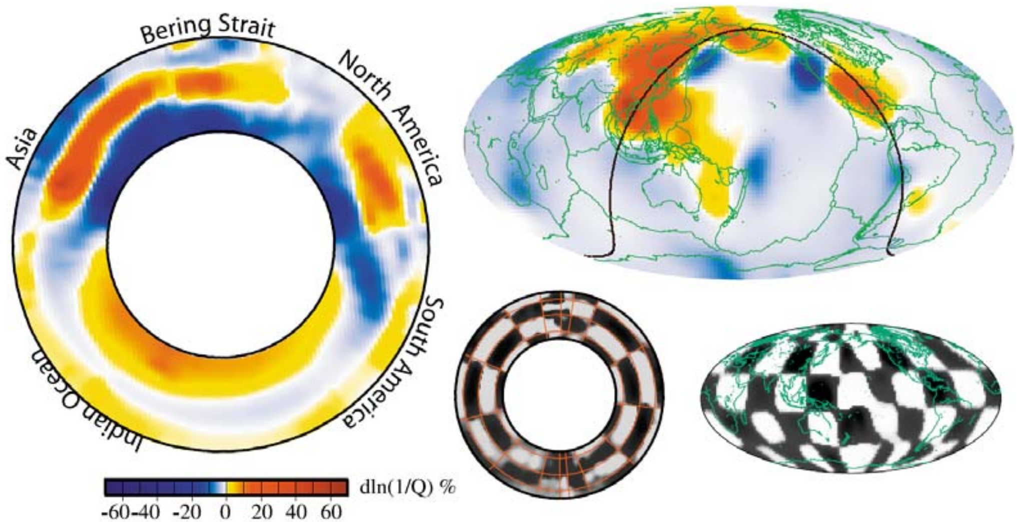
Tetrahedral Occupancy of Ferric Iron in (Mg,Fe)O: Implications for Point Defects in the Lower Mantle

Kazuhiko Otsuka (*Yale Univesity)*
Catherine McCammon *(Bayerisches Geoinstitut)*
Shun-ichiro Karato (*Yale Univesity)*

Motivations

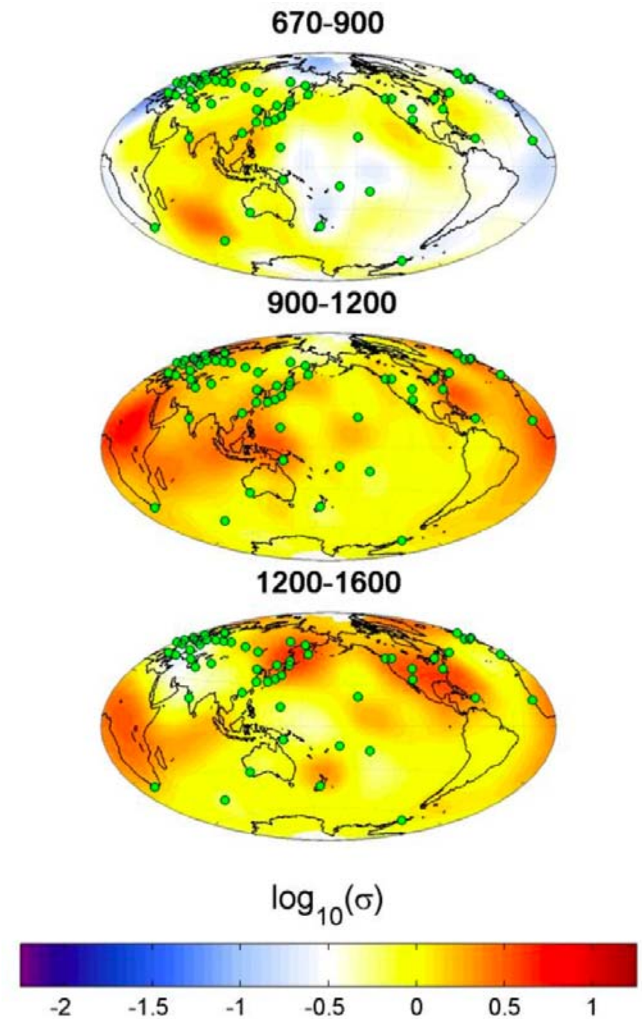
Seismic wave attenuation

Lawrence and Wysession (2006)



Electrical conductivity

Kelbert et al (2009) submitted



Mineral physics basis is needed for interpreting **geophysical observations**.

