

## Mississippian seawater temperature and ice volume variations revealed by $\delta^{18}\text{O}$ and Mg/Ca values of brachiopod shell calcites (late Viséan, SW Spain)

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### Introduction

The late Palaeozoic ice age, one of the most remarkable palaeoclimatic crises in Earth history, was characterized by significant seawater temperature variations as well as by notable glacier fluctuations that were registered in the chemical and isotopic compositions of marine carbonates. In order to record palaeoclimatic changes occurred during the Mississippian, a total of 21 exceptionally well-preserved [1] brachiopod shell calcites were analysed for their elemental and stable isotope composition. Combination of  $\delta^{18}\text{O}$  and Mg/Ca proxies could provide an effective method for estimation of ancient seawater temperatures and continental ice sheet formation [2]. The samples were collected along two stratigraphic levels from late Viséan [3] carbonate platform deposits of the Guadiato unit (Pedroches basin, SW Spain).

### Interpreting $\delta^{18}\text{O}$ and Mg/Ca Values

On one hand, mean  $\delta^{18}\text{O}$  values of the brachiopod shell calcites ( $\delta^{18}\text{O}_c$ ) show an overall increase of  $\sim 1\text{‰}$  from oldest to youngest samples (from  $-3.8\text{‰}$  V-PDB to  $-2.9\text{‰}$  V-PDB), which in terms of palaeotemperature implies a drop of seawater temperatures of  $\sim 5.5^\circ\text{C}$ . However, this positive  $\delta^{18}\text{O}_c$  shift ( $\sim 1\text{‰}$ ) can be interpreted to reflect variations in seawater palaeotemperature and/or alternatively differences in continental ice volume. On the other hand, mean Mg/Ca molar ratios of the brachiopod calcites show a  $\sim 30.3\%$  decrease through the studied time interval (from 12.13 to 8.46 mmol/mol). This decline in Mg/Ca ratios indicates a temperature drop of  $\sim 3.3^\circ\text{C}$ , suggesting that other processes besides temperature may have accounted for the  $\delta^{18}\text{O}_c$  shift. According to the  $\Delta T$  obtained from the Mg/Ca data a positive shift in seawater  $\delta^{18}\text{O}$  of about  $0.4\text{‰}$  can be calculated, which may contribute in the remaining  $\delta^{18}\text{O}_c$  shift and likely reflects increasing storage of continental ice.

[1] Armendariz *et al.* (2008) *Palaeogeography, Palaeoclimatology, Palaeoecology* **268**, 65-79. [2] Pérez Huerta *et al.* (2008) *Chemical Geology* **247**, 229-241. [3] Cózar *et al.* (2006) *Sedimentary Geology* **183**, 269-295.

## Silicon isotopes in achondrites and the light element in Earth's core

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Silicon has long been suggested as a major light element in the core, partly due to the superchondritic Mg/Si of the bulk silicate Earth [1]. This is supported by high temperature and pressure experiments [2]. If silicon has entered the core we may expect a fractionation of the isotopic composition because of the major difference in bonding relative to silicates [3].

Georg *et al.* [3] analysed a series of different meteoritic, lunar, and terrestrial samples and found that the Si composition of the Earth and Moon are heavier, by  $\sim 0.2\text{‰}$ , than both chondritic and achondritic meteorites. This points to some fractionation event that has only affected the Earth-Moon system such as high temperature and pressure core formation. Silicon isotopic measurements of experimental silicate-metal charges are in accord with this conclusion [4].

There have been a number of subsequent Si isotope studies comparing analyses of terrestrial and meteoritic samples [5-9]. Some find differences between BSE and meteorites which are smaller than  $0.2\text{‰}$  and some that claim that the difference is irresolvable. Chondrites, as representing Earth's precursor material, have been the focus of most of these meteorite analyses. However, the Si isotopic signatures of achondrites are important in constraining whether the Earth-Moon system suffered a unique event.

Measurements made at Oxford using the Nu Plasma HR for a suite of Martian and HED meteorites give an average differentiated achondrite value of  $\delta^{30}\text{Si} = -0.43 \pm 0.05\text{‰}$  (1SD) which is within error of our chondrite average of  $-0.45 \pm 0.06\text{‰}$ . The offset between our meteorite values and the BSE value of  $\delta^{30}\text{Si} = -0.27 \pm 0.04\text{‰}$  (1SD) [9] points to some process in Earth's history such as high pressure core formation that does not extend to some smaller differentiated bodies.

[1] Allègre *et al.* (1995) *EPSL* **134**, 515-526 [2] Wade & Wood (2005) *EPSL* **236**, 78-95 [3] Georg *et al.* (2007) *Nature*, **447**, 1102-1106. [4] Shahar *et al.* (2008) *GCA* **71**, A848. [5] Fitoussi *et al.* (2008) *GCA* **71**, A273. [6] Armytage *et al.* (2009) *LPSC XXXX* #1167 [7] Chakrabarti & Jacobsen (2009) *LPSC XXXX* #2089 [8] Ziegler *et al.* (2009) *LPSC XXXX* #2446 [9] Savage *et al.* (2009) *GCA*, this volume.