TOPICAL REVIEW

Monohydrocalcite: a promising remediation material for hazardous anions

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Abstract

The formation conditions, solubility and stability of monohydrocalcite (MHC, CaCO₃·H₂O), as well as sorption behaviors of toxic anions on MHC, are reviewed to evaluate MHC as a remediation material for hazardous oxyanions. MHC is a rare mineral in geological settings that occurs in recent sediments in saline lakes. Water temperature does not seem to be an important factor for MHC formation. The pH of lake water is usually higher than 8 and the Mg/Ca ratio exceeds 4. MHC synthesis experiments as a function of time indicate that MHC is formed from amorphous calcium carbonate and transforms to calcite and/or aragonite. Most studies show that MHC forms from solutions containing Mg, which inhibits the formation of stable calcium carbonates. The solubility of MHC is higher than those of calcite, aragonite and vaterite, but lower than those of ikaite and amorphous calcium carbonate at ambient temperature. The solubility of MHC decreases with temperature. MHC is unstable and readily transforms to calcite or aragonite. The transformation consists of the dissolution of MHC and the subsequent formation of stable phases from the solution. The rate-limiting steps of the transformation of MHC are the nucleation and growth of stable crystalline phases. Natural occurrences indicate that certain additives, particularly PO₄ and Mg, stabilize MHC. Laboratory studies confirm that a small amount of PO₄ in solution (> 30 µM) can significantly inhibit the transformation of MHC. MHC has a higher sorption capacity for PO₄ than calcite and aragonite. The modes of PO₄ uptake are adsorption on the MHC surface at moderate phosphate concentrations and precipitation of secondary calcium phosphate minerals at higher concentrations. Arsenate is most likely removed from the solution during the transformation of MHC. The proposed sorption mechanism of arsenate is coprecipitation during crystallization of aragonite. The arsenic sorption capacity by MHC is significantly higher than simple adsorption on calcite.

Keywords: monohydrocalcite, arsenate, phosphate, formation, solubility, stability, sorption
1. Introduction

Water pollution by inorganic anionic species has become a serious environmental problem around the world. Particularly worrying is the contamination of drinking water by arsenic ions [1, 2]. More than 100 million people are exposed to unsafe As levels by drinking untreated groundwater in Bangladesh, India, China, Myanmar, Pakistan, Vietnam, Nepal, and Cambodia [1] which urges the development of effective remediation methods for arsenic. Phosphate ions (hereafter referred to as PO₄) are an important nutrient having several agricultural applications. Phosphate fertilizers can significantly increase food production. However, when they dissolve in water, the dissolved PO₄ ions cause eutrophication of aquatic environments and adversely affect the ecological system of lakes. Therefore, a method of removing phosphates from water thereby reducing the eutrophication of lakes is required [3].

Water is the most important transport medium on Earth’s surface, and therefore, the mobility of elements must be related to their solubility in water [4, 5]. The elements are released to the aqueous environment by desorption from mineral surfaces or dissolution of minerals, and they are removed from the solution by adsorption to the mineral surface or coprecipitation of minerals [4–6]. From the geochemical viewpoint, both the release and removal of elements occur simultaneously in nature. If the release is more than the removal, then water pollution occurs. This implies that Earth purifies itself from hazardous elements via water–mineral interactions. Therefore, careful observation of natural processes can suggest effective remediation schemes against pollution.

The important materials that participate in the removal of dissolved toxic elements are oxides, clay minerals and carbonate minerals, which are all formed at relatively high rates on Earth’s surface. Most of these minerals occur as fine particles and have a high specific surface area (up to hundreds m² g⁻¹). Four iron oxides—hematite, goethite, ferrihydrite and schwertmannite—are the most important naturally occurring sorbents of anionic species [7–12]. Of these, hematite and goethite are crystalline phases, whereas ferrihydrite and schwertmannite are metastable phases with poor crystallinity [13]. Metastable ferrihydrite and schwertmannite have a much higher surface area and reactivity towards the anionic species [14, 15]. Figure 1(a) shows the adsorption isotherm of arsenate on goethite as a function of pH [16]. Arsenate contains pentavalent arsenic, and thus, for simplicity, we label arsenate as As(V). The adsorption capacity for As(V) on goethite is approximately 10 g·kg⁻¹ of goethite at pH 4.5, and it decreases with increasing pH. This pH dependence relates to the surface charge behavior of goethite [6]. Under acidic conditions, the surface adsorbs protons and acquires a positive charge, which decreases with pH. The surface charge becomes negative at pH higher than the point of zero charge of goethite (approximately pH 8 [17]). Because dissolved arsenate are negatively charged (anionic) species, except at extremely low pH [9], the amount of adsorption decreases with increasing pH. Iron oxides are the most effective adsorbents for many anionic species under acidic or neutral pH condition, but not under alkaline condition. In addition, the redox condition must be considered when iron oxides are used as adsorbents because they are unstable under reducing conditions [13].

