

Carbon Dioxide as Mediating Compound Between Organic and Inorganic Matter**

Armin Reller*

The role of carbon dioxide within the natural cycles of matter and energy is shortly discussed. Possibilities for the generation of organic carbon compounds by the catalyzed reaction of molecular hydrogen with natural metal carbonates are displayed. Together with the exothermal recarbonatization of the so-formed metal oxides, a closed cycle for conversions of organic and inorganic carbon compounds is obtained, within which no fossil carbonaceous matter takes part.

1. Introduction

Carbon dioxide represents not only the thermodynamically stable carbon compound of various degradation processes of organic material such as respiration, combustion, fermentation or putrefaction, but also an indispensable parent product for the photosynthetic formation of essential biomolecules. Natural cycles of matter are so to say specialized in the use of this molecule as carbon storage, i.e. as carbonate deposits, and as ubiquitously disposable reagent, i.e. as gaseous or dissolved carbon dioxide. All the complicated and mutually integrated conversions constitute the dynamic equilibrium of natural processes and therefore play a key role in the material fundamentals of life. Within the global ecosystem, the necessary energy is supplied by the sun.

The extensive use of fossil carbon compounds such as coal, oil or gas has led to an increase of the atmospheric concentration of carbon dioxide in the range of 1.5 ppm/year⁽¹⁾. The possible influences on the

global ecosystem are the object of controversial discussions. There is, however, no doubt, that carbon dioxide represents a waste product within the present human energy concept.

As it is displayed in Fig. 1, this account focusses on the role of carbon dioxide and its possible conversions within a framework made up of the globally present compounds water and calcite as well as of their constituents respectively conversion products. Calcite has been chosen due to the fact, that it is one of the most abundant natural carbonate deposits. It has to be mentioned, that within these natural metal carbonates 10^4 – 10^5 times more carbon is stored than within the fossil carbon deposits coal, oil, and gas⁽²⁾. Moreover, they are readily accessible and – as it is shown in Section 3 – their formation is much faster than the formation of fossil carbon compounds. The displayed framework reveals as well, that the carbon compounds with relevance for technical and industrial use are predominantly carbohydrates and methane. The importance of the inorganic chemistry of carbon dioxide and its conversion products, however, has not yet been taken into account sufficiently.

In the following, investigations on the conversion of inorganic carbon compounds into organic materials as well as the uptake of gaseous, e.g. atmospheric carbon dioxide by means of heterogeneous solid state reactions are presented. The results are discussed with respect to possible technical applications and with respect to ecologically relevant concepts of closed cy-

Armin Reller: Born 1952 in Winterthur. Studied chemistry at the Universität Zürich; Ph.D. in 1981 with Prof. H.R. Oswald. Postdoctoral research at the Department of Physical Chemistry, University of Cambridge, England (Prof. J.M. Thomas). Since 1983 again at the Institute of Inorganic Chemistry, Universität Zürich, where he presently is appointed as Lehrbeauftragter der Philosophischen Fakultät II.

cles of matter. Finally, the presented processes are reviewed with respect to an integration into the global ecosystem. This means, that no waste products should be formed and that the required energy should – in principle – be supplied by the sun.

2. The Formation of Organic Carbon Compounds from Metal Carbonates

Natural metal carbonates have been and still are important parent products for the generation of technically useful materials such as metal oxides or, after subsequent reduction, for metals. In general, these

