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Solubility Products of M(II) - Carbonates

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Rolf Grauer[†]

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PREFACE

The Laboratory for Waste Management at the Paul Scherrer Institut is performing work to develop and test models as well as to acquire specific data relevant to performance assessments of planned Swiss nuclear waste repositories. These investigations are undertaken in close co-operation with, and with the financial support of, the National Co-operative for the Disposal of Radioactive Waste (Nagra). The present report is issued simultaneously as a PSI-Bericht and a Nagra Technical Report.

FOREWORD AND SUMMARY

The geochemical behaviour of elements of importance plays an important role in safety assessments of radioactive waste repositories. Carbonate, hydroxide and oxide anions form perhaps the most important complexants and concentration-limiting solids among a large variety of relevant compounds. In many cases, complexes and solids including these anions form the backbone of the thermodynamic data bases used in geochemical modelling. Therefore, defensible and reliable thermodynamic data for these compounds are of key importance in waste management.

All his life, Professor Rolf Grauer maintained a strong interest in the chemistry of transition metal carbonates and published many studies on this topic. However, being a chemist of the old school, he was very much disturbed by the many inconsistencies in the solubility data for transition metal carbonates which he found even in "critical" data compilations. He finished the present critical comments on these findings very shortly before his unexpected demise in September 1994. Unfortunately, he was not granted the privilege of presenting this, his very last work, to a broader audience, because it was only provisionally issued as a PSI internal report written in German (TM-44-94-05).

The aim of an update of the PSI geochemical data base which was recently begun is not only to improve the quality of data sets for individual elements, but also to provide a comprehensive picture, with chemical consistency among the various elements. Previous studies have shown that chemical consistency is just as important as the numerical precision of individual equilibria.

This critical review by Rolf Grauer represents an essential cornerstone of this particular scientific area. It analyses and quantifies the solubility data available for transition metal carbonates with meticulous attention to detail. Frequently, thermodynamic data compiled in tables are not sufficiently well documented and commented upon. Therefore, the author traces them back to the original publications, judges the experimental methods applied, and discusses the solid phases used in the experiments. In addition, he gives appropriate weight to the conversion of experimental results to standard conditions, as well as to error limits. In his summary, Rolf Grauer presents a new, chemically consistent and comprehensively supported picture of the solubility of transition metal carbonates.

Because of my conviction that this study deserves special attention from experts in this field, I decided to prepare an English translation to open it a broader audience. Along with the scientific facts and terms, the translation also tries to capture the expressive style of Rolf Grauer's original German text. Therefore, very few clarifications and supplementary comments were added.

PSI, December 1998

U. Berner

Translation of original summary: Many solubility data for M(II) carbonates commonly compiled in tables are contradictory and sometimes obviously wrong. The quality of such data has been evaluated based on the original publications and reliable solubility constants have been selected for the carbonates of Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb with the help of cross-comparisons.

VORWORT UND ZUSAMMENFASSUNG

Das geochemische Verhalten der beteiligten Elemente spielt in den Sicherheitsanalysen für die radioaktiven Abfälle eine zentrale Rolle. Als wohl wichtigste Komplexbildner in Lösung und als Anionen in konzentrationslimitierenden Festkörpern sind vor allem die Carbonate, Hydroxide und Oxide zu erwähnen. Komplexe und Festkörper dieser Anionen bilden üblicherweise auch das Rückgrat der für die geochemische Modellierung verwendeten thermodynamischen Datenbasen. Zuverlässige und gut abgestützte thermodynamische Daten dieser Substanzklassen sind deshalb im Waste Management von wesentlicher Bedeutung.

Professor Rolf Grauer hat sich zeitlebens für die Chemie carbonatischer Übergangsmetallkomplexe und –Festkörper interessiert. Er hat zu diesem Thema auch mehrere Studien veröffentlicht. Als anorganischer Chemiker der alten Schule haben ihn die leider auch in "kritischen" Datenkompilationen festgehaltenen Inkonsistenzen in den Löslichkeiten von Übergangsmetallcarbonaten besonders gestört. Kurz vor seinem unerwarteten Tod im September 1994 hat er deshalb die vorliegenden kritischen Betrachtungen als allerletzte seiner Arbeiten verfasst. Leider war es ihm nicht mehr vergönnt, die vorerst in Deutsch abgefasste PSI-interne technische Mitteilung (TM-44-94-05) auch als Publikation einer weiteren Öffentlichkeit vorzustellen.

Ziel einer kürzlich begonnenen Überarbeitung der geochemischen PSI Datenbank ist nicht nur die qualitative Verbesserung einzelner Datensätze, sondern auch eine elementübergreifende, chemische Konsistenz der verwendeten Gleichgewichte. Die bisherigen Studien haben nämlich gezeigt, dass dieser chemisch konsistenten Betrachtungsweise mindestens ebensoviel Bedeutung zukommt, wie der zahlenmässigen Präzision einzelner Gleichgewichte.

