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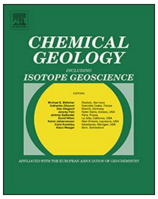

Precipitation behaviour in the system Ca^{2+}-Co^{2+}-CO_3^{2-}-H_2O at ambient conditions — Amorphous phases and $CaCO_3$ polymorphs

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ABSTRACT

The crystallisation behaviour of calcium carbonate phases in the system Ca^{2+}-Co^{2+}-CO_3^{2-}-H_2O was examined in batch reactors. Experiments with different initial ratios of Co^{2+}/Ca^{2+} (from 0 to 1.0) in the aqueous solution were performed to examine precipitation and mineral transformations under ambient conditions. The solids recovered from the aqueous solution after different ageing periods (ranging from 5 min to 2 months after precipitation) were characterised by X-ray diffraction, transmission and scanning electron microscopy and EDX microanalyses. The evolution of the aqueous solutions was also followed by measuring their pH and their chemical composition by UVA–visible spectroscopy. Our experimental data indicate that there are two sequences of solvent-mediated transformations in aged carbonates, one involving Co-rich phases and another involving calcium carbonates. Both sequences are characterised by the initial formation of amorphous or poorly crystalline hydrated phases, which transform into crystalline and anhydrous phases with ageing *via* a dissolution and re-precipitation mechanism. The stability and solubility of the phases are concerned with the incorporation of Co in Ca-bearing phases and Ca in the Co-bearing phases. Co-rich carbonates evolve from a hydrated amorphous hydroxycarbonate ($Co_2CO_3(OH)_2 \cdot H_2O$) to the crystalline phase $Co_2CO_3(OH)_2$. The transformation from the amorphous to crystalline phase ($Co_2CO_3(OH)_2$) was increasingly delayed as the initial Co/Ca ratio lowered. The sequence of Ca carbonates is affected by the amounts of Co^{2+} in the initial solution, and instead of the sequence ACC (amorphous calcium carbonate) → vaterite (Vtr) → calcite (Cal) obtained for control experiments, we observed ACC → monohydrocalcite → aragonite (Arg). Moreover, the Co^{2+}/Ca^{2+} ratio controls the earliest calcium carbonate phases to appear and the subsequent polymorph transformation reactions. In terms of cobalt incorporation into the solids, monohydrocalcite and Arg incorporate a certain amount of cobalt into their crystalline structures. The thermodynamic solubility products of cobalt hydroxide carbonates (amorphous and crystalline) were determined. This experimental study advances the progress of understanding carbonate precipitation-dissolution-recrystallisation reactions under ambient conditions.

1. Introduction

Understanding the stability of the main phases is essential to predict the transformations that occur during rock-forming processes. Vast areas of the Earth's surface are covered by carbonate rocks, the main mineral in which is calcite (Cal). Furthermore, many carbonates are minerals with a particular economic interest. Although only a few carbonates are primary or secondary ores of, for example, Mg, Sr, Fe, and Co, carbonates, and specifically calcium carbonates, are among the most important industrial minerals because of their extensive and diverse uses in different industries: construction, glass, ceramic, plastic, paper, food, health and many others. Not only in nature but also in industry or laboratory conditions, most carbonates form by reaction-precipitation in aqueous solution, and therefore, the precipitation of carbonates from aqueous solution has been of great interest in the scientific literature.

A key aspect of calcium carbonate crystallisation is linked to the subject of $CaCO_3$ polymorphism and its hydrated phases. As is known, Cal is the stable phase at the Earth's surface conditions, but aragonite (Arg), vaterite (Vtr), monohydrocalcite, ikaite and amorphous calcium carbonate (ACC) can also form, influenced by biochemical and geochemical factors. For instance, some polymorphs (ACC, Arg, Vtr) are found in the skeletons of numerous organisms as several organic compounds can control the nucleation and growth of calcium carbonate polymorphs. However, geochemical conditions such as the presence of dissolved ions or salinity allow the metastable precipitation of calcium carbonates (Monohydrocalcite, ikaita, Arg). Among the numerous factors that influence the precipitation of calcium carbonate polymorphs,

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one of the most determinant is the presence of foreign ions or molecules in the aqueous solution from which the carbonate precipitates. For example, it has been observed that some divalent cations such as Mg^{2+} and Sr^{2+} favour Arg formation instead of Cal (Lippmann, 1973; Reddy and Wang, 1980); some oxyanions such as SO_4^{2-}, SeO_4^{2-} and CrO_4^{2-} favour the stabilisation of Vtr (Fernandez-Diaz et al., 2010; Fernandez-Gonzalez and Fernandez-Diaz, 2013; Sánchez-Pastor et al., 2011); other compounds such as different organic molecules stabilise ACC (see Gower and Odom, 2000).

In this work, we focus on the cobalt (II) ion and its influence in calcium carbonate precipitation. Experimental studies (Barber et al., 1975; Katsikopoulos et al., 2008; Wada et al., 1995) have shown that the presence of Co^{2+} in fresh or salt water in which $CaCO_3$ precipitates promotes the formation of amorphous phases and, at specific ratios of Co^{2+}/Ca^{2+}, favours the stabilisation of Arg. It has also been observed, at the molecular level, that Co^{2+} inhibits the nucleation and growth of Cal (Freij et al., 2004), and macroscopic studies suggest that it is incorporated into Cal surface layers, leading to the formation of a cobalt-bearing surface (González-López et al., 2017b). The published experimental studies are mainly based on precipitation, but the evolution of the precipitated phases and the eventual transformations that can occur in the aqueous solution after precipitation remain unstudied. In this study, we designed a set of experiments in which after precipitation in the system Ca^{2+}-Co^{2+}-CO_3^{2-}-H_2O, the precipitated solids were aged in the remaining aqueous solution under ambient conditions (temperature and atmospheric CO_2 partial pressure). The nature and crystallisation behaviour of the solids and the evolution of the aqueous solution chemistry with increasing reaction times were investigated. Furthermore, the thermodynamic solubility products of cobalt hydroxide carbonates (amorphous and crystalline) were also determined. The ageing precipitation experiments along with the solubility data obtained from this study provide crucial insight into the calcium carbonate polymorphic transformation processes that occur in presence of cobalt in an aqueous environment.

