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Kinetics of iron oxidation-reduction in hydrous silicic melts

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ABSTRACT

The kinetics of Fe oxidation-reduction in two hydrous rhyolitic melts, one metaluminous and the other peralkaline, have been studied at 800 °C, 2kb, for melt water contents from ~5 wt% to saturation and f_{O_2} between NNO-2 and NNO + 3 (NNO = nickel-nickel oxide redox buffer). The metaluminous melt (~1 wt% FeO_T) reached redox equilibrium after 10 hours and the peralkaline one (~3 wt% FeO_T) after 3 hours. The kinetics of Fe oxidation and reduction are similar and unaffected by the presence or absence of a hydrous fluid phase. No redox front is observable in the glass as the Fe^{3+}/Fe^{2+} ratio evolves, implying that the Fe redox kinetics in hydrous silicic melts is rate-limited neither by the diffusion of H_2 nor by the mobilities of divalent cations, as observed for anhydrous basaltic melts. We propose a two-step reaction mechanism that involves: (1) virtually instantaneous diffusion of H_2 in the sample, followed by (2) slower structural/chemical reorganizations around Fe atoms. The overall redox process involving iron and hydrogen in Fe-poor, H_2O-rich melts is thus reaction-limited and obeys a first-order logarithmic rate law. The relatively slow kinetics of oxidation/reduction explains why melt Fe^{3+}/Fe^{2+} can be readily quenched in laboratory experiments. Simulation of oxidation of magmas due to H_2 exchange with wall rocks is performed using these new kinetics laws and two D_{H_2} values extracted from the literature. We demonstrate that the metaluminous composition is not significantly modified whereas the peralkaline composition undergoes important and fast changes of Fe^{3+}/Fe^{2+} during short processes such as ascent prior to Plinian-style eruptions.