HIGH TEMPERATURE FORMATION OF FEO-RICH OLIVINE IN THE EARLY SOLAR SYSTEM:
EXPERIMENTAL SIMULATION WITH THERMODYNAMIC AND KINETIC ANALYSIS OF A SOLID-
SOLID REACTION MEDIATED BY A GAS PHASE. R. Dohmen, S. Chakraborty, H. Palme and W.
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Olivine with FeO-contents below 1% is the first major silicate mineral to condense from a cooling solar nebula. Condensation calculations predict higher FeO-olivine only at rather low temperatures predominantly by the reaction of metallic FeNi with pyroxene which requires solid state diffusion [1]. The presence of forsteritic olivine with fayalitic rims and sharp compositional FeO-zoning in type 3 carbonaceous chondrites [2] is not expected from equilibrium thermodynamic calculations. As a solution high temperatures and more oxidizing conditions than those assumed for the canonical solar nebula have been proposed. Vaporized chondritic material would have to deliver the excess oxygen [3]. We show that a solid-gas reaction mechanism can satisfactorily account for all of these factors. Addition of foreign oxygen is not even required.

To study the kinetics and mechanism of the reaction of forsterite with a gas phase, we have carried out several Knudsen-cell mass-spectrometry (KMS) experiments in a special configuration: The principle is that Fe-metal and poly- or single crystals of olivine which are not in physical contact are heated simultaneously in a Knudsen-cell. Therefore, a reaction of Fe-metal with olivine is only possible via the gas phase. The experiments were carried out at 1400°C for 20 hours and KMS allowed us to observe the reaction progress continuously and in situ by monitoring the identity and concentration of chemical species in the gas phase. Polycrystals of forsterites were found to contain 4 to 74 mol% FeO after the experiments, depending on redox conditions. This requires Mg-loss via the gas-phase, which is actually observed with KMS. On single crystal surfaces (synthetic forsterite, San Carlos) spectacular fayalitic films, up to 0.5 mm thick and with fayalite contents of up to 95 mol% were formed. The fayalitic films resemble those observed in chondrules of C3-chondrites around forsterite.

Thermodynamic calculations and reaction modeling show that the observations are consistent with available thermodynamic data and allow us to determine the parameters controlling reaction progress. A key parameter is the ratio \( \frac{P_{Fe}}{P_{Mg}} \), which determines the fayalite content of olivine according to the exchange reaction:

\[
Fe(g) + MgSiO_3(s) = Mg(g) + FeSiO_3(s) \quad (1)
\]

In our experiments \( P_{Fe} \) is fixed by the presence of Fe-metal. Continuous effusion of Mg out of the Knudsen-cell shifts reaction (1) progressively to the right, until the ambient Fe-pressure, the olivine composition and the flux of Mg out of the cell attain a steady-state, pseudo-equilibrium condition. Redox conditions influence the reaction indirectly. An increase of oxygen fugacity results in a decrease of the partial pressure of Mg through the equilibrium constant \( K = \frac{P_{Mg}}{P_{SiO}^2 \cdot P_{O_2}^{3/2}} \) of the evaporation reaction:

\[
Mg_2SiO_4(s) = 2Mg(g) + SiO(g) + 3/2O_2(g)
\]

Thus, with increasing oxygen fugacity we obtain larger \( \frac{P_{Fe}}{P_{Mg}} \) which in turn results in an increase of the fayalite content of product olivine.

Non-equilibrium reaction modeling was performed in an iterative sequence of “reaction” and “transport” (gas flux) steps. It shows that the time-dependent evolution of the gas phase and the FeO-content of olivine not only depends on temperature, but also on various other parameters, like the size of the reaction system or the reactive surface area of olivine. The latter explains the difference between poly- and single crystal experiments. Further, local variations in modal abundances or any of the other controlling parameters can cause local fluctuations in oxygen fugacity or \( \frac{P_{Fe}}{P_{Mg}} \) causing the production of Fa-rich olivines of various compositions.