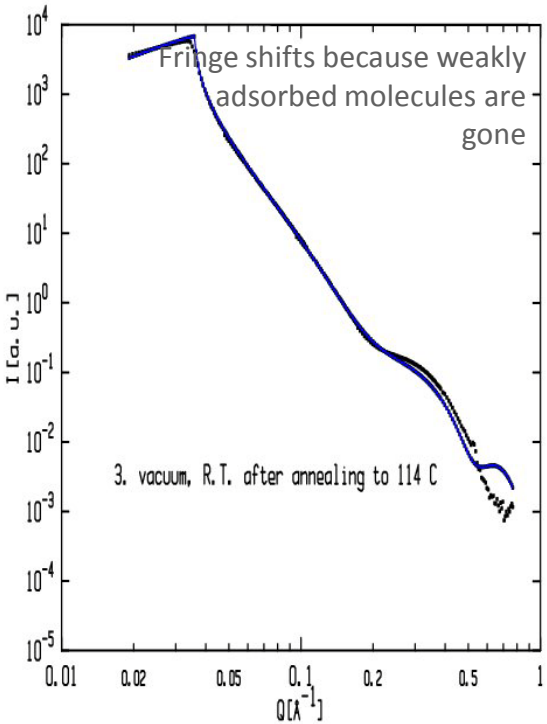
Task 1: Filling ballast from a CO2 liquid siphoning cylinder

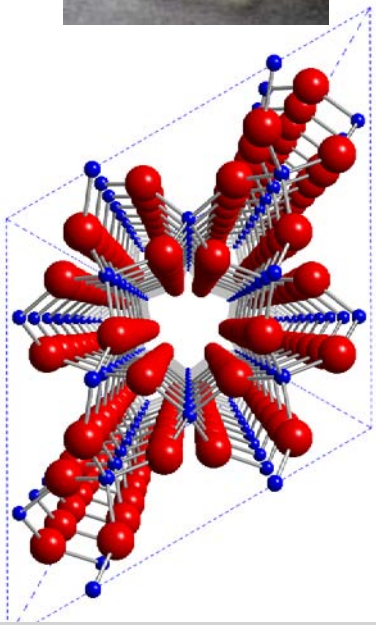




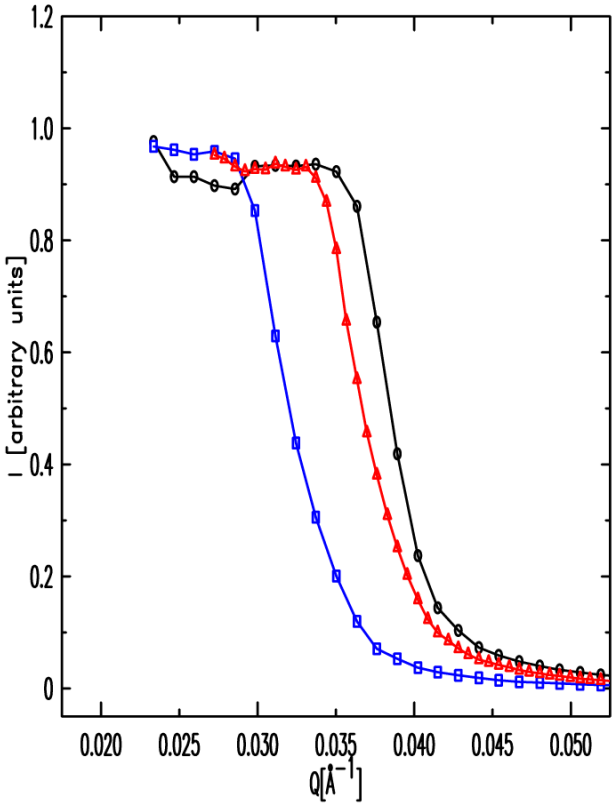
Task 2: Filling the x-ray cell from a ballast

Proof of Principle Experiment Quartz (0001)



