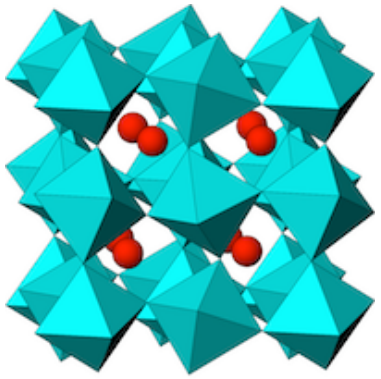
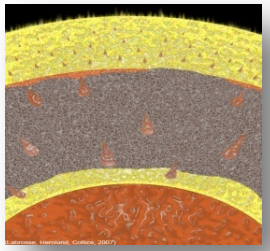
Electronic Structure of Iron in Magnesium Silicate Glass at high pressure



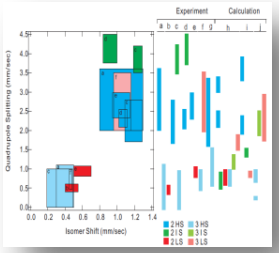
Chen Gu

Supervisor: Sang-Heon Dan Shim

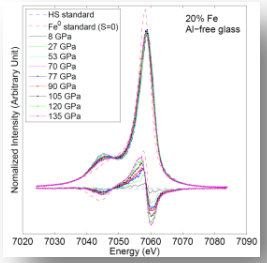
This presentation introduces the electronic structure of iron in magnesium silicate glass.



- Research motivation – Magma ocean, silicate mantle differentiation

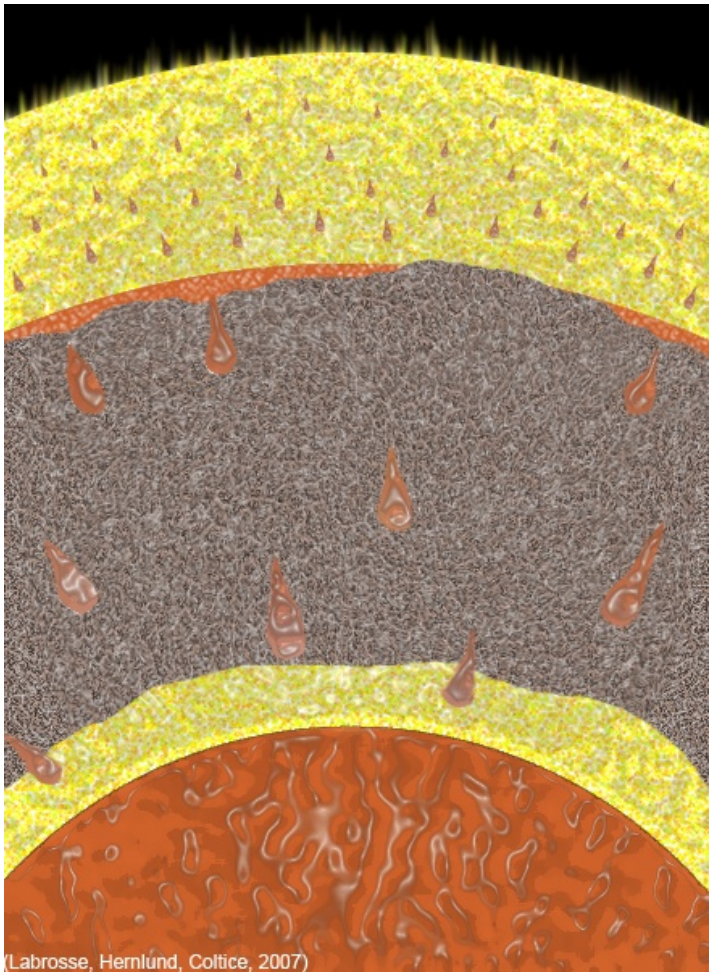


- Experiment methods – X-ray emission spectroscopy (XES) and synchrotron Mössbauer spectroscopy (SMS)

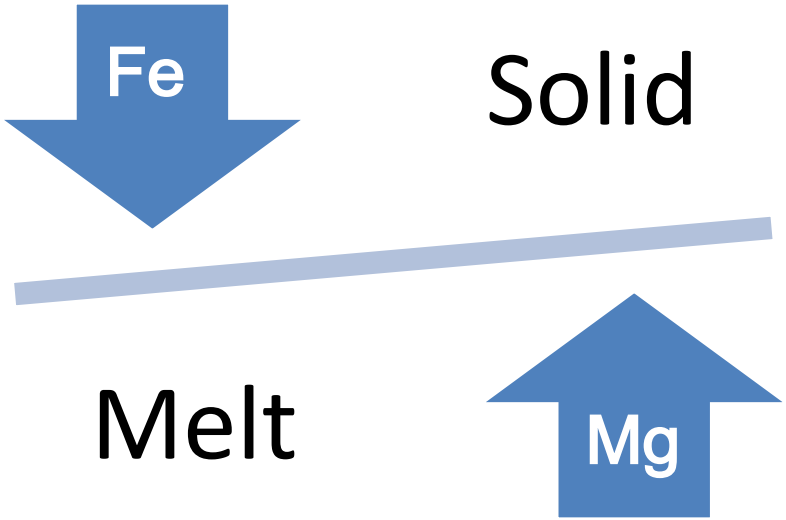


- Results and discussion – Gradual and fractional spin crossover in iron

Fe/Mg partition change could lead to a density crossover between melt and solid.

