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Zn isotopes as tracers of anthropogenic pollution from Zn-ore smelters The Riou Mort–Lot River system

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ABSTRACT

Zn isotopes were used to trace the anthropogenic sources in the Lot watershed (Aveyron, SW France) where a small river, the Riou Mort drains an industrial exploitation of zinc ore. The zinc isotopes in industrial tailings are highly fractionated relatively to Zn ore (δ^{66}Zn ~ 0.16‰), due to metallurgical processes, reaching δ^{66}Zn values up to +1.49‰. Zn extraction yields for these samples were calculated using presumable conservative elements (Fe, Ca, Mg, K, Na and Mn) and vary from 95.4% to 99.4%. Extraction yields are related to the intensity of Zn isotopic fractionation. Different Rayleigh isotope fractionation scenarios for Zn refining yielded $\alpha_{\text{ore-tailings}}$ ranging from 1.00012 to 1.00062. The δ^{66}Zn of the Riou Mort sediments downstream from the former Zn-ore facility is presently +0.91 ± 0.04‰, i.e. significantly different from the signature of upstream sediments and of the regional geochemical background, +0.31 ± 0.06‰, (2SD, $n = 3$). Sediment core δ^{66}Zn values in the 40 km downstream Cajarc hydroelectric reservoir are also consistently 'heavier' (+0.75 to +1.35‰) than the regional geochemical background. Both top-core Zn concentrations and isotopic signatures can be explained by the contribution of 9% of present-day Riou Mort sediments. δ^{66}Zn variations in the ^{137}Cs-dated downcore sediments are suggested to reflect historical changes in metallurgical processes of the Viviez facility, such as improved Zn extraction efficiency and the related evolution of tailings. In sediments deposited during 1952–1972, the mean δ^{66}Zn is +0.95 ± 0.08‰, representative of the combined electrolysis and thermal process used at that time for the Zn extraction. In sediments deposited during the late seventies, δ^{66}Zn increases, reaching a maximum of 1.35‰ during the eighties. These heavier δ^{66}Zn are likely related to further increased Zn extraction after replacement of thermal waste processing by electrolysis in 1976/77. The nature of the extraction processes, especially electrolysis, may therefore play a major role in the Zn isotopic fractionation produced. The soils located on the Lot riverbanks have chemical and Zn isotopic compositions (+0.74‰ to +0.96‰) close to the Cajarc sediments, indicating that they were also impacted by tailings erosion and leaching. The soils located in the vicinity of the plant display lower δ^{66}Zn (+0.40‰ to 0.48‰). That corresponds to mixtures of several atmospheric sources like coal fly ashes, ore and tailing dusts. The relation between Zn isotopic fractionation, extraction yields and/or extraction processes clearly demonstrates the efficiency of δ^{66}Zn as tracer of environmental contamination.

1. Introduction

The first measurements of Zn isotope variations in geological materials were performed fifty years ago (Blix, 1957) and limited analytical precision of ~0.1% lead to the conclusion that there was no isotopic fractionation of Zn in terrestrial samples (Rosman, 1972). Recent development of analytical instrumentation such as multiple collector ICP-MS (MC-ICP-MS) has induced a great expansion of the knowledge of the transition metal isotope geochemistry (Halliday et al., 1995; Rehkämper et al., 2001; Johnson et al., 2004). Analytical protocols for Zn isotope analysis by MC-ICP-MS have been developed in the late 1990s (Marechal et al., 1999) and early 2000s (Marechal and Albarede, 2002; Archer and Vance, 2004; Chapman, 2006) and document substantial natural isotopic variations.

