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Research paper

Nanostructured calcite precipitated under hydrothermal conditions in the presence of organic and inorganic selenium

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ABSTRACT

Selenium is an important trace metalloid, whose global cycle is controlled by fluid–rock interactions in the Earth's upper crust, interactions with bio-molecules in soils and living systems, and atmospheric transport in ashes. The cycling of selenium is often intimately associated with carbonate phases, with Se being generally incorporated as an impurity in calcite crystals or adsorbed on carbonate nanoparticles. In order to better understand the interaction of aqueous selenium species with carbonates, we studied the precipitation of calcite under hydrothermal conditions (30–90 °C, 25–90 bar) in a CO_2–H_2O–$Ca(OH)_2$ medium in the presence of aqueous inorganic and organic selenium compounds. Aqueous carbonation reactions in the presence of selenium at elevated temperatures and pressures, relevant for long-term CO_2 sequestration in reservoirs and other natural geological systems, have until now not been investigated to the best of our knowledge. Electron microscopy (FESEM and TEM) and synchrotron X-ray absorption spectroscopy (XAS) were used in a complementary manner to investigate crystal size, structural order (crystallinity), morphology of crystal faces, crystal organization, and selenium speciation in the calcite samples. XAS data analysis showed clear evidence for the incorporation of selenite oxyanion (SeO_3^{2-}) into the calcite crystal structure. At low Se content (1.3 mg/g calcite), a single site was observed with Se surrounded by six Ca atoms, whereas additional sites, probably corresponding to surface sorption sites, were found with increasing Se content. XAS also showed that seleno-L-cystine (Secys) was chemically fragmented during carbonation, and the solid phase contained elemental and oxidized Se, in hexagonal or amorphous form depending on the experimental conditions, with a minor proportion of Se(IV). Moreover, FESEM and TEM measurements revealed a very complex effect of Secys on the particle size and aggregation/agglomeration process, leading to the following calcite morphologies: rhombohedra, elongated rhombohedra (*c*-axis elongation), scalenohedra, star-like and shell-like crystal aggregates, and irregular calcite polycrystals. The aggregates and irregular polycrystals, which we designate as nanostructured calcite material, were constituted of nanometer-sized calcite crystallites (<100 nm). The star and shell-like crystal aggregates, which were observed only in the presence of Secys, may be due to crystal growth in the presence of associated secondary organic compounds due to a simultaneous chemical fragmentation of Secys. Overall, the results from this study show that selenium (of biotic or abiotic origin) can be integrated into the crystallographic structure of calcite under hydrothermal conditions. This has relevance for geological processes in diverse environments, such as hydrothermal systems along mid-ocean ridges, or underground reservoirs associated with massive injection of CO_2 for long-term geological sequestration.

1. Introduction

The biotic and abiotic (i.e. inorganic) formation of carbonates plays a crucial role in the global carbon cycle. Moreover, carbonate minerals often sequester various trace elements (actinides and lanthanides), metalloids, and heavy metals, and thus control in part their global cycling (e.g. Paquette and Reeder, 1995; Stumm and Morgan, 1995; Sigg et al., 2000; Stipp et al., 2006; Stumpf et al., 2006; Heberling et al., 2008; Schmidt et al., 2008, 2009). Selenium is one of these elements that can be taken up by carbonate phases. In addition to carbonates, selenium also occurs in many diverse geological environments: magmas, sulfide deposits associated with hydrothermal systems, oil and gas reservoirs, coal beds, and clays in black shales (Fouquet et al.,

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1996; Martens and Suarez, 1997; Malisa, 2001; Wen and Qiu, 2002; Rouxel et al., 2004; Yudovich and Ketris, 2006; Orberger et al., 2007). Selenium is also often considered to be a contaminant in the environment, and can be present in soils, ground waters, and the atmosphere. The source of contamination may come from natural selenium-rich geological formations that are altered naturally or anthropogenically, or from fly-ash leachates generated from the combustion of coal in electric power plants. Moreover, Se is also a long-lived, mobile fission product present in nuclear wastes, and thus has the potential to migrate into the far-field geological environment.

