



Hydrology, Environment (Surface Geochemistry)

Osmium isotopic tracing of atmospheric emissions from an aluminum smelter

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ABSTRACT

We present for the first time the use of osmium isotopic composition as a tracer of atmospheric emissions from an aluminum smelter, where alumina (extracted from bauxite) is reduced through electrolysis into metallic aluminum using carbonaceous anodes. These anodes are consumed in the process; they are made of petroleum coke and pitch and have high Re/Os elementary ratio. Due to the relatively large geological age of their source material, their osmium shows a high content of radiogenic ^{187}Os produced from *in situ* ^{187}Re radioactive decay. The radiogenic isotopic composition ($^{187}\text{Os}/^{188}\text{Os} \sim 2.5$) of atmospheric particulate emissions from this smelter is different from that of other typical anthropogenic osmium sources (that come from ultramafic geological contexts with unradiogenic Os isotopes, e.g., $^{187}\text{Os}/^{188}\text{Os} < 0.2$) and also different from average eroding continental crust $^{187}\text{Os}/^{188}\text{Os}$ ratios (ca. 1.2). This study demonstrates the capacity of osmium measurements to monitor particulate matter emissions from the Al-producing industry.

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1. Introduction

The chemical element osmium (Os, atomic number 76) has seven stable isotopes, of which ^{187}Os has a wide range of relative abundances in nature because part of the ^{187}Os found in a geological sample comes from the radioactive decay of ^{187}Re (half-life of about 42 billion years; Smoliar et al., 1996) and varies as a function of both lithology and geological age. Osmium has a limited number of anthropogenic uses, which should theoretically limit its dispersal in the environment. Nevertheless, osmium contamination does occur and the principal sources of osmium inputs to the environment seem to be derived from the industrial production of metals (Chen et al., 2009; Rodushkin et al., 2007), automotive exhaust catalysts (Rauch et al., 2004;

Poirier and Gariépy, 2005) and biomedical facilities emitted from hospital incinerators due to the use of OsO_4 as a fixative for electron microscopy of organic material (Esser and Turekian, 1993). High osmium concentrations have been reported in coastal and estuarine sediments, and observed shifts in isotopic compositions have supported the conclusion that anthropogenic Os contamination into the environment is occurring (Esser and Turekian, 1993; Ravizza and Bothner, 1996). Dissolved aquatic Os is believed to be rapidly scavenged onto particle surfaces in reducing environmental redox settings, so that Os dispersion in such aquatic environment is controlled by particle transfers (Williams et al., 1997). Surface seawater was even reported as having been globally contaminated by anthropogenic Os (Chen et al., 2009). This chemical behaviour has quickly generated interest in the $^{187}\text{Os}/^{188}\text{Os}$ ratio as a tracer of anthropogenic inputs to sediments (Esser and Turekian, 1993; Ravizza and Bothner, 1996; Williams et al., 1997).

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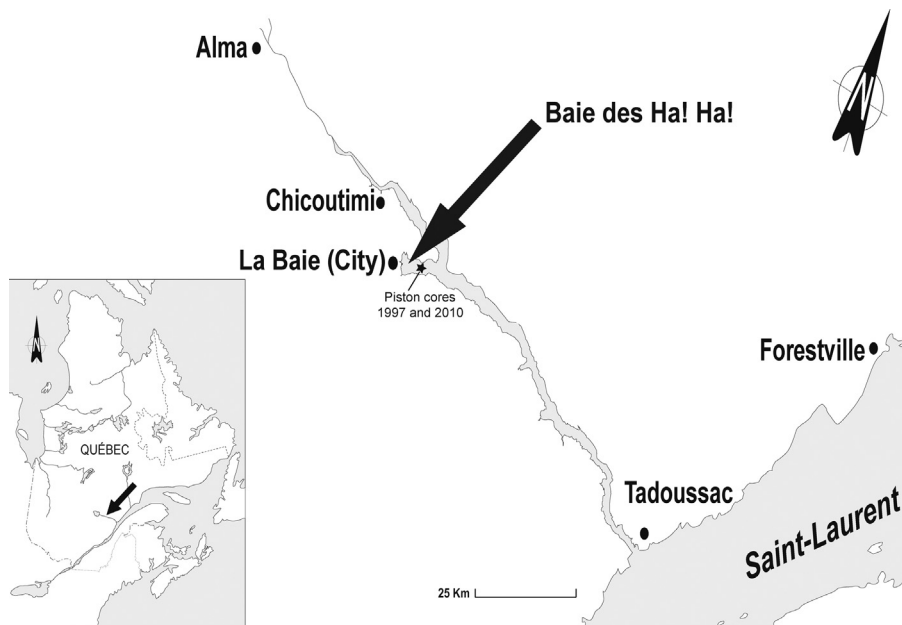


Fig. 1. Grande-Baie aluminum smelter location.

