#6029

Silicon Bonding in Mercury's Magmas

SW Parman[1], BA Anzures[1], JT Cukjati[1], RF Cooper[1], N Dygert[2], MD Mouser[2], H Ohldag[3]

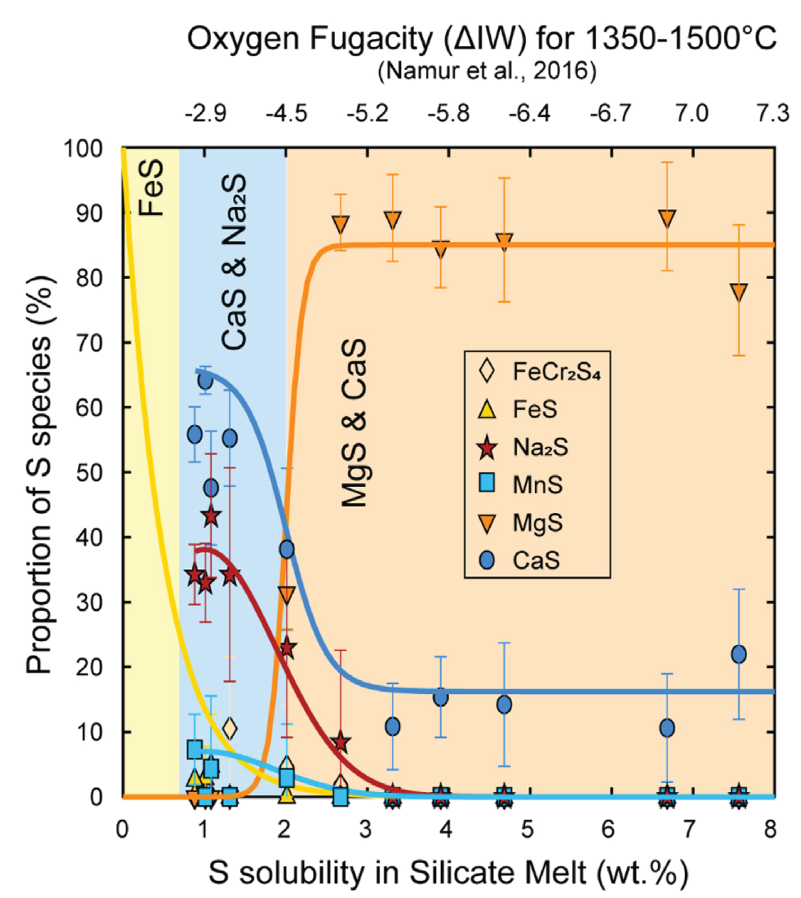
[1]Brown Univ., Providence, RI; [2]Univ. Tennessee, Knoxville, TN; [3]ALS, LBNL, Berkeley, CA

Motivation

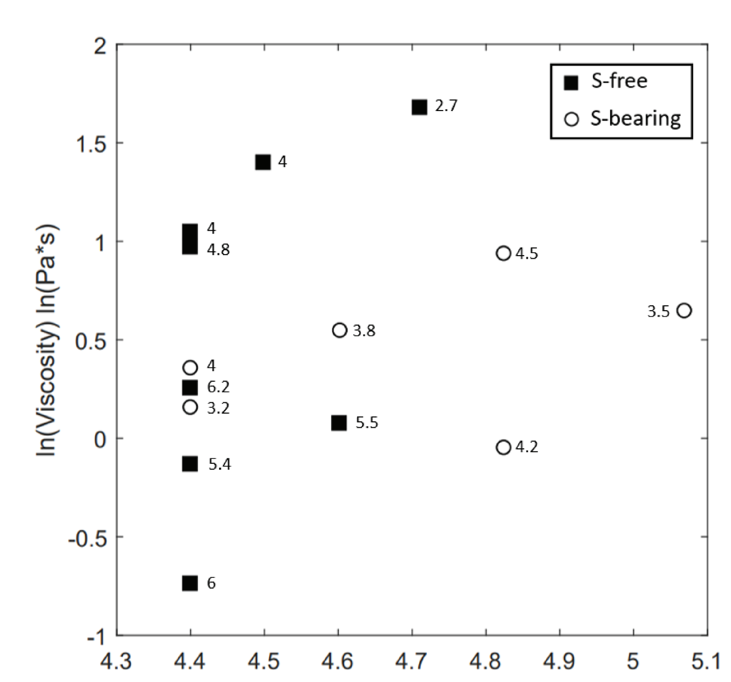
Decreasing oxygen fugacity causes dramatic changes in S and Fe solubility, S speciation and viscosity of silicate melts. Here we explore whether Si valence may also be changing within the silicate melt. If present, Si suboxide (valence<+4) would lower magma viscosity and affect phase equilibria.

