

## Controls of oxygen fugacity on trace element diffusion in rutile

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Rutile is a key mineral in petrology and geochemistry. For example rutile [Zr] is used as a thermometer and the budgets of Nb and Ta in crustal and mantle rocks are commonly controlled by rutile. Recently, we demonstrated that Nb and Ta can fractionate significantly by diffusion in rutile during partial melting [1]. We extended our experimental study to the variation of Zr, Hf, Nb, and Ta diffusion in synthetic rutile as a function of  $fO_2$ , and  $T$  employing the same methods as in [1]. Diffusion anneals were carried out at  $P = 0.1$  MPa in gas mixing furnaces at controlled  $fO_2$  (IW to NNO, and air). Depth profiles of the diffusion couples were measured using a Cameca ims 3f ion microprobe, and fitted numerically.

The diffusion coefficients determined so far at  $fO_2 = WM$  show the following:  $D(Nb)$  and  $D(Ta)$  are consistent with [1] and  $D(Zr)$  is indistinguishable from  $D(Nb)$ . The significant difference between diffusion of Nb and Ta is confirmed and our new results indicate a slightly higher activation energy for  $D(Ta)$  compared to  $D(Nb)$ .  $D(Hf)$  is a factor of  $\sim 2$  smaller than  $D(Zr)$  indicating a weaker diffusive fractionation of Zr-Hf compared to Nb-Ta in rutile. Preliminary data indicate that rutile diffusion coefficients determined here are strongly sensitive to  $fO_2$ . For example, at 1080 °C,  $D(Nb)$  at atmospheric  $fO_2$  is a factor of  $\sim 100$  smaller compared to WM.  $D(Zr)$  and  $D(Hf)$  determined for the  $fO_2 = WM$  deviate significantly from the results of [2], who did not find any significant  $fO_2$  dependence for Zr and Hf diffusion. Our data are more consistent with Zr diffusion coefficients of [3].

The diffusion coefficients of the studied HFSE and their dependence on  $fO_2$  can be interpreted in terms of the point defect chemistry of  $TiO_2$ , which is a non-stoichiometric phase better described by the formula  $TiO_{2-x}$  where  $x$  depends on  $fO_2$  (e.g., [3]). The observed  $fO_2$  dependence is consistent with a vacancy diffusion mechanism. For a given  $fO_2$ , a critical level of heterovalent substitution of Ti exists (e.g., by  $Al^{3+}$ ,  $Fe^{3+}$ ) at which the concentration of Ti vacancies is affected. Calculations based on point defect thermodynamics will be presented to illustrate these effects.

[1] Marschall *et al* (2013) *EPSL*, **375**: 361–371. [2] Cherniak *et al* (2007) *EPSL*, **261**: 267–279. [3] Sasaki *et al* (1985) *J Phys Chem Sol*, **46**: 1267–1283