SUPPORTING TEXT S1 for

A template-free, ultra-adsorbing, high surface area carbonate nanostructure

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**S1 Overview of earlier work**

For many geologists, the anhydrous magnesite is a conspicuous rock with unclear genesis.[1](#_ENREF_1)Although magnesium carbonates are abundant in nature in the form of minor traces in most geological structures, they rarely exist as monomineralic magnesite in economically viable deposits. In fact, there are only two types of magnesite deposits in the world: the sparry magnesite of Vietsch type, which constitutes 90% of world’s reserves and forms nearly monomineralic lenses within marine platform sediments, and the less common but highly valued Kraubath type magnesite of superior quality. The Kraubath type consists of veins (300-400 meter deep) and stockworks (80 meter deep) of cryptocrystalline “bone” magnesite, also sometimes referred to as gel-magnesite.[1](#_ENREF_1) It commonly occurs together with ultramafic rock structures such as serpentine ((Mg,Fe)3Si2O5(OH)4) and olivine ((Mg,Fe)2SiO4) minerals, and the formation of Kraubath type magnesite is suggested to occur through a so-called epigenetic-hydrothermal route,[2-4](#_ENREF_2) wherein hydrothermal fluids of moderate temperature and low salinity carrying CO2 interact with ultramafic rocks. Most of the silica and iron derived from the decomposition of ultramafic rocks are carried to the surface, whereas the veins of magnesite precipitate *in situ* as a gel. It should, however, be stressed that X-ray amorphous forms of MgCO3 are not known to occur in nature.

Interestingly, magnesite has aroused problems not only for geologists, but also for chemists. Anhydrous MgCO3 can be easily produced at elevated temperatures. However, numerous authors, among them Berzelius,[5](#_ENREF_5), [6](#_ENREF_6) Soubeiran,[7](#_ENREF_7) Fritzsche,[8](#_ENREF_8) Nörgaard,[9](#_ENREF_9) Marignac,[10](#_ENREF_10) Beckurts,[11](#_ENREF_11) Genth & Penfield [12](#_ENREF_12), Pfeife [13](#_ENREF_13), Knorre [14](#_ENREF_14), Doelter, Cornu & Redlich,[15](#_ENREF_15) Leitmeier,[16](#_ENREF_16) Wells,[17](#_ENREF_17) Wilson & Ch'iu,[18](#_ENREF_18) and Walter-Lévy19 have described unsuccessful attempts to precipitate anhydrous magnesium carbonate from magnesium bicarbonate solutions kept at room temperature and under atmospheric pressure. Instead, hydrated magnesium carbonates or one of the more complex basic magnesium carbonates precipitated under such conditions, leading to what has been branded as *"the magnesite* *problem"*. Significant improvements to produce anhydrous crystalline magnesium carbonate at temperatures below 100 °C were presented in 1999 by Deelman[20](#_ENREF_20" \o "Deelman, 1999 #1293) who precipitated magnesite from a suspension of artificial sea-water containing NaCl, MgCl2•6H2O, MgSO4•7H2O, KCl, CaCO3 and urea at 40 °C. Titration with dilute ammonia together with CO2 bubbling through the suspension caused dissolution of the components and precipitation of magnesite after 14 consecutive dissolution-precipitation cycles. However, it should be noted that pure magnesite was not obtained; the precipitates contained both magnesite and different forms of calcium carbonates. This has later been repeated by Dos Anjos et al.[21](#_ENREF_21)

For detailed discussion on the different methodologies employed to obtain MgCO3, the reader is directed to Deelman.[22](#_ENREF_22) For methodologies on the manufacturing of pharmaceutical grades of MgCO3, the reader is directed to Truitt.[23](#_ENREF_23)

To circumvent *“the magnesite problem”*, some authors have tried to synthesize anhydrous MgCO3 in organic solvents and, in particular, in alcohol suspensions since the latter tend to form alkyl esters with alkaline earth metal oxides. The works by the Hungarian chemist Emerich Szarvasy are particularly interesting in this respect. In 1897, Szarvasy has consecutively published 3 articles in *Berichte der Deutschen Chemischen Gesellschaft* (Proceedings of the German Chemical Society) in which he for the first time described several new substances, including magnesium hydroxymethylate (MgOHOCH3), magnesium methylate (Mg(OCH3)2), magnesium dimethylcarbonate (Mg(OCOOCH3)2), and magnesium dimethylsulfite (Mg(OSOOCH3)2).[24-26](#_ENREF_24) A key substance during Szarvasy’s studies was magnesium methylate, which could be obtained either through direct interaction of magnesium nitride Mg3N2 or metallic Mg with methanol. Upon interaction with CO2 or SO2, Mg methylate formed Mg dimethylcarbonate and Mg dimethylsulfite, respectively:[26](#_ENREF_26)

