Oxygen Fugacity in Large Metal Capsules

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The oxygen fugacity in experimental samples encapsulatedin in metals with and without added metal oxide is freqeuntly assumed to be set by the respective metal-oxide buffer. The oxygen fugacity in the sample interior is, however, not usually directly examined. Equilibration of the samples is assumed to be diffusive, but it is not clear what the diffusing species is. This is a particular concern in large capsules used for deformation and seismic property experiments, with capsule diameters of 8 - 12 mm.

To determine the fO2 in large capsules, we performed experiments with olivine encapsulated or wrapped in four different metals (Fe, Ni70Fe30, Ni and Pt). Small Pt particles mixed with olivine powder were used as fO2 sensors via the partitioning of Fe or Ni between olivine and Pt-metal alloy. The results show an ordering of the fO2 in the sample interior that is consistent with the enclosing metals, i.e. the fO2 is lowest in Fe and highest in a Pt. However, fO2 values in the interior of the more oxidizing metal capsules are substantially below their respective metal-oxide buffers. For example, the oxygen fugacity of olivine encapsulated in Ni is more than two orders of magnitude below Ni-NiO at 1200ºC and 0.3 GPa after a 24 hour experiment.

Sample-capsule interfaces in Pt and Ni capsules show two distinct diffusive gradients: Fe loss of olivine into the metals extends to over 100 micron into the samples with Mg# at the interface increased from 90 to 98. Analysis of the PtFe particles in a band perpendicular to the capsule surface show gradients in fO2 extending 1.5 mm into the sample in Pt and <0.5 mm in Ni. These fO2 gradients may result from reduction of Fe at the capsule surface and consequent diffusion of the excess oxygen into the interior via grain boundaries. A third diffusive timescale is inferred from the fact that fO2 changes with metal capsule. The spatial scales of the three processes imply diffusivities that differ by at least four orders of magnitude.

Full equilibration of the oxygen fugacity in sample interiors with a metal oxide buffer may therefore be governed by the timescale of grain boundary diffusion of oxygen.