Carbonate reaction experiments at carbonated and bicarbonated springs as a natural analogue field of CO₂ geological sequestration

Masao Sorai*, Munetake Sasaki

National Institute of Advanced Industrial Science and Technology, Higashi 1-1-1, Tsukuba, Ibaraki 305-8567, Japan

Abstract

To improve prediction accuracy of the long-term geochemical simulation, we measured carbonate growth rates at carbonated or bicarbonated springs as a natural analogue field of CO₂ geological sequestration. Seeding experiments, specially focusing on the effect of the Mg-ion as an inhibitor of calcite growth, indicated that the formation phase changed from calcite to aragonite with an increase of the Mg/Ca ratio, whereas that neither dolomite nor magnesite grew in the present range of the Mg/Ca ratio corresponding to typical aquifer conditions. On the other hand, there was no correlation between the calcite growth rate and the Mg/Ca ratio: the impact of the Mg ion alone seems to be diminished in nature. Regarding this, we also found that the calcite growth rate at field conditions was much lower than the literature values mainly based on laboratory experiments. These results suggest that various other factors besides the Mg-ion affect the natural carbonate kinetics intricately; which in turn can cause a significant error on the predicted timescale of the mineral trapping.

Keywords: CO₂ geological sequestration; Mineral trapping; Natural analogue; Carbonated spring; Growth rate; Carbonate

1. Introduction

Carbon dioxide geological sequestration (CGS) into aquifer formations involves various geochemical processes starting from dissolution of injected CO₂ in underground waters. Among such processes, carbonate reactions are most important from both perspectives of storage potentials and leakage risks: the growth of carbonates contributes to the fixation of CO₂ as a mineral trapping, whereas the dissolution of pre-existing carbonates around injection wells or in cap rocks has the potential to form a leakage path of...
injected CO₂. However, these processes generally have a long timescale, and thus there have remained many uncertainties on their kinetics under conditions of CGS. Specifically, several rate-controlling factors, such as the degree of saturation and the concentration of inhibitor ions, as well as the precipitation conditions for each carbonate species should be well compiled.

Facing such problems, we developed new experimental approach to measure reaction rates in a condition cloth to CGS. The approach has two important concepts. First, we focus on carbonated or bicarbonated springs as a reaction field because they are exactly regarded as a natural analogue of CGS. In this method, we can get natural data much more realistic than in laboratory. Moreover, carbonates already existing there provide the knowledge about what carbonate species should be formed under that condition as a result of long-term geochemical reactions. Another point is that seed crystals are introduced into spring waters artificially, thereby allowing us to get highly reliable reaction rates in a short time by observing surface configuration changes on a nanoscale. This also ensures more accurate judgment whether any target mineral can be formed or not. In this study, as a first trial of this method, we analyzed both reaction rate and formation condition of various carbonates directly in nature.

2. Experimental methods

2.1. Reaction experiments

The test sites include 15 hot spring facilities over 6 areas of Japan: Nagayu hot spring in Oita prefecture, two hot springs in Wakayama city, Shirahama hot spring in Wakayama prefecture, Masutomi hot spring in Yamanashi prefecture, six hot springs in Gunma prefecture, and Aobori hot spring in Chiba prefecture. These spring waters, belonging to the Na-Cl type or Na-Cl-HCO₃ type, range from 8.8 to 39.1°C in temperature, 6.4 to 8.8 in pH, 4,600 to 16,000 mg/l in chlorine concentration, and 2,200 to 8,000 mg/l in bicarbonated ion concentration. The saturation index with respect to each carbonate mineral, \( \log Q/Keq \) (the degree of saturation, where \( Q \) is ion activity product and \( Keq \) is equilibrium constant), was calculated using the geochemical modeling code of the Geochemist's Workbench.

Target minerals are four carbonate species in the Ca-Mg binary system: calcite and aragonite (CaCO₃), dolomite (CaMg(CO₃)₂), and magnesite (MgCO₃). We performed two types of experiments with different timescales: the short-term experiment within 24 hours and the longer-term experiment over up to a month. The former mainly focuses on the reaction of calcite, which has the highest reaction rate of four carbonates, whereas the latter targets other carbonate minerals with lower reactivity. Following crushing each single mineral, we selected cleaved samples of a few mm size with fresh surface, and gummed up them on a stainless plate. On the short-term experiment, a part of the seed surface was covered with a gold thin film by sputtering for a reference plane. We also used seed samples with myriad of growth hillocks on their surfaces, which were grown in a properly-adjusted supersaturated solution in advance of field experiment. On the other hand, the long-term experiment adopted the samples, a part of whose surface was pressure-bonded by gum not to bring into contact with solutions. In either case, those seeds were dipped into hot spring waters, and then, the sample was taken out one by one at predetermined time. Any fluid component on a seed surface was blown off by compressed air immediately after taking out of the water.

2.2. Analytical methods

Following the observation of the sample surface by a differential interference microscope (Olympus, BX51), we analyzed its configuration changes on a nano- to microscale using a phase-shift interferometer.
(Olympus, Fabulous) or a laser microscope (Keyence, VK-8510). These optical tools enabled to measure a temporal profile of the height level difference between the reference plane (i.e., the gold coating area or the original crystal surface which had been blocked by gum in solution) and the reacted surface. Reaction rate is estimated from the slope of the linear fitting function to the height change divided by the molar volume of each carbonate [1].

