## Zircon as a Raman spectroscopic pressure sensor

## C. SCHMIDT<sup>1</sup>, M. STEELE-MACINNIS<sup>2</sup> AND M. WILKE<sup>1</sup>

<sup>1</sup>Deutsches GeoForschungsZentrum (GFZ), Telegrafenberg, 14473 Potsdam, Germany (hokie@gfz-potsdam.de, max@gfz-potsdam.de)

<sup>2</sup>Department of Geosciences, Virginia Tech, Blacksburg, VA 24061, USA (mjmaci@vt.edu)

Experiments using diamond-anvil cells have been crucial in understanding minerals and fluids at high pressure (*P*) and temperature (*T*) because sample properties can be studied *in situ*. Pressure in these cells must be determined indirectly, e.g. from the shift in wavenumber of a Raman line of a phase inside the sample chamber. The 464 cm<sup>-1</sup> Raman line of quartz has frequently been applied as pressure sensor because of its fairly large shift with  $P (\partial v/\partial P \sim 9 \text{ cm}^{-1}/\text{GPa})$  and relatively small shift with  $T (\partial v/\partial T \sim -0.014 \text{ cm}^{-1}/\text{K})$  [1]. However, its use is limited by phase transitions and high solubility of quartz in many fluids and melts. In such situations, zircon represents an option because it is stable over a larger range in *P*, *T*, and fluid composition (e.g. [2]).

In this study, we calibrate the shifts in wavenumber of the  $v_3$ -SiO<sub>4</sub> (~1008 cm<sup>-1</sup>) Raman band of fully crystalline synthetic zircon with T and P. The relationship between wavenumber and T from 22 to 950 °C is described by the equation v (cm<sup>-1</sup>) =  $7.26*10^{-9}*T$  (°C)<sup>3</sup> -  $1.58*10^{-5}*T$  (°C)<sup>2</sup> - $2.893*10^{-2*}T$  (°C) + 1008.64. At ~25 °C, the  $\partial v/\partial P$  slope to 6.6 GPa is 5.69 cm<sup>-1</sup>/GPa, and that to 2 GPa is 5.81 cm<sup>-1</sup>/GPa. The latter does not significantly change with temperature, as determined using a Bassett-type hydrothermal diamond-anvil cell [3], with the pressure based on the EoS of H<sub>2</sub>O [4]. The observed  $\partial v/\partial P$  slopes are 5.88 cm<sup>-1</sup>/GPa for the 700 and 600 °C isotherms, and 6.08 cm<sup>-1</sup>/GPa along the 500 °C isotherm. The zircon pressure sensor was used to obtain isochores for aqueous fluids with 6 wt% NaAlSi<sub>3</sub>O<sub>8</sub>, 16 wt% Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, 28 wt% Na2Si13O36, or 64 wt% Na2Si3O7 to 800 °C and 1.43 GPa. Except of the experiment with  $H_2O + 6$  wt% NaAlSi<sub>3</sub>O<sub>8</sub>, these isochores were at significantly higher pressures (by up to ~700 MPa) than calculated from the liquid-vapor homogenization temperature using the EoS of H<sub>2</sub>O [4]. The actual sample temperature should be well known for accurate determination of *P* using this sensor  $(\partial v/\partial T \sim -0.038 \text{ cm}^{-1}/\text{K})$ .

 Schmidt & Ziemann (2000) Am. Mineral. 85, 1725–1734.
Finch & Hanchar (2003) Rev. Min. Geochem. 53, 1–25.
Bassett et al. (1993) Rev. Sci. Instrum. 64, 2340–2345.
Wagner & Pruß (2002) J. Phys. Chem. Ref. Data 31, 387– 535.

## Fractionated enrichment of Zr-Hf and Nb-Ta in ferromanganese crusts

## K. SCHMIDT, MICHAEL BAU AND ANDREA KOSCHINSKY

Jacobs University Bremen, Earth and Space Sciences, 28759 Bremen, Germany (k.schmidt@jacobs-university.de)

The very slow growth rate of and the high adsorption capacity attracting dissolved elements from seawater makes marine hydrogenetic ferromanganese (Fe-Mn) crusts generally suitable for the investigation of environmental and paleooceanographic conditions in the past. However, a detailed unterstanding of enrichment processes and possible fractionation mechanisms of elements and isotopes during the accumulation of the crusts is required. Here we report on the distribution of the geochemical twin elements Zr-Hf and Nb-Ta in ferromanganese crusts from the Northern and Southern Central Pacific, the Eastern North Atlantic and from the hydrothermal vent field Logatchev-1. Recent studies [e.g. 1] dealing with the distribution of Zr-Hf and Nb-Ta in the Pacific Ocean show a fractionation of these elements relative to chondritic values throughout the water column, with distinct signatures in different water masses. Our investigated depth profiles of ferromanganese crusts cover up to 20 Ma and are characterized by highly variable distributions of Zr, Hf, Nb, and Ta, accompanied by changing and fractionated Zr/Hf and Nb/Ta ratios. The Zr/Hf ratios in crust surfaces are always lower compared to the range of Zr/Hf ratios in modern deep seawater. Thus, ferromanganese crusts do not inherit the Zr/Hf (and Nb/Ta) signature of the water mass at the location of crust formation and the ratios cannot be used as paleooceanographic tracers. The elements are almost exclusively bound to the Fe oxyhydroxide fraction of the crust and are probably enriched via surface precipitation. While the Fe oxyhydroxide colloids and particles accumulating in the crusts may have formed away from the crust location and would then carry a different, integrated signal [2], the always lower than seawater Zr/Hf ratios in the crusts also indicate the preferred enrichment of Hf relative to Zr during accumulation in the crust and thus a fractionation of the dissolved seawater Zr/Hf ratio. Seawater data for Nb-Ta are scarce, but a preferential enrichment of Nb in the Fe-Mn crusts can be suggested. The different particle reactivity of the geochemical twin elements is related to the different electron structure causing differences in complex stabilities and the type of chemical bonding. Further, the contribution of hydrothermal Hf to the marine Hf budget will be discussed.

[1] Firdaus, M.L. Minami, T. Norisuye, K. & Sohrin, Y. (2011) *Nature Geoscience* **4**, 227–230. [2] Bau, M. & Koschinsky, A. (2006) *Earth & Planetary Science Letters* **241**, 952–961.

Mineralogical Magazine

www.minersoc.org