Background

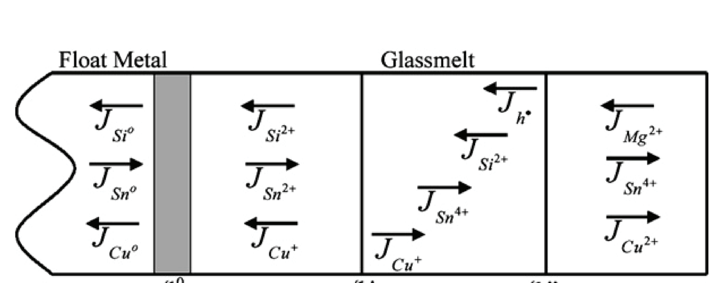
S-speciation - As fO_2 decreases below IW-3, S undergoes a shift from mostly Fe-S bonding, to mostly Ca- and Na-S, to Mg- and Ca-S, in basaltic melts (Anzures et al, 2020).



Viscosity - In-situ falling sphere experiments show that S-rich, highly reduced magmas have low viscosity, relative to S-free experiments (Mouser et al, 2020). However, it is not clear why S should lower viscosity substantially.

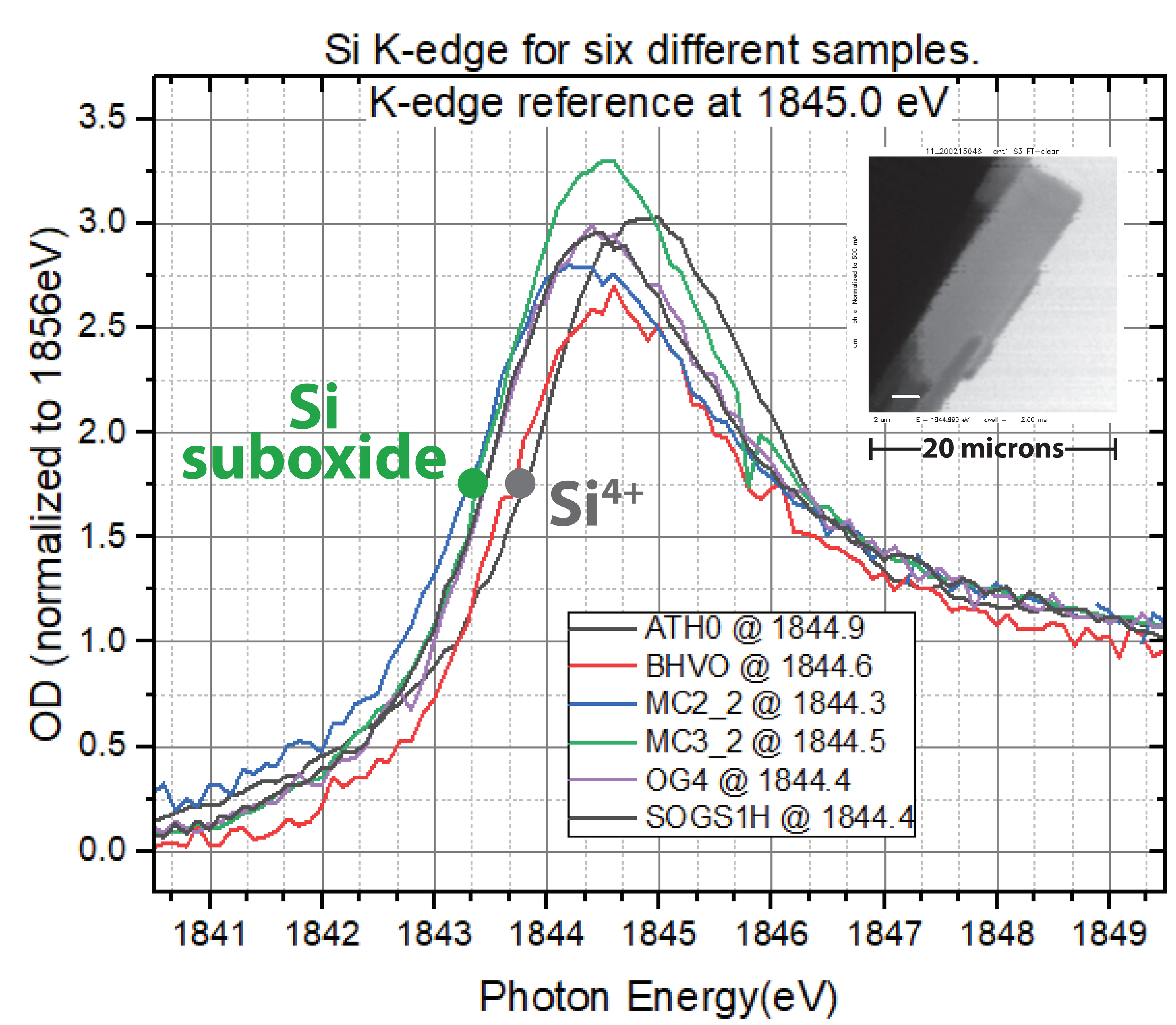


Si suboxide - Experiments on industrial and natural silicate melts indicate that Si^{2+} (or other Si suboxide), is present in highly reduced melts (Peterson and Cooper, 2008; Cooper et al, 2010).



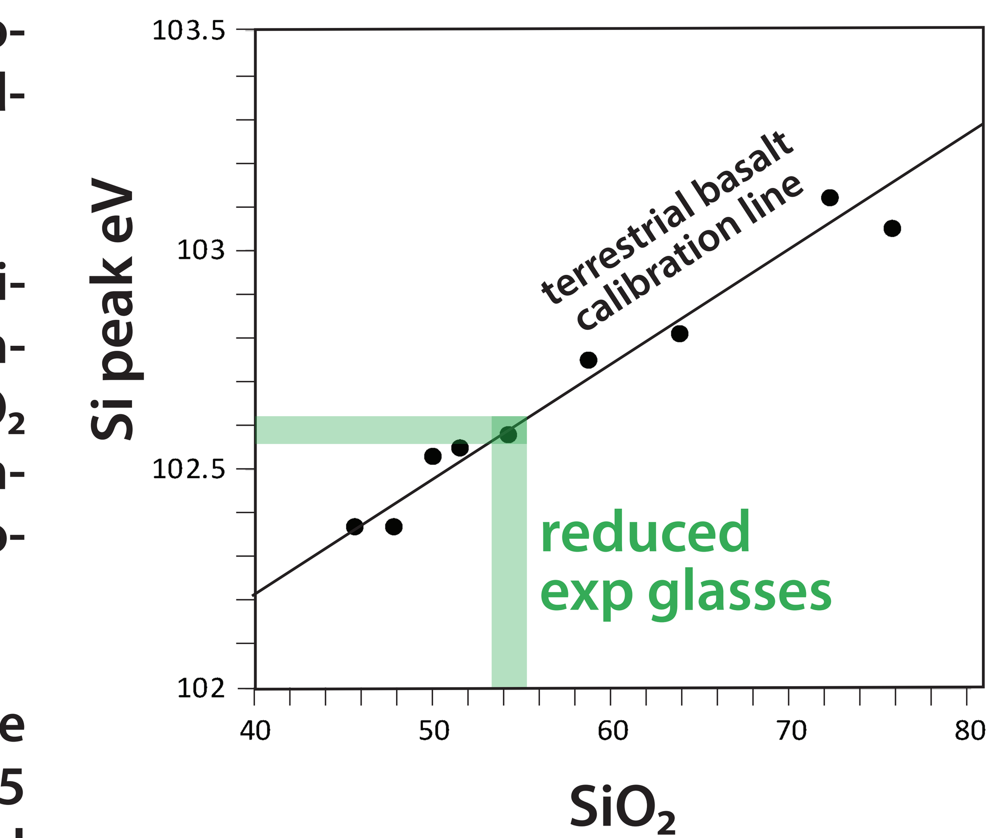
XAS (at ALS)