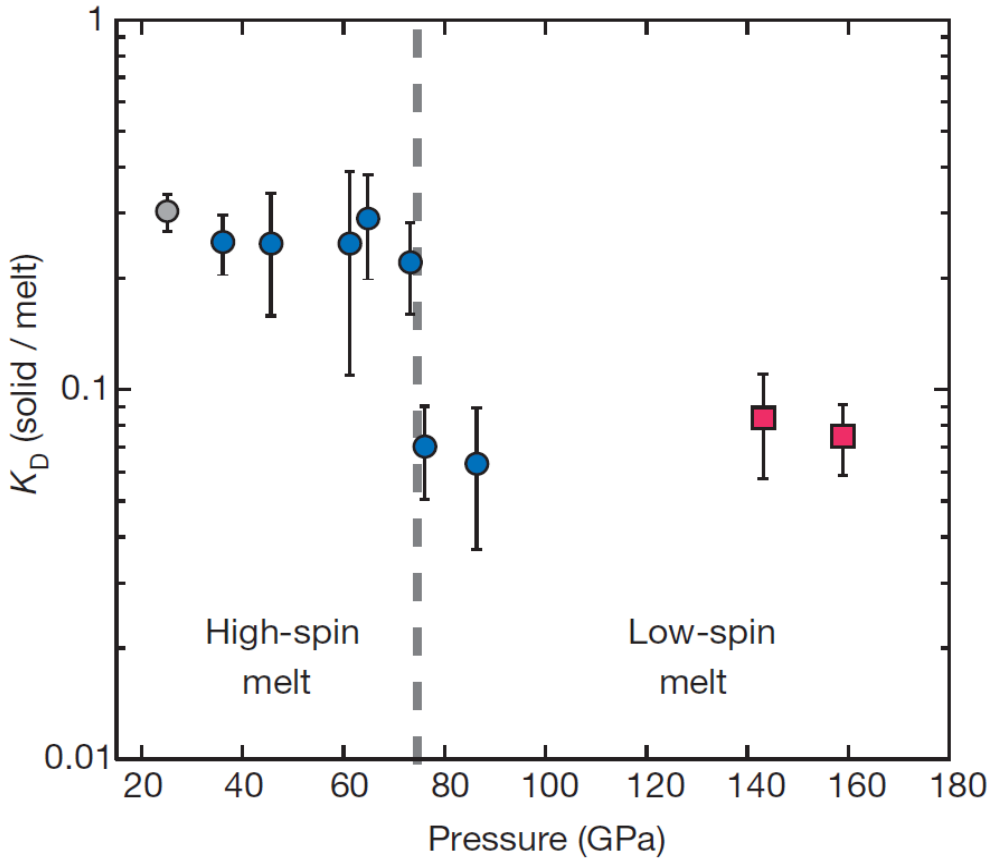


$$K_D = \frac{[Fe^{solid}]/[Mg^{solid}]}{[Fe^{melt}]/[Mg^{melt}]}$$



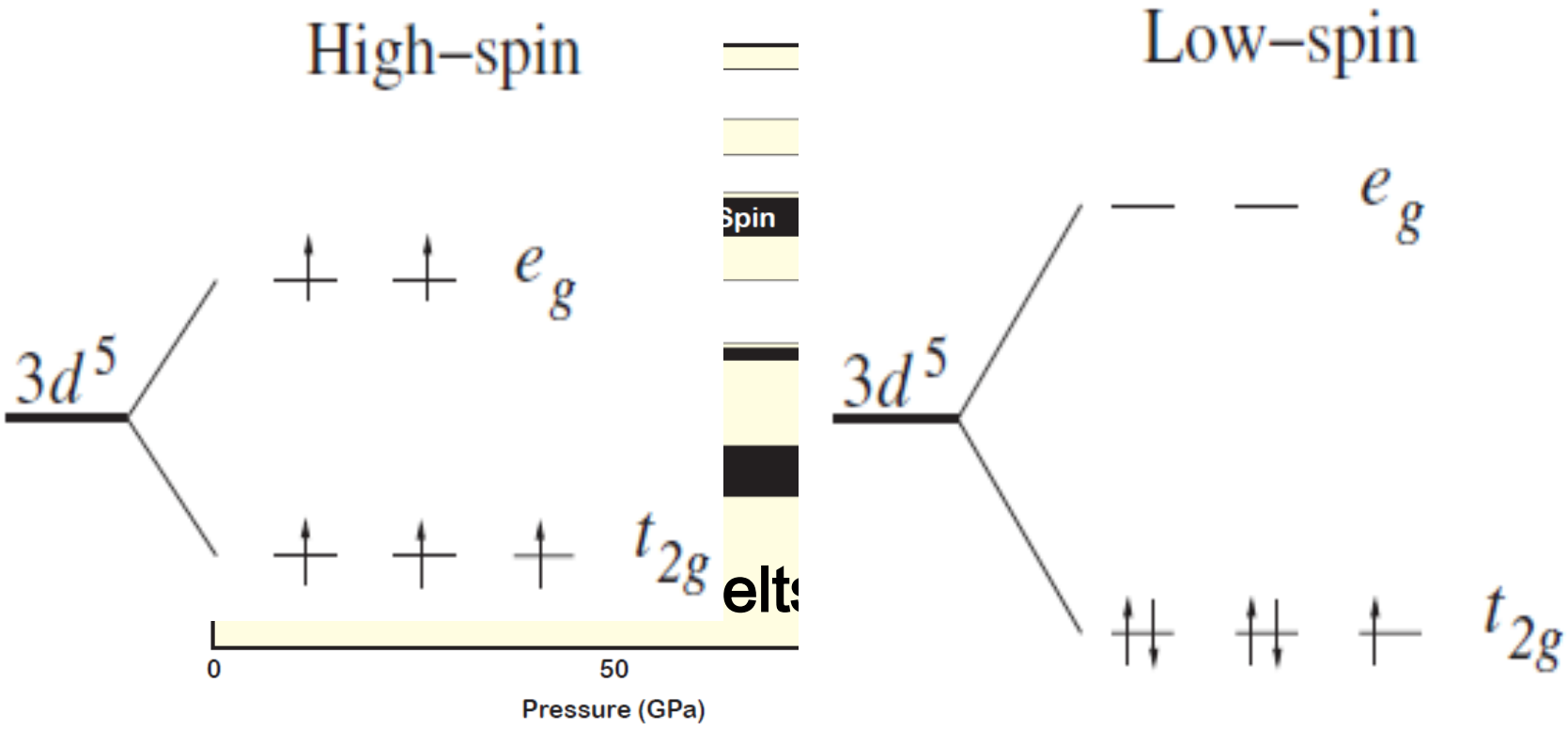
Nomura et al. (2011) attributed the K_D drop to spin crossover of iron in melts.

$(Mg_{0.89}Fe_{0.11})_2SiO_4$



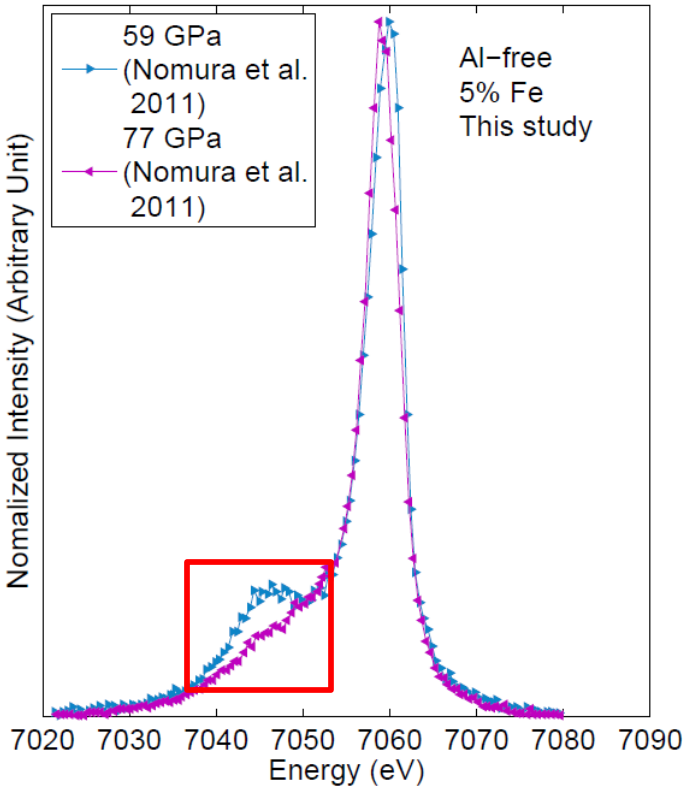
Nomura et al. (2011) attributed the K_D drop to spin crossover of iron in melts.

- **Spin crossover** has been found in silicates and oxides.

