

## A new strategy for the production of homogeneous standards for microbeam techniques

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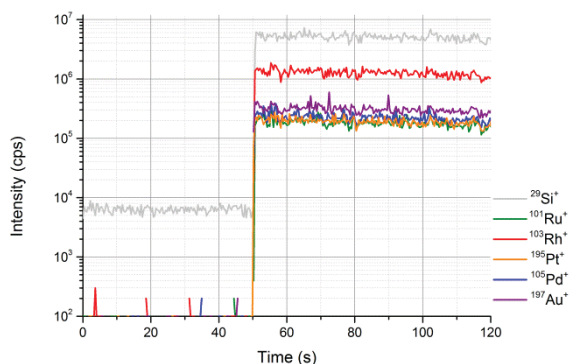
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The glass series of NIST 61x have been the major standard materials particularly useful for quantification for laser ablation – inductively coupled plasma mass spectrometry (LA-ICP-MS) [1]. However, heterogeneities have been reported in some sample charges [2]. Furthermore, geologically important elements such as Ti, Fe, and Mg are very low in concentration; platinum group elements (PGE) are either absent in these materials or present in very low concentrations. Therefore, alternative methods for the production of standard materials were investigated with the aim to extend quantifiable elements in the NIST glass series, in particular the PGEs, and to provide materials which overcome the reported heterogeneities.

A novel approach now provides standard materials with heterogeneities in the size range of 20-50 nm. This approach further provides PGE concentrations in the range of 500 mg/kg; multiple analyses of these novel standard materials confirm a RSD for PGEs in the order of 1-3 %.



**Figure:** Transient LA-ICP-MS of the PGE-doped silicate.

The glass series NIST 61x and the newly synthesized materials provide identical ablation characteristics. The setup of production, preliminary results and first figures of merit will be discussed.

[1] K.P. Jochum et al. (2011), *Geostand Geoanal Res.*, **35**, 397

[2] S.M. Eggins and J.M.G. Shelley (2002), *Geostand Geoanal Res.*, **26** 269

## <sup>13</sup>C-<sup>18</sup>O bonds in dissolved inorganic carbon: Toward a better understanding of clumped isotope thermometer in biogenic carbonates

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Application of the ‘clumped isotope’ thermometer in biogenic carbonates yields invaluable information regarding paleotemperatures [1]. Most biogenic carbonates analyzed so far appear to be free of clumped isotope vital effects [1], except for some surface corals [2,3]. This contrasts against ubiquitous oxygen isotope vital effects in biogenic carbonates, and potentially constitutes another advantage of clumped isotope thermometer. To better understand the incorporation of clumped isotope signals in biogenic carbonates, we present new experimental and theoretical constraints on equilibrium and kinetic clumped isotope fractionations among different dissolved inorganic carbon (DIC) species.

Sodium (bi)carbonate solutions of different pH were prepared and equilibrated at 25°C and 50°C, and the DIC species in each solution were then quantitatively precipitated as barium carbonate (yields >95%). Based on clumped isotope analyses of these precipitates, we determined, relative to statistical distribution, the abundance anomalies of <sup>13</sup>C-<sup>18</sup>O bonds in CO<sub>3</sub><sup>2-</sup>(aq) are 0.392±0.016‰ and 0.354±0.020‰(2σ) respectively at 25°C and 50°C (assuming the clumped isotope fractionation during phosphoric acid digestion of barium carbonate is 0.015‰ smaller than calcite [4]). These values are 0.041±0.014‰ and 0.009±0.029‰(2σ) lower than those in HCO<sub>3</sub><sup>-</sup>(aq) equilibrated at the same temperatures, consistent with our latest theoretical estimation of the equilibrium clumped isotope fractionations among different DIC species. This could potentially explain the general absence of clumped isotope vital effects in most biogenic carbonates [5,6]. We note, however, the oxygen isotope fractionation between dissolved HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> we determined from our experiments are 0.3-0.4‰ smaller than those reported in previous studies [7,8].

We also estimated the kinetic fractionations of clumped isotope species associated with CO<sub>2</sub> hydration and hydroxylation reactions based on first principles transition state theory, and will discuss their implications for clumped isotope thermometry in biogenic carbonates.

[1] Eiler (2011) *Quaternary. Sci. Rev.* **30**, 3575-3588; [2] Ghosh et al. (2006) *Geochim. Cosmochim. Acta* **70**, 1439-1456; [3] Saenger et al. (2011) *AGU Fall Meeting*, Abstract PP41A-1726; [4] Guo et al. (2009) *Geochim. Cosmochim. Acta* **73**, 7203-7225; [5] Guo et al. (2009) *AGU Fall Meeting*, Abstract PP34B-07; [6] Thiagarajan et al. (2011) *Geochim. Cosmochim. Acta* **75**, 4416-4425; [7] Beck et al. (2005) *Geochim. Cosmochim. Acta* **69**, 3493-3503; [8] Kim et al. (2006) *Geochim. Cosmochim. Acta* **70**, 5790-5801.