



## **Speciation of C-O-H volatiles in reduced magmas applicable to early terrestrial and planetary deep volatile cycles**

Lora Armstrong and Marc Hirschmann

Dept. Earth Sciences, U. Minnesota MN 55455 United States (Marc.M.Hirschmann-1@umn.edu)

The speciation and solubility of C-O-H volatiles in reduced magmas are of great importance for volatile behavior in the early Earth and other planets determining partitioning between Earth's earliest atmospheres, mantle, and cores, as well as influencing volcanogenic degassing on reduced planetary bodies such as Mars and the Moon. In mafic and ultramafic magmas, C is soluble chiefly as carbonate under oxidizing conditions, but when  $fO_2$  is below that required for graphite (or diamond) saturation, carbonate solubility diminishes severely. This has left the question as to what, if any, species may host dissolved C in magmas under reducing conditions. Initial results suggested that the principle species may be  $CH_4$  (Mysen et al. 2009), but experiments at well-defined thermodynamic conditions have shown that  $CH_4$  solubility is very small except under conditions of very high  $H_2$  fugacity (Ardia et al. 2012). More recent experiments (Wetzel et al. 2013; Stanley et al. 2014) have identified Fe-carbonyl-like species as possibly the most stable. To clarify the relative stability of these species, we have conducted additional high pressure experiments at 1.2 GPa and 1400°C with graphite-saturated martian and terrestrial (MORB) basalt compositions, over a range of oxygen fugacities, paying careful attention to the availability of  $H_2O$ . FTIR and Raman analyses reveal a range of distinct species that predominate as a function of  $fO_2$  and availability of  $H_2O$ . At comparatively oxidizing conditions, carbonate is the most abundant species but within 1 log unit of iron wustite (IW), carbonyl-like species predominate, provided that conditions are comparatively dry. At yet more reducing conditions, carbonyl is absent and instead N-H associated species (perhaps amides?) are more important. Methane is observed only when quenched glasses have appreciable  $H_2O$  (approaching  $\sim 1$  wt.%). In all cases, solubilities are small when conditions are reduced, with  $<100$  ppm C at IW or below.