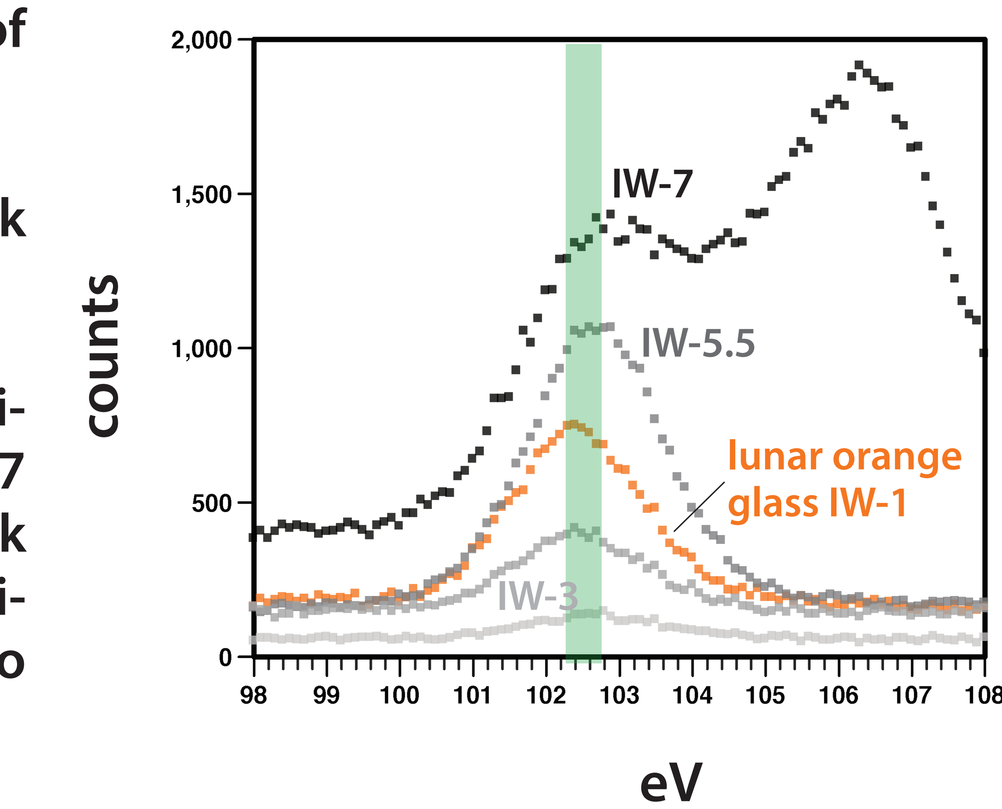
- Synchrotron-based Si K-edge x-ray absorption spectroscopy (XAS) can detect changes in Si bonding and valence in silicate melts.
- Decreasing Si valence below +4 appears as decreases in photon energy of the K-edge (filled circles in figure below).
- In the figure below, the XAS data for two terrestrial basalt glass standards (ATHO and BHVO) are compared to the XAS for four reduced experiments.
- A measurable shift of 0.3-0.6 eV is observed (filled circles), suggesting that some Si suboxide (valence < +4) is present.
- The small size of the shift suggests there is less than ~10 atom% suboxide Si, though this estimate depends on the exact distribution of valences of Si in the melt.
- Inset shows an image of one of the samples. Image is ~ 20 microns across. Samples has been ion thinned to be x-ray transparent for the analyses.



XPS (at Brown)

- XPS (X-ray photoelectron spectroscopy) can also detect changes in Si bonding and valence.
- The top figure shows the Si peak positions for nine terrestrial basalt standards as a function of their SiO_2 conent. The energy of the Si peak increases with increasing SiO_2 and polymerization of the melt.
- The reduced experiments in the bottom figure have SiO_2 between 52.5 and 53.5 wt%. If they were terrestrial basalts, they should have Si peaks of 102.6+/- 0.1 (green region).
- Si suboxide should appear as peak shifts to lower energies.
- The experiments have oxygen fugacities from IW-3 (light gray) to IW-7 (black), but do not show clear peak shifts to lower energies. An experiment on lunar orange glass is also shown, with an fO_2 of IW-1.





Implications & Future Work

- **Both theory and the XAS data suggest a small amount of Si suboxide is present in Mercurian magmas.**
- **XPS analyses does not detect the Si suboxide, which may be below detection limits.**
- **Reduced Si would depolymerize melts and lower their viscosities, as is observed. This could help explain the extensive flood basalts of the smooth plains, even though the magmas are Si-rich.**
- **Si suboxide would also lower SiO_2 activity in the magmas and decrease the stability of SiO_2-rich phases.**
- **Ongoing experiments will measure Si bonding with NMR.**

References: *Anzures et al (2020) GCA 286: 1-18; Mouser et al (2020) LPSC 50, abs# 2030; Peterson and Cooper (2008) J Non-Cryst Solids 354: 3194-3206; Cooper et al (2010) Am Min 95: 810-824.*