Due to active participation of Zn in multiple biological and low-temperature inorganic-chemical reactions, isotopic variations of Zn may be used as a tracer of biogeochemical and chemical processes. Marechal et al. (2000) have first applied Zn isotopes as a marine biogeochemical tracer of biological activity. Pichat et al. (2003) reported δ^{66}Zn values in deep-sea carbonates varying from +0.31‰ to +1.34‰ and Bermin et al. (2006) recently determined a δ^{66}Zn profile in a seawater column showing values of +0.35 ± 0.08‰. This suggests that Zn isotopes may be used as tracer of marine sediments provenance (Bentahila et al., 2008) or to identify the role of Zn as a micronutrient in the oceans (Vance et al., 2006). Experiments by Pokrovsky et al. (2005) showed minor Zn isotopic fractionation (±0.2‰) during Zn adsorption

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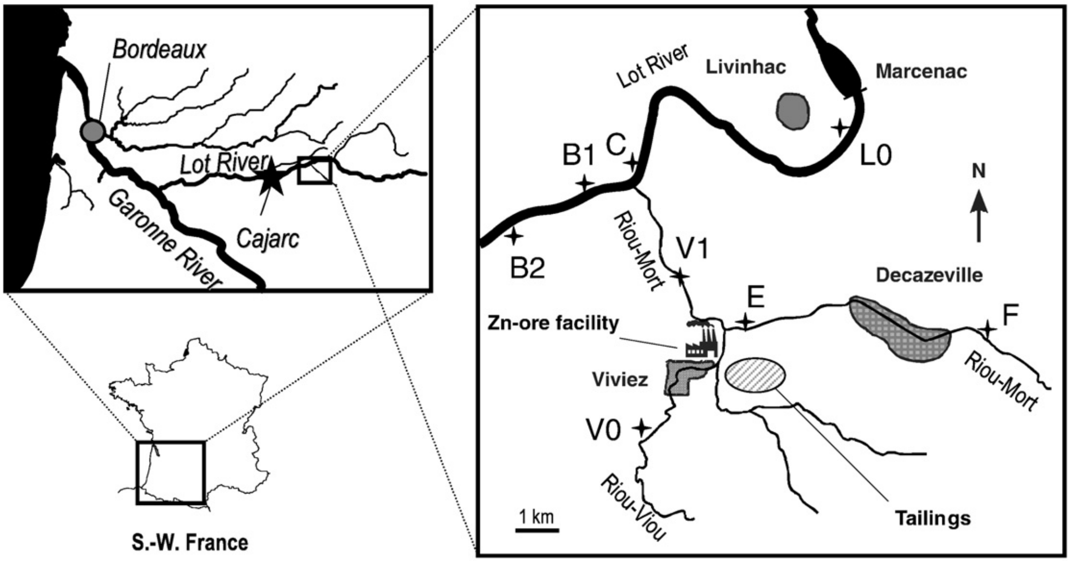

Fig. 1. Map of the study area and location of sampling sites (black stars). The hatched zone represents the tailings.

onto oxy(hydr)oxides and anhydrous oxides surfaces under abiotic conditions. Within a continental environment analyses were performed on rocks, such as loess, mantle-derived materials (Ben Othman et al., 2001, 2003, 2006), ore deposit samples (Wilkinson et al., 2005; Sonke et al., 2008) and volcanic-hosted massive sulphides (VHMS; Mason et al., 2005), giving a wide range of δ^{66}Zn values: from −0.43‰ to +1.33‰ (Cloquet et al., 2006a, and references therein). Biological processes may also induce fractionation between Zn isotopes. For instance, Zhu et al. (2002) have reported Zn fractionation of +1.1‰ for Zn proteins synthesized by yeast, relatively to δ^{66}Zn in the nutrient solution. Gelabert et al. (2006) demonstrated that irreversible incorporation of Zn in cultured diatom cells (*Thalassiosira weisflogii*) induces an enrichment in heavy isotopes ($\Delta^{66}\mathrm{Zn}_{\mathrm{solid\text{-}solution}}$=+0.3 to +0.4‰, compared to the growth media) attributed to the change of chemical status of the metal inside the cells. Weiss et al. (2007) reported large variations of δ^{66}Zn in peat cores (up to +1.05‰), partially related to biological Zn cycling in peat. In plant roots, heavy Zn isotope enrichments of up to +0.27‰ and +0.76‰ were observed relative to the litter layer (Weiss et al., 2005; Viers et al., 2007), whereas negative δ^{66}Zn values were obtained for tree leaves.

