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Heterogeneous microchemistry between $CdSO_4$ and $CaCO_3$ particles under humidity and liquid water

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HIGHLIGHTS

- Raman analysis of chemical reactions between $CdSO_4$ and $CaCO_3$ particles.
- Under humid air no changes of morphology and chemical composition were observed.
- Condensation of liquid water generates an insoluble $CdCO_3$ layer on $CaCO_3$ surface.
- Addition of water previously equilibrated with $CaCO_3$ generates $CdCO_3$ and $CaSO_4$.

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ABSTRACT

Laboratory experiments using *in situ* Raman imaging combined with *ex situ* TOF-S-SIMS demonstrate the behavior of $CdSO_4{\cdot}8/3H_2O$ microparticles in contact with $\{10\bar{1}4\}$ $CaCO_3$ (calcite) surface under three different experimental conditions representative of unpolluted atmosphere. The contact of $CdSO_4{\cdot}8/3H_2O$ particles with $CaCO_3$ surface in humid air (RH ~ 40–80%) does not induce any chemical reaction. In contrast, the condensation of a water drop on $CdSO_4{\cdot}8/3H_2O/CaCO_3$ interface causes the free dissolution of $CdSO_4{\cdot}8/3H_2O$ particle in the drop. A $CdSO_4{\cdot}8/3H_2O$ microcrystal is reformed after gentle drying with a $CdSO_4{\cdot}H_2O$ coating of the $CaCO_3$ surface. The TOF-S-SIMS image of the $CaCO_3$ surface provides evidence of a thin layer corresponding probably to insoluble coating of $CdCO_3$ (otavite) or $Cd_xCa_{1-x}CO_3$ solid solution at the liquid–solid interface. This layer armours the $CaCO_3$ from further dissolution and stops the reaction. The deposition of $CdSO_4{\cdot}8/3H_2O$ particle in water drop previously in contact with $CaCO_3$ for a long time generates $CdCO_3$ small rhombohedral crystals while gentle drying provokes the crystallization of bar shape crystals of $CaSO_4{\cdot}2H_2O$ (gypsum). These laboratory results provide valuable chemical prediction for a possible fate of cadmium rich particles emitted in the atmosphere and thus, can contribute to realistic assessment of human exposure to Cd hazard.

1. Introduction

European REACH Regulation (EC 1907/2006 of European Parliament and of the Council of 18 December 2006) recommends managing the environmental and sanitary risks induced by substances of very high concern such as some metals and metalloids. Although cadmium has been classified with arsenic, lead and mercury at the top of the priority list of the most hazardous metals, cadmium is currently used in a wide variety of applications such as nickel–cadmium rechargeable batteries, pigments, plastics and pesticides. The principal industries that use cadmium are metal smelting, electronics, nuclear power stations, paint pigment productions, and other metal working and refining companies [1]. Cadmium is a by-product of the smelting of other metals such as zinc, lead, and copper. Cadmium is released into the environment from metal processing operations, burning fuels, or making, using and disposing of metal products [2]. Particularly, metal processing industries using pyrometallurgic techniques, industrial waste, burning coal and oil may release cadmium in the atmosphere [3]. Cadmium is primarily emitted as airborne particles as sulfide (CdS), oxide (CdO), chloride ($CdCl_2$) or sulfate ($CdSO_4$) in the micrometer and submicrometer size range [4,5]. People living near industry that conducts any of these activities may be exposed particularly to water soluble $CdCl_2$ and $CdSO_4$ particles [6,7]. Once Cd containing particles including $CdSO_4$ particles are in the atmosphere, they can be transported over long distances by the wind. During their atmospheric transport, the size and chemistry of $CdSO_4$ particles can change through heterogeneous chemical processes. Finally, cadmium deposits on ground as wet or dry deposits and can be resuspended in air by wind and

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manipulation [8]. Deposition in the lungs of the inhaled cadmium depends on the size of the airborne particles while absorption in the lungs depends on the chemical composition and the solubility of particles. Cadmium exposure even at low levels can cause adverse health effects [9–11]. The heterogeneous chemistry of $CdSO_4$ particles occurs under tropospheric conditions through gas–particle and particle–particle chemical reactions after agglomeration with airborne particles and particularly, with mineral dust.

$CaCO_3$ (calcite) is an important and ubiquitous mineral of Earth. The adsorption and retention of divalent metals in aqueous solutions including Cd^{2+} by $CaCO_3$ surfaces has been well studied due to its significant environmental relevance [12–16]. Water pollution due to heavy metals such as cadmium and lead is a serious global problem [17]. Cadmium in water tends to sink and accumulate in bottom sediments [18,19]. The affinity of $CaCO_3$ for Cd^{2+} not only makes it of interest for its role in environmental processes [20], but also for its potential practical use as a material to sequester Cd produced during anthropogenic activity [21–23]. The incorporation of Cd^{2+} into $CaCO_3$ structure to form solid solution is presumably facilitated by the similarity between the ionic radii of Ca^{2+} and Cd^{2+} [24]. In contrast to extensive work done on the removal of Cd^{2+} and divalent metals from aqueous solutions by $CaCO_3$, few papers has revealed the interest of the knowledge of interfacial reactivity between $CaCO_3$ particles and heavy metal salt particles under atmospheric conditions. Mineral dust and heavy metal particles have the potential to undergo various reactions with natural components of atmosphere including water and anthropogenic air pollutants such as NO_x. A huge quantity of $CaCO_3$ particles is uplifted from earths' crust into the atmosphere by strong wind and powdered $CaCO_3$ is also a major component of many engineered systems [25]. Calcite particles represent a reactive component of the mineral aerosol present in the troposphere and indoor environments [26,27]. Several field measurements show that aerosol particles based on mineral dust including $CaCO_3$ are typically in the micrometer size regime in atmosphere while airborne cadmium containing particles are both in the sub- and micrometer size domains [28]. Field observations also suggest that the mixing of natural mineral aerosols and anthropogenic metal particles promote heterogeneous chemistry during their transport in atmosphere [29]. The reactivity of airborne particles is generally done under humidity of ambient air where multiple wet-dry cycles can occur as function of temperature. Some scarce laboratory experiments have demonstrated the role of humidity and liquid water condensation at level of individual particle in the reactivity resulting from collision of micrometer-sized particles [29–32].