In contrast to iron oxides, carbonate minerals are stable under alkaline condition [6] and the stability does not depend on the redox state. Calcite and aragonite are two important and abundant calcium carbonates. The concentrations of soluble reactive phosphates are much lower in the pore waters of calcium carbonate rich sediments than in sediments with little or no calcium carbonate [18]. Adsorption of As and PO₄ on calcite and aragonite has been considered in a number of studies [19–23]. Sø et al [22, 23] investigated the sorption of As(V), arsenite and PO₄ on calcite in a series of batch sorption experiments in a wide range of pH, alkalinity, calcium concentration and ionic strength. They showed little or no arsenite sorption on calcite within 24 h but As(V) adsorbed well on calcite. The amount of As(V) sorption on calcite increases with decreasing alkalinity and ionic strength, but the effect of pH on As(V) sorption is small. PO₄ sorbs to a greater extent than As(V), and the amount of PO₄ sorption on calcite increases with decreasing alkalinity and ionic strength, similar to As(V). The amount of PO₄ sorption increases with pH. Millero et al [19] conducted PO₄ sorption experiments on calcite and aragonite. They showed that aragonite is a...
more effective sorbent of PO$_4^{3-}$ than calcite. These studies concluded that calcium carbonates are effective sorbents of As(V) and PO$_4^{3-}$, but the adsorption efficiency is weaker for calcite and aragonite than for iron oxides. Figure 1(b) shows the adsorption isotherm of As(V) on calcite measured by Alexandratos et al. [21]. The adsorption capacity for As(V) is approximately 500 mg kg$^{-1}$ of calcite, which is significantly lower than that for goethite. In summary, the use of carbonate minerals such as calcite and aragonite for the remediation of hazardous anionic species appears promising, but a higher sorption capacity is desired.

The reactivity is usually higher for metastable than stable phases [24]. Therefore, the metastable minerals ferrihydrite and schwertmannite are more effective sorbents than the stable goethite and hematite, as mentioned above, and one can expect a higher reactivity towards the anionic species for metastable calcium carbonates than for the stable calcite and aragonite. Six forms of calcium carbonate occur in nature: three anhydrous (calcite, aragonite and vaterite) and three hydrated forms (monohydrocalcite (MHC), ikaite and amorphous calcium carbonate (ACC)). Of these minerals, calcite is the most stable phase under Earth’s surface conditions. Although aragonite is less stable than calcite, it usually persists under Earth’s surface conditions for a long time. Vaterite, ikaite and ACC are unstable, so that ikaite and ACC transform within several days [26] to calcite or aragonite in a solution at ambient conditions. Therefore, vaterite, ikaite and ACC are rarely preserved in geologic media and are hardly suitable for remediation. The stability of MHC has long been debated [27]. Some laboratory studies indicate that MHC transforms to aragonite or calcite in solution within several days [27–29]. However, natural observations show that MHC has been preserved in ancient sediments formed more than a thousand years ago [30, 31]. Moreover, the natural MHC obtained under sedimentary conditions contained 4–6 g kg$^{-1}$ PO$_4^{3-}$ [31], suggesting that MHC is an efficient, long-term oxyanion sorbent. Understanding the physico-chemical properties of MHC should help us apply it as a remediation material. In this paper, we review the formation conditions, solubility and stability of MHC, as well as the sorption behavior of toxic anions on MHC to assess this material for environmental purification.

2. Mineralogical properties and natural occurrence

The chemical composition of MHC is CaCO$_3$·H$_2$O. Effenberger [32] determined the structure of synthetic MHC as follows. MHC belongs to the rhombohedral (trigonal) subclass. The space group of the substructure is $P3_112$ with the cell parameters $a = 0.60931$ and $c = 0.75446$ nm, and the parameters of the $P3_1$ primitive supercell are $a = 1.05536\ \text{Å}$ and $c = 0.75446\ \text{nm}$. Swainson [33] refined the primitive supercell parameters as $a = 1.05547$ and $c = 0.75644\ \text{nm}$ using natural specimens from lakes Butler and Fellmongery.

MHC is a rare mineral in geological settings. It has been most frequently found in saline lakes (figure 2) and was first reported in carbonate deposits in the shore zone of Lake Issyk-Kul in Kyrgyzstan by Sapozhnkov and Tsvetkov [34]. It was also found in beach rocks of lakes Fellmongery and Butler in Australia [27], surface sediments in Walter Lake in Nevada [35, 36], in Nam Co in Tibet [37], in East Basin Lake in southern Australia [38] and in Tsgan-Tyrm Lake in the west Baikal region [39]. The water temperatures of those lakes range from 0 to 25 °C, and therefore are not an important factor for MHC formation [27]. Table 1 summarizes the water chemistry of the saline lakes where MHC occurs [27], [36–40]. The pH is usually higher than 8 and the Mg/Ca ratio exceeds 4. As indicated below, the formation of MHC requires a high Mg/Ca ratio.

In addition to saline lakes, the presence of MHC has been reported as ikaite tufa debris in the seawater environment.
X-ray diffraction (XRD) patterns and infrared spectra of the solution were agitated for 10 s in an ultrasonic bath and the respective Mg solution was added to the artificial seawater resulting in crystallization of stable calcium carbonates. MHC was first prepared by Brooks [39], Kralj and Brecevic [40], while the others characterized MHC as a precursor or intermediate product in the MHC synthesis [41]. The Na ratios of 5.3 and 1.2. The solution was agitated for 10 s in an ultrasonic bath and left overnight in a refrigerator. The suspension was filtered through a 0.45 µm membrane. The solids were washed several times with small amounts of water and a portion of absolute ethanol, and then dried in air for several hours. X-ray diffraction (XRD) patterns and infrared spectra of the resulting solid showed only signals belonging to MHC.

