

## The effect of light elements on metal/silicate partitioning

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The accretion of the Earth was marked by the high-pressure segregation of most of its core, accompanied by dissolution of about 10% of one or more “light” elements into the metallic phase. Various light elements have been proposed including S, Si, C and O, with each having an effect on the partitioning behaviour of the trace elements. Metallurgical data indicate that dissolution of even small amounts of light elements in liquid Fe can have profound effects on the activities of some trace components. For instance, significant partitioning of Si into the core of the growing Earth should have affected the observed Mo<sup>1</sup> content of the mantle.

Here, we use the epsilon model of non-ideal interactions in Fe liquids ( $\epsilon$ )<sup>2</sup>. We present interaction parameters ( $\epsilon$ ), derived from 1.5GPa, 1650°C metal-silicate equilibration experiments, for W, Ni, Co and Mo in liquid Fe alloyed with C, S and Si.

At oxygen fugacities above IW-3, we can safely assume a 6+ valence for W and 4+ for Mo<sup>3</sup>. In the system Fe-S we can then derive Ni, Co, W and Mo interaction parameters. For example, our W interaction parameter ( $\epsilon_{W}^S$ ) is 8.4(±1), as opposed to the literature value of 6.1<sup>4</sup>. This means that at fixed oxygen fugacity, W becomes less siderophile with increasing metallic S content. However, for Mo in the same system we derive  $\epsilon_{Mo}^S$  to be 0.5 (±1.7); the partitioning behaviour of Mo is therefore significantly less sensitive to the S content of the metallic phase. In contrast to W, the metal-silicate partitioning of Ni and Co are relatively insensitive to both S and C contents of the metal. Mars is proposed to possess a sulphur rich core, which would imply the primitive martian mantle possesses a higher W/Mo ratio than Earth's if the core's S content is taken into account.

[1] Ono-Nakazato *et al.* (2007) *ISIJ Int* **47**, 365-369 (2007).

[2] Wagner. *Thermodynamics of Alloys* (1962). [3] Wade *et al.* (2012) *Chem Geol* **335**, 189-193. [4] Steelmaking, J. S. f. t. P. o. S. a. t. t. C. o. *Steelmaking Data Sourcebook* (1988).

## Reconstruction of Holocene climate variability using stalagmites from the Herbstlabyrinth, central Germany

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The Herbstlabyrinth cave system lies at an elevation of 435 m asl in a small limestone area in Central Germany. The cave has a length of about 7 km and is well decorated with speleothems.

The chronology of two Holocene stalagmites is established by precise <sup>230</sup>Th/U dating using a NU Plasma MC-ICPMS at the Max Planck Institute for Chemistry, Mainz. The age model is constructed using StalAge [1]. Trace element concentrations and stable isotope ratios have been analysed at a temporal resolution of ~50 years.

In order to support the interpretation of the proxies in terms of past climate variability, we set up an extensive cave monitoring program to understand the processes occurring in the cave system.

In both stalagmites, P, Ba and U are positively correlated with each other and negatively correlated with  $\delta^{13}C$ . This suggests that these proxies reflect the productivity of the vegetation above the cave. In contrast, Mg, which is interpreted as a proxy for effective precipitation above the cave [2], is negatively correlated with P, Ba and U. This indicates that the vegetation is more productive during more humid phases.

The  $\delta^{18}O$  values of precipitation in the research area show a strong positive correlation to the winter North Atlantic Oscillation (NAO) index [3]. Due to strong evapotranspiration during summer months, summer precipitation does not contribute to the recharge of the cave system. Thus, the  $\delta^{18}O$  values of the dripwater and speleothem calcite reflect winter precipitation. Therefore, the  $\delta^{18}O$  values recorded in the speleothems from Herbstlabyrinth may give us the opportunity to reconstruct the NAO, with more positive values reflecting NAO+ conditions and vice versa.

[1] Scholz & Hoffmann (2011), *Quaternary Geochronology* **6**, 369-382 [2] Fairchild & Treble (2009), *Quaternary Science Reviews* **28**, 449-468 [3] Baldini, McDermott, Foley & Baldini (2008), *Geophysical Research Letters* **35**, L04709