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## Cadmium isotope fractionation of materials originating from different industrial processes

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Cadmium is present in most terrestrial samples such as minerals, ores and coal. These materials are used in human induced activities such as smelting, burning etc. Of great importance is also the application of Cd as a pigment and corrosion-resistant coating for metals. As a consequence of all these processes, Cd is released to the environment and it results in a pollution of adjacent areas and possibly poses a risk to human health. Our study represents a Cd isotope inventory of waste materials resulting from different industrial activities such as coal burning, smelting, car battery recycling, glass production and plating. Using  $\epsilon^{114/110}$  Cd values, obtained data could help us to track Cd origin and to study its behaviour in the environment.

We have found that all studied industrial processes generated isotopically fractionated materials compared to  $\epsilon^{114/110}$  Cd<sub>NIST3108</sub> values of primary sources used in the companies. Primary sources (ore samples-two sphalerites, one galena, coal and pigment) exhibited  $\epsilon^{114/110}$  Cd<sub>NIST3108</sub> values of  $1.0 \pm 0.2$ ,  $0.2 \pm 0.2$ ,  $1.3 \pm 0.1$ ,  $-2.3 \pm 0.2$  and  $-0.1 \pm 0.3$ , respectively and our data show that these  $\epsilon^{114/110}$  Cd<sub>NIST3108</sub> values are clearly distinguishable from the  $\epsilon^{114/110}$  Cd<sub>NIST3108</sub> values of industrial materials. In more detail, we have observed several  $\epsilon^{114/110}$  Cd<sub>NIST3108</sub> values with very different isotopic signature compared to the rest of our results. These data include Cu and Sn waste material after Pb refinement resulting from battery recycling plant ( $-13.9 \pm 0.1$  and  $-23 \pm 2.5$ , respectively). Clearly different  $\epsilon^{114/110}$  Cd<sub>NIST3108</sub> values exhibited also slag ( $58.6 \pm 0.9$ ), ash ( $-8.6 \pm 0.1$ ) and deposit (mixture of ash and slag;  $24.8 \pm 0.1$ ) originating from coal combustion. The slag, coming from smelting activity ( $5.1 \pm 0.04$ ) and solids from electroplating bath ( $-6.3 \pm 0.1$ ), showed significantly different isotopic composition as well. All these waste materials exhibit specific isotope fingerprints that cannot be confused with other materials. The  $\epsilon^{114/110}$  Cd<sub>NIST3108</sub> values of the rest of studied waste materials fall within the range from  $-5.1$  to  $4.4$  and are not clearly distinguishable from each other in terms of differences among industrial activities. If more Cd sources would be located at the same locality, the Cd tracing could be difficult. Therefore, every study dealing with tracing of a compound using isotope approach must consider possible mixing of local sources. Nevertheless, concerning every single industrial process, clear differences are found between primary source material and waste products.

We have also found that the technology in use plays an important role in Cd isotope fractionation. According to condensation-evaporation theory,  $\epsilon^{114/110}$  Cd<sub>NIST3108</sub> values of ash exhibit shift to light values compared to slag that is supposed to exhibit heavy  $\epsilon^{114/110}$  Cd<sub>NIST3108</sub> values. Nevertheless, we have observed the effect of introduction of the cooling system behind the furnace that probably caused the atypical shift to the heavy  $\epsilon^{114/110}$  Cd<sub>NIST3108</sub> value of ash.

Detailed insight into each industrial process, clear and quantitative material flows could be included in further detailed study. Nevertheless our objective was to investigate Cd fractionation during different industrial processes in comparison to the isotopic composition of raw materials.

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