Note on magnesite formation
(Studies on irreversible geochemical reactions Nº 9)

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Abstract: In recent laboratory experiments magnesite ($MgCO_3$) has been synthesized at a temperature of 313ºK (= 40ºC). The experiments have demonstrated that irreversible reactions are involved in the low-temperature formation of magnesite. Fundamental to such irreversible reactions is a requirement for fluctuations, i.e., alternations between precipitation and dissolution. But unequivocal evidence for the necessity for fluctuations in order to produce such irreversible geochemical reactions can be demonstrated only by static control experiments. The present note describes several static control experiments on the low-temperature synthesis of magnesite. The first experiment consisted of adding the total amount of ammonia (used in the original experiment in 14 different titration steps) in a single action: only magnesium hydroxide carbonate formed, not magnesite. In the second experiment the possible reaction between magnesium chloride, ammonia and carbon dioxide in solution was studied at 318ºK (= 45ºC): magnesium hydroxide formed, not magnesite. The third static control experiment involved the reaction between magnesium chloride and ammonium carbamate; this time nesquehonite formed, not magnesite. The implications of these static control experiments in relation to the low-temperature formation of magnesite and dolomite in the sedimentary environment are discussed.

Key Words: Magnesite, dolomite, irreversible geochemical reactions.

Résumé : *Note sur la formation de magnésite (Études de réactions géochimiques irréversibles Nº 9).-* Au cours d'expériences récentes en laboratoire, de la magnésite ($MgCO_3$) a été synthétisée à une température de 313ºK (= 40ºC). Ces expériences ont démontré que la formation de magnésite à basse température implique des réactions irréversibles. L'alternance de phases de précipitation et de dissolution est une exigence pour que de telles réactions se produisent. Toutefois, la preuve sans équivoque de la nécessité de ces phénomènes d'alternance pour produire de telles réactions géochimiques irréversibles ne peut être établie que par le truchement d'expériences statiques de contrôle. Cette note décrit une série d'expériences statiques aboutissant à la formation de magnésite de synthèse à basse température. La première expérience consiste en l'ajout de la quantité totale d'ammoniaque requise en une seule fois (à l'origine, l'ammoniaque était introduite en 14 étapes) : seul du carbonate de magnésium a été produit, pas de magnésite. Dans une deuxième expérience, la réaction entre le chlorure de magnésium, l'ammoniaque et le gaz carbonique en solution a été étudiée à 318ºK (= 45ºC) : on obtient ainsi de l'hydroxyde de magnésium, non de la magnésite. La troisième expérience statique de contrôle implique la réaction entre le chlorure de magnésium et le carbamate d'ammonium ; cette fois-ci, c'est de la nesquehonite qui a été produite, et non de la magnésite. Les conséquences de ces expériences statiques de contrôle sur la formation de magnésite et de dolomite à basse température dans un contexte sédimentaire (et non plus dans des conditions de laboratoire) sont discutées.

Mots-Clefs : Magnésite ; dolomite ; réactions géochimiques irréversibles.

Introduction

For too long it has been thought, that the formation of dolomite at low temperatures takes place by way of a reaction between previously deposited calcium carbonate and magnesium chloride and/or magnesium sulfate in solution. Furthermore it has been suggested that dolomite is capable of reacting with magnesium in solution to give magnesite (ALDERMAN & VON DER BORCH, 1963). However the hypothetical "dolomitization reaction" has never been shown to take place at room temperature (around 298ºK = 25ºC) and atmospheric pressure. On the contrary, many chemical laws are against the suggested reaction taking place under low-temperature conditions. Ultimately reproducible laboratory experiments, not theoretical speculations, led to a solution of "the dolomite problem".

When duplicating experiment nº 57 of LIEBERMANN (1967) at temperatures between 298 and 333ºK (= 25 and 60ºC), but using ammonia instead of a solution of sodium carbonate for the titrations, magnesite, dolomite or huntite will form (DEELMAN, 1999). The experiments as such consists essentially of 14 intervals of dissolution alternating with 14 discrete titrations with dilute

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ammonia, after which in each instance the titrated solution is left for a time at constant temperature until the start of the next interval of dissolution. Alternations between the intervals of dissolution and additions of ammonia (titrations until pH = 8.0) have been claimed to be fundamental to the irreversible geochemical reactions involved in the low-temperature nucleation of dolomite, magnesite and huntite.