(Mg,Fe)O

- [1] Control **transport properties** in the lower mantle?
  - Higher **atomic diffusivity** than perovskite (e.g., Holzapfel et al., 2003; Van Orman et al., 2009; Yamazaki and Irifune 2003)
  - Lower **viscosity** than perovskite (e.g., Poirier et al., 1986; Yamazaki and Karato, 2001)
  - Higher **electrical conductivity** than perovskite (e.g., Dobson et al., 1997; Ohta et al., 2007; Wood and Neil, 1991 ; Xu and McCammon, 2002)

- [2] Change dominant positive **point defects** with *P*?

  (Bolfan-Casanova et al., 2002; 2006)

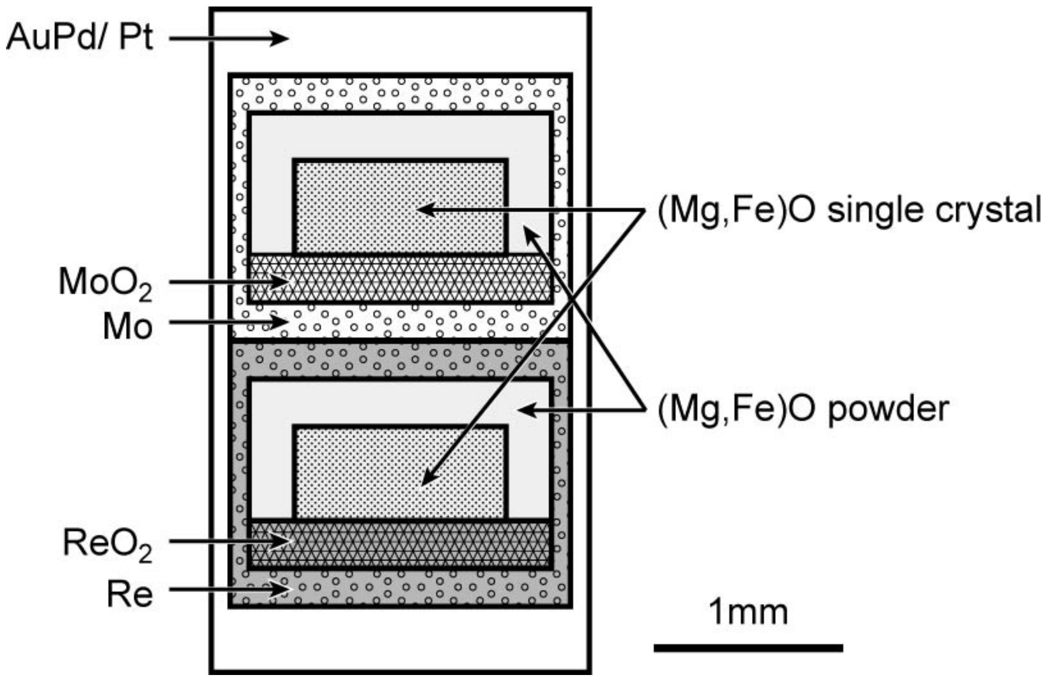
