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Review

Reactivity of the calcite–water-interface, from molecular scale processes to geochemical engineering

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ABSTRACT

Surface reactions on calcite play an important role in geochemical and environmental systems, as well as many areas of industry. In this review, we present investigations of calcite that were performed in the frame of the joint research project "RECAWA" (reactivity of calcite–water-interfaces: molecular process understanding for technical applications). As indicated by the project title, work within the project comprised a large range of length scales. The molecular scale structure of the calcite (1 0 4)–water-interface is refined based on surface diffraction data. Structural details are related to surface charging phenomena, and a simplified basic stern surface complexation model is proposed. As an example for trace metal interactions with calcite surfaces we review and present new spectroscopic and macroscopic experimental results on Selenium interactions with calcite. Results demonstrate that selenate (SeO_4^{2-}) shows no significant interaction with calcite at our experimental conditions, while selenite (SeO_3^{2-}) adsorbs at the calcite surface and can be incorporated into the calcite structure. Atomistic calculations are used to assess the thermodynamics of sulfate (SO_4^{2-}), selenate (SeO_4^{2-}), and selenite (SeO_3^{2-}) partitioning in calcite and aragonite. The results show that incorporation of these oxo-anions into the calcite structure is so highly endothermic that incorporation is practically impossible at bulk equilibrium and standard conditions. This indicates that entrapment processes are involved when coprecipitation is observed experimentally. The relevance of nano-scale surface features is addressed in an investigation of calcite growth and precipitation in the presence of phosphonates, demonstrating the influence of phosphonates on the morphology of growth spirals and macroscopic growth rates. It is investigated how physical properties of limestone containing cement suspensions may influence the workability of the cement suspensions and thus the efficacy of limestone in industrial applications. The largest scale is reached in iron filtration experiments in a water-purification-pilot-plant using limestone as filter material, which appeared to be highly effective for removing iron from drinking water. Investigations presented cover a whole series of methods to study the calcite–water-interface. Many calcite related topics are addressed, demonstrating how broad the field of calcite–water-interface research is and how manifold the applications are, for which calcite–water-interface phenomena are of major relevance.

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1. Introduction

Calcite is the most common polymorph of calcium carbonate and the thermodynamically most stable at standard conditions (room temperature and atmospheric pressure). Calcite is one of the most common minerals in the earth's crust, and the main component of limestone. Due to its ubiquity, surface reactions on calcite play an important role in geochemical and environmental systems.

The exchange of carbonate ions of calcite with the aqueous solution phase defines to a large degree the chemical milieu of ground and surface waters. The buffering effect of bicarbonate has a major influence on the chemical behaviour of soils and sediments. Numerous studies have shown that trace elements adsorb at the calcite surface and can thereafter be incorporated into the calcite crystal structure (e.g. Cheng et al., 1997, 1999; Curti, 1999; Curti et al., 2005; Elzinga et al., 2006; Heberling et al., 2008a,b; Reeder et al., 1994, 2004; Rouff et al., 2006; Staudt et al., 1994; Tesoriero and Pankow, 1996). The reactivity of its surface makes calcite a potentially important sink for heavy metals, metalloids and other contaminants in aquifers (Dong et al., 2005; Wang et al., 2005) and soils (Wang and Liu, 2005; Zheng et al., 2003), in travertine (Le Guern et al., 2003; Winkel et al., 2013), lacustrine-, or marine sediments (Rumolo et al., 2009), as well as in water purification plants (TrinkwV, 2001). The surface charging behaviour of calcite can determine its efficacy in industrial applications and has a major influence on contaminant adsorption.

Beside the natural processes, calcite is used in many industrial processes, such as paper- and cement production, and plays a prominent role in geochemical engineering projects like nuclear waste (Arcos et al., 2008) and CO_2-storage, or even oil production (Kan and Tomson, 2012). The fields of applications, that are directly involved in the production or the conversion of calcium carbonate, in which calcium carbonate is used as a process chemical (mainly filling material), or for which the properties of calcite are of major importance in some other context, is large.