Irreversible geochemical reactions

One of the first papers describing an irreversible geochemical reaction (DEELMAN, 1979) involved the laboratory synthesis of anatase (TiO_2) at a temperature of 298ºK (= 25ºC). Until 1979 anatase could be made in the laboratory only above a temperature of 343ºK (= 70ºC). Inspiration for the use of an automatic laboratory set-up capable of introducing periodical alternations between wet and dry conditions had been found in the observations made by WALKER *et alii* (1969) on the weathering of an ultrabasic lava on the Hawaiian island of Kauai. Anatase is not present in the unweathered lava at Kauai, but can be found in certain parts of the surface exposures of the titaniferous-ferruginous latosols there. WALKER (1964) had noted that anatase was present when the soil was subject to alternating wet and dry conditions. Similarly HUTTON *et alii* (1972) described anatase from Australia in desert areas undergoing repeated cycles of wetting and drying. On Kauai anatase was found only where vegetation was absent; amorphous hydrated titanium oxide was found in soils under a forest cover (WALKER *et alii*, 1969).

The low temperature synthesis of anatase was achieved by dipping once per hour a piece of cellulose acetate filter into a dilute TiO_2 suspension, immediately withdrawing it and leaving it to dry at 298ºK (= 25ºC). Every hour the sequence was repeated automatically. The active role of the periodical alternations between wet and dry conditions in the low-temperature formation of anatase was shown by way of a static control. "In order to identify a possible crystalline phase formed in the solution itself without the aid of the dipping sequences, the TiO_2 suspension left behind in the glass beaker was dialysed to remove all HCl. After three days of dialysis, a test with a solution of silver nitrate indicated the absence of chloride anions. The dialysed suspension was slowly evaporated for several days at a constant temperature of 50ºC and X-rayed. No line or band whatever could be observed: the suspension itself was still X-ray amorphous" (DEELMAN, 1979, p. 258).

Reproducible laboratory syntheses of eitelite $Na_2CO_3.MgCO_3$ (DEELMAN, 1984) provided evidence against the possibility that the hydration of magnesium cations might constitute a barrier against the low-temperature nucleation of dolomite and/or magnesite (LIPPMANN, 1973; SAYLES & FYFE, 1973). Eitelite would form in the laboratory when once every half hour 2 ml of a magnesium bicarbonate solution was added to a mixture of Na_2CO_3 plus $NaHCO_3$. A heat lamp and fan insured complete desiccation at a constant temperature of 298ºK (= 25ºC). After one half hour of desiccation another 2 ml of the magnesium bicarbonate was added by an automatic set-up. In this case too a static control experiment showed the active role of the artificially introduced fluctuations. When a saturated magnesium bicarbonate was added in one action to the same mixture of sodium carbonate plus sodium hydrogen carbonate, not eitelite but magnesium hydroxide carbonate formed (DEELMAN, 1984).

The low-temperature synthesis of eitelite may have great significance as regards the possible mode of formation of dolomite and magnesite in nature. One of the few occurrences of eitelite in nature is found in the (Eocene) Green River Formation (BRADLEY, 1973; EUGSTER & HARDIE, 1975), which bears all the hallmarks of a playa-lake deposit. The deposits of the Green River Formation formed, "on a broad playa fringe, in a shallow-water lake which underwent frequent periods of desiccation": LUNDELL & SURDAM (1975, p. 493).

Static controls

Unequivocal evidence for the active role of alternations between precipitation and dissolution in low temperature reactions can be demonstrated only through comparison with a static control experiment. But in the investigation of how magnesite forms problems will inevitably be encountered in trying to devise a static control experiment. LIEBERMANN's (1967) experiment involves two fundamentally different and discrete steps. The first step consists of bubbling CO_2 through artificial sea water for 12 hours. The second step starts after titration with ammonia until pH = 8.0 is reached. It consists of heating the solution to a constant temperature (for example 308ºK = 35ºC) for the next 60 hours. The complete experiments involves 14 cycles of the first step, always followed by the second step. It was not possible to add the total amount of CO_2 plus the total amount of NH_4OH in a single action to the artificial sea water, because the quantity of carbon dioxide used was not measured.

Nonetheless attempts have been made to perform a static control experiment. To this end the total amount of the ammonia solution used in the series of titrations was measured. Ingredients identical to those of LIEBERMANN's experiment nº 57 were used, and after saturating the solution with CO_2 at atmospheric

pressure, the measured amount of ammonia was added in one action. The precipitate formed consisted of magnesium hydroxide carbonate at both 333ºK (= 60ºC) and 313ºK (= 40ºC).