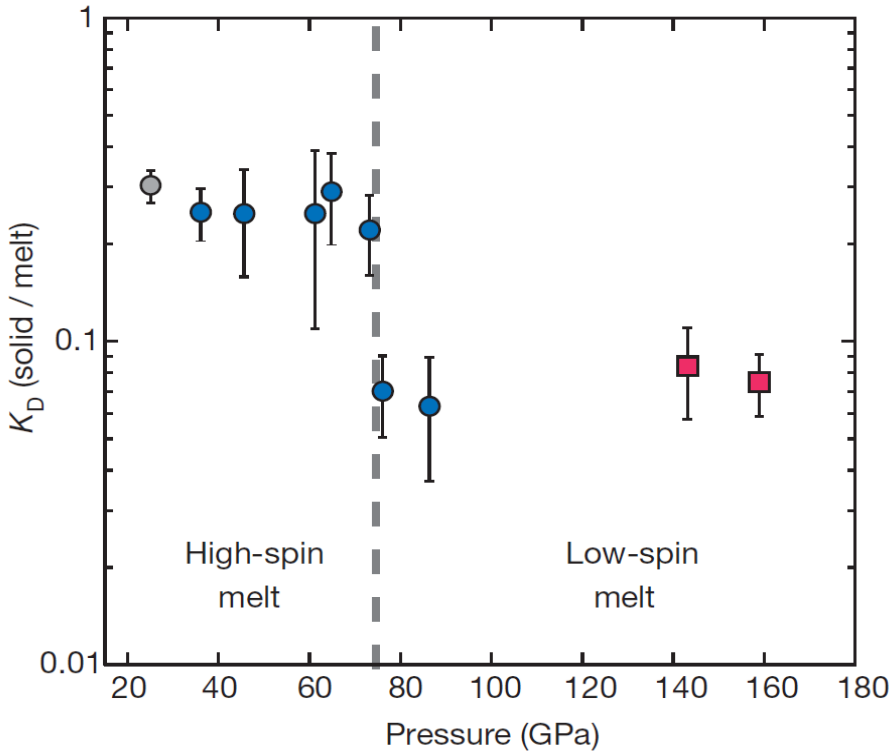


Nomura et al. (2011) attributed the K_D drop to the spin crossover of iron in melts.

$(Mg_{0.95}Fe_{0.05})SiO_3$



$(Mg_{0.89}Fe_{0.11})_2SiO_4$



We conducted both XES and SMS on both Al-free and Al-bearing glasses.

X-ray emission spectroscopy (XES)

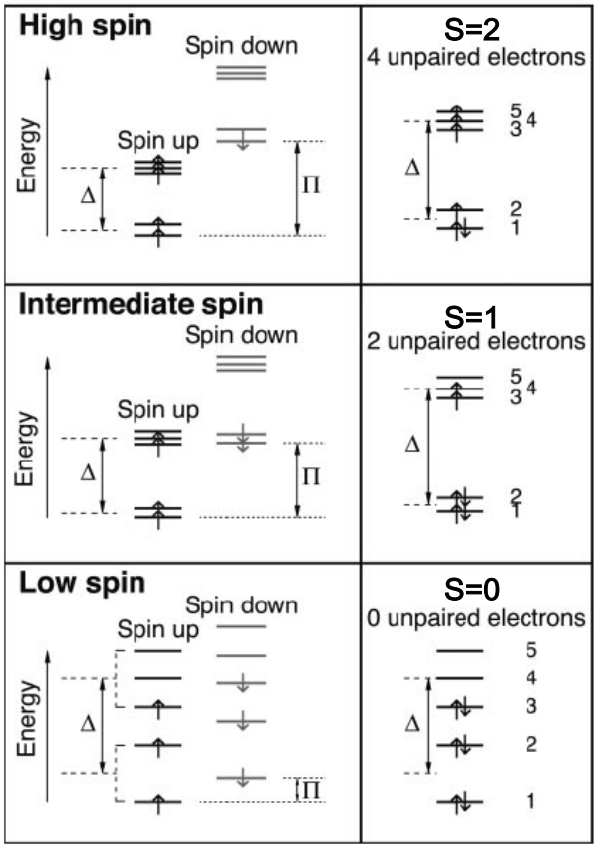
- $(Mg_{0.8}Fe_{0.2})SiO_3$
- $(Mg_{0.8}Fe_{0.2})(Al_{0.1}Si_{0.9})O_3$

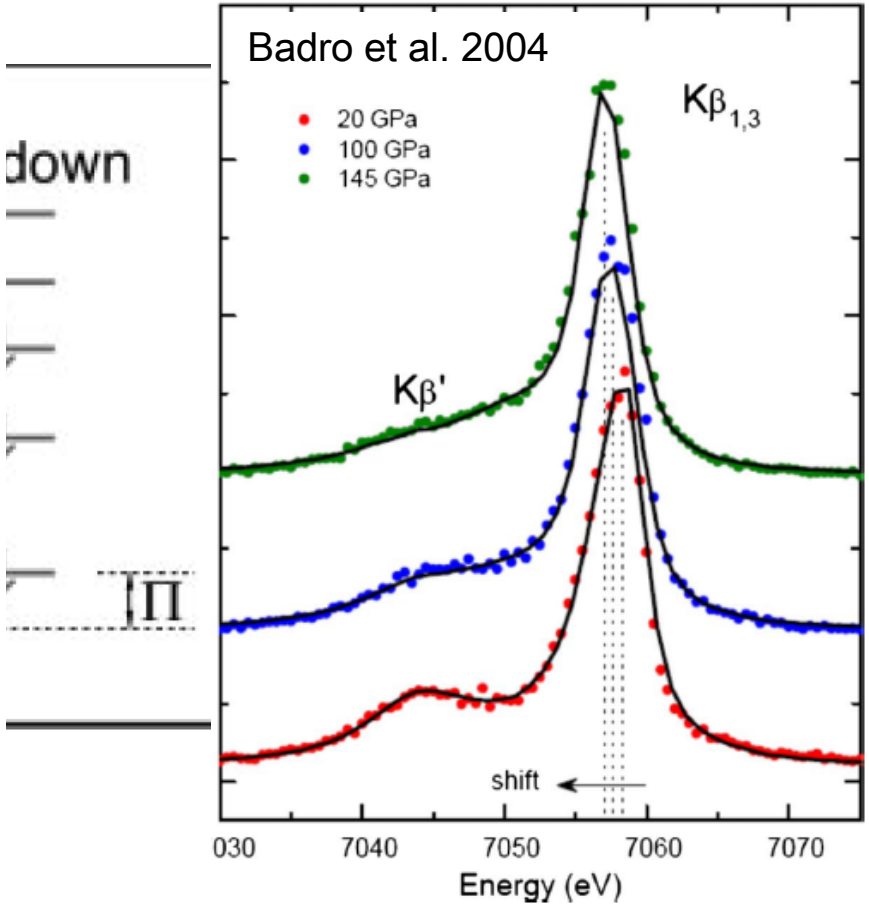
synchrotron Mössbauer spectroscopy (SMS)

- $(Mg_{0.8}Fe_{0.2})SiO_3$
- $(Mg_{0.8}Fe_{0.2})(Al_{0.1}Si_{0.9})O_3$

X-ray emission spectroscopy is sensitive to the average spin number of iron (S).

