

## SILVER AND COPPER FRACTIONATION IN MORB

Portnyagin M.<sup>1,2</sup>, Sushchevskaya N.<sup>2</sup>, Shishkina T.<sup>2</sup>, Kamenetsky V.<sup>3</sup>, Taylor R.<sup>4</sup> & Garbe-Schönberg D.<sup>5</sup>

<sup>1</sup>GEOMAR Helmholtz Centre for Ocean Research Kiel, Kiel, Germany

<sup>2</sup>V.I.Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, Russia

<sup>3</sup>School of Physical Sciences, University of Tasmania, Hobart, Australia

<sup>4</sup>Ocean and Earth Science, University of Southampton, Southampton, UK

<sup>5</sup>Institute of Geosciences, Christian-Albrechts-University of Kiel, Kiel, Germany

Ag and Cu are strongly chalcophile elements, and their behavior in magmatic systems is highly dependent on the presence of solid or liquid sulfide phase in magmas and their sources (e.g., Li & Audetat, 2012). A recent study of Jenner & O'Neill (2010) revealed a nearly uniform  $1000\text{Ag}/\text{Cu} = 0.28 \pm 0.04$  (2s, N=338) in MORB glasses, similar to that in the Earth mantle (0.25-0.35; McDonough & Sun, 1995; Wang & Becker, 2015). Because Cu and Ag have very high and similar in magnitude partition coefficients between sulfide and silicate liquids (~1000; e.g., Patten et al., 2013; Li & Audetat, 2012), the constancy of Ag/Cu in MORB has been explained by a major control of sulfide liquid on the partitioning of these elements in MORB magmas during mantle melting and low-pressure fractionation (Jenner & O'Neill, 2010; Li & Audetat, 2012).

Here we report results of a new survey of Cu and Ag abundances in MORB from several active and abandoned ridge segments (e.g., Reykjanes Ridge, 15°20'N, Bouvet triple junction and TAG area in Atlantic, Macquarie Island, EPR and paleo Kula-Pacific Rift in Pacific). All samples were relatively primitive basaltic glasses with Mg#=0.4-0.7 of N- and E-MORB types. The analyses were performed in the Institute of Geosciences at the University of Kiel by LA-ICP-MS (Agilent 7500s, 193nm GEOLAS Pro). A thoroughly elaborated protocol for analysis allowed limit of detection below 1 ppb for Ag and long-term reproducibility within 15%.

The measured contents are 52-139 ppm Cu and 0.016-0.037 ppm Ag in N-MORB, and 35-151 ppm Cu and 0.015-0.046 ppm Ag in E-MORB. The concentrations decrease with decreasing Mg#. The highest Cu and Ag at given Mg# were found in Reykjanes Ridge glasses. Despite of the relatively wide range of concentrations, N-MORB have nearly constant  $1000\text{Ag}/\text{Cu} = 0.32 \pm 0.02$  (2s, N=50), which are similar to those reported by Jenner & O'Neill (2010). E-MORB glasses have  $1000\text{Ag}/\text{Cu}$  ranging from 0.29 to 0.61, on average  $0.40 \pm 0.07$  (2s, N=43), which is significantly higher than in N-MORB. A strong positive correlation was found between Ag/Cu and indices of source enrichment in highly incompatible elements (K/Ti, La/Sm etc.).

Because Ag/Cu ratio in basalts is not easy to fractionate, we propose that the elevated Ag/Cu in E-MORB reflect the composition of their mantle source metasomatised by a melt component enriched in highly incompatible elements and Ag. The origin of such component is uncertain but may be related to small-degree low-temperature hydrous mantle melting in the presence of solid sulfide (monosulfide solid solution, mss). Because Ag is much less compatible in mss compared to Cu (e.g., Li & Audetat, 2012), such melts are expected to be enriched in Ag and have high Ag/Cu as observed in E-MORB.

### References

- Jenner F.E., O'Neill H.S.C. (2012): Analysis of 60 elements in 616 ocean floor basaltic glasses. *Geochem. Geophys. Geosyst.*, **13**, Q02005.
- Li Y., Audetat A. (2012): Partitioning of V, Mn, Co, Ni, Cu, Zn, As, Mo, Ag, Sn, Sb, W, Au, Pb, and Bi between sulfide phases and hydrous basanite melt at upper mantle conditions. *Earth Planet. Sci. Lett.*, **355**, 327-340.
- McDonough W.F., Sun S.S. (1995): The Composition of the Earth. *Chem. Geol.* **120**(3-4), 223-253.
- Patten C., Barnes S.-J., Mathez E.A., Jenner F.E. (2013): Partition coefficients of chalcophile elements between sulfide and silicate melts and the early crystallization history of sulfide liquid: LA-ICP-MS analysis of MORB sulfide droplets. *Chem. Geol.* **358**, 170-188
- Wang Z., Becker H. (2015): Abundances of Ag and Cu in mantle peridotites and the implications for the behavior of chalcophile elements in the mantle. *Geochim. Cosmochim. Acta*, **160**, 209-226.