  transport properties sensitive to

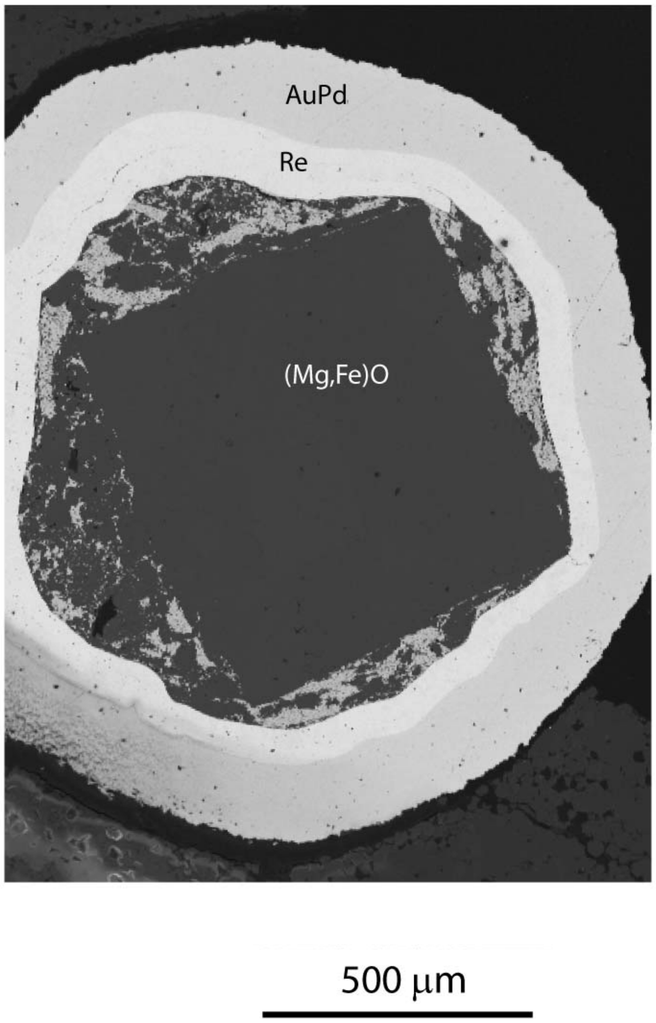
  - **Fe^{3+} at low *P*** → **Fe^{3+} content (oxygen fugacity)**
  - **H^+ at high *P* (?)** → **H^+ content (water fugacity)**

Goals: To characterize the **concentration** and **site occupation** of Fe^{3+} in order to explore **solubility crossover** between Fe^{3+} and H^+

Experiments

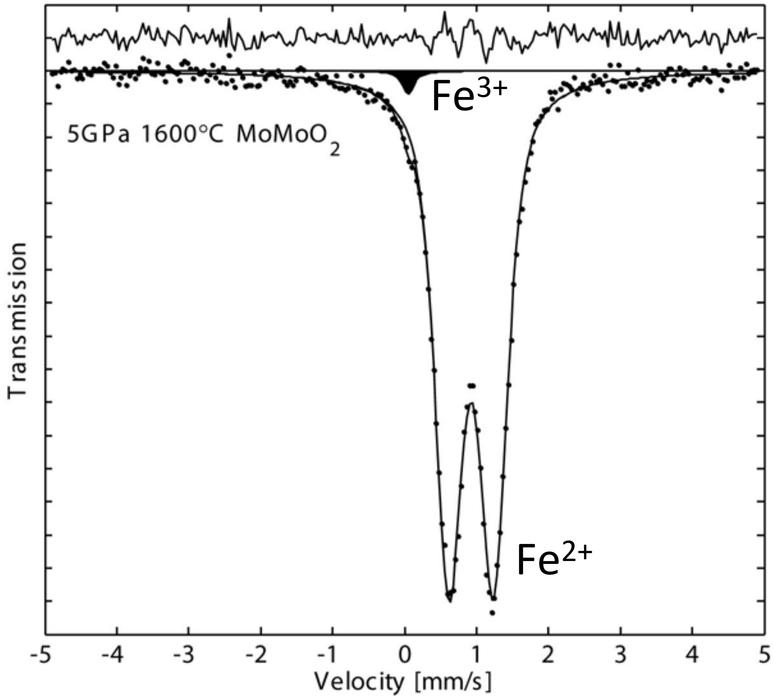
- With a Kawai-type **Multi-anvil apparatus**
- Sample: (Mg,Fe)O with Mg# 80
- Conditions: **1674-2273K; 5-15 GPa**
- fO_2 buffer: **Mo-MoO$_2$; Re-ReO$_2$**