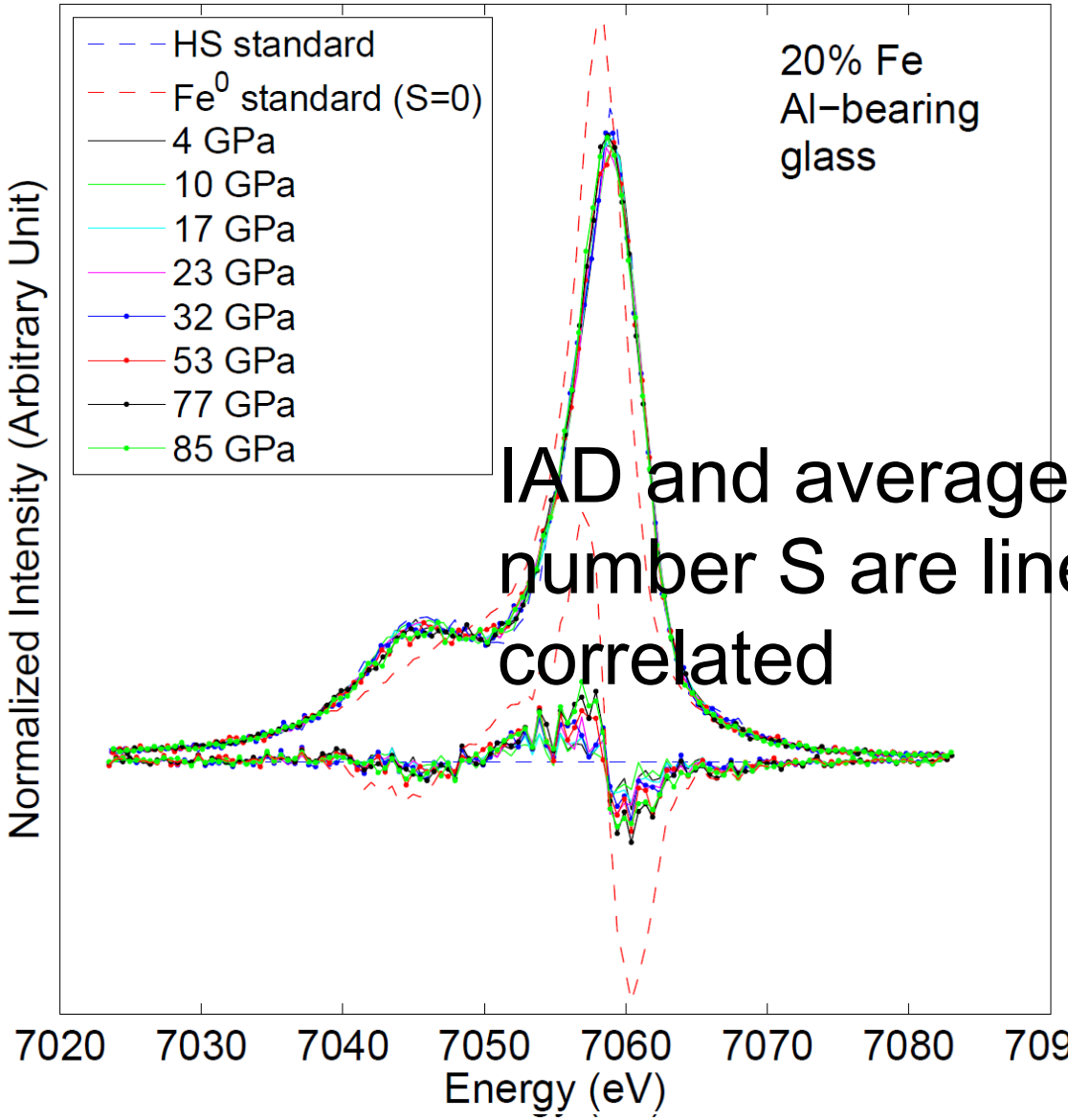
- The average spin number (**S**) equals half of unpaired electron in the *3d* sub-shell of iron.





Source: Li et al. 2004

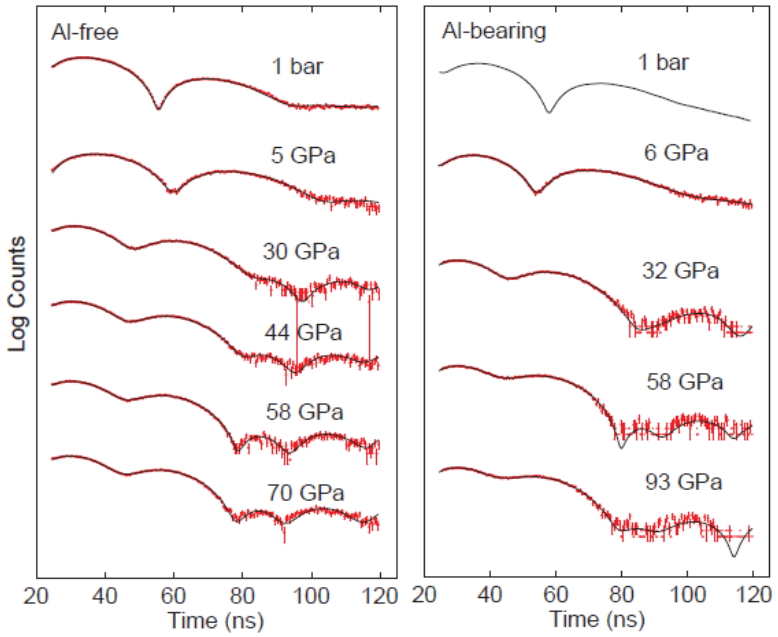
IAD refers to the integral of absolute spectra difference, which is linearly correlated to *S*.



IAD and average spin number S are linearly correlated

Two SMS parameters – 'IS' and 'QS' – reflect the electronic structures of iron.

- Isomer Shift (IS) ← s-electron density of iron
- Quadrupole Splitting (QS) ← 3d-electron distribution and coordination environment of iron
- We can also obtain the population of iron sites with different IS and QS values.

