

## Natural mass-dependent Cd isotopic variations determined by TIMS

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We present a high-precision double spike (DS) technique for Cd isotopes in which the Cd is measured by thermal ionisation mass spectrometry (TIMS). Since we observe anomalous odd-even isotope mass bias during measurement, we utilize even isotopes of Cd only. The "natural" fractionation is expressed as deviations in  $^{112}\text{Cd}/^{110}\text{Cd}$  (in parts per  $10^4$ ) from our JMC Cd shelf standard. The commonly-used "JMC Münster Cd" standard lies at  $-1.11 \epsilon^{112/110}\text{Cd}$  on this scale. The external reproducibility (2SD) for double-spiked JMC Cd shelf (100 ng) is  $\pm 0.14 \epsilon^{112/110}\text{Cd}$  (i.e.  $\pm 7$  ppm/amu) which is a factor of 4 to 10 times better than that reported in previous MC-ICP-MS studies (e.g. Wombacher *et al.*, 2003; Lacan *et al.*, 2006; Ripperger and Rehkämper, 2007).

We have analyzed  $\epsilon^{112/110}\text{Cd}$  in over sixty samples from different terrestrial reservoirs and environments (MORB, OIB, loess, Fe-Mn nodules, continental and hydrothermal sulphides). Our study confirms the limited variations found by Wombacher *et al.* (2003) in terrestrial materials—the total range is  $\sim 5 \epsilon^{112/110}\text{Cd}$ , but most samples lie between  $-1.0$  and  $+1.0$ . Three mid-T hydrothermal sulphides differ by  $\sim 4 \epsilon^{112/110}\text{Cd}$ , suggesting significant Cd isotopic fractionation occurs in this setting, though other sulphides are much more tightly clustered. Analyses of 31 hydrogenous Fe-Mn deposits (and phosphorites) worldwide range from  $-0.6$  to  $+2.0$ , and display isotopically heavier Cd (by 1 to  $2 \epsilon^{112/110}\text{Cd}$ ) in the top 2000 m than in the deeper ocean. These differences might reflect shallow inorganic scavenging of Cd by Fe-Mn oxides and its remineralization at depth. However, allowing for interlab bias, three shallow seawater samples of Ripperger and Rehkämper (2007) have  $\epsilon^{112/110}\text{Cd}$  of  $+0.5$  to  $+2.2$ . These data are quite consistent with our shallow Fe-Mn nodule data, implying that only minor Cd isotope fractionation occurs on Fe-Mn oxide precipitation from seawater. The principal cause of the heavy Cd in the surface ocean then appears to be partitioning of light Cd into phytoplankton, entirely consistent with the sense and magnitude of the fractionation factor ( $7 \pm 3 \epsilon^{112/110}\text{Cd}$ ) determined by Lacan *et al.* (2006). Overall, these considerations suggest that  $\epsilon^{112/110}\text{Cd}$  is potentially useful as a paleoproductivity proxy, in much the same way as Cd/Ca.

### References

- Lacan F., François R., Ji Y. and Sherrell R. M. (2006), *Geochim. Cosmochim. Acta* **70**, 5104-5118.  
 Ripperger S. and Rehkämper M. (2007), *Geochim. Cosmochim. Acta* **71**, 631-642.  
 Wombacher F., Rehkämper M., Mezger K. and Münker C. (2003), *Geochim. Cosmochim. Acta* **67**, 4639-4654.

## Zircon U-Th ages from Laacher See indicate coeval crystallization of coerupted carbonatite and silicate magmas

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In order to constrain the origins of spatially associated carbonatite and silicate magmas and to quantify the time scales during which they interacted in a shallow magma system, we are employing U-Th dating of individual zircon crystals by secondary ionization mass spectrometry (SIMS). Laacher See (Germany) erupted a suite of crystal-rich xenolithic clasts that range from carbonate-free intermediate (dominantly syenitic) compositions to carbonatites (sövites). Because of the youthful age of the Laacher See eruption ( $\sim 12,900$  a BP), SIMS U-series geochronology can be applied which provides unrivaled temporal resolution in the order of  $\sim 10^3 - 10^4$  years for individual grains or grain domains that are analyzed *in situ* (thin-section) at  $\sim 30 \mu\text{m}$  lateral resolution and crater depths  $< 5 \mu\text{m}$ . Our initial results from three syenitic sövite clasts yield overlapping U-Th zircon isochron ages that average  $15.8 \pm 2.7$  ka ( $1\sigma$ ; MSWD = 0.45; 30 spot analyses). This age overlaps within uncertainty with the U-Th isochron age for zircons from early erupted Laacher See differentiated phonolite and late-crystallized zircons in vesicles of carbonate-free syenite ejecta clasts ( $17.1 \pm 1.3$  ka; Schmitt, 2006).

These results indicate coeval crystallization of carbonatite and differentiated silicate magmas that were stored at the top of a shallow magma body. Thus far, the zircon record lacks unequivocal evidence for protracted (several  $10^3$ 's to  $10^4$ 's ka) pre-eruptive crystallization within a long-lived shallow Laacher See magma chamber and rather suggests crystallization and differentiation at most within few ka prior to eruption. The geochronological results are also in line with trace element evidence that indicate a close chemical affinity between carbonatites and Laacher See phonolites (Liebsch, 1996). Coeval zircon crystals in both, Laacher See carbonatites and phonolites/syenites have indistinguishable initial ( $^{230}\text{Th}/^{232}\text{Th}$ ) ratios ( $0.885 \pm 0.013$  and  $0.894 \pm 0.010$ , respectively). This further supports the hypothesis of consanguineous carbonatite and silicate melts in the Laacher See magma chamber that originated by liquid immiscibility.

### References

- Liebsch H., (1996) *PhD thesis, University of Göttingen*, 1-111.  
 Schmitt A.K., (2006) *Geology* **34**, 597-600.