The grown phase on seed samples was identified using an imaging-plate X-ray diffractometer (Rigaku, R-AXIS IV++). For this measurement, we ripped a minute amount of surface material off carefully not to damage the original seed surface, gummed them up in globular shape using adhesion bond, and then mounted it on a needle tip 10μm in diameter set in the X-ray sample holder.

3. Results and discussion

3.1. Formation condition of carbonate minerals

The present study revealed that the aspect of changes on seed surfaces differed greatly according to location. For example, on the calcite seed, the seed mineral of calcite grew at Masutomi hot spring, whereas the metastable phase of aragonite formed at Nagayu hot spring. On the other hand, some organic matter instead of carbonates covered seed surfaces at Aobori hot spring. Several sites, where log \( \Omega \) is relatively lower, showed little or no changes of surface during experiments. Similarly, on dolomite and magnesite seeds, we could not observe a clear evidence of their own growth at all test sites.

To highlight such a difference of results, Fig. 1 plots the site condition on the Matsuda (2009)'s diagram for the stability range of calcite and dolomite, where the horizontal axis is the Mg/Ca molar ratio and the vertical axis is the salinity normalized by the seawater [2]. The Mg/Ca ratio is surely responsible for the species of the grown carbonate: only calcite is preferred at the lower Mg/Ca ratio, whereas aragonite forms at the higher Mg/Ca ratio. Intermediate region corresponds to the transition zone, where both calcite and aragonite are formed. The boundary Mg/Ca ratio dividing calcite and aragonite is derived as about 1-2, which shows a good agreement with the phase boundary of high-Mg calcite and aragonite after Matsuda (2009) [2].

On the other hand, we could not observe the dolomite growth as mentioned above. In fact, almost all sites in this study locate within the calcite stability region, although they are more or less supersaturated with respect to dolomite. This suggests that dolomite would never grow in the calcite stability region and require extremely high values of both log \( \Omega \) and Mg/Ca ratio for its growth. Therefore, considering the fact such that there exist little spring waters corresponding to the dolomite stability region in the database of hot spring waters, we can conclude that the precipitation of dolomite (and probably also magnesite) should not be incorporated in the geochemical simulation of CGS at least into typical aquifers except for the geochemically-specific setting, such as the formation including high-alkaline waters.
3.2. Growth rates of carbonate minerals

Figure 2 shows the log $\Omega$ dependence of growth rate of the calcite grown on calcite seed surfaces. The present experiment does not allow us to compare rate data directly because each site has different temperature and pH values. Therefore, first all data were converted to those at 40°C and pH 7, using the empirical rate function of temperature dependence (activation energy $E = 23.5$ kJ mole$^{-1}$) from the USGS reaction rate database [3]. In fact, the calcite growth rate is constant in the neutral pH range at constant temperature [3]; so the resultant data do not include the conversion by the pH variation.

In Fig. 2, we found some data scattering at several sites besides a rough trend such that calcite growth rate increased with an increase of log $\Omega$. Here, an inhibitor effect caused by dissolved ions, such as the Mg ion, can be responsible for the scattering of data. However, our checking showed no correlation between the calcite growth rate and the Mg/Ca ratio (Fig. 2). Furthermore, the data was correlated with neither the salinity nor the CO$_2$ concentration. Regarding this, we are now considering the possibility of an impurity effect due to another trace element. Figure 2 also depicts the calculated results of the calcite growth rate mainly based on laboratory experiments from the above USGS database (log $k = -5.81$ mole m$^{-2}$ s$^{-1}$, where $k$ is rate constant at 25°C and pH=0) [3]. It is noticed that our growth rates are much lower than these literature values. One possibility for such a discrepancy is that the traditional function form for the log $\Omega$ dependency of reaction rate is not suitably adjusted to field conditions. If this assumption is true, the present result can become an important constraint to avoid an overestimate of mineral trapping on CGS. However, other physical factors, such as the flow rate and the condition of crystal surface, also have a potential to reduce growth rate. Therefore, hereafter we should analyze in detail the cause for the reduction of growth rate based on additional experiments: that varying flow rate at field and that using the similar seed mineral in laboratory.
By the way, the aragonite grown on aragonite seed surfaces indicated the growth rate higher than that of calcite at the same log $\Omega$. Therefore, contrary to our prediction such that the mineral carbonation is reduced by the Mg ion, the present result comes to derive another aspect: the aragonite formation rather enhances the growth rate of calcium carbonate itself.

4. Conclusions

The present study performed field experiments at carbonated or bicarbonated springs as a natural analogue of CGS; we measured growth rates of various carbonate minerals directly in nature as well as analyzing the formation condition of each carbonate. The purpose in this study is to obtain various key parameters and knowledge with high reliability toward an improvement of prediction accuracy of the long-term geochemical processes on CGS. Seeding experiments, specially focusing on the effect of the Mg-ion as an inhibitor of calcite growth, indicated that the formation phase changed from calcite to aragonite with an increase of the Mg/Ca ratio. However, the high Mg/Ca ratio did not necessarily reduce the calcite growth rate and rather increased the growth rate of calcium carbonate itself via the aragonite formation. On the other hand, we found that calcite growth rate at field conditions is much lower than the literature values mainly based on laboratory experiments. Regarding this, we should identify the factors affecting reaction rates and quantify their impacts, hereafter. The present study used seed crystals, but that might have produced apparently higher growth rate. Rather, the real carbonation rate would be much slower because the nucleation of carbonate minerals requires the additional activation energy. Therefore, determinations of both the nucleation rate and the critical log $\Omega$ value for each carbonate are also important future problems.
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References

