Ni-Fe isotope fractionation during cooling of sulfide liquid

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Ni isotopic composition varies significantly among ore deposits [1]. In the absence of redox reactions (Ni occurs only as Ni^{2+}), this variation is attributed to mass fractionation by chemical reactions at high temperatures [1]. To better constraint the nature of these reactions, *in situ* analyses of large (>100 µm) Ni-bearing sulfides would be required. However, these are relatively rare in the crust.

Recently, we recovered exceptionally large sulfides in the lower crust of the 810-m-deep IODP Hole U1473A into the Atlantis Bank ocean core complex (OCC) along the Southwest Indian Ridge (33.7°S, 57.3°E). These are composed of pyrrhotite [$Fe_{1-x}S$; 75-85 vol.%], chalcopyrite [$CuFeS_2$; 5-20 vol.%], and pentlandite [$(Fe,Ni)_9S_8$; 2-10 vol.%] exsolved from a cooling sulfide liquid [2]. For comparison, we studied ten hydrothermal monophasic pentlandites from peridotites of the Kane Megamullion OCC along the Mid-Atlantic Ridge (23.4°N, 45.4°W) described by Ciazela et al. [3]. We measured pentlandite δ^{62}Ni (relative to NIST SRM 986) and δ^{56}Fe (relative to IRMM-014) *in situ* with femtosecond laser ablation coupled to a NeptunePlus MC-ICP-MS at the Leibniz University of Hannover using the procedures outlined in Weyrauch et al. [4] and Oeser et al. [5], respectively.

While the average for the hydrothermal pentlandites from the Kane Megamullion (0.1 ± 0.1‰ δ^{62}Ni; 1SE) is close to the Bulk Silicate Earth (BSE) value of 0.0-0.1‰ δ^{62}Ni, the magmatic pentlandites from Atlantis Bank show variable δ^{62}Ni between -1.5 and 0.0‰. In contrast, δ^{56}Fe in the Atlantis Bank pentlandites exhibits heavy isotope signatures of 1.1-2.4‰. Such low δ^{62}Ni and high δ^{56}Fe signatures cannot be explained by equilibrium fractionation. Instead, our results suggest kinetic isotope fractionation due to Fe-Ni exchange diffusion between pyrrhotite and newly-formed pentlandite during cooling at <650 °C with transport of light Ni from pyrrhotite to pentlandite and light Fe from pentlandite to pyrrhotite. These findings are confirmed by slightly negative δ^{56}Fe (-0.4 to +0.1‰) of the pyrrhotites.

[1] Tanimizu & Hirata (2006) *JAAS* **21**, 1423-1426. [2] Ciazela (2018), *ECORD News.* **31**, 23-25. [3] Ciazela *et al.* (2018), *GCA* **230**, 155-189. [4] Weyrauch *et al.* (2017), *JAAS* **32**, 1312-1319. [5] Oeser *et al.* (2014) *Geostand Geoanal Res.* **38***,* 311-328.