Kinetic Isotopic Fractionation of Cd and Zn during Condensation

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Introduction

The isotopic composition of metals (Zn, Cd, Cu) varies in terrestrial and extra-terrestrial samples resulting most probably from phase transformations (solid-gas-solid) and/or biogenic fractionation. Up to now, very few experiments were conducted in order to document isotope fractionation during evaporation and condensation of metals. In this study, we report Cd and Zn elemental and isotopic variations measured in fly ashes collected from an urban waste combustor (UWC) equipped with various ash and flue gas filtration devices, including a heat transfer system (Figure 1). In the evacuation system, temperature drops from ca. 1000 to 200 degree Celsius. This temperature range allows the evaporation and then condensation of Cd and Zn and probably fusion and oxido-reduction reactions.

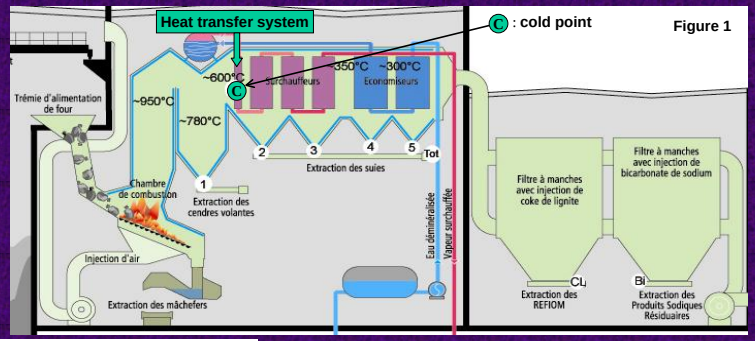

Figure 1

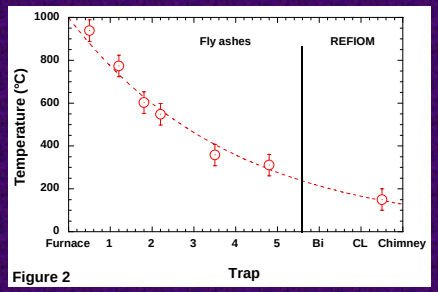

Figure 2

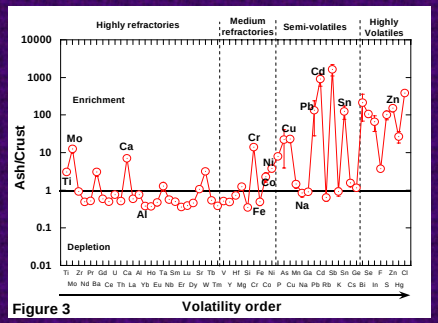

Figure 3

Elemental Behaviour

Different samples were collected from traps 1 to 5 and their integrated sample Tot (fly ashes), CL and Bi traps (flue gases), (Figure 1), along the 1000°C to 200°C temperature gradient of the fumes evacuation system (Figure 2). Concentrations in Tot samples are coherent with elemental volatility. Most refractory elements normalized to the natural upper crust (Taylor and Mc Lennan, 1995) yielded a ratio of ca. 1, whereas the more volatile elements (including Pb, Cd, Zn) showed a significant enrichment of up to 3 orders of magnitude (Figure 3). The distribution of metal contents in samples from the different traps showed major enrichments for flue gases and/or micro-particles (CL trap) and significant enrichment for ashes from trap 2 (Figure 4). A leach-residue study for the different fly ashes clearly indicated that Cd, Zn and Pb condensed on more refractory particles as soluble salts. The elemental behaviour of these elements suggests massive condensation early in the evacuation system of the UWC, probably before trap 2, traps 3 to 5 recording gravity particle settling. Mass balance calculations between flue gases, fly ashes and residual materials suggest that more than 20% Pb, 35% Zn and 90% Cd volatilized in the combustion chamber of the UWC.