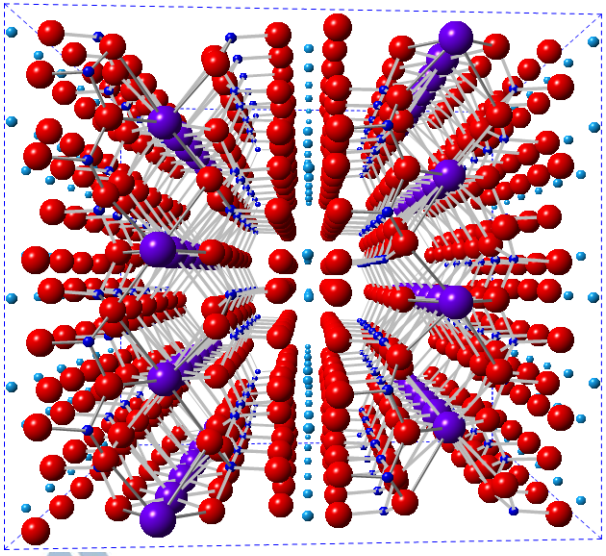


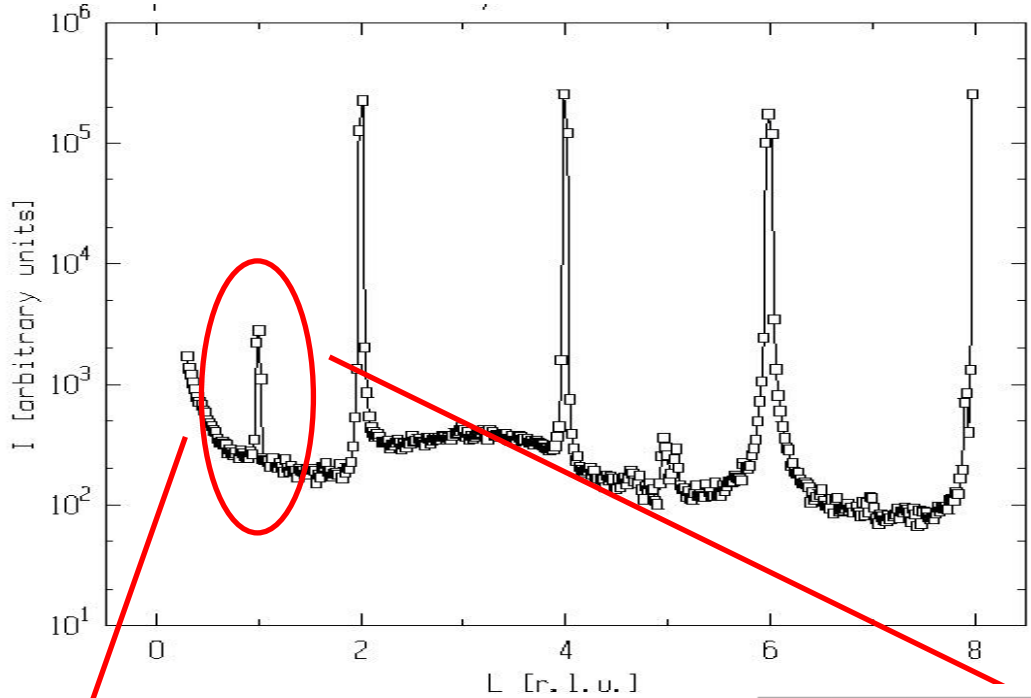
Critical angle changes

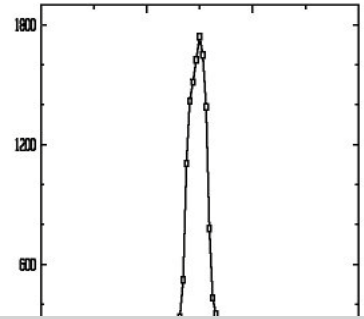


- The surface roughness <1 nm.
- No measurable dissolution or roughening under static $scCO_2$-H_2O