One of the reasons for studying Se uptake by calcite is that selenium is a beneficial trace element in living organisms (dietary deficiency for humans occurs at intakes less than 40 μg/day); on the other hand, it is deleterious to health (i.e. toxic) at elevated concentrations (>400 μg/day intake for humans); see Aurelio et al. (2010) and Levander and Burk (2006). Therefore, understanding selenium's mobility and its global cycle are necessary for better predicting its effect on the environmental quality of natural soils, as well as surface and ground water systems.

Selenium most commonly occurs in four different oxidation states in natural geological environments, namely −2, 0, +4, and +6. It can easily form compounds with metals. About fifty naturally-occurring minerals containing selenium have been identified. Past studies have shown that the fate and transport of Se in contaminated sites are influenced by its chemical form and speciation (see, e.g., Montes-Hernandez et al., 2008a, 2008b; Fernandez-Martinez and Charlet, 2009; and references therein). Selenium can also exist in organic molecules. For example, selenocystine (containing two amine and two carboxylic acid groups) is an analog to selenocysteine amino acid present in most living systems. It is naturally synthesized by several plants and can accumulate in soils (Martens and Suarez, 1997).

Carbonate minerals can be formed in natural or artificial environments by three different mechanistic pathways and/or conditions (e.g., Montes-Hernandez et al., 2010): (1) aqueous nucleation growth in homogeneous or heterogeneous systems, e.g., chemical or biogenic formation of carbonates in lakes, oceans, CO_2 storage sites, natural caves; (2) gas–solid carbonation of alkaline minerals (fine particles) in the presence of adsorbed water (water humidity conditions, 0<water activity<1), e.g., carbonate formation in water-unsaturated soils, in terrestrial or extraterrestrial aerosols; (3) dry gas–solid carbonation of granular/porous materials (dry conditions, water activity ≈ 0), e.g., the industrial mineralization, recovery, or capture of CO_2 at high temperatures in the presence of alkaline oxides (CaO, MgO) or metastable nanoparticle alkaline silicates. A brief description concerning the aqueous mineralization of CO_2 or aqueous carbonate formation in natural and industrial systems is provided in the supporting information (see text SI-1).

The nucleation growth of calcite has been widely studied in homogeneous (solution–solution interactions) or heterogeneous (solid–solution interactions) systems at atmospheric pressure and at moderate temperatures (<70 °C). Typical studies have used classical macroscopic, microscopic, or atomistic models to explain nucleation and growth (see e.g., Seifritz, 1990; Dove and Hochella, 1993; Lackner et al., 1995; Stumm and Morgan, 1995; Paquette and Reeder, 1995; Jonasson et al., 1996; Gower and Tirell, 1998; Teng et al., 1998; Temman et al., 2000; Dousi et al., 2003; Pastero et al., 2003; Freij et al., 2004; Fujita et al., 2004; Chrissanthopoulos et al., 2005; Dalas et al., 2006; Lee and Reeder, 2006; Menadakis et al., 2007; Montes-Hernandez et al., 2007; Nehrke et al., 2007). The incorporation of various oxyanions (e.g., selenite, selenate, arsenite, arsenate) into calcite has also been investigated in homogeneous or heterogeneous systems (e.g. Paquette and Reeder, 1995; Cheng et al., 1997, 1999; Roman-Ross et al., 2006; Alexandratos et al., 2007). For example, Reeder et al. (1994) have shown that selenate (SeO_4^{2-}) oxyanion substitutes for carbonate anion (CO_3^{2-}) in calcite. Other tetrahedral oxyanions, including CrO_4^{2-} and AsO_4^{3-}, have been found to substitute for CO_3^{2-} in calcite (Alexandratos et al., 2007; Tang et al., 2007). In all of these studies, the Ca shell was fitted with two Ca sub-shells, suggesting that the metal(loïd) was off-centered compared to the position of the carbon atom from the carbonate group in pure calcite.