A solution of sodium carbonate used instead of ammonia in the titrations of LIEBERMANN's experiment nº 57 formed no magnesite, dolomite or huntite. Therefore ammonia must play an active role in the low-temperature nucleation of these three carbonates. Only when

the exact role of ammonia has been determined will a definite conclusion concerning the effects of fluctuations be reached. Perhaps a clue can be found in a process from the chemical industry for in the production of soda a precipitation of magnesite occurs. When sea water instead of the usual pure NaCl brines is used in the ammonia soda process (SOLVAY method) various magnesium

Location	Author(s)	Mg/Ca	Salinity (‰)	pH
Coorong Lagoon (Australia)	ALDERMAN & VON DER BORCH (1961)	-	32	10
	ALDERMAN (1965)	20 - 100	-	10
	ALDERMAN & VON DER BORCH (1963)	-	3 – 10	8 - 9
Great Salt Lake (USA)	GRAF *et alii* (1961)	-	-	-
	BISSELL & CHILINGAR (1962)	0,05	-	-
Tuz Gölü (Turkey)	IRION (1970)	> 140	max.	-
Sabkha El Melah (Tunisia)	PERTHUISOT (1971)	± 100	200 - 500	6 - 6.5
Sabkha Persian/Arabian Gulf	KINSMAN (1967)	-	-	7
	BUSH (1973)	5 - 235	500 - 700	-
Lake Yao (Chad)	GAC *et alii* (1977)	-	> 200	9.7
Clipperton Atoll, Pacific Ocean	BOURROUILH-LE JAN *et alii* (1985)	-	34	6.5
Playa Guallar (Spain)	PUEYO MUR & INGLES URPINELL (1987)	450	-	7.5
Saline lakes, British Columbia (Canada)	RENAUT (1990) RENAUT & LONG (1989)	7.7	30 -100	8.5 - 10.5

Table 1: Some occurrences of Recent magnesite.

salts will be precipitated including magnesite (HOU, 1942). Precipitation of $MgCO_3$ takes place at a stage of the SOLVAY process known as the ammoniation of the saturated brine. The brine has a temperature of around 313ºK (= 40ºC) due to the introduction of a mixture of hot NH_3 and CO_2 gas. The details of this reaction can be found in the patent claim of WAESER (1923-1926), which has its origin in the ammonia soda process. WAESER (1923-1926) stated, that the reaction

$$MgCl_2 + 2\ NH_3 + CO_2 + H_2O = MgCO_3 + 2\ NH_4Cl$$
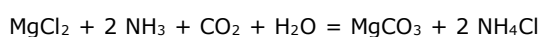
would become reversible at temperatures exceeding 303ºK (= 30ºC). However WAESER (1923-1926) was not quite clear concerning the

nature of the precipitate (WAESER used "$MgCO_3$" in the equation cited, but only a few sentences later he wrote "$MgCO_3$ or basic magnesium carbonate").

In order to test WAESER's claim, the following experiment was performed: in 0.5 litre demineralized water 0.1 mol $MgCl_2.6\ H_2O$ was dissolved; this solution was saturated with CO_2 gas (industrial grade), by bubbling CO_2 through the solution at room temperature (around 293ºK = 20ºC) for 48 hours. After closing the glass bottle with the carbonated solution, it was equilibrated at 318 ± 1ºK (= 45 ± 1ºC). At the same time a closed bottle containing 28 grams of a 25 % NH_4OH solution (p. A., MERCK art. Nº 5432) was equilibrated at 318ºK (= 45ºC). This amount of ammonia corresponds with the

amount needed to convert all of the magnesium chloride in solution into $MgCO_3$. All of the ammonia solution was added in one action to the magnesium chloride solution. Immediately a precipitate formed and filtered off after standing for one hour at 318°K (= 45°C). After washing with 2 litres of demineralized water the filter was dried at room temperature. Because the filter paper remained wet, additional re-suspension, filtration and washing was needed. Finally a dry precipitate was obtained to be used in X-ray diffraction. The precipitate was found to consist of $Mg(OH)_2$.

In subsequent laboratory experiments ammonia gas and carbon dioxide gas were not used to react with a solution of magnesium chloride; a solution of the stoichiometric equivalent ammonium carbamate $NH_4CO_2NH_2$ (p. A., MERCK art. N° 1134) was substituted. In 0.5 litre water 0.1 mol $MgCl_2.6\ H_2O$ (p. A. quality) were dissolved, and in another 0.5 litre water 0.2 mol $NH_4CO_2NH_2$. The two solutions were equilibrated at 318°K (= 45°C), and only then poured (in one action) into a 1 litre glass beaker. After 2 hours a precipitate was seen to have been formed. The suspension was filtered off, and washed with 1 litre demineralized water (during which a large part of the precipitate dissolved). The filter paper was dried at room temperature (no extra heating). X-Ray diffraction showed the result from this test to consist of $MgCO_3.3\ H_2O$ (nesquehonite).