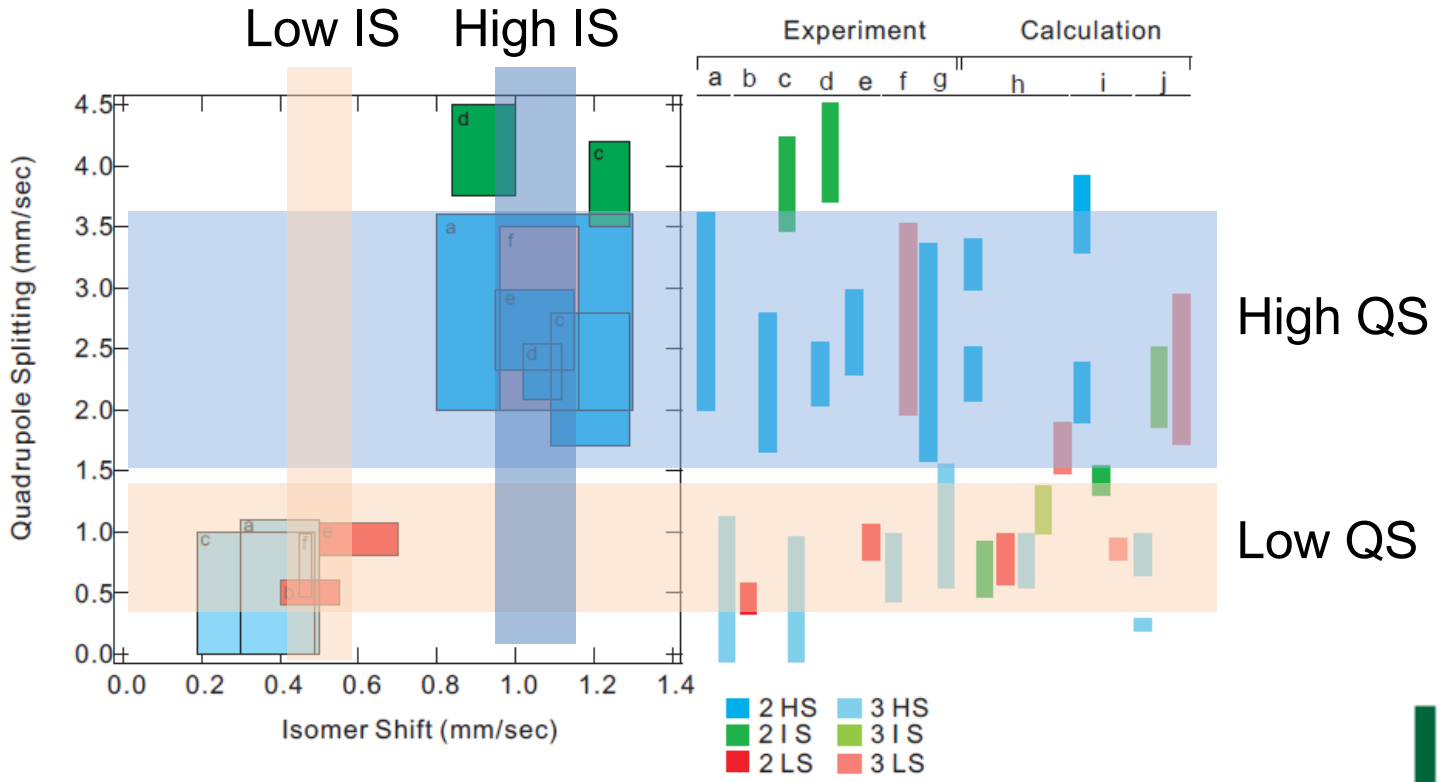


We summarize the SMS parameter ranges of iron with different valence and spin states.

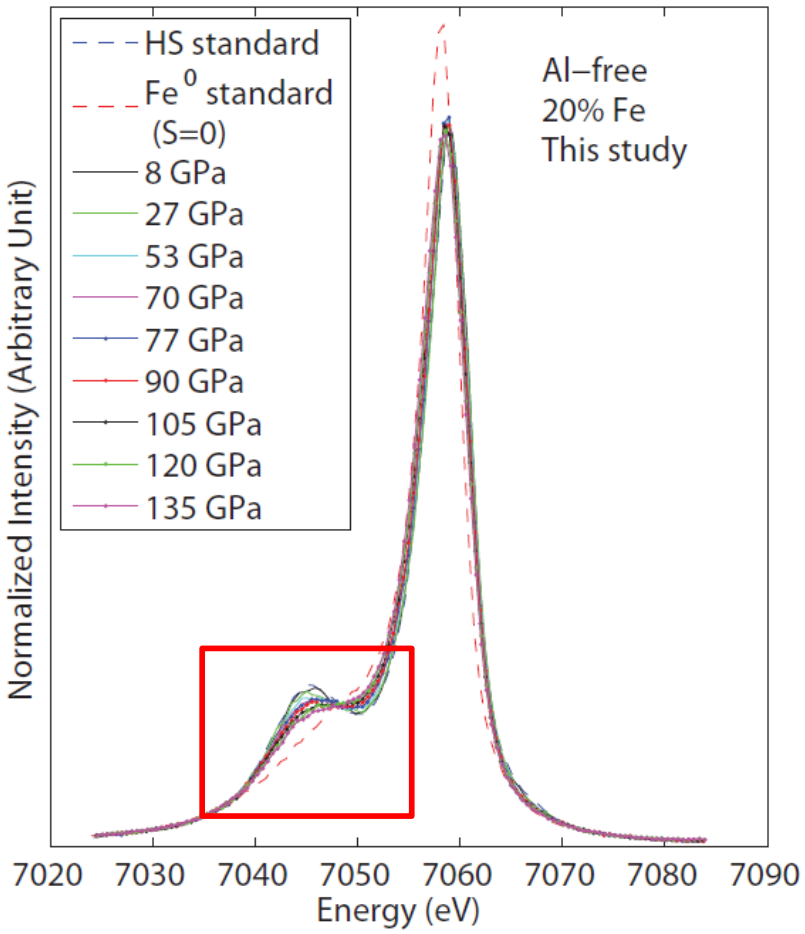
- We notice two obvious QS overlaps:

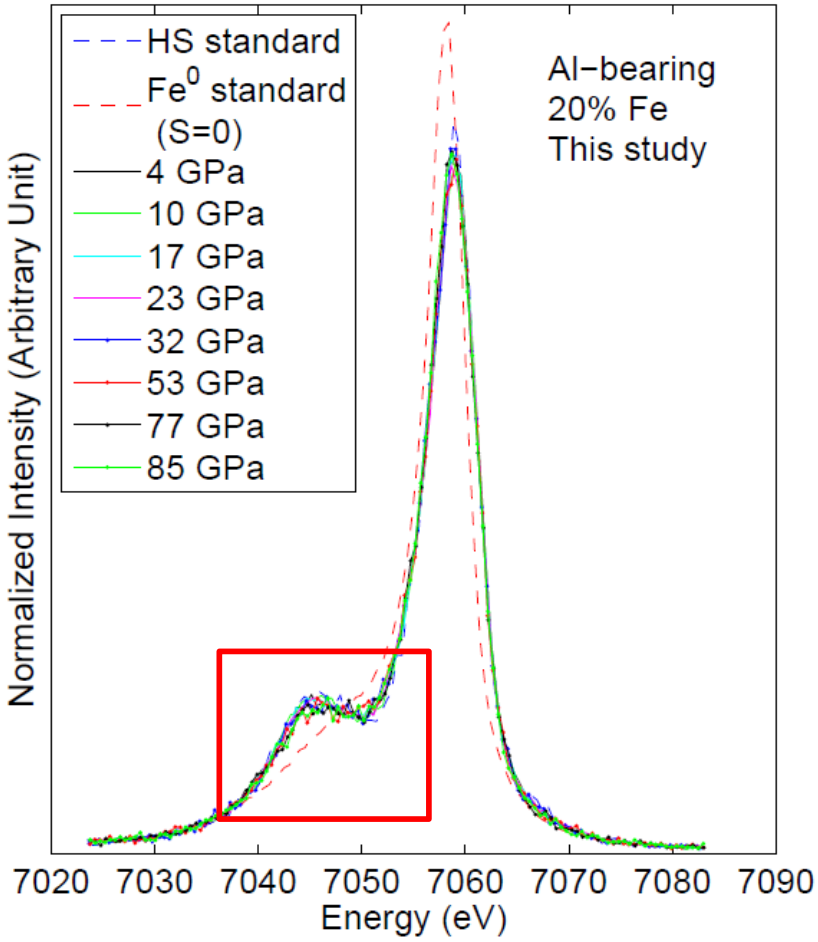
  high-spin Fe^{2+} and intermediate- or low-spin Fe^{3+}