CH3•O•C•O•O•Mg•O•O•C•O•CH3

CH3•O•S•O•O•Mg•O•O•S•O•CH3

It should also be mentioned that Szarvasy did not describe the monomethyl hydroxycarbonate salt of Mg or its methyl ester;

HO•Mg•O•O•C•O•CH3

CH3•O•Mg•O•C•O•O•CH3

which would otherwise be expected to exist considering the structure of Mg dimethylcarbonate. Magnesium dimethylsulfite could also be obtained by passing sulphur dioxide through the methanolic solution of magnesium dimethyl carbonate by substituting the weak acid ester of carbonic acid by an ester of a stronger acid. As a part of characterisation, Szarvasy also described the following: upon addition of a few droplets of water to magnesium dimethylcarbonate, a white jelly-like precipitate is formed, which can be dissolved in excess water. When the produced clear water solution is boiled, white powder precipitate is formed which is reminiscent of magnesium carbonate. According to Szarvasy, the only water-soluble substance which would precipitate into magnesium carbonate from water upon heating is magnesium hydrocarbonate. Therefore, it was concluded that magnesium dimethylcarbonate should be analogous to magnesium hydrocarbonate, except for the hydroxyl groups being substituted by methoxy groups. Szarvasy also predicted that since magnesium methylate can be produced from direct interaction between metallic Mg and methanol, other alkaline earth metals such as Ca, Sr, and Ba will also form their respective alcoholates.

In 1908, Neuberg and Rewald[27](#_ENREF_27" \o "Neuberg, 1908 #1195) claimed that the addition of carbonic acid to a methanolic suspension of an alkaline earth metal oxide (e.g. CaO) under mild warming resulted in the dissolution of metal oxide and formation of a colloidal suspension after filtrating away the solid residue. Upon long-standing and moderate stirring in an icebox, the above solution formed a thick starch-like gel, which was rather opaque. The authors stated that the gel was so thick that it could be turned upside down in a glass tube. Upon reaction with acid, such as sulphuric, phosphoric or oxalic acid, this product formed the respective calcium sulphate, phosphate, or oxalate and produces CO2 gas, which led the authors to believe that the product may be CaCO3. The experiments with MgO, however, turned out differently since when CO2 was bubbled through methanolic suspensions of MgO no gel was formed. This led Neuberg and Rewald to doubt that MgCO3 can be obtained from methanolic suspensions due to the more likely formation of magnesium dimethyl carbonate,[27](#_ENREF_27) as reported earlier by Szarvasy.[26](#_ENREF_26) Not so long after, the experiments by Neuberg and Rewald were repeated by Buzágh in 1926.[28](#_ENREF_28) Buzágh, another Hungarian chemist, criticised the approach by Neuberg and Rewald as it evidently led to the formation of dimethyl carbonates also for Ca, Ba, and Sr, as it would be anticipated from the teachings of Szarvasy. Then, instead of using oxides, Buzágh suggested to use the respective hydroxides to form pure carbonates of Ca, Ba, and Sr. Yet it remains unclear why Buzágh did not report any data on the reaction of Mg(OH)2 with CO2 in methanol.

Significant contribution to understanding the properties of dimethylcarbonates of alkali and alkali earth metals was made by Kurov who studied in total 46 different salts of alkyl and alkenyl carbonic acids and their thermal degradation patterns, both with respect to the type of the alcohol used (same metal-different alcohol) and the type of the metal (same alcohol-different metal).[29-36](#_ENREF_29) Kurov’s results reveal that in a homologous row of alcohols the most stable salts are dimethylcarbonates and the least stable ones are those of di-n-butylcarbonates; among the monovalent salts the most stable ones are those of Na and the least stable ones are those of Rb; among the divalent salts the most stable ones are those of Ba and least stable ones are those of Mg. The thermal degradation of Mg(OCOOCH3)2, which was conducted in a sealed ampoule at ~200-300 ˚C, produces MgCO3, CO2, and CH3OH (main components) and traces of (CH2)2O and CH2OH but no CO or C2H4, as it is the case with monovalent alkali metals.[32](#_ENREF_32)

The thermal degradation patterns of mono and di-glycolcarbonic acid salts studied by Franz and Gattow[37](#_ENREF_37" \o "Franz, 1977 #1379) confirmed the general mechanism of thermal degradation proposed by Kurov also for glycolcarbonic salts.