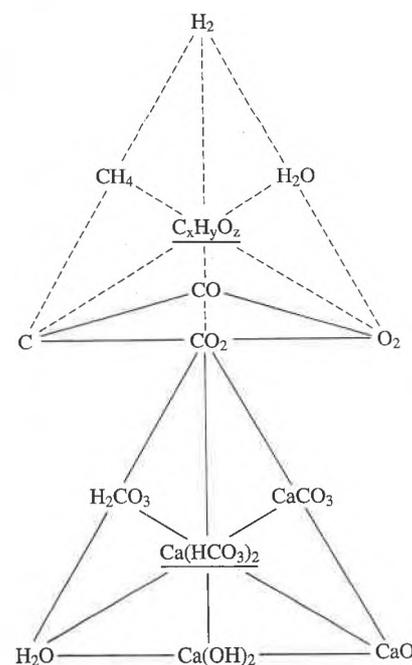
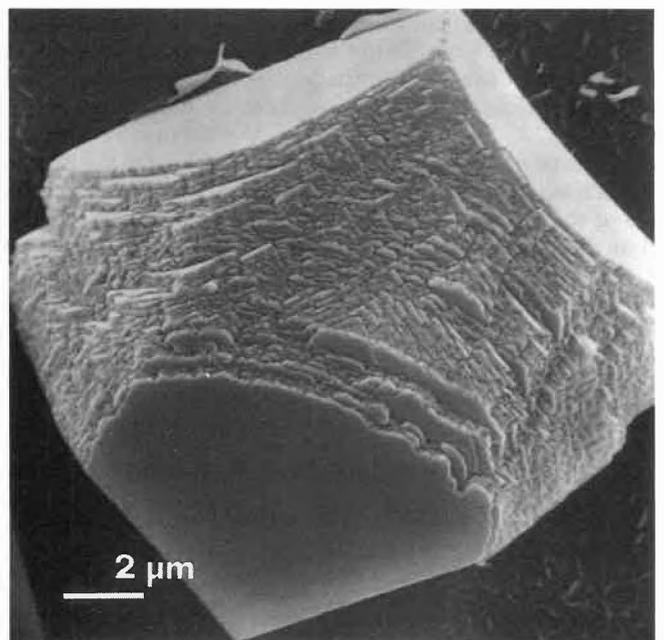
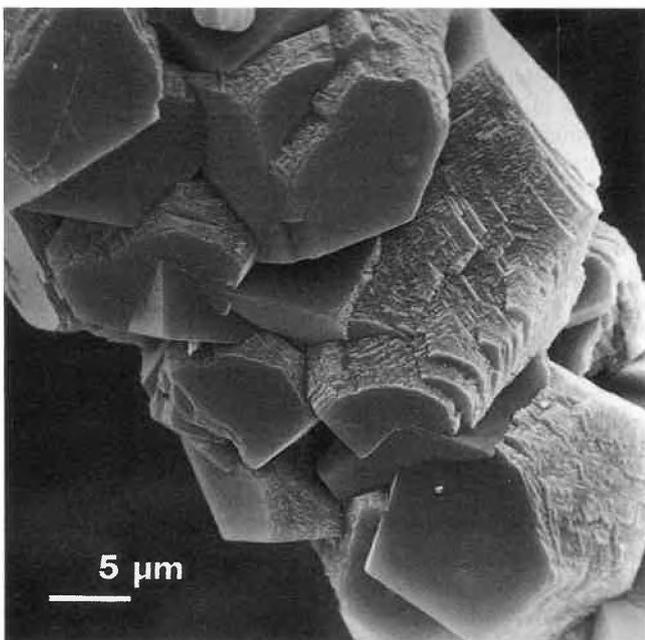
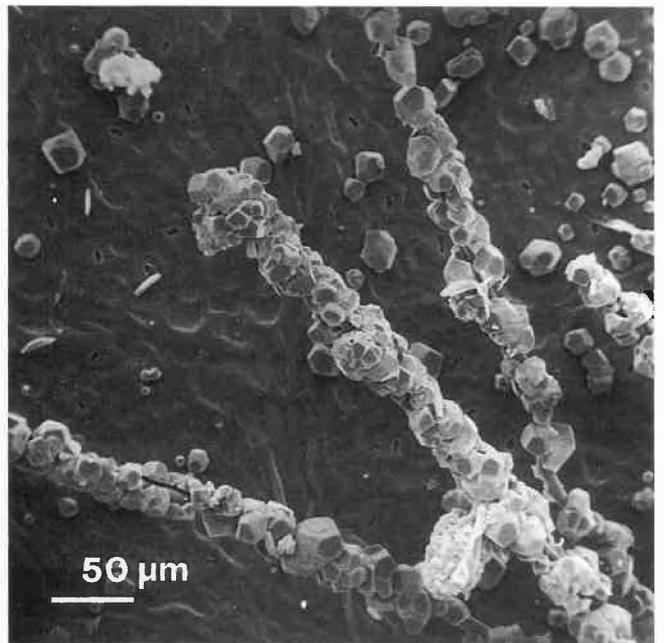
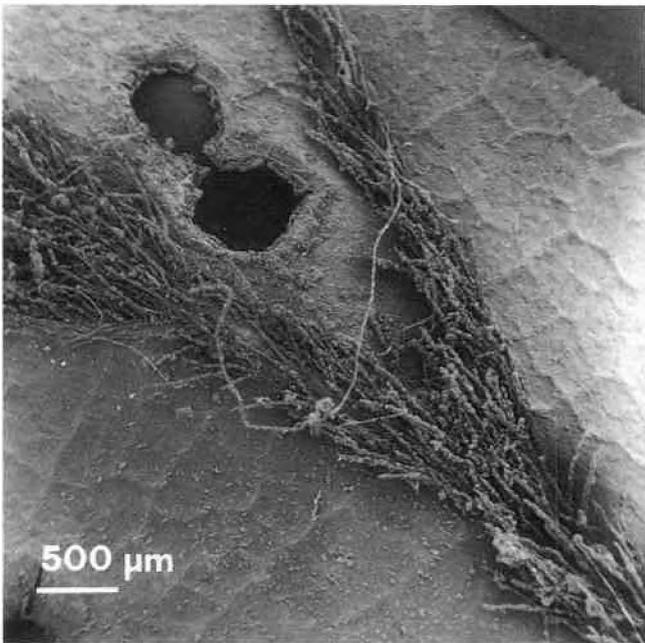