  high-spin Fe^{3+} and intermediate- or low- spin Fe^{2+}

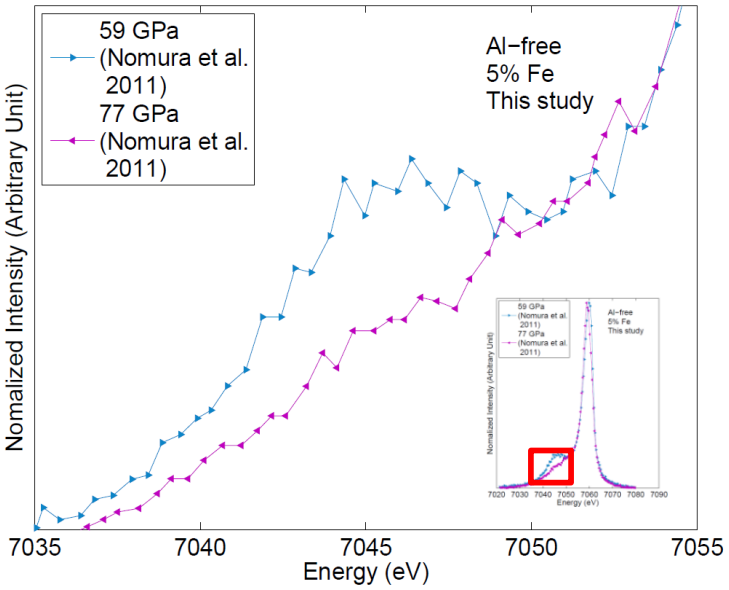


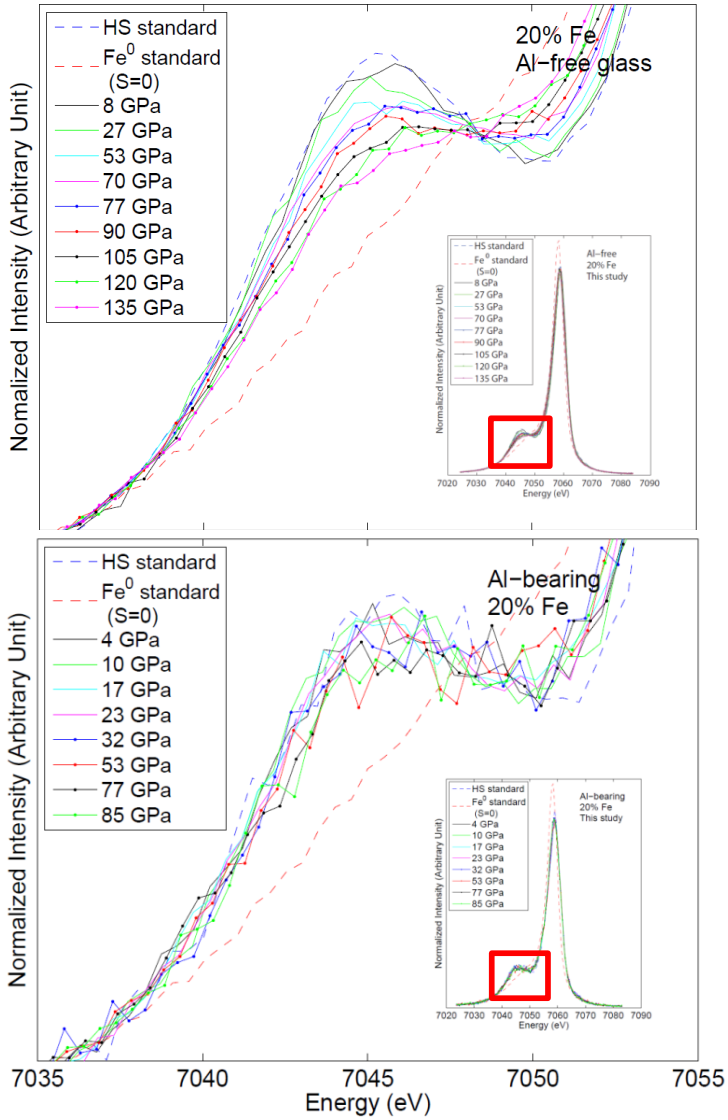
The satellite peak does not vanish in either of the two glass samples up to 135 GPa.





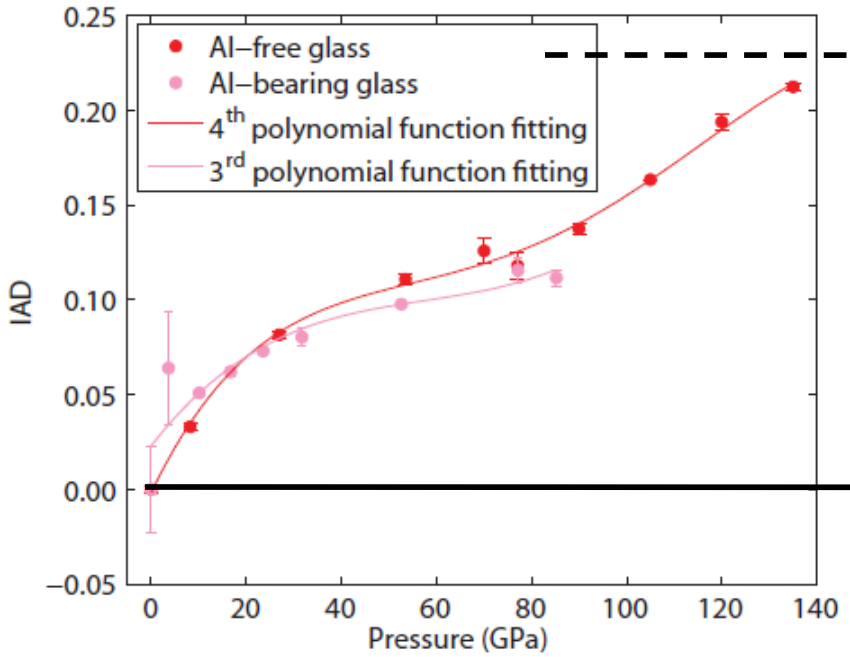
We do not find a sharp satellite peak drop in either of the two glasses.





Quantitative IAD analysis indicates a gradual spin moment decrease of iron.

