

## $^{238}\text{U}/^{235}\text{U}$ variations in high- and low-temperature uranium deposits

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$^{238}\text{U}/^{235}\text{U}$  ratio was analysed by high-precision MC-ICP-MS method using  $^{233}\text{U}$ - $^{236}\text{U}$  double spike. Double spike was prepared from monoisotopes  $^{233}\text{U}$  and  $^{236}\text{U}$  and calibrated relative to CRM-112A standard in which  $^{238}\text{U}/^{235}\text{U}$  value was accepted as  $137.844 \pm 24$  according to [1]. Long-term reproducibility ( $\pm 2\text{SD}$ ) of  $^{238}\text{U}/^{235}\text{U}$  results estimated for three reference samples (total 87 analyses) is better than 0.07%.

High-T U-deposits from some regions previously dated by U-Pb method were involved in this study. 1) Transbaikalia, Russia: the Streltsovsky, Ochyabrsky and Antei deposits in volcanogenic Streltsovsky ore field (Mz); the Khadatkanda skarn deposit (Pz). 2) Erzgebirge, Germany: the Schlema-Alberoda granite-related deposit (Pz). 3) Tyan-Shan, Uzbekistan: the Chauli volcanogenic deposit (Pz). 4) Athabaska Basin, Canada: the Shea Creek and McArthur "unconformity" deposits (Prz). 5) Cage district, Canada: uraninite ore showing (Prz).

$^{238}\text{U}/^{235}\text{U}$  ratio was measured in pitchblende (more rarely in uraninite and coffinite) local microsamples of 10-50  $\mu\text{g}$  weight separated directly from polished sections.  $^{238}\text{U}/^{235}\text{U}$  values for listed deposits (total 44 analysed samples) yield 137.710-137.828 interval (i.e. 0.86%) which only in part coincides with range for zircons 137.772-137.908 [2]. At the same time the individual deposits display 0.12-0.70% variations. Owing to analyses of local microsamples the distinctions of  $^{238}\text{U}/^{235}\text{U}$  ratio up to 0.45% were documented for different pitchblende spherulites growth zones as well as for U-mineral phases formed during different periods of mineralization.

Ore samples from low-T U-deposits of "sandstone" (or "paleo-valley") type Dybryn and Khiagda (Vitim region, Russia) demonstrated wider range of  $^{238}\text{U}/^{235}\text{U}$  values 137.738-137.881 (i.e. 1.0%) which is statistically "heavier" as compared with high-T U-deposits. This data are in agreement with results obtained for 40 concentrates of "sandstone" type ores from USA, Canada and some other regions [3].

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[1] Condon *et al.* (2010) *Geochim. Cosmochim. Acta* **74**, 7127-7143. [2] Hiess *et al.* (2012) *Science* **335**, 1610-1614. [3] Brennecka *et al.* (2010) *Earth Planet. Sci. Lett.* **291**, 228-233.

## Near-infrared measurements of water speciation in hydrous $\text{Na}_2\text{Si}_2\text{O}_5$ melt using HDAC

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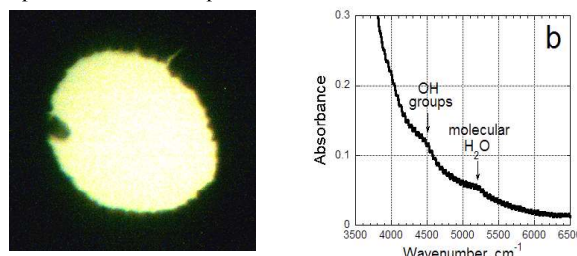
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*In situ* study of water speciation in silicate melts is important for the construction of water solubility models and prediction of physical properties of hydrous melts at high temperature and high pressure. Water speciation in  $\text{Na}_2\text{Si}_2\text{O}_5$  melt (anhydrous NBO/T = 1, structural analogue of basaltic melt) was examined by FTIR spectroscopy in an externally heated diamond anvil cell (HDAC) [1]. Hydrous  $\text{Na}_2\text{Si}_2\text{O}_5$  glass, containing up to 5.9 wt% water, was used as starting material without any additional pressure medium. Experimental pressure was monitored with the pressure- and temperature-dependent Raman shift of  $^{13}\text{C}$  diamond [2].

At temperatures above 650 °C and at pressures above 1.6 GPa only a homogeneous melt phase was observed (Fig. 1a). Near-infrared spectra of this phase contain absorption peaks corresponding to molecular  $\text{H}_2\text{O}$  (at  $\sim 5200\text{ cm}^{-1}$ ) and structurally bound OH groups (at  $\sim 4500\text{ cm}^{-1}$ ). Assuming a constant ratio of molar absorptivities for these bands and knowing the total water content in the melt, concentrations of water species are estimated to be 2.0 wt% as molecular  $\text{H}_2\text{O}$  and 3.9 wt% as OH groups at 800 °C and 2 GPa.

Comparison of the OH/ $\text{H}_2\text{O}$  ratio in the quenched glasses at ambient conditions and in the melts at high temperature shows significant increase of OH species concentration with temperature. At this point, it is difficult to evaluate the effect of pressure on water speciation.



**Fig. 1:** (a) Sample chamber of HDAC with hydrous  $\text{Na}_2\text{Si}_2\text{O}_5$  melt (5.9 wt% water) and  $^{13}\text{C}$  diamond pressure marker.

(b) Near-infrared absorption spectrum of the melt at 800 °C.

[1] Bassett *et al.* (1993) *Rev. Sci. Instr.* **64**, 2340-2345. [2] Mysen & Yamashita (2010) *Geoch. Cos. Acta* **74**, 4577-4588.