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Dissolution and solubility of trace metals from natural and anthropogenic aerosol particulate matter

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Abstract

An open flow reactor is used to simulate the dissolution process of mineral aerosol particles in atmospheric water droplets. Data on dissolution kinetic and solubility are provided for the major trace metals from two kinds of matrix: alumino-silicated and carbonaceous sample. The results emphasise that the metals contained in the carbonaceous aerosols are easier dissolved than in the alumino-silicated particles. The released concentrations are not related to the total metal composition or the origin of particles, but are directly associated with the type of liaisons whereby the metals are bound in the solid matrix. Thus, the metals coming from carbonaceous particles are adsorbed impurities or salts and hence are very soluble and with a dissolution hardly dependent on pH, whereas the metals dissolved from alumino-silicated particles are less soluble, notably the ones constitutive of the matrix network (Fe, Mn), and with a dissolution highly influenced by pH. Consequently, in the regions with an anthropogenic influence, the dissolved concentrations of metals found in the atmospheric waters are mainly governed by the elemental carbon content. Moreover, it appears that the dissolution kinetic of metals is not constant as a function of time. The dissolution rates are very rapid in the first 20 min of leaching and then they are stabilised to lower values in comparison to initial rates. By consequence, the total dissolved metal content is provided after the first 20 min of the droplet lifetime. For this reason, the effects of trace metals on the atmospheric aqueous chemistry and as atmospheric wet input to the marine biota are maximal for "aged" droplets.

Keywords: Trace metals; Dust; Fly-ash; Dissolution kinetic; Leaching; Atmospheric water

1. Introduction

Several researches are revealed that trace metals play an important role in marine productivity (Morel et al., 1994; Whitfield, 2002). Most of the studies show a nutrient-depleted profile in the upper ocean for these metals and in particular Fe, Cu, Co, Cd and Zn (Butler, 1998). Over the past two decades, many studies stated that the dry and wet atmospheric aerosol depositions are significant, and sometimes the only, source of these compounds in coastal and remote regions (Guerzoni et al., 1999; Spokes et al., 2001). The atmospheric input of the trace metals to the ocean is so governed by the origin of aerosols and the water/particle interaction, in particular in the rain droplets (Chester et al., 1997). The particulate fraction dominates the dry deposition of all metals. However, in wet deposition, the dissolved fraction of trace metals, directly available for the phytoplankton, becomes dominant (Chester et al., 1999). There is now a relative large database on the chemical

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composition of the aerosol from a variety of marine regions. For example, Chester and Johnson (1971), Chester et al. (1999) and Guieu et al. (1997) have shown that western Mediterranean aerosols are characterised by an European background signature upon which Saharan inputs are superimposed. On the contrary, few data exist on the particle/atmospheric water reactivity and the partitioning between dissolved and particulate trace metals within the rain droplet is obviously needed to be documented.

Furthermore, dissolved trace metals are implied to different chemical processes in the atmospheric liquid phase. It has been emphasised that iron (Faust and Hoigné, 1990) copper (Sedlak and Hoigné, 1993) and manganese (Berglund and Elding, 1995) may react as catalysts in the oxidation of S(IV) in cloud droplets. Several authors also pointed that these metals might significantly influence free radicals budget because they are expected to react efficiently with many of the oxidising and reducing agents in atmospheric waters such as HO_2/O_2^- (Zuo and Hoigné, 1993; Losno, 1999). The reactivity of these transition metals is closely related to their concentrations in the aqueous phase. Thus, even if Cu reacts at much faster rates with hydroperoxyl and superoxide radicals, Fe is likely as significant as Cu in the HO_x cycles because the concentrations of dissolved Fe in atmospheric waters are at least one order of magnitude higher than those of Cu (Losno, 1999). It has been showed that a twofold increase of dissolved iron concentrations could multiply by a factor of 2 the oxidation rate of S(IV) (Clarke and Radojevic, 1987). Large uncertainties arise from estimations of trace metals concentrations in tropospheric waters. The chemical composition of cloud water varies according to the incorporation of atmospheric aerosols and gaseous species, and some products of chemical reactions taking place within the droplets. The presence of trace metals in cloud water depends exclusively on dissolution of aerosols particles through heterogeneous multiphase chemical reactions. It has shown that droplet conditions, such as pH, and the nature of incorporated aerosol particles govern these dissolution processes and hence the soluble fraction of aerosol particles (Jickells et al., 1992; Zhuang et al., 1992; Spokes et al., 1994; Desboeufs et al., 1999). Consequently, it is of particular importance to relate the aerosol particles origin and dissolved trace metals concentrations to assess their significance in the liquid droplets chemistry.

In this paper, we present the results of several experimental leaching measurements which have been carried out on mineral aerosol particles in atmospheric water conditions. The experimental system enables both to quantify the soluble fraction of mineral aerosol particles, and to study their dissolution kinetics. Thus, the objective of this work is to use the study of trace metals dissolution from mineral aerosol particles to estimate the relationship between the parent character of aerosols and their solubility in trace metals.

2. Method and materials

All dissolution rates and solubilities obtained in the present work were performed using an open flow reactor perfected for the aerosol particles dissolution study in cloud droplets (Desboeufs et al., 1999). In this reactor, 20 mg of particulate matter are leached by a flow of an aqueous solution. This inlet solution is MilliQ® water acidified with Suprapur® sulphuric acid (H_2SO_4) which is a typical atmospheric acidifying agent (Fuzzi, 1994). The pH is fixed to 4.7, median pH in the atmospheric waters (Li and Aneja, 1992). About 30 ml of the outlet solution, containing dissolved trace metals from particulate matter, was sampled all the 2 min during the first 30 min of leaching then at 45, 60, 90 and 120 min. These liquid samples were analyzed by atomic emission spectrometry coupled with plasma (ICP-AES) (Desboeufs et al., 2003a). All experiments and analysis were conducted in ultra-clean rooms and under benches (class 10) to avoid metal contamination. From measured dissolved concentrations, dissolution rates and solubilities (ratio between the dissolved metal concentration and the total metal content in solid sample) of trace elements are calculated according to the way described elsewhere (Desboeufs et al., 1999, 2001).

Natural and anthropogenic particulate matter were used for the dissolution experiments. Two types of mineral dust were investigated as windblown natural particles: (1) Loess of Cape Verde (Loess), which are analogue of Saharan aerosol particles (diameter 2–20 μm), mainly constituted of alumino-silicated mineral (quartz, feldspars, clays, pyroxenes) (Desboeufs et al., 2003b) and (2) Arizona dust (AD) which is the fine fraction of air floated sand (quartz and clays) from the Salt River Valley in Arizona (diameter 0.6–12 μm) provided by Powder Technology Inc. Two types of anthropogenic particles emitted from industrial activities were also investigated: (3) The <100 μm fraction of Porcheville Fly-Ash (PFA) emitted by heavy fuel oil combustion, and collected in the electrostatic filters of the thermal power station of Porcheville (France); which the major constituent is graphite C associated with low contents of cristoballite (SiO_2) and mullite ($3Al_2O_3$, $2SiO_2$) and (4) Vitry Fly-Ash (VFA, diameter 2–100 μm) emitted by coal combustion in the thermal power station of Vitry (France). To the difference of PFA which is produced from fuel, the VFA, emitted from coal, are principally constituted of alumino-silicates (quartz and mullite). (5) The last sample, urban particulate matter (UP, diameter 30 nm to 10 μm) provided by NIST as standard reference (SRM 1648), is a mixture of anthropogenic pollution and natural material (sludges, fly-ash