In diesem wissenschaftlichen Umfeld stellt die Studie von Rolf Grauer einen wesentlichen Eckpfeiler dar. Sie analysiert und quantifiziert das vorhandene Datenmaterial zur Löslichkeit der Übergangsmetallcarbonate in fast schon akribischer Art und Weise. Der Autor verfolgt die in der Literatur vielfach ungenügend kommentierten Zahlenwerte zurück bis zu den Originalarbeiten, bewertet die angewandten experimentellen Methoden und diskutiert die im Experiment verwendeten Festphasen. Einen angemessenen Stellenwert erhalten neben der Umrechnung der Messdaten auf Standard-Bedingungen auch die Fehlergrenzen. Schliesslich werden die gewonnenen Erkenntnisse in einer Empfehlung zusammengefasst. Hier präsentiert der Autor die Löslichkeiten der Übergangsmetallcarbonate in einem neuen, chemisch konsistenten und umfassend abgestützten Bild.

Ich bin überzeugt, dass die vorliegende Studie für die entsprechenden Fachleute von grossem Interesse sein wird. Aus diesem Grund habe ich mich entschlossen, einem breiteren Fachpublikum eine englische Übersetzung zugänglich zu machen. Diese Übersetzung versucht, neben den reinen fachtechnischen Fakten auch den ausdrucksvollen Stil von Rolf Grauers deutschem Text so gut wie möglich wiederzugeben. Nur an sehr wenigen Stellen wurden Ergänzungen in Form von Fussnoten oder kursiven Einschüben vorgenommen.

PSI, im Dezember 1998
U. Berner

Originalzusammenfassung: Die Löslichkeitsdaten für die M(II)-Carbonate in gängigen Tabellenwerken sind widersprüchlich und zum Teil offensichtlich falsch. Anhand der Originalarbeiten wurde die Datenqualität beurteilt, und mit Hilfe von Quervergleichen konnten für die Carbonate von Mn, Fe, Co, Ni, Cu, Zn, Cd und Pb verlässliche Werte für die Löslichkeitskonstanten ausgewählt werden.

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1 INTRODUCTION

A search for solubility data on transition and heavy metal carbonates with the composition $M(II)CO_3$ revealed significant discrepancies among different compilations. Further, it became obvious, that particular solubility products are wrong (Figure 1).

For instance, the extreme difference between the solubility products of $CoCO_3$ and $NiCO_3$ is in clear contradiction to the well known similarity between the two elements.

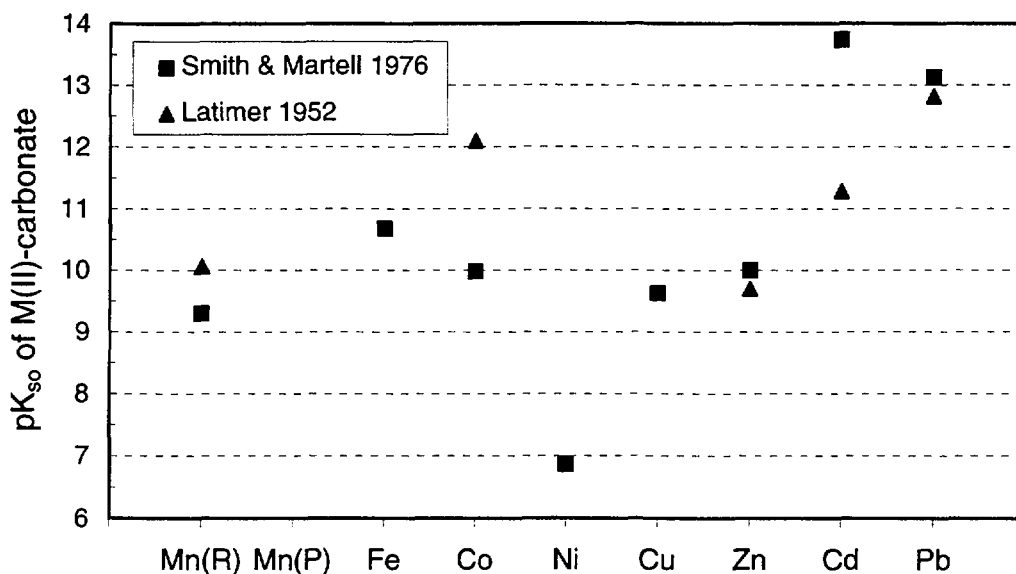


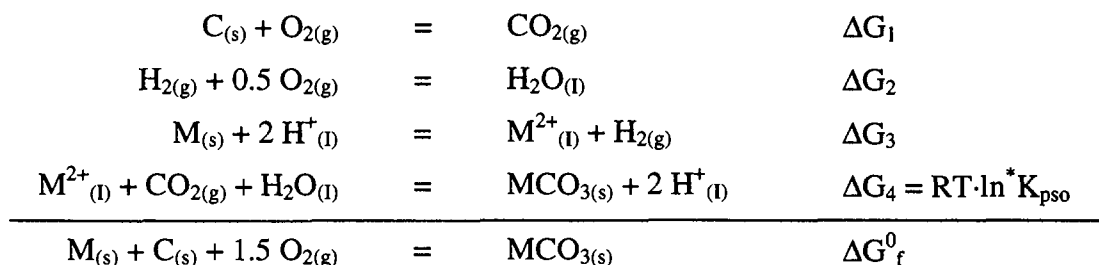
Figure 1 Solubility data of heavy metal carbonates with the composition $M(II)CO_3$, taken from SMITH & MARTELL 1976 and LATIMER 1952. pK_{so} is defined as $-\log((M^{2+}) \cdot (CO_3^{2-}))$.

