

## Redox kinetics of olivine revealed by diffusion profile of oxygen fugacity and its implication to the redox evolution of the uppermost mantle

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The evolution of the redox state of the mantle through time has been a focus of hot debate. Recent study implies that the redox budget of the slab may not be significantly changed during subduction [1]. Thus, ferric iron transported by oxidized slab is expected to change the redox state of the upper mantle. However, concentrations of Cr, V, and the V/Sc ratio of the oldest known rocks indicate that the uppermost mantle has remained at approximately FMQ over the past 3.5 Gyrs [2, 3]. Therefore, it seems that although oxidized slab is continuously subducted into mantle, the redox state of the upper mantle does not change systematically. It is possible that the mantle represents an almost infinite buffer reservoir and renders the addition of oxidized slab ineffective. On the other hand, the possible extremely slow reaction speed between slab and the uppermost mantle materials might disable the oxidized component to be an effective redox changer. However, the mechanism of the interaction between them remains unclear, which is of great urgent to investigate.

Olivine ( $\text{MgO}$ ,  $\text{SiO}_2$  and  $\text{Fe}_2\text{O}_3$  oxide mixture) with 5 wt% Pt powder used as oxygen sensor was first synthesized using gas mixture furnace at iron-wustite (IW) buffer and Ni-NiO (NNO) buffered condition at 1300 °C. Diffusion couple method is adopted to investigate the redox kinetics of olivine, within which pre-sintered piece of oxidized and reduced olivine was stacked face to face. Diffusion experiments were conducted for different durations at 1 GPa, 1100-1300 °C using piston cylinder apparatus. After recovery, oxygen fugacity profiles were calculated from iron fraction in Pt alloy and iron content in olivine measured by EPMA [4]. Diffusion coefficients were obtained using Boltzmann-Matano method through fitting and calculation of iron content in Pt alloy as a function of distance from Matano interface. Water content after diffusion was measured using FTIR.

Except one couple, the water content of all the other couples shows < 10 wt. ppm. Redox process in olivine could be viewed as a diffusion-controlled process. Diffusion coefficient in oxidized olivine shows obvious oxygen fugacity dependence, while that in reduced one shows small dependence. The activation enthalpy is calculated to be 235 kJ/mol, which is comparable with that for Fe-Mg diffusion in olivine. However, the magnitude is 2-4 orders higher. Since the activation enthalpy and magnitude are comparable with that of diffusion of hydrous defects related to Mg-vacancies [5], it is possible that even extremely small amount of water could dominate redox kinetics in olivine. The diffusion length calculated indicate that the influence exerted by slab on the reduced mantle is very limited (< 4 km at 1600 °C even for 4500 Ma' s stagnation in the upper mantle). Therefore, it is possible that the extremely slow redox process prevents subducted slab to change the redox state of the upper mantle. Once subducted more, the oxidized slab can bring redox budget to deep mantle as it keeps dry condition.

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