Our study area is the surroundings of the Grande-Baie aluminum smelter (G-B), operated by Rio Tinto Alcan (RTA) near the town of La Baie (Québec, Canada). Located on the shores of the Baie des Ha!-Ha! (BHH, Fig. 1), this smelter started operating in 1980. Aluminum smelting is a major industrial process within the realm of base metal production. The process of aluminum production involves the electrolytic reduction of alumina to Al (liquid) by reacting with a carbon anode in a cell containing a bath of molten alumina and cryolite (Na_3AlF_6), used as a fusion flux. In this specific case, the main process atmospheric emissions are, in order of abundances: CO_2 , gaseous fluorides, sulfur dioxide (SO_2) and dust (Divan Junior et al., 2008). Thus, the hundred-meter-long pot rooms are subject to dust emission associated with the produced gases. Raw pot gases and dust are recovered directly from the cells and then scrubbed at gas treatment centres (GTC), with bag filters and injections of fresh alumina that reacts with the fluoride in the gas (part of that fluorinated alumina is then re-used for the electrolytic reduction). This process is > 99.5% efficient at removing dust and gaseous or particulate fluorides (Boullemant, 2011). Emitted dust comes mainly from alumina and molten bath particulate matter entrained to stacks with the carbon dioxide created during anode consumption. During maintenance operations on pots (especially during anode replacing), particulate matter that is neither recovered nor treated can be emitted via roof vents. These emissions are most probably deposited in the local environment of G-B (emissions of low velocity and low temperature “large” particles—i.e. > 2.5 μm). The fume treatment centre (FTC), located in another area of the plant, recovers fumes from the anode-baking furnace, where green anodes from the paste plant – where the anode paste (pitch and coke) is crushed, ground, and mixed – are shaped and baked (Boullemant, 2011). The fumes are then scrubbed

with the same process as GTC. G-B smelter also has two effluents: 1201 for rainwater and 1202 for wastewater from the plant. They join together to form the 1203A effluent, which successively discharges into two artificial sedimentation lakes (Neree and Poleon lakes) and emerges as 1203B effluent to join BHH via the Mars river (Fig. 2).

Osmium is present as a significant natural impurity in the anode, because of its fossil fuel origin (i.e. distillation residue from petroleum refining). The emission process of this heavy metal (atomic mass ~ 190.2 g/mol) will not change the isotopic composition of the metal to any significant degree. Thus, depending on the age and composition of local country rock and soils, the isotopic signature of the emitted dust can be different and detectable from the surrounding environment. The carbon anode is an essential component of the electrolysis process used in aluminum smelters. The fact that it is fully consumed during the oxygen exchange reaction ($2\text{Al}_2\text{O}_3 + 3\text{C}_{\text{anode}} \rightarrow 4\text{Al}_{(l)} + 3\text{CO}_{2(g)}$; see below) suggests that trace elements present in it can be emitted at the stacks or the roof vent, being drawn in and transported by the generated gas. The anode being a carbon-rich by-product of petroleum refining industry (petroleum coke and pitch), one can expect it to contain a significant amount of radiogenic osmium (e.g., Selby et al., 2005). Coke and pitch have high Re/Os elementary ratios, and thus, over their burial time (many million years) develop large quantities of ^{187}Os from *in situ* disintegration of ^{187}Re . Consequently, the $^{187}\text{Os}/^{188}\text{Os}$ ratio of coke/pitch will be much higher than those of ultramafic deposits, which are the typical anthropogenic platinum group metal sources and have $^{187}\text{Os}/^{188}\text{Os}$ ratios closer to that of the Earth's mantle (0.1–0.2). Therefore, it should be possible to follow emissions of osmium in the atmosphere from smelters using its isotopic fingerprint. An anode used in aluminum smelting at G-B was measured at $^{187}\text{Os}/^{188}\text{Os} = 2.393 \pm 0.005$ (2σ)

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