The next experiment was designed to test the claim of WAESER (1923-1926): 0.6809 g of a pure sample of natural magnesite (from Radenthein, Austria) was left in contact during 14 days with a solution of 0.5 mol (= 28 g) NH_4Cl (p. A., MERCK art. N° 1145) in 0.5 litre water at a temperature of 333°K (= 60°C). After washing and filtering off a precipitate weighing 0.4839 g was obtained, which was subjected to X-ray diffraction and found to consist of magnesite. After 14 days some 29 % of the initial amount of magnesite had been dissolved (as magnesium chloride most probably): at 333°K (= 60°C) only the dissolution of magnesite into the ammonium chloride solution takes place. Therefore it has been proven that the reaction claimed by WAESER (1923-1926) is not reversible.

Conclusions

The static control experiments described here have demonstrated the validity of my earlier suggestion: that the low-temperature formation of magnesite requires fluctuations in solution chemistry (DEELMAN, 1999). The fact that in this case an irreversible geochemical reaction appeared to be involved has a number of consequences:

1. The nucleation of magnesite (or dolomite) cannot be explained in terms of classical chemistry. As shown in Table 1, there is no common factor in terms of Mg/Ca ratios, salinities or pH values among the environments in which modern magnesite has been found.

2. It has now been made clear, why only the metastable equivalents of magnesium carbonate precipitate in all classical (i.e., static) laboratory experiments. The irreversible reaction requires large-scale fluctuations to take place in the chemical composition of the solution before detectable amounts of magnesite will form under low-temperature conditions.

3. There is no need to invoke a supposed "dehydration barrier" to explain the difficulty in the formation of magnesite in low-temperature laboratory experiments. Even when it was proposed such a "dehydration barrier" seemed unlikely, because calcium cations are nearly as hydrated in aqueous solution as magnesium cations.

4. The need for an irreversible geochemical reaction explains why the solubility concept fails in the low-temperature nucleation of magnesite (and dolomite). Although magnesite has a much lower solubility product than its metastable equivalents nesquehonite or magnesium hydroxide carbonate (see for example LANGMUIR, 1965), it fails to precipitate at room temperature under static conditions. But then the concept of a solubility product is founded on the assumption of equilibrium.

5. Static control experiments demonstrate that only fluctuations are capable of overcoming the "kinetic barrier". Reaction kinetics instead of classical (equilibrium) thermodynamics appear to control the formation of magnesite in the sedimentary environment.

Discussion

The laboratory data presented above appear to justify the conclusion that the low-temperature nucleation of magnesite does indeed require fluctuations. Not merely fluctuations in a closed system near equilibrium, but large-scale alternations between intervals of precipitation and intervals of dissolution. By definition these large-scale alternations can take place only in an open system. The actual mechanism which forms the stable phase magnesite instead of the metastable phases nesquehonite or magnesium hydroxide carbonate, is as simple as it is effective (DEELMAN, 2001). The intervals of dissolution alternating with the intervals of precipitation are responsible for the dissolution of more and more of the metastable phase. By definition such metastable phases have a higher rate of precipitation, and conversely a higher rate of dissolution, than the stable phase.

Thermodynamic calculations make it clear that magnesite must be considered more stable than nesquehonite, which in turn is more stable than magnesium hydroxide carbonate (LANGMUIR, 1965). Brucite will have to be excluded from these considerations, because usually it reacts with carbon dioxide to give magnesium hydroxide carbonate. The relation between stability or metastability and precipitation and dissolution rates was introduced originally by Wilhelm OSTWALD. As MORSE & CASEY (1988) have stressed, mineral paragenesis is not as much controlled by (classical) thermodynamics as such, but rather by reaction rates. Only when intervals of precipitation alternate with intervals of dissolution is the lower dissolution rate of the stable phase sufficiently favoured so that more and more of the stable mineral develops at the expense of the metastable one. Equilibrium thermodynamics do not allow for such considerations, but open systems during disequilibrium (i.e., fluctuations) have been shown to initiate irreversible geochemical reactions such as the one leading to the low-temperature formation of magnesite.

Acknowledgements

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