

INTRODUCTION

"L'expérience est la source unique de la vérité: elle seule peut nous apprendre quelque chose de nouveau; elle seule peut nous donner la certitude. Voilà deux points que nul ne peut contester."

H. Poincaré (1912, *La Science et l'Hypothèse*, p.167)

In July 1791 a letter by the French Count Déodat De Dolomieu to his friend *monsieur* Picot de la Peyrouse was printed in Volume XXXIX of the *Observations et Mémoires sur la Physique, sur l'Histoire naturelle, et sur les Arts et Métiers* (later renamed into the *Journal de Physique*). The letter described, how De Dolomieu had discovered a new carbonate rock (new in that it would not effervesce with dilute hydrochloric acid), in buildings in the old city of Rome and in vast masses in the mountains south of the Brenner Pass (N.Italy). The newly described mineral was named "*dolomie*" after its discoverer in a paper by N. Th. de Saussure one year later. In the years that passed since, various authors have described syntheses of the calcium-magnesium double carbonate, now known as dolomite. All of those syntheses involved temperatures above 373 K, and in some instances high pressures as well. Meanwhile occurrences of dolomite in modern sediments, soils and caves became known, where most certainly no such high temperatures and/or high pressures have reigned. This obvious discrepancy between laboratory syntheses requiring a minimum temperature of at least 373 K and finding dolomite there, where no such high temperatures can possibly have existed, is the essence of the dolomite problem.

But the low-temperature formation is not the only scientific puzzle more than two centuries old. Much the same situation exists in the case of the mineral magnesite. Magnesium carbonate as a compound found in nature, was known many years before dolomite was described for the first time. According to a review paper by De Fourcroy(1789) magnesium carbonate from rocks had been described by Bergman(1774) as well as Black(1775). Apparently it was Delamétherie(1795), who used the name "*magnesite*" for the first time (to describe not only magnesium carbonate, but magnesium sulfate, magnesium nitrate and magnesium chloride as well), but it has been Karsten(1808), who gave the name to magnesium carbonate found as a mineral. (At the same time it should be realized, that even today the name "*giobertite*" given to magnesium carbonate by Beudant, 1824 is still being used in French speaking countries.) The comparison with the dolomite problem is complete: magnesite too has been found in sediments, which show no traces at all of high temperatures and/or high pressure. The thought may come to mind, that perhaps the dolomite problem and the magnesite problem are related in some way. Such a connection seems likely, when realizing, that dolomite is in fact a calcium *magnesium* double carbonate. No major problems are known in relation to the dissolution and precipitation of calcium carbonate; even though calcium carbonate has three polymorphs in clear contrast to magnesium carbonate, which has none. The hard core of both the dolomite problem and the magnesite problem seems to be the difficulty to precipitate anhydrous magnesium carbonate from an aqueous solution at room temperature and under atmospheric pressure.

The method used by me to investigate the low-temperature formation of magnesite and dolomite, was that of laboratory experiments. The inspiration for the multitude of tests came from

mere deduction of one of the factors from descriptions of the situation found in nature. At a later stage numerous theoretical aspects of the problem were grouped together into chapters for a planned book. After collecting facts, theories, and speculations, an attempt was made to create a historical perspective. This endeavour made it necessary to consult much of the 19th century literature on dolomite, not in the least because most current concepts and theories on dolomite formation originated at that time. In a number of instances this historical approach itself led to surprising results. To mention only one example: from the existing literature it became clear, that there is no factual evidence in support of the so-called *Haidinger reaction*, the supposed reaction between pre-existing calcium carbonate and solutions of magnesium sulfate, often used as the underlying principle for theories on "dolomitization". In 1847 Von Morlot had recounted, how Haidinger had suggested, that dolomite forms upon the contact between calcium carbonate and a solution of magnesium sulfate. Three years earlier Haidinger had endorsed the observations made by Mitscherlich and Gmelin on the reaction between powdered dolomite and a solution of calcium sulfate leading to calcium carbonate plus a solution of magnesium sulfate. The laboratory experiments by Von Morlot showed, that the reaction between calcium carbonate and a solution of magnesium sulfate must take place at temperatures of at least 200 ° R (= 523 K) in order to lead to any dolomite. Von Morlot was quite explicit in pointing out, that a definite minimum temperature exists for the formation of dolomite. But the rhetorics of Haidinger and his followers came to prevail over the experimental evidence. Thus was laid the basis for what is now known as a variety of "dolomitization theories".

Mere deduction led to the conclusion, that all it took to form dolomite in the sedimentary environment was some form of fluctuation in free energy, of periodicity in changes of temperature, pressure or concentration. But the causal relation between the low-temperature formation of dolomite and fluctuations in free energy in terms of a specific nucleation process as proposed by me (Deelman, 1975 A), turned out to have been without foundation. Exactly how magnesite and dolomite form under conditions of low temperature and atmospheric pressure, has meanwhile been described by me in a paper in the *Neues Jahrbuch für Mineralogie* (Deelman, 1999). The fact remains, that fluctuations (notably in pH) play an essential role in the process. It must be stressed here, that only through a multitude of laboratory experiments "the dolomite problem" has been solved.

Most of the text of this publication had been prepared prior to publishing the paper on the low-temperature nucleation of magnesite and dolomite. Over the years much information has been gathered, and all the while laboratory experiments were conducted. The leading principle in composing the text was that of the historical perspective, not in the least because chronology is the first element of deduction. As a consequence large numbers of original papers, of historical publications, of old books and nearly forgotten dissertations had to be consulted. An attempt was made towards an almost encyclopaedic degree of completeness. This has made the text as such of course quite *recherché*. The ultimate goal of completeness proved very difficult to reach; and, it must be admitted here, has not been reached. A number of publications on dolomite and magnesite could not be consulted, because of reasons such as accessibility, language barriers, and financial limitations. Despite serious efforts (and desires) there are limits to one's resources. Visits to the libraries of the Technische Universiteit Delft, Technische Universiteit Eindhoven, Rijksuniversiteit Utrecht, Rijksuniversiteit Leiden, Rijksuniversiteit Groningen, Katholieke Universiteit Nijmegen, Universiteit van Amsterdam, Octrooiraad Rijswijk, AKZO Hengelo, Rijks Geologische Dienst Haarlem, Teylers Museum Haarlem, Geologisch Bureau Heerlen, Koninklijke Militaire Academie Breda, Rijksinstituut voor het Visserijonderzoek IJmuiden, Koninklijke Bibliotheek Den Haag,

Koninklijk Nederlands Metereologisch Instituut De Bilt (The Netherlands), Universität Heidelberg, Universität Freiburg, Universität Tübingen, Universität Jena, Universität Göttingen, Rhein-Ruhr-Universität Bochum, Staatsbibliothek Bamberg, Bayerische Staatsbibliothek München, Universität München, Bibliothek Bergbauforschung Essen (Germany), British Library London (United Kingdom), the Bibliothèque National de France Paris and the Bibliothèque Nationale et Universitaire Strasbourg (France) eventually made it possible to write this publication.