

Trace elements in Catanda carbonatitic massif (SW Angola)

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The Catanda carbonatite massif (SW Angola) is built mainly of lapilli and lapilli-ash tuffs, ash tuffs, carbonatites and granulated carbonatites.

The studies covered 43 samples of rocks of the massif. Concentrations of Sc, Y, Li, Ta, Zr, Nb, Th, As, Ba, Co, Cr, Cu, Ga, Hf, Mo, Ni, Pb, Rb, Sr, U, V, Zn and REE were determined by the ICP-MS and ICP-OES methods after dissolving the rocks in aqua regia.

Concentrations of radioactive elements are rather low. U concentrations range from 1 to 20 ppm. Mean levels in tuffs (8.6 ppm) is higher than in lavas (5.9 ppm). Th contents range from 5 to 52 ppm. Mean levels of Th tend to be higher in lavas (30.4 ppm) than in tuffs (28.8 ppm). Nb concentrations range from 14 to 652 ppm, with mean levels equal 383 ppm for tuffs and 285 ppm for lavas. Li contents range from 9 to 55 ppm, attaining 21 ppm at the average. Cr concentrations range from 25 to 161 ppm, being markedly higher in tuffs (49 ppm) than in lavas (33 ppm). Cu contents range from 11 to 356 ppm, being much lower in tuffs than in lavas (29 and 48 ppm at the average, respectively). V concentrations range from 33 to 222 ppm (98 ppm at the average). Zn contents change from 57 to 551 (124 ppm at the average). Ba concentrations change from 250 to 1700 ppm (950 ppm at the average). Sr contents change from 0.08 to 0.54%, with mean levels clearly higher in carbonatite lavas (0.21%) than in tuffs (0.16%). Concentrations of Ga, Hf, Ni, Pb, As and Co are low and poorly differentiated as they appear generally unrelated to petrology. The rocks are also enriched in REE, especially LREE (La, Ce, Pr and Nd). Sum REE contents range from 0.25 to 0.95%. The concentrations were found to be markedly higher in tuffs (avg. 0.33%) than in carbonatite lavas (0.21%).

Carbonatite lavas of the Catanda Massif are characterized by higher mean levels of Cu, Zr, Th and HREE and the tuffs – by higher mean levels of Cr, U, V, Rb, Mo, Zn, Nb, Li and LREE. In turn, concentrations of As, Ba, Ga, Hf, Ni, Pb, Y and Sc appeared not related to the types of rocks of that massif.

Mass-(in)dependent Cd isotope fractionation during evaporation

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Here, we investigate large mass-dependent (MDF) and very small mass-independent fractionations (MIF) of Cd isotopes that result from the evaporation of liquid Cd into vacuum at 10⁻⁴ mbar and ~180°C [1].

Cadmium stable isotope data were obtained using a Neptune MC-ICP-MS. To resolve small mass-independent anomalies, residual Cd metal samples were analysed at high ion beam intensities typically >20V for ¹¹⁴Cd and long analysis times (30 min.).

MDF in the residual Cd metal samples from vacuum evaporation experiments are well described by Rayleigh distillation with a vapor-residue fractionation factor $\alpha = 0.9900$ for ¹¹⁴Cd/¹¹⁰Cd (i.e. 10.0‰) [1]. The observed fractionation is much less than predicted from kinetic theory ($\alpha_{kin} = (\text{mass } ^{110}\text{Cd} / \text{mass } ^{114}\text{Cd})^{0.5} = 0.9823$; i.e. 17.7‰), a mismatch that is frequently observed, e.g. [2].

The accurate quantification of mass-independent fractionation (MIF) in residual Cd metals required that the large mass-dependent fractionation is accurately corrected. This is facilitated using the generalized power law and normalization to ¹¹⁰Cd/¹¹⁴Cd of the starting material [1]. After correction, deficits ranging from 8 to 28 ppm were well resolved for ¹¹¹Cd/¹¹⁴Cd, ¹¹³Cd/¹¹⁴Cd and ¹¹⁶Cd/¹¹⁴Cd. The observed pattern is in accord with predictions from nuclear charge radii and thus indicate nuclear volume effects [3-6]. The preferential evaporation of ¹¹¹Cd, ¹¹³Cd and ¹¹⁶Cd may result from their more tightly bound 5s electrons and hence weaker metallic bonds in the liquid as previously suggested for Hg [7,8], another group 12 element. The observation of nuclear volume effects thus suggests that (metallic) bonding in the melt results in reduced fractionation factors.

[1] Wombacher *et al.* (2004) *GCA* **68**, 2349–2357. [2] Richter *et al.* (2009) *Chem. Geol.* **258**, 92–103. [3] Bigeleisen (1996) *J. Am. Chem. Soc.* **118**, 3676–3680. [4] Schauble (2007) *GCA* **71**, 2170–2189. [5] Fujii *et al.* (2009) *Chem. Geol.* **267**, 157–163. [6] Rehkämper *et al.* (2011) *Handbook Environ. Isotope Geochem.*, Chap. 8, 125–154. [7] Estrade *et al.* (2009) *GCA* **73**, 2693–2711. [8] Ghosh *et al.* (2013) *Chem. Geol.* **336**, 5–12.