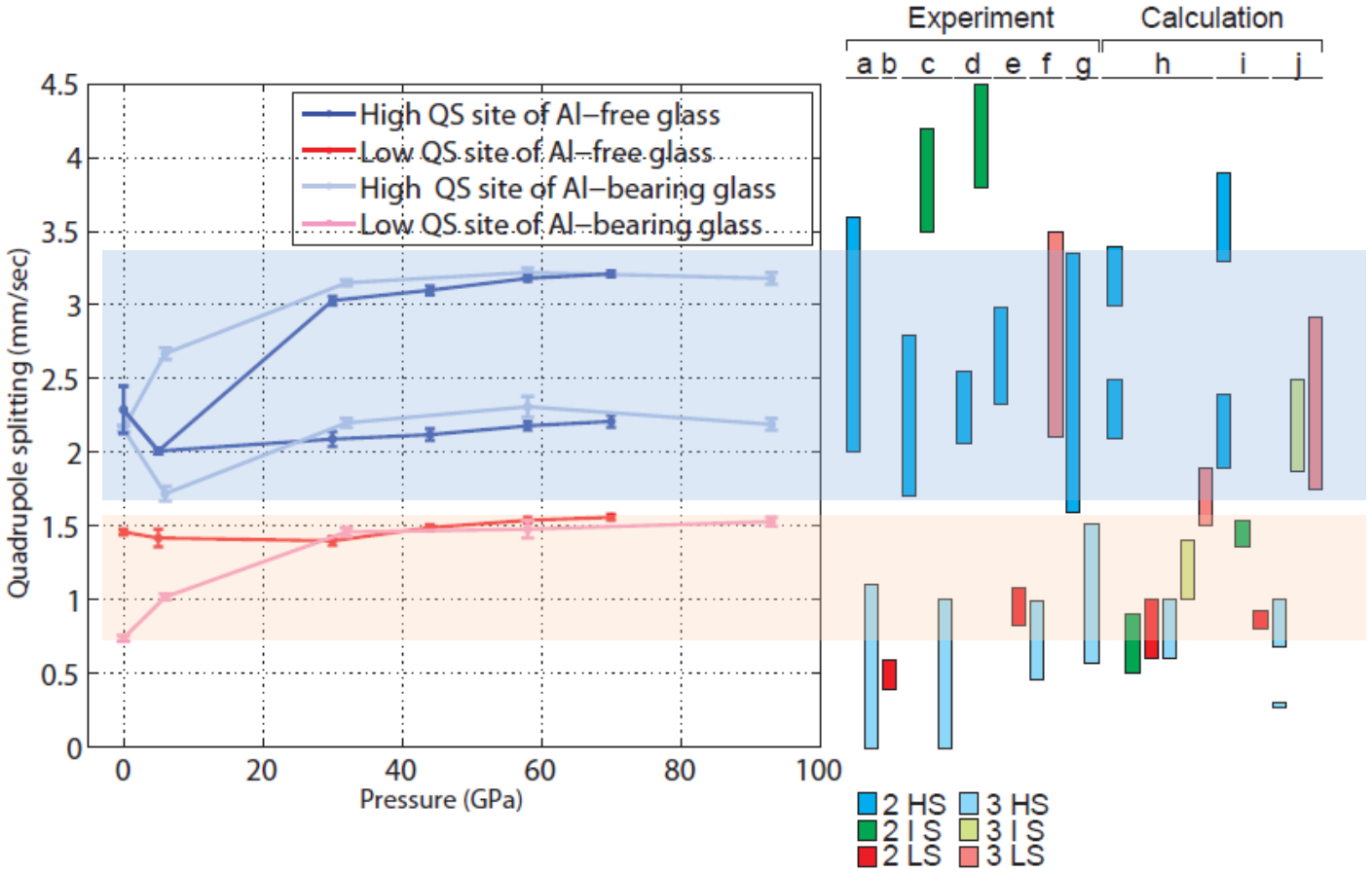
- The gradual IAD changes for both the two glasses are observed.
- We cannot convert the IAD values to the absolute S values only with the high-spin standard.



Low spin:
Unknown up to
135 GPa

High spin:
S=2 for Al-free glass
S≈13/6 for Al-bearing glass

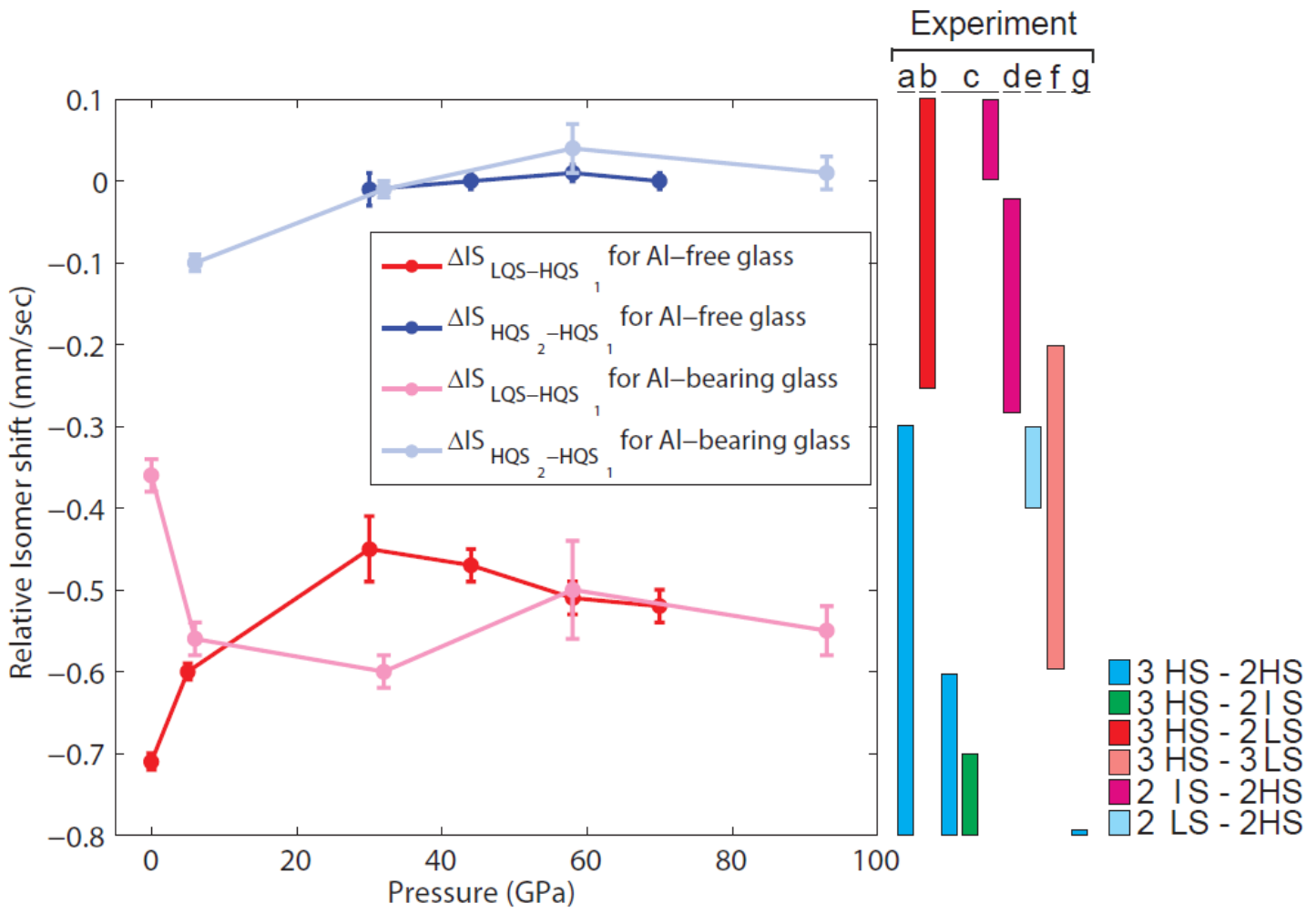
There exist two kinds of sites in both of the two glasses: the high-QS and low-QS sites.



Low-QS sites also show low ΔIS relative to the IS of the high-QS sites.