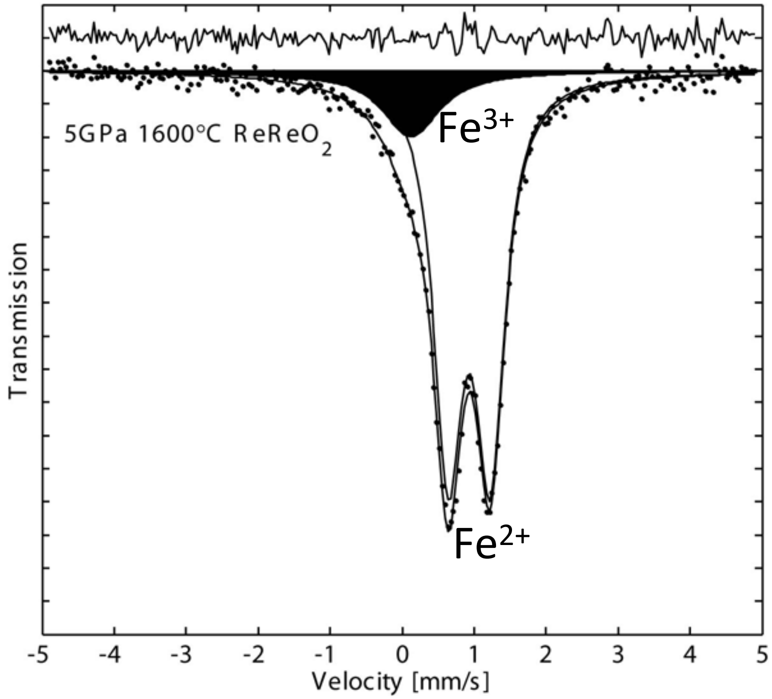




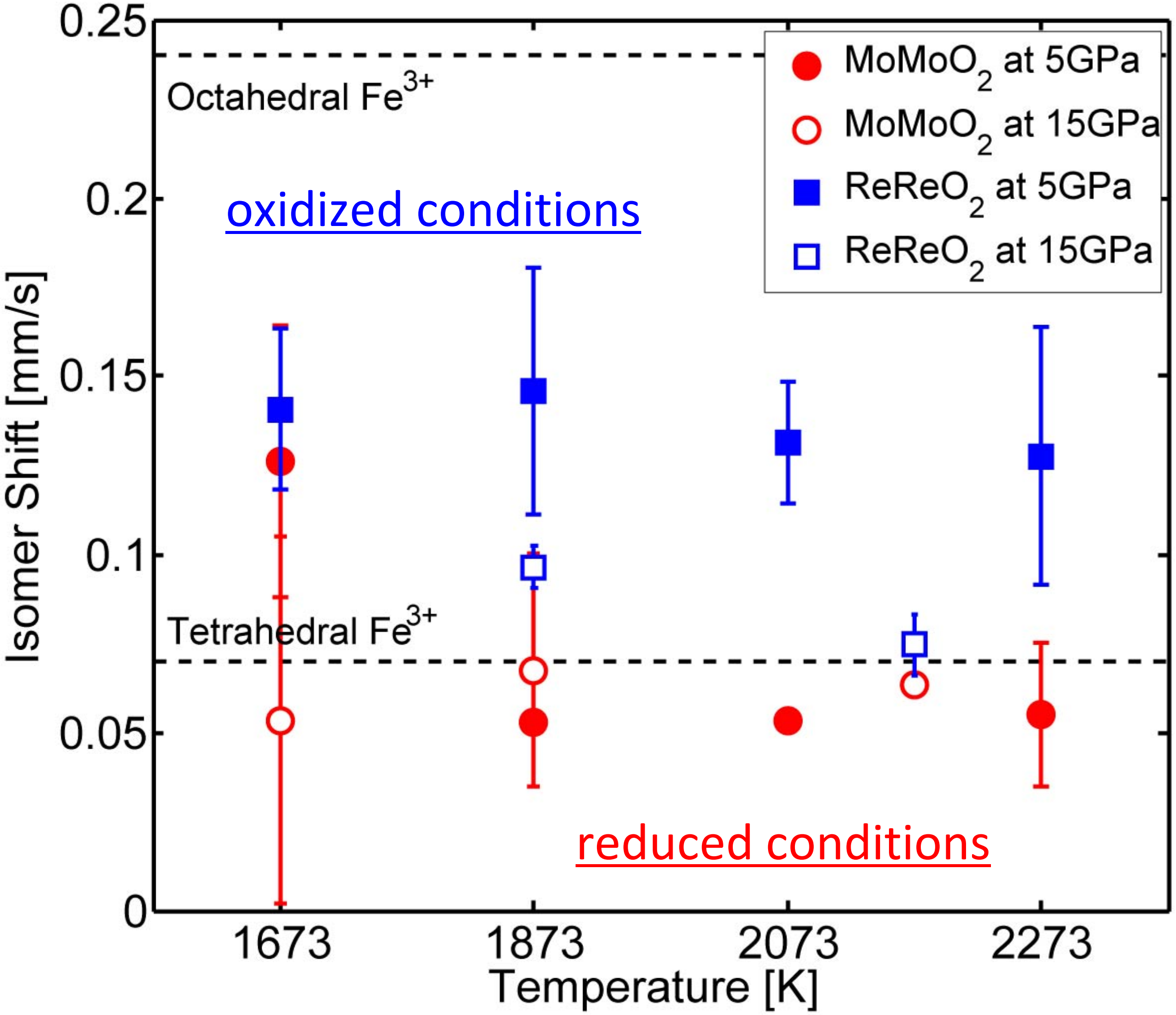
Mössbauer Spectra

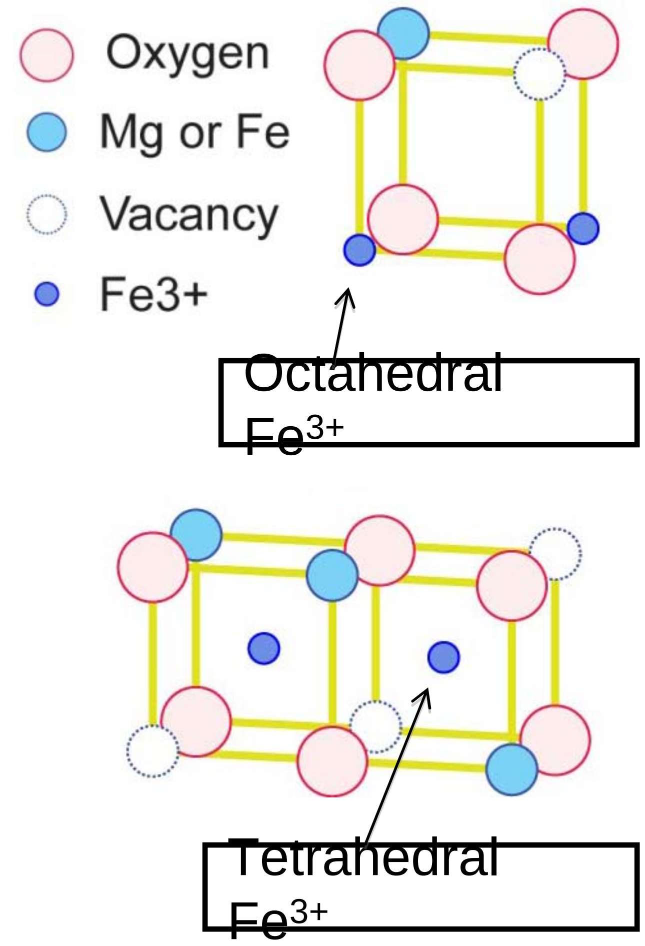
- **Reduced condition**
  - low $Fe^{3+}/\Sigma Fe$
  - low IS
- **Oxidized condition**
  - high $Fe^{3+}/\Sigma Fe$
  - high IS





Isomer Shift (IS)