Dejehet et al [45] prepared MHC using a procedure similar to that of Kralj and Brecevic [46]. The Na2CO3 solution was added to the solution containing Na, K, Ca, Mg, Sr and Cl. A Na2CO3 solution was added to the artificial seawater resulting in the respective Mg/Ca and CO3/Cl ratios of 5.3 and 1.2. The solution was agitated for 10 s in an ultrasonic bath and left overnight in a refrigerator. The suspension was filtered through a 0.45 µm membrane. The solids were washed several times with small amounts of water and a portion of absolute ethanol, and then dried in air for several hours. X-ray diffraction (XRD) patterns and infrared spectra of the resulting solid showed only signals belonging to MHC.

MHC was prepared from an artificial seawater in a guinea-pig bladder stone (reviewed in [41]).

Table 1. Water chemistry of some MHC-producing lakes.

| Lake Name             | pH  | Unit        | Na (mmol kg⁻¹) | K (mmol kg⁻¹) | Mg (mmol kg⁻¹) | Ca (mmol kg⁻¹) | Cl (mmol kg⁻¹) | SO4 (mmol kg⁻¹) | HCO3 (mmol kg⁻¹) | Mg/Ca | References               |
|-----------------------|-----|-------------|----------------|---------------|----------------|----------------|----------------|-----------------|-----------------|-------|--------------------------|
| Lake Fellmongery      | 8.6 | mmol kg⁻¹   | 246            | 6.09          | 38.7           | 2.35           | 282            | 17.0            | 9.2             | 16.5         | Taylor [27]              |
| Walker Lake           | 9.4 | mmol kg⁻¹   | 135.7          | 4.19          | 5.59           | 0.270          | 63.8           | 21.5            | 46.7            | 20.7         | Benson et al [36]        |
| Nam Co                | 8.04–9.72 | mmol l⁻¹   | 7.10–0.485     | 1.75–0.160    | 1.21–1.56      | 7.12–10.9      | 10.9           |                 |                 | 135.7         | Li et al [37]             |
| East Basin Lake       | 9.15 | mmol l⁻¹   | 708            | 15            | 49             | 0.80           | 625            | 4.50            | 32.8            | 61.8         | Last [38]                 |
| Tsagan-Tym Lake       | 8.60 | mmol l⁻¹   | 163            | 13.9          | 25.5           | 1.02           | 127            | 41.6            | 17.7            | 24.9         | Solotchina et al [39]     |
| Lake Issyk-kul        | 8.7 | mmol kg⁻¹   | 66.3           | 1.80          | 12.9           | 3.08           | 44.6           | 22.3            | 5.78            | 4.2          | Vollmer et al [40]        |

aAveraged over 35 observations.
bAt 0–90 m depth at 5 different sites.
cEstimated from the charge difference between cations and anions.

d| of the Ikka Fjord in Greenland [41] and in the cold waters of Shioyakka Spring in Japan [42] (figure 2). MHC was recovered from deep sediments formed at least several thousand years ago in Lake Hovsgol in Mongolia [30] and Lake Kivu in Central Africa [31]. MHC has been reported as a constituent of speleothems in limestone caves, precipitates from biochemical processes in the so-called moonmilk assemblage and a component of vertebrate otoliths and in a guinea-pig bladder stone (reviewed in [41]).

3. Laboratory synthesis of MHC

MHC was first prepared by Brooks et al [29], and many studies have followed [28, 43–48]. Some of them focused on the MHC synthesis [28, 29, 46], while others characterized MHC as a precursor or intermediate product in the crystallization of stable calcium carbonates [43, 44, 47, 48].

Kralj and Brecevic [46] synthesized MHC for use in dissolution experiments. MHC was prepared from an artificial seawater containing Na, Mg, Ca, Sr and Cl. A Na2CO3 solution was added to the artificial seawater resulting in the respective Mg/Ca and CO3/Cl ratios of 5.3 and 1.2. The solution was agitated for 10 s in an ultrasonic bath and left overnight in a refrigerator. The suspension was filtered through a 0.45 µm membrane. The solids were washed several times with small amounts of water and a portion of absolute ethanol, and then dried in air for several hours. X-ray diffraction (XRD) patterns and infrared spectra of the resulting solid showed only signals belonging to MHC.

Dejehet et al [45] prepared MHC using a procedure similar to that of Kralj and Brecevic [46]. The Na2CO3 solution was added to the solution containing Na, K, Ca, Mg, Sr and Cl. Although the solution compositions generally corresponded to seawater, the ratio of the components was varied: Mg/Ca from 0.1 to 3.48 and CO3/Ca from 2.83 to 6.37. The solutions were aged for approximately 15 days. The resulting solid phases contained spherulites of 100 µm diameter. The spherulites were separated from white gangue by dissolving the gangue in 0.1 N HCl or by sieving and rinsing with water. XRD confirmed that the obtained spherulites were mainly composed of MHC. Aragonite was present in the samples prepared from the solutions with Mg/Ca < 1. Scanning electron microscopy (SEM) observations showed that MHC had spherical morphology. The spherulites were surrounded by a layer with a Mg concentration 5 times higher than in the bulk, which was suggested to play a protective role.