ΔIS between two high-QS sites

ΔIS between the high-QS and the low-QS sites

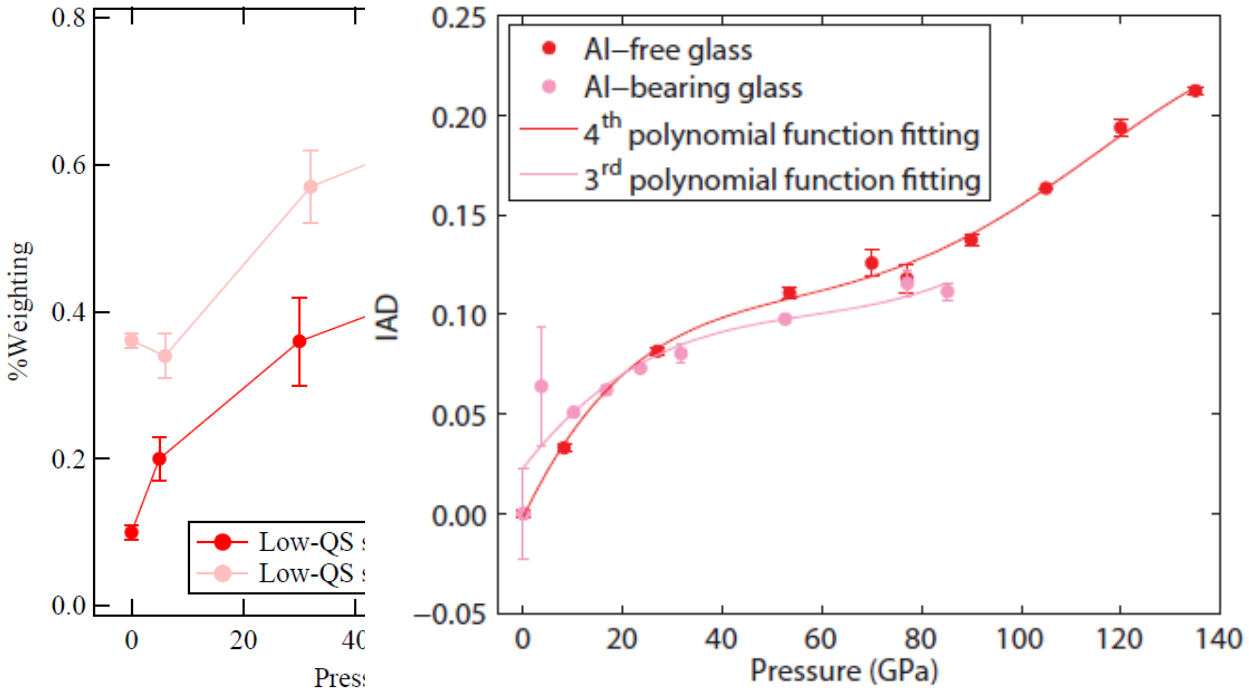


The population of the low-QS sites increases with the pressure.

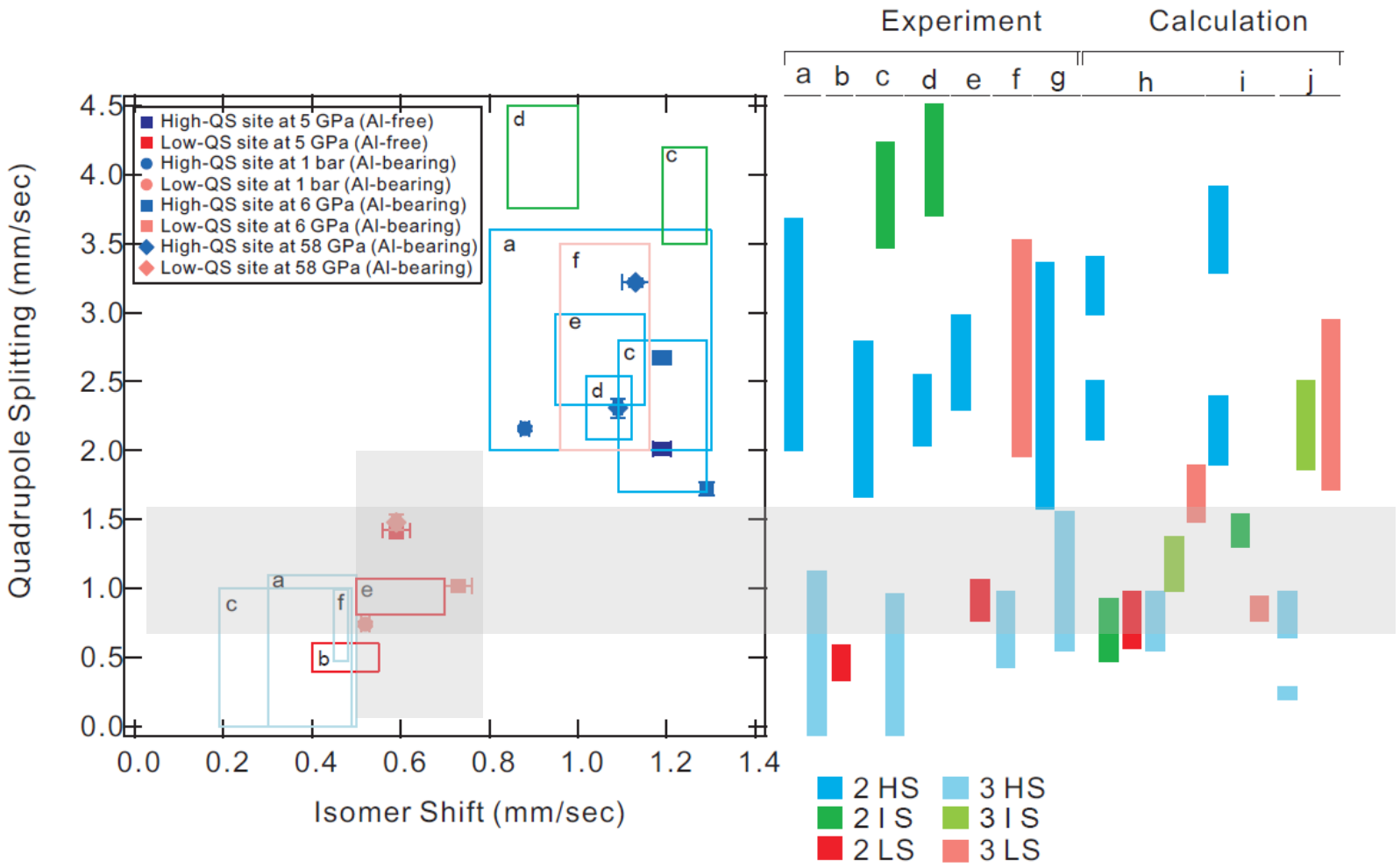
- We notice two obvious QS overlaps:

  High QS: high-spin Fe^{2+} and intermediate- or low-spin Fe^{3+}

  Low QS: high-spin Fe^{3+} and intermediate- or low- spin Fe^{2+}



The low-QS sites locate at a region never reported by previous experimental studies.



We expect a gradual, incomplete and fractional spin crossover of iron in glasses.

- The XES suggested a gradual and incomplete spin crossover of iron for both Al-free and Al-bearing glasses.
- The SMS indicated a gradual and fractional high-spin to intermediate- or low- spin transition of iron.
- The successful combination of XES and SMS provide more constraints to determine the electronic structures of iron.

Our study finds:

- A gradual spin crossover for a fraction of Fe^{2+} occurs in our magnesium silicate glass.
- The Fe^{2+} undergoes the gradual and fractional high-spin to intermediate- or low- spin change over a wide range of pressure.
- Spin effect may be minor (and gradual) for density crossover and iron partitioning in Fe-rich melts.