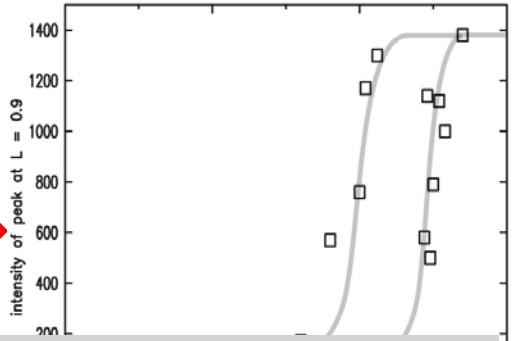
Intercalation of Water Into Muscovite Under $scCO_2$





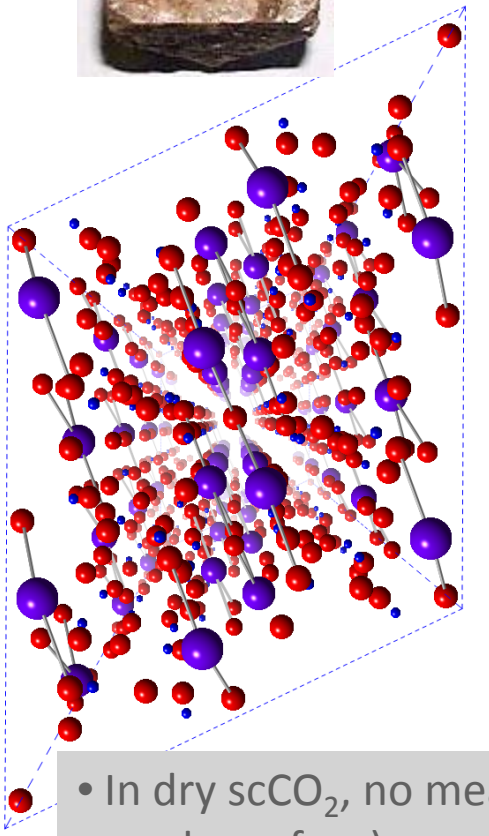


1022 psi, 140° C
$scCO_2 + H_2O$

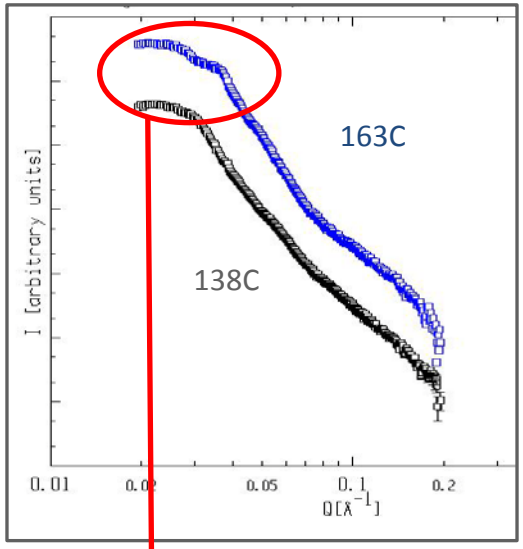


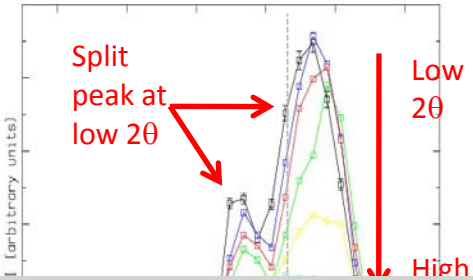
- In dry $scCO_2$, no intercalation.
- In $scCO_2$-H_2O, intercalation/de-intercalation observed.