Munemoto and Fukushima [28] synthesized MHC for use in transformation experiments. A solution containing 0.06 M CaCl₂ and 0.06 M MgCl₂ was prepared at room temperature, and Na2CO3 was added to it to result in 0.08 MCO3⁻. The Mg/Ca and CO3/Cl ratios in the mother solution were 1 and 1.3, respectively. Immediately after Na2CO3 was added to the solution, a whitish suspension was formed. It was stirred, aged for 48 h and filtered through a 0.2 µm membrane. The white paste collected on the filter paper was washed several times with an ample amount of deionized water and the resulting solid was air-dried. XRD showed only the MHC diffraction lines. Ca and Mg concentrations in the dried MHC were measured by wet chemical analysis as 8.31 and 0.46 mmol g⁻¹, respectively.

Yagi and Fukushima [49] synthesized MHC for use in adsorption experiments. The precipitation conditions were the same as those used by Munemoto and Fukushima [28]. After aging for 48 h, the solid was dialyzed for 3 days at 13 °C and freeze-dried. XRD confirmed the purity of the synthesized materials. The Ca and Mg concentrations were measured by wet chemical analysis as 8.49 ± 0.05 and 0.19 ± 0.01 mmol g⁻¹, respectively, and the CO3 and H2O contents were determined as 8.68 ± 0.16 and 8.77 ± 0.39 mmol g⁻¹, respectively, by thermogravimetry. The BET surface area was 16.4 m² g⁻¹.

Kinsman and Holland [43] examined the mineralogical compositions of calcium carbonates, precipitated from seawater upon slow addition of dilute Na2CO3 solutions, as functions of temperature and aging time. The reaction temperature ranged from 3 to 96 °C; however, the samples produced at above 30 °C were dried at 110 °C. According to stability studies [28], MHC instantaneously transforms to stable anhydrous calcium carbonate at temperatures above 50 °C. Therefore, we reviewed only the experiments conducted at 3 and 16 °C. They were carried out using the seawater collected near Sea Girt, NJ, which had the Mg/Ca ratio of 5. Diluted Na2CO3 or NaHCO3 solutions (250 ml) were slowly added to 600 ml of seawater to yield the 0.001 to 0.02 M CO3 concentrations in the final solutions. The CO3/Ca ratio ranged from 0.4 to 3 and the experiments lasted between 42 and 430 h. Then, the contents of the reaction vessels were filtered, washed with double-distilled water and dried at 30 °C. The structure of the precipitates was analyzed by XRD. Twenty-four batches were prepared at 3 and 16 °C by varying
Figure 3. Changes in XRD diffraction intensities of MHC and aragonite with time [44].

Kamiya et al [44] conducted two types of synthesis from the solutions of CaCl₂, (NH₄)₂CO₃ and MgCl₂. One set of experiments aimed to study the effect of the Mg/Ca ratio on mineral formation. The CO₃/Ca ratio was fixed as 1 and the Mg/Ca ratio was varied from 0 to 5. The solutions were sealed and aged for two months at 19–29 °C; the temperature variation did not affect the mineralogical compositions of the products. XRD showed that the precipitates obtained from the solutions with a Mg/Ca ratio >2.5 consisted of MHC and aragonite, but MHC was absent at lower Mg/Ca ratios. Another set of experiments assessed the effect of aging time on mineral formation. The starting solutions contained 0.1 M CaCl₂, 0.1 M (NH₄)₂CO₃ and 0.5 M MgCl₂ and had the Mg/Ca and CO₃/Ca ratios of 5 and 1, respectively. The obtained suspensions were filtered after 1, 2, 3, 4, 6, 8, 10, 15, 20 and 27 days. Figure 3 shows the change in XRD intensities, representing the contents of MHC and aragonite in the precipitates, as a function of time. The solids obtained after 3 days were amorphous, and after 4 days, the MHC peaks appeared. After 6 to 20 days, the XRD pattern consisted of MHC reflections only, with no amorphous phase, and the peak intensity was maximum after 10 days. The 111 reflection of aragonite appeared after 27 days, indicating MHC-aragonite transformation.

Loste et al [47] conducted syntheses of calcium and magnesium carbonates from the solutions of CaCl₂, MgCl₂·6H₂O and NaHCO₃. They used a bicarbonate solution for the source of carbonate and examined the effect of Mg/Ca ratio (between 0 and 10) on the mineralogy of the formed precipitates. The solutions were combined in a dish for crystallization and stirred for 2 min. The formed precipitates were then analyzed as the aging time progressed up to several days. The precipitates accumulated at the air–water interface and at the base of the dish. These were isolated and analyzed separately. ACC formed first in all the cases and then transformed into various crystalline carbonate minerals depending on the Mg/Ca ratio and aging time. MHC with calcite and aragonite was observed from the precipitates collected from the air–water interface of the solutions with Mg/Ca = 3 and 4 after 72 h. At Mg/Ca = 10, MHC with MgCO₃·3H₂O and magnesium calcite appeared at the air-water interface after 14 days.