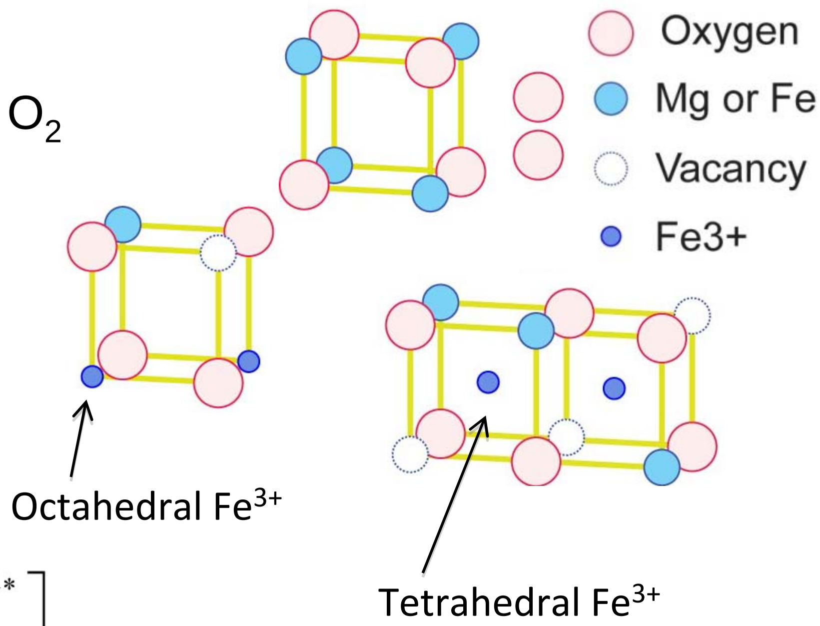




IS Fe^{3+} in octahedral: 0.24; tetrahedral 0.06 [mm/s] from Waychunas (1983)

Thermodynamic Models

- **System**:
  – ${}^{VI}[Mg, Fe^{2+}, Fe^{3+}, V]^{IV}[V, Fe^{3+}]_2[O]$ and O_2



- **Stoichiometric Relations**:

$$2Fe_{VI}^{\times} + \frac{1}{2}O_2{}^{f} = 2Fe_{VI}^{\bullet} + V_{VI}^{''} + 2V_{IV}^{\times} + O_O^{\times}$$

$$2Fe_{VI}^{\times} + \frac{1}{2}O_2{}^{f} = 2Fe_{IV}^{\bullet\bullet\bullet} + 3V_{VI}^{''} + O_O^{\times}$$

