INTRODUCTION

In concentrations ranging from parts per million to weight percent, hydrogen is always present in natural minerals or melts in the form of a variety of species with different redox states (H+, OH–, H2O, or H2) (Ingrin and Skogby 2000; Johnson et al. 1994; Schmidt et al. 1998; Stolper 1982). The identification of the nature and the mobility of the different H species is a key for understanding the Earth because H incorporation in mineral or melt dramatically modifies their physical properties. In nominally anhydrous minerals (NAM), the kinetics and mechanisms of H incorporation or extraction have been and still are studied intensively. Water-derived species incorporation/extraction in NAM recently has been revealed to evolve through a two-stage process (Kohlstedt and Mackwell 1998). The fastest stage was demonstrated to be related to redox processes involving H motion as protons and electronic defects related to Fe3+-Fe2+ exchange (Kohlstedt and Mackwell 1998; Hercule and Ingrin 1999). Therefore, both the H content and Fe 3+/Fe2+ ratio in NAM are strongly interdependent parameters. The slower stage does not involve redox exchanges and seems to be associated with intrinsic defect mobility (Kohlstedt and Mackwell 1998).

With respect to silicate melts, it is generally accepted that

H-bearing species diffuse as H2O molecules (e.g., Zhang et al. 1991; Behrens and Nowak 1997). However, at low water contents (<0.8 wt%) the mobile water-derived species may be NaH2O+, H3O+, or H+ (Stanton et al. 1990). Schmidt et al. (1998) have also identified the possibility of hydrogen incorporation as H2 molecules in Fe-free silicate melts. In natural melts, which all contain H and Fe, redox interactions occur between H2-H2O and Fe3+-Fe2+ (Gaillard et al. 2002). Currently, the mechanisms and the mobilities of the species involved in these interactions are still not known accurately.

Gaillard et al. (2002) studied the kinetics of Fe redox reactions at 2 kb in H2O-rich (5–6 wt%), Fe-poor (1–3 wt% FeOtot) melts that occur in response to variations of hydrogen fugacity (fH2). No redox fronts were observed. The kinetic data were interpreted in terms of a two-step reaction mechanism that involves first a virtually instantaneous diffusion of H2 in the sample and then slower structural/chemical reorganizations, involving slower interactions of water-derived species with Fe in the melt. Oxidation-reduction of Fe in these low-Fe, high-H2O rhyolitic melts is reaction-limited, in contrast to the diffusion-limited process identified by Cooper et al. (1996) for the oxidation of dry basaltic melts.

From these two studies, it is clear that the redox mechanisms in silicate melts strongly depend on the presence or absence of hydrogen (as H2 and OH/H2O). In addition, another major difference concerns the Fe concentration of the studied melts. Both factors make direct comparisons between the two studies difficult.