While many studies focus on Zn isotopes during natural biogeochemical cycling, fewer deal with the use of Zn isotopes to trace anthropogenic contamination, which is a timely topic: significant variability of δ^{66}Zn was reported in epiphytic lichen and aerosols samples near an urban area affected by aerosols or flue gases from a waste combustor (Cloquet et al., 2006a, and references therein), but the lack of systematic variation did not allow distinguishing between pollution sources. Dolgopolova et al. (2006) also measured δ^{66}Zn in lichens around a mining and mineral facility and reported Zn isotopic signatures up to +1.40‰ heavier than the natural dust derived from the local host rocks. Weiss et al. (2007) used the Zn isotopic signature of peat surface layers affected by atmospheric Zn contamination to estimate those of the probable sources, a mining site ($\delta^{66}\mathrm{Zn}_{\mathrm{JMC}}$= +0.32±0.18‰, 2SD) and a smelting site ($\delta^{66}\mathrm{Zn}_{\mathrm{JMC}}$=+0.66±0.16‰, 2SD). These values are ‘heavy’ compared to the negative $\delta^{66}\mathrm{Zn}_{\mathrm{JMC}}$ values measured by Mattielli et al. (2006) in smelter airborne particles ($\delta^{66}\mathrm{Zn}_{\mathrm{JMC}}$=−0.02 to −0.52‰). Riverine suspended particulate matter (SPM) and sediments are both pivotal compartments for pollution transport and accumulation in hydrosystems, but only one study of anthropogenic Zn isotopic variations in SPM and sediments has been published so far (Petit et al., 2008). Cloquet et al. (2008) recently proposed a review of the known variations in the isotopic composition of zinc in the environment.

The aim of the present study was to understand and evaluate the impact of metallurgic activity on Zn isotopic fractionation and to assess the potential of Zn isotopes as a tracer of anthropogenic Zn at a river system scale. For this, Zn isotopic compositions of surface soils, smelting/mining wastes, river and reservoir sediments from a river system (Lot River, SW France) impacted by Zn-ore metallurgy were determined using MC-ICP-MS. Zinc isotopic signatures of the anthropogenic sources and polluted compartments (soils and river/reservoir sediments) were compared. Links between Zn-extraction processes, Zn-extraction yields and Zn isotopic fractionation are discussed.

2. Field settings

The Riou Mort and the Riou Viou Rivers drain the Decazeville basin (Aveyron, SW France) and are affected by heavy metal pollution while running through a former (1842–1987) industrial Zn-ore treatment plant (Fig. 1). The contaminated Riou Mort River exports important amounts of various metals into the downstream Lot–Garonne–Gironde fluvial-estuarine system (e.g. Audry et al., 2004a,b; Schafer et al., 2006), contributing 23% of the total Zn flux into the downstream Gironde estuary, whereas its hydrological contribution is only 0.4% (Audry et al., 2004b).

During 145 years of Zn-ore treatment industrial processes evolved continuously allowing the processing of increasing amounts of Zn ores with growing extraction yields. Zinc was produced from $ZnCO_3$ until 1922 by a thermic reduction with coal. After 1922, the company processed sphalerite (ZnS), coming from major Zn ores around the world. This ore was thermically oxidized (roasted), and the ZnO obtained was solubilised with sulphuric acid (lixiviation) and metallic Zn extracted by electrolysis. The produced residues were then re-processed by a coal-fired thermic process, which was replaced by a second electrolysis-based process from the late 1970s. Zn production at Viviez increased progressively and reached a maximum of 100,000 tons Zn per year in 1985 (Audry, 2003). The Zn extraction was stopped after an accidental pollution in 1987.

During 1987–1990, remediation work was performed by confining part of the waste deposits in storage basins with underlying and overlying mud (Audry et al., 2004c). Nevertheless, large parts of the tailings are still submitted to chemical and physical erosion, so that metal mobilization can occur via (i) fluvial particulate matter transport, (ii) solubilisation by the infiltrated waters or (iii) airborne dissemination of small, Zn-rich particles. Furthermore, both the Zn-ore metallurgical plant and a local power plant have burnt, for