

## **Hydrogen in diopside: Diffusion, kinetics of extraction-incorporation, and solubility**

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### **ABSTRACT**

The kinetic of H extraction-incorporation in diopside single-crystals ( $\text{Ca}_{0.97}\text{Na}_{0.02}\text{Cr}_{0.01}\text{Mg}_{0.97}\text{Fe}_{0.036}\text{Si}_{1.99}\text{O}_6$ ) deduced by monitoring OH infrared absorption bands for samples heated from 973 to 1273 K at 0.1 atm and 1 atm of  $\text{pH}_2$ , is independent of crystallographic orientation,  $P_{\text{O}_2}$ , and  $\text{pH}_2$ . The diffusion law is  $D = D_0 \exp[-(126 \pm 24) \text{ kJ/mol}/RT]$ , with  $\log D_0$  (in  $\text{m}^2/\text{s}$ ) =  $-6.7 \pm 1.1$ . Hydrogen self-diffusion obtained from H-D exchange in the same diopside samples over 873–1173 K, and along directions [001] and [100]\* at 1 atm total pressure is two orders of magnitude faster than H uptake and follows the diffusion law  $D_{\text{H}} = D_0 \exp[-(149 \pm 16) \text{ kJ/mol}/RT]$ , with  $\log D_0$  (in  $\text{m}^2/\text{s}$ ) =  $-3.4 \pm 0.8$ . Self-diffusion along [010] follows the diffusion law  $D_{\text{H}} = D_0 \exp[-(143 \pm 33) \text{ kJ/mol}/RT]$ , with  $\log D_0$  (in  $\text{m}^2/\text{s}$ ) =  $-5.0 \pm 1.7$  and is one order of magnitude faster than H uptake. The kinetics of extraction incorporation of H in this diopside follows the reaction  $\text{Fe}^{3+} + \text{O}^{2-} + 1/2\text{H}_2(\text{g}) = \text{Fe}^{2+} + \text{OH}^-$  and are not rate limited by the mobility of protons but more probably by the mobility of electron holes connected with the Fe oxidation-reduction process. The results suggest that the kinetics of H uptake in clinopyroxenes will increase with increasing Fe content until it is rate controlled by the kinetics of H self-diffusion. We predict a rate for H exchange in diopside appropriate to the upper mantle almost as fast as H exchange in olivine. The insensitivity of H solubility on temperature and  $P_{\text{O}_2}$  for samples recovered from low-temperature conditions (below 1273 K) and/or rapidly quenched samples let us suggest the use of OH concentration measurements in diopside as a potential  $\text{pH}_2$  sensor.