Fig. 1. Graphic representation of the position respectively interrelations of carbon dioxide within a reaction framework made up of ecologically relevant compounds. The lower «inorganic triangle» consists of water, calcia, and carbon dioxide as well as their mutual conversion products. The upper «organic triangle» is made up of hydrogen, oxygen, and carbon as well as their mutual conversion products. Note the important role of the central units $C_xH_yO_z$, respectively $Ca(HCO_3)_2$. – From this scheme, the outstanding role of carbon dioxide as mediating compound between organic and inorganic conversions of matter is readily comprehensible (—: inorganic processes; ---: organic processes).

* Correspondence: Dr. A. Reller
Anorganisch-chemisches Institut der
Universität Zürich
Winterthurerstrasse 190
CH-8057 Zürich

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technically important materials are obtained by thermal decomposition of the initial carbonates in air. Effects of the ambient atmosphere on the course of the thermal degradations have only been studied on the basis of scientific interest. No attention has been paid to the volatile products CO and predominantly CO₂, which represent potential parent products for the generation of useful carbon compounds.

By combined thermogravimetric/mass spectrometric techniques, however, it has been found that the actual inert, oxidizing or reactive (e.g. CO₂) atmosphere influences the decomposition temperature. Concomitantly the mechanistic and kinetic course and – as an important feature – the morphology of the solid products formed also depend upon the ambient atmosphere^[3]. For calcite, the most pronounced differences are found between the thermal degradation in carbon dioxide and the one in vacuum: Under CO₂, sintering processes take place and the reaction temperature is well above 1000 K; under vacuum conditions, however, the decomposition takes place at temperatures as low as 800 K and as product, microcrystalline calcium oxide with particle sizes below 1 µm is obtained. These facts are of importance with respect to the kinetics of the recarbonatization (see Section 3).

Under the mentioned experimental conditions, carbon dioxide is the main volatile product. Taking the initially mentioned statements into consideration, one could think about the conversion of so-formed carbon dioxide into partly or fully reduced, i.e. technically useful carbon compounds. The catalytic conversion of CO₂ is presently elucidated by various groups (see e.g.^[4-6] and references cited therein).

In a recent study, we investigated the decomposition of natural metal carbonates, i.e. calcite CaCO₃, dolomite Mg-Ca(CO₃)₂, and magnesite MgCO₃ in reducing atmosphere, i.e. in molecular hydrogen^[7]. As combined thermogravimetric/mass spectrometric measurements reveal, the decomposition temperatures of the said carbonates are lowered by more than 150 K compared to the analogous reactions in inert or oxidizing atmospheres. High-resolution electron microscopic investigations give evidence for the formation of the pure or mixed metal oxides MgO respectively CaO as conglomerates of microcrystalline domains with diameters in the range of 10–20 nm. During the decomposition of magnesite the evolution of even amounts of carbon monoxide and carbon dioxide is observed. For calcite, however, carbon monoxide is detected as main volatile carbon compound (CO:CO₂ > 10:1). The decomposition temperature as well as the ratio of the gaseous products formed for dolomite are between the values measured for the two pure car-

bonates. These observations indicate, that the mechanism changes remarkably, i.e. reduction processes of the carbon oxide species take place. Considering the role of carbon monoxide as parent carbon compound in the Fischer-Tropsch synthesis of organic carbon compounds, these results open up a further possibility for the conversion of inorganic carbonates into organic materials (see e.g.^[8]).