Jimenez-López et al [48] conducted syntheses under closed system conditions from solutions containing NaHCO₃ and CaCl₂. The pH of the solutions was maintained by adjusting the partial pressure of NH₃ gas. Precipitation was carried out in isolated environmental chambers held at 25 °C and 1 atm inside a glovebox filled with argon. Each chamber contained four watch glasses mounted on supports approximately 5 cm above the bottom of the chamber. The initial solutions contained 0.33 M NaHCO₃ and 0.0023 M CaCl₂ and had a pH of 7.24 and the CO₃/Ca ratio of 143. The initial solutions and stock ammonium acetate solutions were placed in a glovebox containing 19 environmental chambers. After purging the system with argon, the solutions were loaded into the watch glasses of each chamber. Ammonium acetate solution was then poured on the bottom of each chamber, and the chambers were sealed with lids in a CO₂-free environment. The ammonium acetate solution released NH₃ gas into the chambers, which were then left to equilibrate for various periods up to 1440 min. At a certain time, the suspensions were filtered through a 0.1 µm membrane and dried at 40 °C for 6 h. According to the XRD patterns, MHC appeared after 30 min, followed by the formation of calcite and gradual disappearance of MHC, which was completed after 300 min.

Synthesis experiments as a function of time indicated that MHC is an intermediate phase—MHC formed from ACC and transformed to calcite and/or aragonite [44, 50], although in the studies by Jimenez-López et al [48], MHC was the first mineral to precipitate from solution. In most experiments, MHC formed from Mg-containing solutions; however, Jimenez-López et al [48] observed MHC formation even without Mg, followed by disappearance after 6 h. These results indicate that Mg acts as an inhibitor of the formation of stable calcium carbonates. Whereas the effects of the Mg/Ca ratio and duration on the formation of MHC have been extensively studied, the effect of temperature and CO₃/Ca ratio are still unclear.

4. Solubility of MHC

The dissolution reaction of MHC can be written as

\[ \text{CaCO}_3 \cdot \text{H}_2\text{O} = \text{Ca}^{2+} + \text{CO}_3^{2-} + \text{H}_2\text{O}. \]

The corresponding mass action equation is given as follows:

\[ K_{\text{MHC}} = \frac{a_{\text{Ca}^{2+}}a_{\text{CO}_3^{2-}}a_{\text{H}_2\text{O}}}{a_{\text{CaCO}_3 \cdot \text{H}_2\text{O}}}, \]

where \( K_{\text{MHC}} \) denotes the solubility product of MHC, and \( a_i \) is the activity of the \( i \)th species. The activities of pure solids and water are set to 1 by convention. The activities of dissolved species are related to the concentration in solution (measured in mol l⁻¹) via the activity coefficients. There are two reports
Kralj and Brecevic [46] measured the solubility in water under a CO$_2$ pressure of 1 atm at 25 °C. They used the natural MHC obtained from beach rocks at Lake Fellmongery, South Australia. The detailed mineralogical properties of MHC are given by Taylor [27]. Samples were suspended in a CO$_2$-saturated solution at 25.0 ± 0.1 °C. Aliquots of MHC suspensions were collected at regular intervals and filtered under CO$_2$ atmosphere. The filtrates were measured for pH and concentrations of Ca, Mg and Na. The solids were analyzed by XRD for the phase transformation. Hull and Turnbull found that the calcium concentration increased steadily to a maximum, where it remained for 20–40 h, and slightly decreased after the formation of calcite. They estimated the activities of Ca$^{2+}$ and CO$_3^{2-}$ from the measured Ca concentration and pH at equilibrium with MHC, and calculated the solubility of MHC as $10^{-7.60±0.03}$ (figure 4).

Kralj and Brecevic [46] measured the solubility of synthetic MHC between 15 and 50 °C. Their method of preparation of MHC is mentioned above. MHC slurry was injected in a closed glass vessel, and the lack of space for air inside the vessel prevented carbon dioxide exchange between the air and the studied system. The temperature was maintained within ±0.1 °C. During the study, the system was continuously stirred and the change in pH was logged. The authors estimated the activities of Ca$^{2+}$ and CO$_3^{2-}$ from the measured pH assuming the closed system, and then calculated the solubility of MHC as a function of temperature (solid circles in figure 4). The solubility decreased with temperature, and at 25 °C, it is about 3 times higher than the value measured by Hull and Turnbull [51]. Kralj and Brecevic [46] attributed this difference to the fact that they studied a synthetic material whereas the samples of Hull and Turnbull were natural. The solubility of MHC is clearly higher than those of calcite, aragonite and vaterite [52], but lower than those of ikaite [53] and ACC [25] at any temperature (figure 4). This trend indicates that MHC is metastable with respect to calcite, aragonite and vaterite and is stable with respect to ikaite and ACC under ambient conditions.