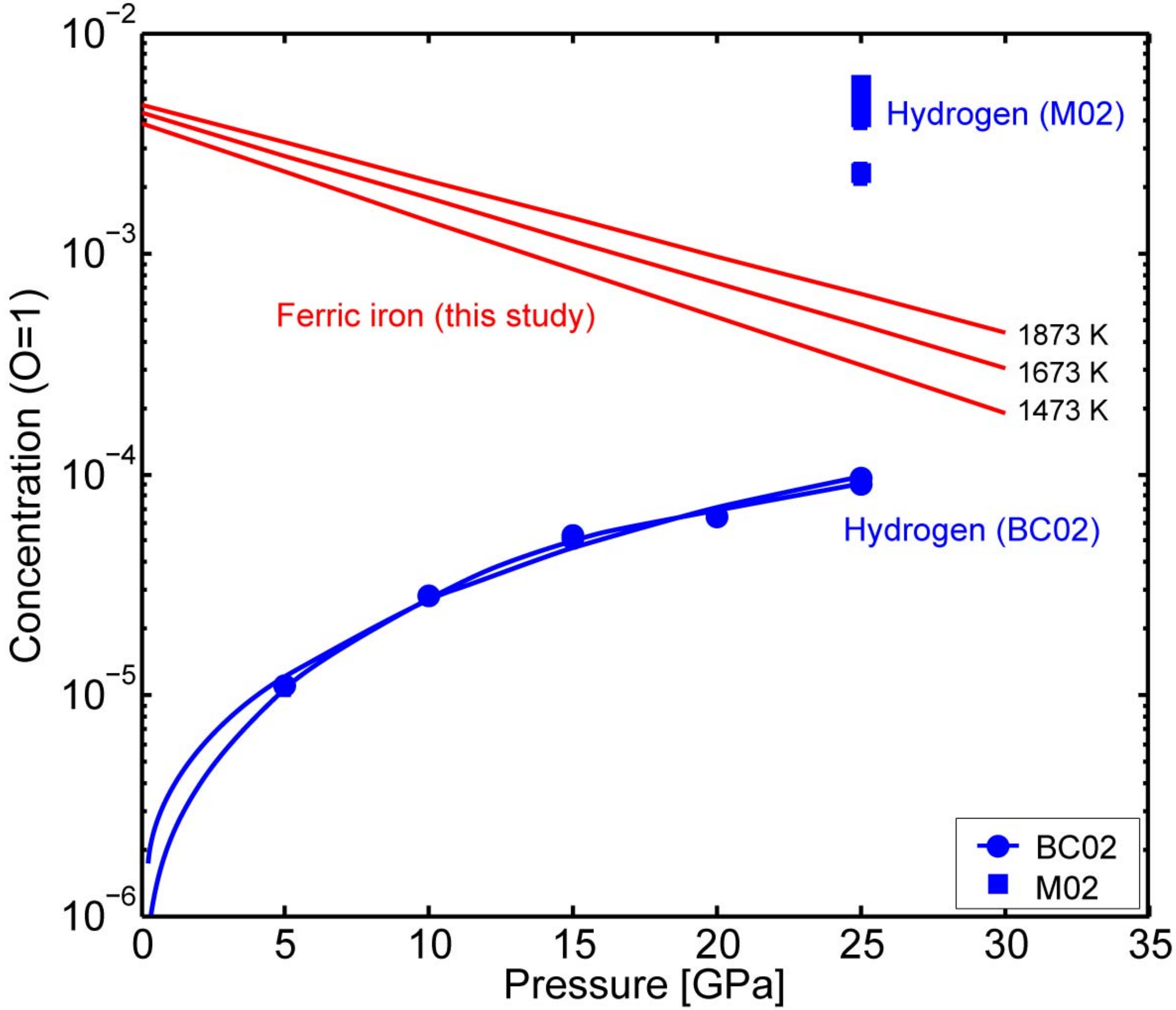
- **Law of mass action**:

$$[Fe^{3+}] = A[Fe_{VI}^{\times}]^{l} f_{O_2}^{m} \exp\left[-\frac{E^* + PV^*}{nRT}\right]$$

	charge neutrality conditions	l	m	n
Octahedral Fe^{3+} :	$[Fe_{VI}^{\bullet}] = 2[V_{VI}^{''}]$	$\frac{2}{3}$	$\frac{1}{6}$	3
Tetrahedral Fe^{3+} :	$6[Fe_{IV}^{\bullet\bullet\bullet}] = 2[V_{VI}^{''}]$	$\frac{2}{5}$	$\frac{1}{10}$	5

Fe^{3+} occupies tetrahedral sites at low fO_2 or high *P*.

Solubility of Fe^{3+} and H^{+}



Experimental data from this study, Bolfan-Casanova et al. (2002); Murakami et al (2002).

Conclusions

- A change in the dominant site occupancy of Fe^{3+}:

