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ScienceDirect

Geochimica et Cosmochimica Acta 170 (2015) 108–125

Geochimica et Cosmochimica Acta

www.elsevier.com/locate/gca

The estuarine geochemical reactivity of Zn isotopes and its relevance for the biomonitoring of anthropogenic Zn and Cd contaminations from metallurgical activities: Example of the Gironde fluvial-estuarine system, France

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Received 3 December 2014; accepted in revised form 11 August 2015; available online 31 August 2015

Abstract

Zinc stable isotopes measurements by MC-ICP-MS, validated by laboratory intercalibrations, were performed on wild oysters, suspended particles and filtered river/estuarine water samples to provide new constraints for the use of Zn isotopes as environmental tracers. The samples selected were representative of the long range (400 km) transport of metal (Zn, Cd, etc.) contamination from former Zn-refining activities at Decazeville (i.e. δ^{66}Zn > 1‰) and its phasing out, recorded during 30 years in wild oysters from the Gironde Estuary mouth (RNO/ROCCH sample bank). The study also addresses additional anthropogenic sources (urban and viticulture) and focuses on geochemical reactivity of Zn in the turbidity gradient and the maximum turbidity zone (MTZ) of the fluvial Gironde Estuary. In this area, dissolved Zn showed a strong removal onto suspended particulate matter (SPM) and progressive enrichment in heavy isotopes with increasing SPM concentrations varying from $\delta^{66}\text{Zn} = -0.02$‰ at 2 mg/L to +0.90‰ at 1310 mg/L. These signatures were attributed to kinetically driven adsorption due to strongly increasing sorption sites in the turbidity gradient and MTZ of the estuary. Oysters from the estuary mouth, contaminated sediments from the Lot River and SPM entering the estuary showed parallel historical evolutions (1979–2010) for Zn/Cd ratios but not for δ^{66}Zn values. Oysters had signatures varying from $\delta^{66}\text{Zn} = 1.43$‰ in 1983 to 1.18‰ in 2010 and were offset by $\delta^{66}\text{Zn} = 0.6$–0.7‰ compared to past (1988) and present SPM from the salinity gradient. Isotopic signatures in river-borne particles entering the Gironde Estuary under contrasting freshwater discharge regimes during 2003–2011 showed similar values ($\delta^{66}\text{Zn} \approx 0.35 \pm 0.03$‰; 1SD, $n = 15$), i.e. they were neither related to former metal refining activities at least for the past decade nor clearly affected by other anthropogenic sources. Therefore, the Zn isotopic signatures in Gironde oysters reflect the geochemical reactivity of Zn in the estuary rather than signatures of past metallurgical contaminations in the watershed as recorded in contaminated river sediments. The study also shows that the isotopic composition of Zn is strongly fractionated by its geochemical reactivity in the Gironde Estuary, representative of meso–macrotidal estuarine systems.

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http://dx.doi.org/10.1016/j.gca.2015.08.004
0016-7037/

1. INTRODUCTION

Zinc is a ubiquitous biolimiting micronutrient, involved as a cofactor in enzymes and regulatory proteins in all living beings (Cloquet et al., 2008) but may become toxic in contaminated environments, where concentrations can exceed background levels by orders of magnitude. This duality observed for many metallic trace elements (MTE), explains why environmental studies using Zn isotopes have focused on both past/present pristine environments (Maréchal et al., 2000; Pichat et al., 2003; Viers et al., 2007; Zhao et al., 2014) and metal contaminated systems (Weiss et al., 2007; Borrok et al., 2008; Chen et al., 2008, 2009; Sivry et al., 2008; Sonke et al., 2008; Mattielli et al., 2009; Bigalke et al., 2010). Both kinds of applications deal with a variation range of δ^{66}Zn values greater than 1‰, which is about more than 20 times the analytical precision achieved with modern MC-ICP-MS measurements.

The similarity of Zn isotope signatures in continental siliciclastic rocks and marine detrital sediments (Maréchal et al., 1999; Albarède, 2004; Cloquet et al., 2008) and the small isotopic difference between natural and common anthropogenic Zn (John et al., 2007; Cloquet et al., 2008; Sivry et al., 2008; Sonke et al., 2008) may explain why Zn isotope studies on estuarine systems are extremely rare (Petit et al., 2006, 2008a). In contrast to the small isotopic variations expected for sedimentary samples in estuaries, a range of δ^{66}Zn values over 1‰ has been observed for dissolved Zn in the Seine (Chen et al., 2008, 2009) and various World Rivers (Little et al., 2014), as well as in coastal and open ocean surface waters (Bermin et al., 2006; Boyle et al., 2012; Zhao et al., 2014). This clearly highlights the importance of studying dissolved Zn isotopes at the ocean/continent interface in order to understand potential fractionation related to biogeochemical processes in these highly dynamic environments. In fact, the partitioning between solids and solution plays a critical role in the distribution, transport and behavior of metals in aquatic environments, with adsorption/desorption processes being a major control on dissolved metal loads in fluvial-estuarine systems (Turekian, 1977; Benoit and Rozan, 1999; Petit et al., 2009), potentially modifying Zn isotopic signatures.