### 5. Stability of MHC

Brooks et al [29] reported that synthetic MHC is unstable and readily transforms to aragonite. Munemoto and Fukushi [28] conducted a systematic study of MHC synthesized by the method described in section 2. Batch alteration experiments were conducted at 10, 25, 40 and 50 °C; 80 mg (0.70 mmol) of MHC powder was added to 40 ml of 0.01 M NaCl electrolyte solutions. After aging, the suspensions were filtered through a 0.2 μm membrane, air-dried at room temperature and analyzed by XRD. The amounts of MHC and aragonite in the dried samples were evaluated by the external standard method.

MHC gradually transformed to aragonite at all temperatures. Calcite was not detected (table 2) despite it being the most stable CaCO$_3$ polymorph. Both the
nucleation and growth of calcite were inhibited by the presence of Mg$^{2+}$ in the solution [54]. Synthetic MHC contains a small amount of magnesium, which is released to the solution during the dissolution of MHC, and this released magnesium may have inhibited the formation of calcite.

The induction time of aragonite formation was estimated by XRD as 1800–3600, 3600–7200, 3600–7200 and 43200 s at 50, 40, 30 and 25°C, respectively (table 2). After aragonite was formed, the peak intensity of MHC decreased with time, whereas that of aragonite increased (figure 5). These results indicate that there are two different rate-limiting processes in the transformation of MHC to aragonite, occurring before (step 1) and after (step 2) the formation of aragonite. The observed alterations can be explained assuming that the transformation of MHC is characterized by the dissolution and precipitation of stable phases. The following three processes are involved in this transformation: (1) dissolution of MHC, (2) nucleation of aragonite and (3) growth of aragonite crystals. The pH of the suspension became highest value immediately after the aging began at 25°C and then gradually decreased (table 2). Because the increase in pH resulted in the release of ions from MHC, the dissolution of MHC is expected to be fast. When MHC is added to the solution, the solution immediately attains equilibrium owing to the high dissolution rate of MHC. Because the solubility must be higher for unstable than stable phases, the solution in equilibrium with MHC must be supersaturated with respect to aragonite. However, aragonite is not formed in this step; therefore, step 1 represents the nucleation of aragonite. In step 2, the relative amount of MHC decreased and that of aragonite increased with time (figure 5(a)). Because the dissolution of MHC must be faster than other processes, step 2 represents the crystal growth of aragonite after nucleation, when the dissolved components that were released from MHC are consumed by the growing aragonite.

The nucleation rate is evaluated from the induction time for the formation of aragonite measured by XRD. They were $(2.7 \pm 0.9) \times 10^3$, $(5.4 \pm 1.8) \times 10^3$, $(3.2 \pm 0.4) \times 10^4$ and $(7.3 \pm 0.4) \times 10^5$ s at 10, 25, 40 and 50°C, respectively. Assuming a zero-order reaction for the aragonite crystal growth, the conventional rate constants were estimated as $(1.0 \pm 0.3) \times 10^{-5}$, $(6.1 \pm 0.8) \times 10^{-5}$, $(1.0 \pm 0.3) \times 10^{-5}$ and $(1.6 \pm 0.3) \times 10^{-6}$ mmol s$^{-1}$ at 10, 25, 40 and 50°C, respectively. The rates of both processes strongly depend on temperature (figure 5(b)).

Figure 6 shows the Arrhenius plots, which are linear for both processes. The regression line for the nucleation of aragonite was calculated as

$$\ln k = 13000 / T - 32 \quad (r = 0.98),$$

and that for the crystal growth of aragonite was

$$\ln k = -9700 / T + 21 \quad (r = 0.99),$$

From the slopes of these lines, the activation energies were estimated as $E_a(n) = 108.1 \text{ kJ mol}^{-1}$ and $E_a(g) = 80.6 \text{ kJ mol}^{-1}$ for the nucleation and growth of aragonite, respectively.

These stability experiments [28] showed that the transformation of synthetic MHC was rapid and completed within an hour at 50°C. Very different results were obtained using natural samples. MHC from Lake Fellmongery transformed slowly into calcite in the presence of water [27]. Natural MHC from Lake Kivu did not transform into calcite at temperatures below 120°C without water [31]. In distilled water, about half of MHC did not transform into calcite at

![Figure 5](image-url)
100 °C for 50 h. The authors found that distinct MHC layers of Lake Kivu contained 0.4–0.6% PO$_4$ and concluded that the presence of phosphate is responsible for the relatively high stability of the Lake Kivu MHC. As mentioned below, laboratory experiments [49] confirmed that even a small amount of PO$_4$ significantly inhibits the transformation of MHC.

6. Hazardous oxyanion sorption

6.1. Phosphate

The behavior and mechanism of PO$_4$ sorption on MHC have been examined via sorption isotherms [49]. Synthetic MHC always contains a small amount of Mg [28], which is released after immersing MHC in water. According to Stumm and Leckie [55], the presence of Mg in solution significantly affects the uptake of PO$_4$ on calcium carbonate minerals. Yagi and Fukushima [49] examined the PO$_4$ sorption on MHC at different Mg concentrations to investigate the behavior and mechanism of PO$_4$ sorption on MHC.