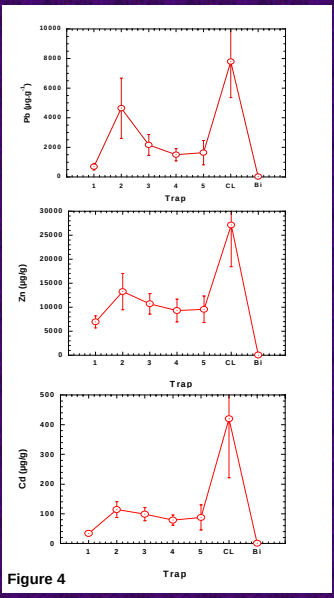

Figure 4

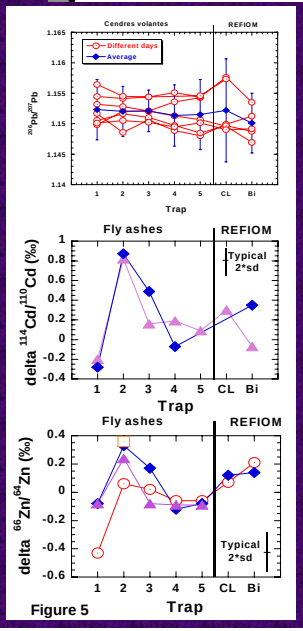

Figure 5

Isotopic variations

The isotopic composition of Pb, Cd and Zn for the fly ash and flue gas trap samples is reported in Figure 5. Lead isotope ratios varied from day to day but, as a whole, the different samples from a single day did not show any systematic variations. On the contrary, Cd and Zn isotopic compositions were highly contrasted between trap 1 and 2 samples with variations as large as 1 per mil in δ^{114}Cd (^{114}Cd/^{110}Cd ratio) and up to 0.5 per mil in δ^{66}Zn (^{66}Zn/^{64}Zn ratio)(Figure 5). Fly ashes from traps 3 to 5 and flue gases yielded intermediate isotopic compositions. More than 90% Cd and 85% Zn present in the evacuation system of the UWC were found in the flue gas trap CL. We suggest that the composition of samples from traps 3 to 5 and CL represents best that of gases prior to condensation. According to the temperature gradient, and then the condensation sequence, samples from trap 1 contained relatively more material condensed at higher temperature (e.g. CdO or $CdSO_4$) whereas samples from trap 2 would contain materials condensed at lower temperature (e.g. $CdCl_2$), mainly because of the cold point of the heat transfer system located between the two traps. Leachates from trap 2 samples had the highest delta Cd and Zn values (Figure 6), favouring this hypothesis. This means that the first condensates were depleted in heavy isotopes whereas the later ones were enriched in heavy isotopes. This situation is only compatible with mass dependant kinetic isotope fractionation during gas condensation, as proposed by Richter (2004) and schematized in Figure 7.

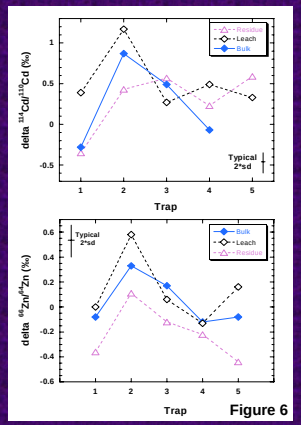

Figure 6

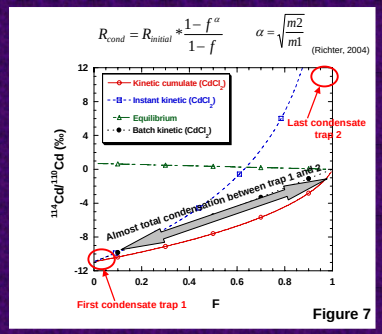

Figure 7

References

Taylor and Mc Lennan,(1995) *Reviews of Geophysics* (*33*), 241-265
Richter, F. M. (2004) *GCA* (*68*), 4971-4992

Perspectives and conclusions

Considering the information on the behaviour observed during the gas cooling and the short time of the reactions, the Cd and Zn isotopic fractionation observed in the fly ashes are interpreted as the result of kinetic isotopic fractionation during condensation. Because the cold point of the heat transfer system is located close to the combustion chamber, most volatile elements such as Pb, Cd and Zn condensed and homogenized early in the evacuation system so that the most isotopically fractionated samples do not reached the environment through the chimney. Rather, non fractionated samples are evacuated in the atmosphere, limiting isotope source tracing.

However, this study confirmed the existence of kinetic isotopic fractionation during condensation of metals, which may have implications for the interpretation of isotope variations measured in extra-terrestrial samples.