**Abstract** Kinetics of hydrogen extraction were investigated by FTIR spectroscopy on a Dora Maira pyrope single crystal. Annealing experiments were performed at ambient pressure, between 1073 and 1323 K, and under two different redox conditions ($p_{O_2} = 0.21$ atm and $p_{O_2} > 10^{-16}$ atm). During hydrogen extraction the two principal OH absorption bands behave independently. The OHa triplet, centred on 3651 cm$^{-1}$, decreases at least five times faster than the OHb band at 3602 cm$^{-1}$. This suggests the presence of two distinct H defects, each with its own kinetics, which are slightly dependent on oxygen partial pressure:

$$D_{\text{OHa}} = D_0 p_{O_2}^{0.119} \exp \left[ \frac{-(277 \pm 22) \text{kJ/mol}}{RT} \right],$$

with $\log D_0 (\text{m}^2\text{s}^{-1}) = 0.5 \pm 1.0$

$$D_{\text{OHb}} = D_0 p_{O_2}^{0.147} \exp \left[ \frac{-(329 \pm 21) \text{kJ/mol}}{RT} \right],$$

with $\log D_0 (\text{m}^2\text{s}^{-1}) = 1.9 \pm 0.9$.

Both kinetics are slower than previous data (Wang et al. 1996), but activation energies are similar. At the same time as the OHa bands decrease, an exchange of hydrogen from OHa to OHb occurs. The extent of this transfer can be modelled by assuming it is directly proportional to the fraction of OHa band which has been removed, independent of temperature. This suggests that OHb defects could be produced by partial dehydrogenation of OHa defects. Activation energies and values of diffusion coefficients are very close to those found by Kohlstedt and Mackwell (1998) for the diffusion of metal vacancies in olivine. Thus it is very likely that cation vacancies control the kinetics of dehydrogenation reactions in pyrope.

**Keywords** Pyrope · Hydrogen · Water · Upper mantle · Diffusion

**Introduction**

The Earth’s upper mantle is essentially composed of nominally anhydrous minerals. Since the early 1970s (Martin and Donnay 1972), it has been known that these phases contain small amounts of hydrogen (tens to a few hundred ppm wt H$_2$O) incorporated as point defects. Many studies have shown that nominally anhydrous minerals play a key role in the water budget of the upper mantle or, more generally, in the water cycle of the Earth’s interior (Bell and Rossman 1992; Thompson 1992; Ingrin and Skogby 2000; Williams and Hemley 2001). Kinetics data on hydrogen mobility in the main upper mantle phases are essential to quantify the dynamics of this cycle.

In garnets, it has been pointed out that several mechanisms of hydrogen incorporation occur and that several types of H-defects coexist (e.g. Geiger et al. 1991; Lager et al. 1989; Rossman et al. 1989; Rossman and Aines 1991; Andrut et al. 2002). The hydrogarnet substitution, which corresponds to the replacement of Si$^{4+}$ by 4 H$^+$ in the tetrahedral site, represents the best-characterized mechanism of hydrogen incorporation (e.g. Cohen-Addad et al. 1967; Harmon et al. 1982; Lager et al. 1987, 1989); but other H defects, like the incorporation of isolated OH or clusters of two or three OH, may also occur (e.g. Cho and Rossman 1993; Khomenko et al. 1994).

Very few kinetics experiments have been performed in garnets. Wang et al. (1996) report the dehydrogenation in air of natural pyrope megacrysts extracted from mantle xenoliths and we recently investigated the kinetics of H–D exchange in pyropes from both mantle...
xenoliths and a metamorphic unit (Blanchard and Ingrin 2004). These works have placed constraints on the extrapolation of hydrogen-exchange kinetics to mantle conditions but give no further constraints on the number and nature of hydrogen defects in pyrope. In this study, we characterize the kinetics of hydrogen extraction in a natural pyrope single crystal that comes from the Dora Maira metamorphic unit (Italian Alps). Experiments were performed under two very different redox conditions in order to investigate a possible dependence on oxygen partial pressure.

**Experimental**

**Starting material**

Pyrope samples used here were prepared from the same single crystal as used for the determination of the H–D exchange kinetics (Blanchard and Ingrin 2004). It is a large, pale pink crystal of about 8 mm in diameter that comes from the ultra high-pressure metamorphic unit of Dora Maira in the Italian Alps (Chopin 1984). The crystal is chemically zoned within the marginal zone of Dora Maira metamorphic unit (Italian Alps). Experiments were performed under two very different redox conditions in order to investigate a possible dependence on oxygen partial pressure.

Heat treatments were carried out at ambient pressure in a horizontal furnace in which the sample was isolated from the heating elements (lanthanum chromite) by an alumina tube of 18 mm internal diameter. Temperature was controlled by a Pt/PtRh10% thermocouple located less than 5 mm from the sample. We estimate the uncertainty in temperature to be less than ± 5 °C.

In order to investigate a possible dependence of hydrogen extraction on oxygen fugacity, two types of experiments were performed: in air and under reducing conditions. For annealing in air, the alumina tube was kept open. In the other case, a 90% Ar + 10% H₂ gas mixture flowed through water before passing into the furnace. The alumina tube was flushed with the gas mixture for 30 min before the heating started. In order to avoid an overshoot, a heating ramp was programmed to reach the final temperature in 60 min.

**Analytical solution**

Because the thickness of the sample is small compared to its width, we assume that diffusion is essentially one-dimensional and can be described by equations for an infinite plate with a homogeneous initial concentration. For this geometry, the solution of the Fick's second law (Carslaw and Jaeger 1959) for a concentration, C, of

![Fig. 1](image)

**Fig. 1** Evolution of infrared absorption spectra with increasing time of heating in the region 3900–3300 cm⁻¹. Sample Dora 6, annealed at 1123 K in air. Spectra were taken with a circular aperture of 600 μm in diameter at a resolution of 4 cm⁻¹.