The MHC used for the examinations was synthesized by the method described in section 2. Sorption isotherms were obtained for three Mg concentrations (0, 0.5 and 1.0 mM as MgCl$_2$) using 0.01 M NaCl solutions. The solid concentration was 2 g L$^{-1}$. Phosphate was added to the solution to adjust the initial PO$_4$ concentrations to 0–210 µM. The reaction was conducted in ambient atmosphere at 25 °C for 24 h. After the reaction, the suspensions were filtered. Both the water chemistry and mineralogy of the reacted samples were examined.

Figure 7 shows the sorption isotherms for PO$_4$ on MHC. The amount of sorbed PO$_4$ increases with PO$_4$ concentration. Initially, the slope decreases with PO$_4$ concentration up to 50 µM. The isotherms are similar for the three Mg concentrations at a low PO$_4$ level. The slopes of the isotherms increase above 50 µM of PO$_4$, and the rate of this increase is higher for zero Mg content.

Figure 8 shows the XRD patterns of representative reacted samples. No MHC peaks are observed at 0 µMPO$_4$, irrespective of Mg concentration, and the patterns are dominated by aragonite. Weak calcite peaks are present in the absence of Mg (figure 8(a) and disappear when Mg is added (figures 8(b) and (c)). Calcite dominates the XRD patterns if 10 µMPO$_4$ is added to the initial solutions, and some aragonite is present provided the solutions contain Mg (figures 8(b) and (c)). The MHC peaks are seen only at 1.0 mM of Mg (figure 8(c)). The transformation to MHC occurs at the PO$_4$ concentration of 30 µM or higher. Mg and PO$_4$ are known to stabilize MHC [27], as confirmed by these results [49]. The mineralogy of reacted solids after transformation is significantly affected by the type of inhibitors. The dominance of aragonite in the PO$_4$-free system can be attributed to the presence of Mg in solution, which inhibits the calcite formation [54]. The appearance of calcite at 10 µMPO$_4$ indicates that small amounts of PO$_4$ promote the formation of calcite or/and inhibit the formation of aragonite even in the presence of Mg.

At 10 µMPO$_4$, MHC mostly transforms to calcite. Under those conditions, more than 90% of the PO$_4$ was removed from the solutions, irrespective of the Mg concentration. Coprecipitation with calcite should be responsible for this removal, as illustrated in figure 9(a). The MHC phase was stable at the initial PO$_4$ concentration of 30 µM and above, which corresponds to 8 µMPO$_4$ in the isotherm. Up to 110 µMPO$_4$ (50 µM in the isotherm), the isotherm has a typical Langmuir-type shape, indicating that PO$_4$ was removed by adsorption on MHC (figure 9(b)). The line in figure 7 corresponds to a Langmuir isotherm calculated for 30–110 µMPO$_4$ assuming monolayer adsorption. The maximum adsorption capacity and adsorption constant of MHC are 36.2 µmol g$^{-1}$ and 0.0671 µmol L$^{-1}$, respectively, and the adsorption of PO$_4$ most likely occurs at the MHC surface. Millero et al [19] showed that the maximum adsorption capacity and adsorption constant of aragonite
at the lowest salinity and 25 °C are 21.6 µmol g⁻¹ and 0.1301 µmol⁻¹, respectively. Although the PO₄ adsorption constant is lower for MHC than for aragonite, the adsorption capacity is significantly higher for MHC.

When the initial PO₄ concentration exceeds 110 µM, the slope of the isotherm rapidly increases and its shape deviates from the Langmuir behavior. The increase in PO₄ loading leads to the increase in the saturation state of calcium phosphates. Christoffersen et al. [56] showed that the initial precipitate, obtained from the solution containing Ca²⁺ and HPO₄⁻ ions, was amorphous calcium phosphate (ACP1) with the stoichiometry Ca(PO₄)₀.₇₄H₂O. Figure 10 shows the saturation index (SI) of the reacted solution with respect to ACP1. The reacted solutions become saturated (SI > 0) with respect to ACP1 at PO₄ concentrations above 50 µM (110 µM of initial PO₄), at which point the deviation from the Langmuir-type isotherm occurs (figure 7). Stumm and Leckie [55] also showed that the formation of calcium phosphates is significantly hindered by Mg. The sorption of PO₄ on MHC at initial PO₄ concentrations above 110 µM clearly depends on the Mg concentration (figure 7). Therefore, the uptake mode at higher PO₄ levels must be precipitation of amorphous calcium phosphate (figure 9(c)).

High pH and Ca concentrations favor the formation of amorphous calcium phosphates. Both pH and Ca concentrations equilibrated with MHC are higher than those obtained with anhydrous calcium carbonate, like calcite and aragonite. Therefore, the formation of secondary calcium
phosphate should be favored in the system containing MHC rather than anhydrous calcium carbonate. The straight and dotted lines in figure 10 show theoretical SI values for ACP1 of the reacted solution with calcite and aragonite, respectively. The SI is higher for the reacted solution with aragonite than with calcite because of the higher solubility of aragonite. The SI of the aragonite system does not reach supersaturation up to 100 μMPO₄, which is significantly higher than that of the MHC system. The PO₄ sorption efficiency is significantly higher if calcium phosphates form in the process than for a simple adsorption (figure 7). Therefore, MHC is a more efficient PO₄ sorbent than anhydrous calcium carbonate at high PO₄ concentrations.