Several studies have established how anthropochemical processes related to the production of metallic Zn account for the diversification of Zn isotopic signatures in commercial products and by-products (John et al., 2007; Sivry et al., 2008; Sonke et al., 2008; Mattielli et al., 2009). The use of Zn isotopes as a tracer of anthropogenic contamination often addresses natural systems affected by Cd contamination (associated to other metals) from pyrometallurgical Zn production. Due to environmental regulation and remediation strategies implemented since the mid-eighties, globally decreasing Cd concentrations and consistent changes of δ^{66}Zn signals in contaminated systems have been observed (Sivry et al., 2008; Sonke et al., 2008; Petit et al., 2008a; Mattielli et al., 2009). However, Zn isotope studies have mainly focused on tracing point-source pollutions in the nearby environment rather than following their long-range transport at the watershed scale. At this scale, the relative proportions of natural and anthropogenic sources vary in time and space due to a complex interplay of transient processes controlled by a combination of natural (floods vs. low discharge periods, mixing between tributaries) and anthropogenic forcing (urban and industrial activity, remediation, reservoir management, dredging, etc.). Studying the evolution of metal-contaminated large scale systems requires long-term and high-resolution monitoring of suspended and dissolved metal loads allowing establishing balanced fluxes at different physical, hydrodynamic and geochemical boundaries of the river-estuary continuum.

Since 1979, the French "Mussel Watch" program (RNO/ROCCH) has been monitoring MTE exposure in French coastal systems using bivalves sampled along the coastline and in estuaries. These organisms are useful sentinels for information on time-integrated bioavailable metal exposure in coastal sites and the related sample banks allow for the monitoring of spatial and temporal trends over decades.

Bivalves from the RNO/ROCCH sample bank have been analyzed for Cd (Claisse, 1989; Chiffoleau et al., 2001), Ag (Chiffoleau et al., 2005; Lanceleur et al., 2011), Ni and V (Chiffoleau et al., 2004), Cr (Chiffoleau and Bonneau, 1994), Pb and Hg (Claisse, 1989), and more recently, Zn and Cd stable isotopes (Shiel et al., 2013). The latter study has shown Cd and Zn isotopic signatures (δ^{66}Zn > 1‰; δ^{114}Cd < −1‰) in two RNO oysters samples from the La Fosse site (Gironde Estuary mouth) clearly different than in bivalves from other French coastal sites under stronger marine influence (δ^{66}Zn ≈ 0.5‰; δ^{114}Cd ≈ −0.5‰). Shiel et al. (2013) have attributed the heavy δ^{66}Zn in Gironde oysters to the resilience and the river-borne resuspension/transport of Cd-contaminated sediments from the Lot River (1‰ < δ^{66}Zn < 1.6‰, Sivry et al., 2008), downstream the former Decazeville metal processing plant (Fig. 1). In the same study, the light δ^{114}Cd values in oysters were explained by airborne emissions of metallic Cd from the former Decazeville industry, presumably characterized by very light Cd isotope signatures, as observed in a Zn smelter in Northern France (Cloquet et al., 2006). However, atmospheric dust from the same smelter had negative Zn isotope signatures (δ^{66}Zn ≈ −0.7‰; Mattielli et al., 2009) and Cd contaminated sediments from the Lot River show δ^{114}Cd values close to 0‰ (Sivry et al., 2006). Given that the main transport of Cd from the Decazeville area to the Gironde Estuary and adjacent coastal area occurs via the Lot–Garonne–Gironde fluvial-estuarine system (Schäfer et al., 2002; Audry et al., 2004b; Dabrin et al., 2009) rather than by atmospheric deposition, a dual transport pathway for Cd and Zn accumulated in Gironde oysters appears unlikely. We hypothesize that other processes must account for the particular Zn and Cd isotopic compositions measured in oysters from the Gironde Estuary.

The potential of metal stable isotopes for fingerprinting and discriminating anthropogenic sources, and the scientific relevance of using bivalves to monitor contamination levels in coastal sites are well established. However, the use of stable metal isotope signatures in coastal biomonitoring of remote metal contaminations must account for