Here are reported results of laboratory investigations concerning reactions between $CdSO_4{\cdot}8/3H_2O$ microparticles in contact with $\{10\bar{1}4\}$ $CaCO_3$ crystal surface under three different experimental conditions related to unpolluted atmosphere: (i) humid clean air, (ii) condensation of pure liquid water on aggregate and (iii) condensation of liquid water on $CaCO_3$ surface and subsequent equilibration prior deposition of $CdSO_4{\cdot}8/3H_2O$ microparticles on wet $CaCO_3$ surface. The reactions were followed by Raman imaging under *in situ* conditions. Time-of-flight static secondary ionization mass spectrometry (TOF-S-SIMS) imaging was conducted under vacuum to assist in the interpretation. The main objective is to explain the chemical reactions that can occur in three different real events in troposphere (i) agglomeration of $CaCO_3$ and $CdSO_4{\cdot}8/3H_2O$ particles in humid air (ii) condensation of liquid water to $CaCO_3$—$CdSO_4{\cdot}8/3H_2O$ aggregate and (iii) agglomeration of $CdSO_4{\cdot}8/3H_2O$ particle with $CaCO_3$ particle previously coated with water film. When Raman spectroscopy is used as an analytical technique the assignment of the Raman signal is crucial. Therefore, the dehydration of $CdSO_4{\cdot}8/3H_2O$, the formation of cadmium basic sulfate and $CdCO_3$ (otavite) from $CdSO_4$ was reinvestigated by Raman spectroscopy.

2. Experimental

2.1. Materials

$CaCO_3$ (calcite) powder, $CdSO_4{\cdot}8/3H_2O$, $CdCO_3$, Na_2CO_3 and NaOH were purchased from Sigma–Aldrich with >99% purities and were used without further purification. $CaCO_3$ slides with $\{10\bar{1}4\}$ plane of 10 mm × 10 mm size were obtained by cleavage. At ambient temperature, $CaCO_3$ is poorly soluble in water ($\sim 1.4 \times 10^{-4}$ mol L^{-1}); $CdSO_4{\cdot}8/3H_2O$ is freely soluble in water (1.8 mol L^{-1}) and $CdCO_3$ is insoluble in water ($pK_s = -12.1$). Deionized water (pH ~ 5.5) and clean air containing atmospheric CO_2 (~0.03% in volume) were used. Pre-equilibrated $CaCO_3$ solution was prepared by mixing excess of $CaCO_3$ powder with deionized water. The mixture was continuously stirred and equilibrated with atmospheric CO_2 for several weeks. The pH of suspension was 8.2. Prior to use, this pre-equilibrated solution was filtered to eliminate $CaCO_3$ particles.

2.2. Preparation of the samples for in situ automated Raman imaging

2.2.1. Reaction in humid air

A freshly cleaved $CaCO_3$ slide $\{10\bar{1}4\}$ was placed on a glass slide. Microcrystals of $CdSO_4{\cdot}8/3H_2O$ were carefully deposited on the $CaCO_3$ surface in ambient air at room temperature. The sample was placed on a plate cooler of Pelletier device with accurate temperature controller in a cylindrical and hermetic chamber. The relative humidity (RH) is controlled with a laminar flow premixed with H_2O/air, further details are given in a previous work [31].

At first, the sample was exposed to a laminar flow of premixed H_2O/air gas (1 L/min clean air) at different RH in the 40–80% range without any liquid water at room temperature and atmospheric pressure. The Raman imaging was performed at different RH.

2.2.2. Condensation of pure liquid water

The condensation of small amounts of liquid water was carried out by cooling the plate supporting the sample to 5 °C for suitable time and by subsequent warming to room temperature. In a supplementary experiment a deionized water drop was carefully added on the surface and submerged the $CdSO_4{\cdot}8/3H_2O$ microcrystals. After different time of contact varying from 1 min to 24 h, the samples were dried under dry air to stop the reaction in the chamber before automated Raman mapping.

2.2.3. Condensation of liquid water and equilibration with $CaCO_3$

The third type of experiment is devoted to liquid water equilibrated with $CaCO_3$ before addition of microcrystal of $CdSO_4{\cdot}8/3H_2O$. The condensation of small amounts of liquid water on $CaCO_3$ crystal was carried out by cooling the plate to 5 °C for suitable time and by subsequent warming to room temperature. After 24 h a microcrystal of $CdSO_4{\cdot}8/3H_2O$ was added. In a supplementary experiment a pre-equilibrated $CaCO_3$ solution drop was carefully added on the surface and submerged the $CdSO_4{\cdot}8/3H_2O$ microcrystals. After different time of contact varying from 1 min to 24 h, the samples were dried under dry air in the chamber before automated Raman mapping.

2.3. Preparation of the samples for ex situ TOF-S-SIMS imaging

After reaction under the three different experimental conditions as previously described above the samples were dried and analyzed using TOF-S-SIMS instrument under high vacuum.