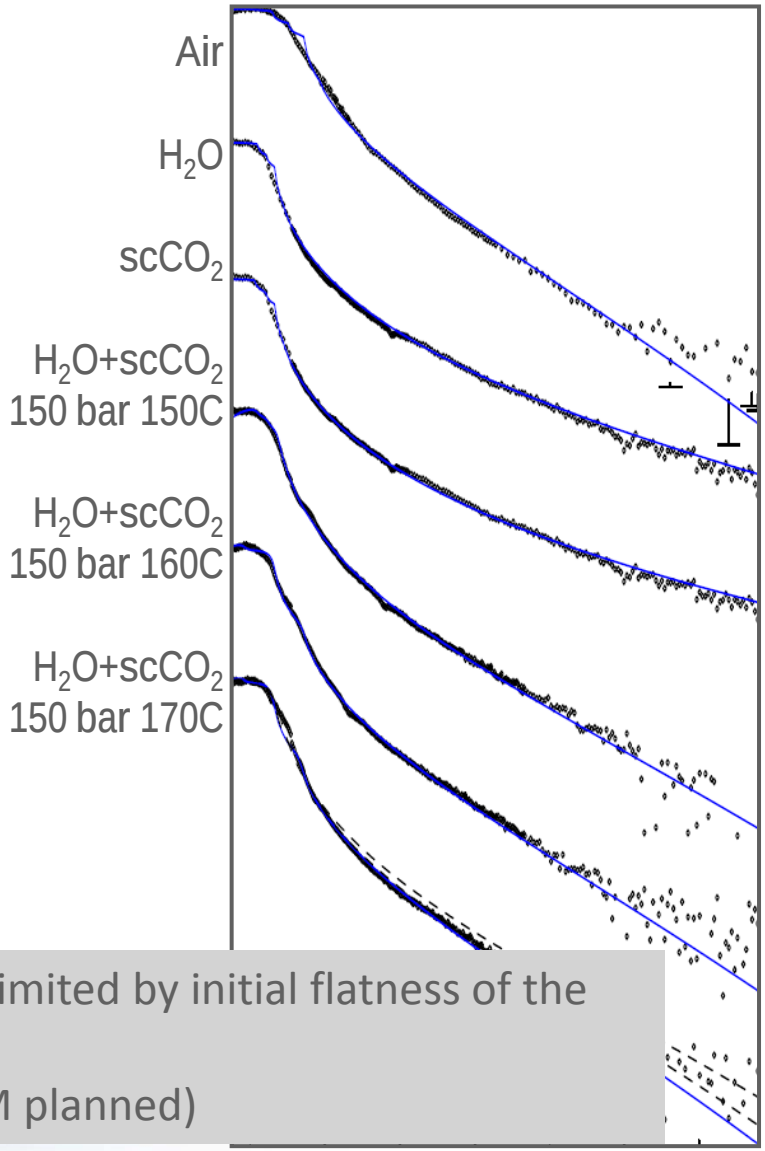
Dissolution of Orthoclase Surface



$KAlSi_3O_8$







- In dry $scCO_2$, no measurable dissolution (accuracy limited by initial flatness of the sample surface)
- In $scCO_2$-H_2O, rapid dissolution was observed. (AFM planned)

Conclusions

- Corrosion in supercritical water
  - Reflectivity show no increase in roughness at supercritical water conditions.
  - Powder diffraction shows the formation of Cr_2O_3 at subcritical conditions. This confirms that subcritical conditions at high pressure is most corrosive to the alloy.
- Dissolution reaction in supercritical CO2 and water
  - Silica surfaces by synchrotron x-ray reflectivity: The surface roughness <1 nm and no measurable dissolution or roughening under static $scCO_2$-H_2O fluids as expected.
  - Mica under $scCO_2$-H_2O fluids in dry $scCO_2$, no intercalation. In $scCO_2$-H_2O, intercalation observed.
  - Orthoclase under $scCO_2$-H_2O fluids: In dry $scCO_2$, no measurable dissolution (accuracy limited by polishing). With water, rapid dissolution was observed.

The END