It is postulated in this work that methyl hemicarbonic acid is an important intermediate formed under mild pressure. By pressurising CO2, the following reactions are potentially enabled:

ROH+CO2↔ HOCOOR (P)

2ROH+CO2↔OC(OR)2+H2O (high P, T, catalysts, desiccants)

In order to form dialkyl carbonates high pressure, high temperature, catalysts (typically metal oxides, including MgO), and desiccants are required.[38](#_ENREF_38) The formation of alkylcarbonic acid in CO2-alcohol systems has been shown in supercritical fluids at 70-100 bar at 20-40 ˚C for 2 days by interacting it with diazodiphenylmethane as a probe to catch acid species.[39](#_ENREF_39) These results also showed that in a homologous row of alcohols the rate of hemicarbonic acid formation is the fastest for methanol and the slowest for tert-butanol. The free methyl hemicarbonic acid was isolated at low temperatures (-70 ˚C) by Gattow and Behrendt.[40](#_ENREF_40), [41](#_ENREF_41)

In the current work, FTIR spectroscopy of the reaction products after 3 hours revealed that the main constituent at this stage is HOMgOCH3 without traces of Mg(OH)2, see Fig. S3 below. It should, however, be noted that magnesium carbonate could also potentially be formed if the product of reaction 1a is Mg methylate rather than Mg hydroxymethylate via formation of Mg dimethylcarbonate as follows:

MgO + 2CH3OH ↔ Mg(OCH3)2+H2O (S1a)

CH3OH+CO2↔CH3OCOOH (S1b)

Mg(OCH3)2+2CH3OCOOH↔H3CO•CO•O•Mg•O•CO•OCH3+2CH3OH (S1c)

H3CO•CO•O•Mg•O•CO•OCH3+H2O → MgCO3+CH3OH +CH3OCOOH (S1d)

The last step (S1d) in this reaction actually resembles what Szarvasy described earlier in his work when he adds a few droplets of water to the magnesium dimethylcarbonate as discussed above. In order to verify this hypothesis, Mg(OCH3)2 was used as the starting material instead of MgO, and water (1:1 mole ratio) was deliberately added to the reaction medium. It was found that indeed an amorphous magnesium carbonate had formed but this material was non-porous and showed a different FTIR spectrum indicating that the short-range order differs from that of Upsalite. Therefore, the reaction scheme 1a-e, i.e. involving HOMgOCH3, is more plausible under the employed mild synthesis conditions.

As it is seen from reactions 1d and S1d, the proposed formation of in situ water will induce hydrolysis of the complex methyl ester Mg methylcarbonate. On the other hand, excessive water will halt the formation of hemicarbonic acid through nucleophillic attack as shown below:

CH3OCOOH+H2O→H2CO3+CH3OH (S1f)

H2CO3↔ CO2+H2O (S1g)

Excessive water is also expected to further hydrolyse HOMgOCH3 to Mg(OH)2. Indeed, we observed that the reaction is extremely sensitive to the presence of water: when water is added deliberately to the methanolic suspension (e.g., 1:1 water/methanol volume ratio) prior to pressurising the reaction vessel, crystalline nesquehonite (Mg(HCO3)(OH)•2H2O) with no traces of residual MgO is obtained (see Fig. S1).

Another important aspect of the proposed reaction of Upsalite formation is the role of CO2 gas pressure. During our synthesis attempts, it became clear that moderately pressurised CO2 gas (>1-3 bar) is necessary in order to convert MgO to MgCO3 in methanol: when CO2 is merely bubbled through a methanolic suspension of MgO, no MgCO3 is formed. Reaction 1b is a result of nucleophile attack by methanol on CO2, which, due to its intrinsic electron deficiency, can be considered as an anhydride of carbonic acid. The product of the reaction 1b is the methyl ester of hemicarbonic acid and the equilibrium in this reaction is shifted strongly to the left hand-side of the reaction under ambient conditions as discussed above. According to Le Chatelier’s principle, increasing the CO2 pressure in reaction 1b will be favourable for shifting the equilibrium in the direction necessary for formation of methyl ester of hemicarbonic acid.

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