6.2. Arsenate

Sakai et al. [57] reported preliminary results for As(V) sorption on MHC. They examined the behavior and mechanism of As(V) sorption on MHC by sorption isotherm measurements. MHC was synthesized by a method similar to that used by Munemoto and Fukushi [28]. Sorption isotherms were measured on 0.01 M NaCl solutions, and the solid concentration was 2 g L⁻¹. As(V) was added to the solution to adjust the initial As concentration between 0 and 200 μM. The reaction was conducted in ambient atmosphere at 25 °C for 24 h. Both water chemistry and mineralogy of reacted samples were studied.

MHC transformed to aragonite in solutions with As(V) concentration less than 108 μM (figure 11), and the transformation was incomplete at higher As(V) concentrations. At As(V) concentrations above 108 μM, the area under the XRD peak of aragonite decreased and that of MHC increased with As(V) concentration. Thus, the transformation of MHC to aragonite is inhibited by As(V) (figures 9(d) and (e)), although the inhibitory effect is significantly weaker for As(V) than for PO₄. Figure 12 shows the sorption isotherm of As(V) on MHC. The As(V) uptake increases with As(V) concentration up to 60 μM of the initial As(V) concentration (that corresponds to 13 μM in solution). The As(V) uptake saturates at 23.4 mmol kg⁻¹ between 60 and 108 μM and decreases at higher initial As(V) concentrations. The sorption was more efficient when MHC transformed to other phases. According to Munemoto and Fukushi [28], the dissolution of MHC results in the formation of aragonite. As(V) is more readily removed during the aragonite formation, and therefore, the sorption mechanism of As(V) should be coprecipitation during the crystallization of aragonite (figures 9(d) and (e)). The maximum arsenic sorption capacity per initial unit mass of MHC is more than 4 times higher than the simple adsorption capacity of calcite (figure 1(b)).
Because of the similar properties of As(V) and P atoms, the AsO₄³⁻ and PO₄³⁻ molecules show similar chemical behavior and adsorption on oxide minerals [8]. However, the inhibitory effect and sorption mechanism on MHC are quite different, with the maximum sorption capacity being much lower for AsO₄³⁻ than for PO₄³⁻.

7. Conclusions

MHC is a rare mineral in geological settings. It has been most frequently found in saline lakes as recent sediments formed from lake waters. The water temperature appears unimportant for MHC formation. The pH of lake waters is usually higher than 8, and the Mg/Ca ratio is higher than 4, as indicated by the synthesis conditions of MHC in the laboratory.

A number of studies of MHC synthesis have been reported. Some of them focused on the synthesis itself, whereas others observed MHC as a precursor or intermediate product during the crystallization of stable calcium carbonates. Synthesis experiments as a function of time indicated that MHC is an intermediate phase—it is formed from ACC and converts to calcite and/or aragonite. In most studies, MHC formed from solutions containing Mg. In the absence of Mg, MHC disappeared after 6 h, indicating that Mg inhibits the formation of stable calcium carbonates. The effects of temperature and CO₂/Ca ratio on the formation of carbonates are still unclear.

Kralj and Breccievic [46] and Hull and Turnbull [51] have studied the solubility of MHC. The former authors measured higher solubilities at 25°C than the latter authors, which is attributed to the difference in sample origin—synthetic and natural, respectively. The solubilities of MHC obtained by both groups are higher than those of calcite, aragonite and vaterite [52], but lower than those of ikaite [53] and ACC [25] at any temperature. This result indicates that MHC is metastable with respect to calcite, aragonite and vaterite under ambient surface conditions, and stable with respect to ikaite and ACC. Similar to calcite, aragonite, vaterite and ACC, but opposite to ikaite, the solubility of MHC decreases with temperature [46].

A systematic investigation of synthetic specimens [28] revealed that the transformation of MHC consisted of the dissolution of MHC and the subsequent formation of stable phases from the solutions. The rate-limiting steps of the MHC transformation are nucleation and growth of stable crystalline phases. That study also evaluated the rates and activation energies for each process. The transformation rates are very different for synthetic and natural samples. Natural samples are impure, which should affect the stability of MHC. A laboratory study confirmed [49] that small amounts of PO₄³⁻ in the solution (> 30 µM) significantly inhibit the transformation of MHC.

The sorption of phosphate on MHC was examined in laboratory experiments [49]. The sorption isotherms are of the Langmuir type at low phosphate loading, indicating that the phosphate uptake proceeds through adsorption on MHC surfaces. The Langmuir parameters suggest that the sorption capacity is significantly higher for MHC than for aragonite and calcite. At higher phosphate loading, the slope of the isotherm rapidly increases and deviates from the Langmuir behavior, and the phosphate sorption likely proceeds through the precipitation of secondary phosphate carbonate minerals. This precipitation is expected to occur only for MHC, but not for calcite and aragonite.

The sorption behavior of arsenate on MHC was examined in laboratory experiments [57]. Arsenate is most likely removed during the transformation of MHC to aragonite, and the proposed sorption mechanism is coprecipitation during the crystallization of aragonite. The arsenic sorption capacity by MHC is significantly higher than simple adsorption on calcite.

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