In order to obtain detailed insights into such decomposition/reduction processes, we performed experiments using mixed Mg,M- respectively Ca,M-carbonates as initial materials (M = Co, Ni, Cu; 10% each). Compared to the analogous degradations of the pure carbonates in non-reducing atmospheres, a lowering of the decomposition temperatures in the range of 200 K to 400 K (for Ca,Ni-carbonates) is registered. Moreover, the composition of the evolved gases changes drastically: Mg, Cu- respectively Ca,Cu-carbonates decompose under evolution of mixtures of carbon monoxide and carbon dioxide. Samples containing Co as transition metal evolve carbon monoxide and methane, but only few percents of carbon dioxide. For the degradation of Mg,Ni- respectively Ca,Ni-carbonates methane is detected as main gaseous carbon compound (> 90%). The solid products are made up of the earth alkali metal oxide and of the respective elemental metals. It has been found, that the Ca,Ni system is a highly active catalyst for the direct conversion of CO₂ into CH₄ under ambient pressure of molecular hydrogen^[9]. This finding gives evidence for the role of the transition metals as catalytically active species. Preliminary investigations on the nature of these catalysts by means of high-resolution electron microscopy, electron diffraction, and electron spectroscopic techniques yielded that the metals are present as highly dispersed, poorly crystalline materials^[10].

Obviously, the combination of heterogeneous solid state reactions with heterogeneous catalysis allows a straightforward approach to the direct conversion of metal carbonates into organic carbon compounds.

3. Carbonatization of Earth Alkali Metal Compounds

The reaction of gaseous or dissolved carbon dioxide with earth alkali metal compounds or ions is an ubiquitously occurring, natural day-to-day process. As illustration, the formation of calcium carbonate by the reaction of atmospheric carbon dioxide with calcium ions dissolved in the water of a natural source is displayed in Fig. 2. The sequence of gradually magnified sections gives evidence for the fact, that the macroscopic phenomenon – the

terrace-like rock – is made up of small CaCO₃ crystals exhibiting an unusual habitus with a pronounced growth zone. X-ray diffraction proves, that the crystalline material consists of pure calcite. No indications for the presence of the other modifications of calcium carbonate – aragonite and vaterite – have been found. The dynamics of the natural process is variable owing to its dependence on many parameters such as the concentration of CO₂ and Ca²⁺ ions as well as on the temperature- and pH-dependent solubility of the calcium carbonate formed (see e.g.^[11]). As it can be seen in Fig. 1, the compound Ca(HCO₃)₂ is of central importance within the mentioned conversions, i.e. precipitation and dissolution of calcium carbonate in aqueous medium. Owing to the metastable character of this hydrogencarbonate phase, it has not yet been isolated nor sufficiently characterized with respect to its structure and its chemical reactivity.

The carbonatization of MgO respectively CaO has been studied by means of thermogravimetry under well controlled atmospheres. In a dry CO₂ atmosphere, MgO does not undergo significant carbonatization at low temperatures. CaO, however, readily reacts with CO₂. In a model experiment, CaCO₃ was decomposed under vacuum (temperature: < 950 K; pressure: 1 Pa). After cooling to 300 K, the reaction of the obtained microcrystalline CaO with dried CO₂ was measured under isothermal conditions. A fast uptake of CO₂ is observed, even in atmospheres containing only few percents of CO₂^[12]. The evaluation of the weight gain reveals, that the carbonatization reaches 70–80% of the stoichiometric conversion. The kinetics of this process depend decisively on the particle size of the initial reactant CaO. X-ray diffractometry and high-resolution electron microscopy give evidence for the formation of amorphous calcium carbonate. This up to now never observed phenomenon is substantiated by the fact, that by heating this amorphous phase, an exothermal reaction corresponding to the crystallization of the amorphous calcium carbonate is registered at ca. 600 K by means of differential thermal analysis as well as temperature dependent X-ray diffraction. The obtained crystalline calcium carbonate consists of conglomerates made up of domains of calcite with domain diameters in the range of 10–20 nm.

