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# The Chemistry of $CO_2$ and $TiO_2$

## From Breathing Minerals to Life on Mars

Springer

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*Someone else always has to carry on the story.*
J. R. R. Tolkien

*To all pilgrims on the path of knowledge…*

# Preface

A broad range of experimental and theoretical work has been devoted to the interaction of carbon dioxide with titania ($TiO_2$) in recent years, not least because of the changing state of the global climate. Carbon dioxide chemistry and $TiO_2$ surface catalysis nowadays find their use in many applications from battling the global warming through technical application, fuel production and energy storage to origin of life studies and synthesis of organic molecules on early Earth, Mars and other terrestrial planets.

The purpose of this book is to show two important aspects of the interaction between gaseous $CO_2$ and the semiconductor mineral surface. Firstly, this book will show that oxygen atoms are exchanged between the oxygen-containing minerals and $CO_2$ in ambient conditions. This surprising feature which is often neglected, shows that the boundary between the gas phase and the solid phase is not inert and that room temperature may be sufficient to allow the interaction to take place.

Furthermore, this oxygen atom exchange is not limited to titanium dioxide. Other minerals may interact with the gas in a similar manner, including many commonly occurring natural minerals. It seems, therefore, that this surprising feature is not unique. Quite the contrary, it is a commonplace process, which affects the ongoing chemistry in the environment and should be considered in every model that features natural processes.

Secondly, in the past four decades, many studies have shown that carbon dioxide can be readily reduced to methane through a process called 'methanogenesis.' The photocatalytic reduction of carbon dioxide to methane, methanol and other carbon-containing compounds is an important process for our planet. If employed on a large-scale basis, it may reduce carbon dioxide content in the atmosphere, capture solar energy, which is the ultimate inexhaustible source of energy (at least until humankind migrates outside the Solar system, if that will ever happen) and produce fuel or chemical reagents. This process is often coupled with water splitting, which produces hydrogen and oxygen, which in turn can again be used as fuels or for chemical synthesis.

The area of research into these solar-powered processes is very big and still growing exponentially. Most work published on this topic, however, is concerned with the material chemistry, doping, photocatalyst efficiency and sensitizing. This book, on the other hand, will show the chemical aspects of the methanogenesis and discuss how they could be exploited to enhance the effectivity of the process. For example, the effect of an acidic proton in the environment will be discussed and we will describe that acidic conditions boost the rate of the reduction reaction.

Such findings can serve a purpose in the environmental chemistry research indeed, but there is a staggering amount of literature on this topic already available. What this book will show is that natural minerals can be used as photocatalysts for the methanogenesis as well and that it may occur in the natural environment on contemporary Earth. Looking back in time, we shall see that this process may have, or indeed, must have taken place on the early Earth, where it must have influenced the redox state of the atmosphere. Consequently, organic synthesis or prebiotic synthesis could have taken place in ways unprecedented to this day and the chemistry of $CO_2$ must have played an important role in the chemical origin of life.

What is more, we will show that this process may be used for the explanation of the presence of methane on Mars and may shed some light on the seasonal variation of $CH_4$, which has been observed recently on Mars. The methanogenesis is probably insufficient to explain these phenomena completely, but it definitely plays its part and again, should be included in any models of planetary chemistries such as there may be.

Overall, this book should neither serve as a definitive answer to humankind problems and resolve the issue of the global change of climate nor should it be used as a manual for the designing of photoreactors. For this, there are books and articles more fitting than our work. Rather this book should be able to show some of the often neglected aspects and processes and review their potential role in the chemistry of the contemporary and early Earth and beyond.

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