2. Materials and methods

2.1. Precipitation + ageing experiments

In this study, we have reproduced some of the precipitation experiments conducted by Katsikopoulos et al. (2008), in which two different solutions of ($CaCl_2$ + $CoCl_2$) and Na_2CO_3 were mixed at room temperature. In this work, 15 different proportions of Co^{2+}/Ca^{2+} were considered, and the solids were separated by filtration and characterised immediately after precipitation. Here, we have selected only 4 of the 15 experiments: those with high Co^{2+}/Ca^{2+} ratios in which the precipitation of a low-crystallinity phase (lcp) was reported to have precipitated together with calcium carbonate polymorphs. Moreover, in the present study, the precipitated solids were not immediately filtered, but instead, they were aged in the remaining water solution for different predetermined periods of time.

Table 1 shows the concentration of the initial aqueous solutions. The labelled E0 experiment (control experiment) was run to follow evolution of calcium carbonate from an aqueous solution free of cobalt.

Table 1
Initial aqueous solutions for the precipitation + aging experiments.

Exp	Aqueous solution 1		Aqueous solution 2	Ratio
	$CoCl_2 \cdot 6H_2O$ (M)	$CaCl_2$ (M)	Na_2CO_3 (M)	Co^{2+}/Ca^{2+}
E0	–	0.05	0.05	–
E1	0.02	0.05	0.05	0.4
E2	0.03	0.05	0.05	0.6
E3	0.05	0.05	0.05	1
E4	0.05	–	0.05	–

For each experiment, 50 mL of a 0.05 M aqueous solution of Na_2CO_3 was mixed with 50 mL of a ($CaCl_2$ + $CoCl_2$) aqueous solution in a polypropylene reactor of 100-mL capacity. After mixing, the reactor was sealed using plastic tape to prevent evaporation and was maintained at 25 ± 0.5 °C under continuous stirring at 100 rpm by means of Teflon® -covered magnetic bar. All solutions were prepared with analytic grade (Panreac®) reactants and deionised Milli-Q® water.

For each experiment, a set of nine identical runs was conducted, and each one was stopped after a predetermined period of ageing. The nine considered ageing periods were 5 min, 1, 5, 24 and 48 h, and 4, 7, 30 and 60 days. After ageing, the solids were separated by filtering the aqueous solutions with a 0.45-μm Millipore® filter, rinsed with Milli-Q® water to avoid excess salts and dried at room temperature. Furthermore, the aqueous filtered phase was kept at 8 °C in a refrigerator. Finally, both solid and aqueous phases were sampled for their analysis. Each run was repeated at least three times to check the reproducibility of the results.

2.2. Solid phases characterisation

After each experiment, a representative sample of the precipitated phase was selected and characterised by different instrumental techniques to determine its chemical and mineralogical composition, morphology, crystallinity and eventual evolution with ageing time. Solids were first analysed by powder X-ray diffraction (XRD) to identify the solid phases and determine their crystallinity. Moreover, in the case of the identified crystalline phases, the observed reflections were indexed, and the corresponding cell parameters calculated and refined.

The diffraction patterns were obtained by scanning from 5° to 80° of 2θ with a step size of 0.02° on a Philips X'PertPro diffractometer using CuKα radiation. The instrument was periodically calibrated with an external Si standard. The collected diffractograms were processed with the X'Pert HighScore Plus (PANalytical B.V.) software.

The morphology and a first estimation of the composition of the precipitates were studied by scanning electron microscopy (SEM) in a JEOL 6610LV microscope equipped with an INCA Energy 350 microanalysis system (EDX) supplied with the Xmax 50 silicon drift detector (PentaFET, Oxford Instruments) fitted with an ultra-thin window that allows the detection of oxygen. Secondary and backscattering electron images allowed the detailed observation of the external morphology and the discrimination of possible compositional inhomogeneities on the solid surfaces. The microanalysis system provided a semi-quantitative chemical analysis of the precipitates. More precise quantitative chemical analyses were performed in a JEOL JEM-2100 transmission electron microscope equipped with an Energy Dispersive X-ray (EDX) micro-analyser.

2.3. Aqueous phase characterisation and modelling

The aqueous solutions were monitored for pH, alkalinity and cobalt and calcium concentrations for the entire reaction time. Both pH and alkalinity were immediately measured after filtration using a CRISON Compact Tritrator S equipped with a CRISON electrode, model 50-14T. The electrode was regularly calibrated with two CRISON buffer solutions of pH 4.01 and 7.

Cobalt and calcium concentrations were determined by UVA-visible spectroscopy in an AquaMate Vis Spectrophotometer (Thermo Scientific). Cobalt determination was performed by the Hach method 8078 with a wavelength of 620 nm, a precision of 95% (0.99–1.01 mg/L Co) and a sensitivity of 0.01 mg/L Co per the 0.010 absorbance change. Calcium analysis was conducted using the Spectroquant® method 14815 at a wavelength of 550 nm with a standard deviation of ± 1.5 mg/L Ca and a sensitivity of 1.4 mg/L Ca per 0.010 absorbance change.

From the analytical data, the aqueous phases of each experiment and for each specific ageing time were modelled with the geochemical code PHREEQC (Parkhurst and Appelo, 1999) and the phreeqcd.dat