4. The Ecological Relevance

The outlined experimental findings allow the principal conclusion of the possible existence of a closed carbon compound cycle without participation respectively integration of fossil carbon deposits. Within this cycle carbon dioxide acts as mediating

Fig. 2. Series of gradually magnified sections (photographs and scanning electron micrographs) illustrating the formation and thus the growth of a natural calcite deposit by the reaction of atmospheric CO₂ with dissolved Ca²⁺ ions respectively Ca²⁺ compounds.

reagent between organic and inorganic matter. As further main constituents of such a cycle, water and calcia must be mentioned. As Fig. 3 shows, these three compounds, i.e. CO_2 , H_2O , and CaO , represent the material fundament for a concept of technically applicable conversions of matter, which could be integrated within the naturally occurring processes. Thus, an ecologically feasible alternative to the present concept – the extensive use of fossil fuels comprising the production of CO_2 as waste material – is imaginable.

Fig. 3 reveals, that hydrogen acts as crucial reactant within the presented scheme of conversions. Moreover, it represents a possible main constituent of future global energy scenarios^[13]. Its production – in an ecologically feasible concept it must be generated by the photovoltaic, electrochemical, or thermal splitting of water – as well as the catalyzed reduction of CO_2 require energy, which can be supplied by the sun. Thus the combination of splitting water as well as reducing carbon dioxide by means of solar energy meets the requirements for closed cycles of matter. From an economic point of view, however, the production of organic carbon compounds by means of a solar receiver/reactor system is at present not competitive, although possible and ecologically reasonable. This situation might change drastically, when the exploitation of fossil carbon deposits becomes increasingly costly or when possible adversary impacts of the present energy concept on the global ecosystem require fundamental alternatives.

Thinking about the problems, which could arise from the increasing concentration of atmospheric CO_2 , the concept sketched out in the present article contains one crucial process. By the «sun-driven» natural convection of the atmosphere, CO_2 is ubiquitously disposable and by its exothermal reaction with dissolved or solid Ca^{2+} compounds, it can be concentrated.

Consequently, this cyclic concept is not an inorganic alternative for the generation

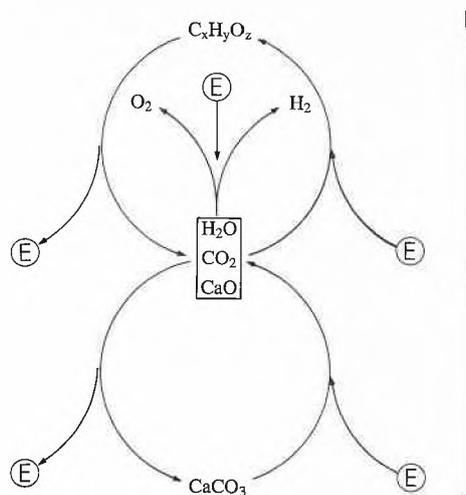


Fig. 3. Schematic representation of a closed cycle of ecologically feasible carbon compound conversions illustrating the possible generation of organic material from metal carbonates, i.e. without participation of fossil carbonaceous matter. In principle, the required energy for the splitting of water into the reactants oxygen and hydrogen as well as the activation (decomposition of CaCO_3) and the catalyzed conversion of CO_2 into $\text{C}_x\text{H}_y\text{O}_z$ can be supplied by solar radiation. The oxidation of $\text{C}_x\text{H}_y\text{O}_z$ as well as the recarbonatization of calcia are exothermal processes. The energy scale on the right is semi-quantitative inasmuch as it refers to the stabilities of the compounds within the global ecosystem.

of combustible carbon compounds and thus for a large-scale production of conventional fuel. It rather represents a sum of mutually integrated chemical conversions, which are not only relevant for natural processes and concomitantly for man's requirements (see e.g.^[14]), but also confirm the importance of carbon dioxide and its

potential conversion products in the fields of heterogeneous solid state reactions and heterogeneous catalysis (see e.g.^[15]).

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