  1) Fe^{3+} in the **tetrahedral site**,

  2) Fe^{3+} in the **octahedral site**, and

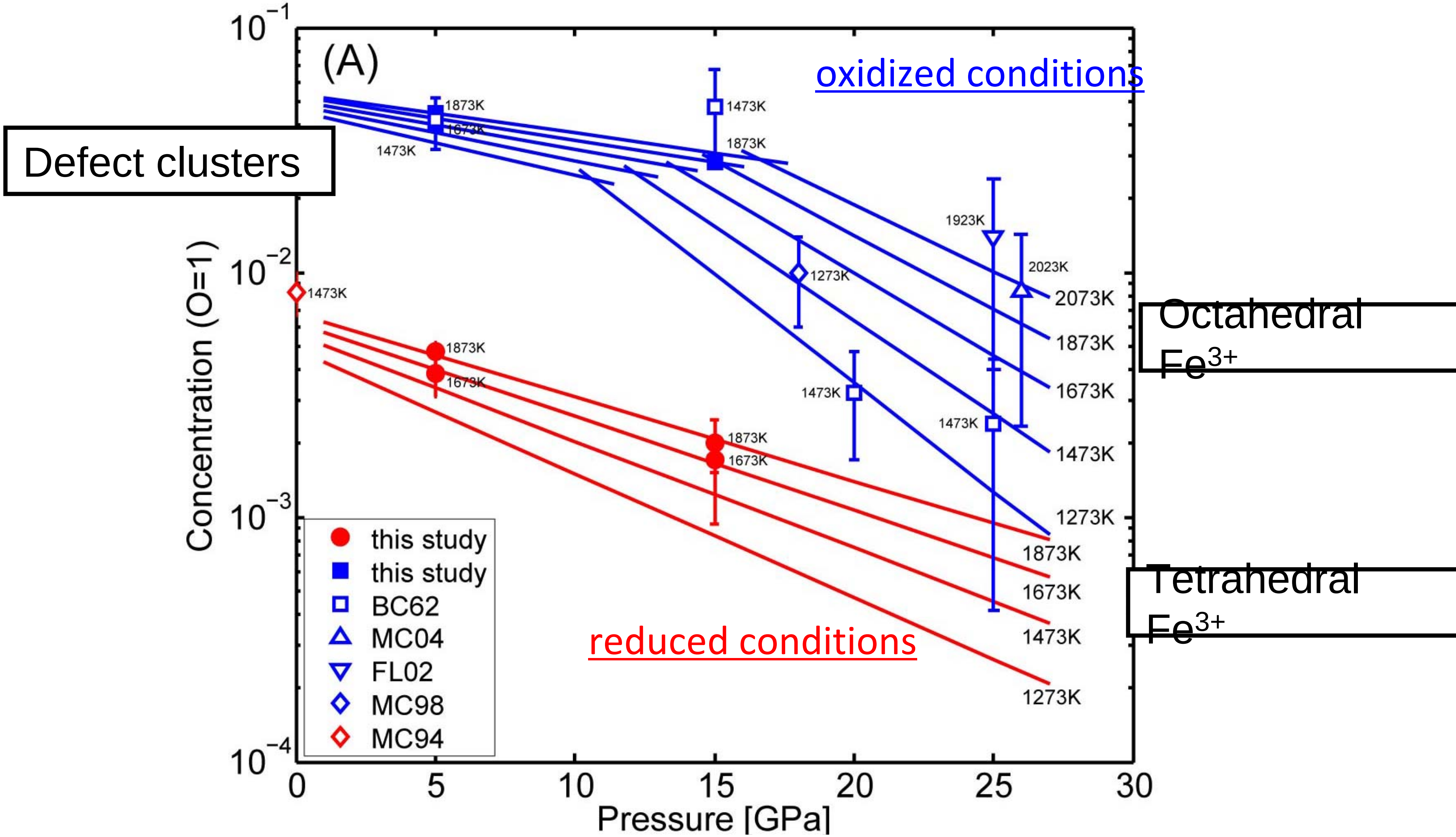
  3) **defect clusters** of Fe^{3+} and cation vacancy,

  in the order of **increasing fO_2** and **decreasing *P***.

- Fe^{3+} in the **tetrahedral site** down to the lower mantle where fO_2 is even lower than the experimental conditions.

- The conditions of **solubility crossover** between Fe^{3+} and H^+ are not constrained.

Fe^{3+} Concentration in $(Mg_{0.8}Fe_{0.2})O$



Experimental data from this study, Bolfan-Casanova et al. (2002:2006); McCammon et al. (1998; 2004); Frost and Langenhorst (2002).