Several studies have demonstrated that the incorporation and/or sorption of inorganic/organic impurities inhibit the crystal growth process of calcite (e.g., Dove and Hochella, 1993; Paquette and Reeder, 1995; Freij et al., 2004; Dalas et al., 2006). Conversely, the nucleation process may be enhanced, leading to a complex aggregation/agglomeration process of small particles, resulting in clusters or crystallites, as observed in present study. When the dimensions of the clusters or crystallites are in the 1 to 100 nm range, the solid is commonly termed a nanostructured material. While the effects of inorganic/organic aqueous selenium on calcite growth at ambient conditions have been previously studied, there is a lack of data on this at hydrothermal conditions. Our study, conducted at elevated temperatures and pressures in a triphasic gas–liquid–solid system, is meant to fill this gap. The experimental conditions used in this study are relevant for geological sequestration sites or geological systems associated with calcite carbonation reactions. Indeed, the mobility and/or uptake of Se and other trace elements contained in native rocks by mineral dissolution can be expected during CO_2 injection in geological formations (or any Ca-rich industrial waste), followed by carbonate precipitation (e.g. Kharaka et al., 2006). In general, hydrothermal conditions are representative of several geological environments in the Earth's upper crust where carbonate and selenium may interact: hydrothermal systems at mid-ocean ridges (Fouquet et al., 1996; Rouxel et al., 2004), black shales (Orberger et al., 2007), deep-seated plutonic rocks incorporating dense calcite vein networks (Malisa, 2001), coal beds (Yudovich and Ketris, 2006), and oil and gas reservoirs where CO_2 is used either as an enhanced oil recovery agent or for underground storage and sequestration (Kharaka et al., 2006).

The aim of the present study is the microscopic and molecular-scale characterization of calcite precipitated from an aqueous CO_2–H_2O–$Ca(OH)_2$ medium containing selenium at hydrothermal conditions. Similar experimental conditions were used in two previous studies, both with specific industrial applications: synthesis of a new calcite/Se^0 composite (Montes-Hernandez et al., 2008a) and removal of oxyanions from synthetic wastewater (Montes-Hernandez et al., 2009). The current study, however, is more fundamental in nature and provides new detailed data on calcite growth in the presence of inorganic and organic Se at hydrothermal conditions. This was achieved by using more sophisticated and higher resolution analytical tools: synchrotron X-ray absorption spectroscopy (XAS), high resolution transmission electron microscopy (HRTEM), and Field Emission Scanning Electron Microscopy (FESEM).

FESEM and HRTEM were used to study the morphology of the crystals, particle sizes, and the physical organization of the calcite nanoparticles. XAS was used to investigate the speciation and sorption/incorporation mechanism(s) of selenium in calcite. In addition, XAS was explicitly used to study the effects of certain physicochemical parameters, such as the initial concentration of the selenium compounds used (sodium selenite and seleno-L-cystine), temperature (30 and 90 °C), gas pressure (CO_2 or CO_2 + Ar mixture, at 20, 55 and 90 bar), and reaction time.

In the present study, novel insights have been gained concerning selenite incorporation into calcite structure, inhibition of calcite growth (leading to a nanostructured calcite), and irregular organization of nanosized crystallites. There are, however, several limitations to the present approach. Based on our experimental setup and on the ex-situ measurements (HRTEM and XAS), it remains difficult to determine whether the nanostructured calcite is the product of multiple nucleation events from a different precursor, such as amorphous calcium carbonate or vaterite. In order to shed more light on this, time resolved in situ measurements would be necessary, by coupling, for example, a reaction cell with XAS, RAMAN, or IR spectroscopic