Thermodynamic data that are wrong have a tenacious hold on life and travel from one compilation to the next. KOTRLÝ & ŠUCHA 1985, for example, have indiscriminately adopted carbonate solubility constants from the "Critical Stability Constants". Since such procedure is the rule rather than the exception, correct values are never obtained by comparing different databases. The only way to judge the data quality is to examine their original source reports.

2 THE ORIGIN OF SOLUBILITY PRODUCTS

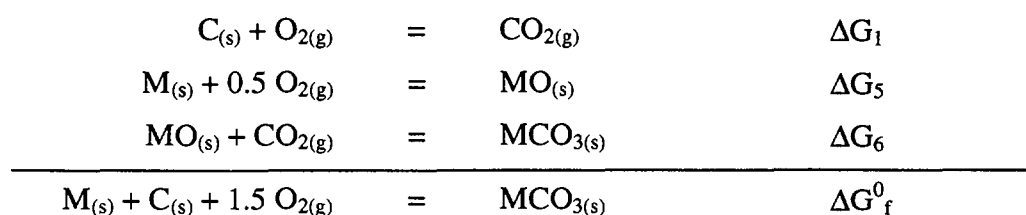
The formalism of equilibrium thermodynamics links equilibrium constants to the heat of reaction, the free energy of reaction and to the entropy of reaction. Hence, a solubility product may be determined in many different ways¹. Of course, there is a clear preference for values derived directly from solubility measurements. Unfortunately, tables do not always identify the methods used for evaluating or determining the constants.

The free energy of formation of a carbonate may be obtained using a simple Carnot cycle (Carnot cycle 1):



The subscript I denotes an aqueous solution with ionic strength I. ΔG_1 and ΔG_2 are sufficiently well known. ΔG_3 is known or can be found very accurately from experiments for several metals, but particularly for Zinc and Cadmium (SCHINDLER ET AL. 1969, GAMSJÄGER ET AL. 1965). ΔG_4 is obtained from solubility measurements at constant ionic strength I. Therefore, Carnot cycle 1 is also suited for converting the solubility product $^*K_{pso}$ to different ionic strength conditions. However, for a series of metals the ΔG_3 values are uncertain (LARSON ET AL. 1968), and it is important to always use consistent and well referenced data when converting equilibrium constants into free energies of formation. Unfortunately, many violate this elementary rule and, by doing so, create "new" values.

The free energy of formation of a carbonate can be calculated with Carnot cycle 2, which is based on calorimetric or thermochemical investigations:



The important thing here is that such investigations produce ΔH values and require auxiliary data for converting them into free energies of reaction. ΔG_5 is known from the heat of hydration of the oxide and ΔG_6 may be obtained from measuring the dissociation pressure at elevated temperatures².

¹ "What then is the use of thermodynamic equations? They are useful precisely because some quantities are easier to measure than others" (MCGLASHAN 1966). A good overview of the determination of thermodynamic data is given by NORDSTROM & MUNOZ 1985.

² The free energy of formation of the carbonate is also derivable from its heat of hydration (by analogy to Carnot cycle 1) using the standard entropies S^0 .

Many literature data are based on Carnot cycle 2. Although this Carnot cycle appears very elegant, it becomes evident when making practical applications that the basic values are usually not sufficiently well known³; their determination often requires extrapolations over several hundreds of degrees K. A systematic error is due to the fact that the decomposition of the carbonate produces a fine powdered oxide; the oxide in reaction 5 is thermodynamically different from that in process 6.

Hence, discrepancies among solubility products from thermochemical data and those from solubility measurements are the rule. Uncritical combination of values and auxiliary data of different quality and origin especially produce uncertain or even erroneous results. This has been comprehensively documented for cadmium carbonate by STIPP ET AL. 1993.

3 ASSESSMENT OF SOLUBILITY DATA

Broad experience is required for the precise determination of solubilities because there is a great variety of sources of mistakes. Similar experience is also needed to judge the quality of solubility measurements. The following paragraphs list several important aspects which have impacts on the reliability of a solubility constant.

a) Characterisation of the Solid Phase

The solid phase plays a principal role in solubility measurements, and, a comprehensive characterisation of its properties is fundamental (quantitative analysis, X-ray diffraction, specific surface area). Checks for impurities and for a homogeneous distribution of particle sizes are best performed using electron microscopy.

Often, solubility measurements must be performed under conditions where the solid phase is metastable. Further, it is possible that the metal may form a mixed hydroxide salt with the anion dominating the solution (GRAUER & SCHINDLER 1972). Therefore, additional X-ray and electron microscope analyses should be performed at the end of the experiment. In many studies, little or no attention is paid to these recommendations and, occasionally, even ill-defined trade products are used. Such studies should be viewed with great scepticism because there may be substantial discrepancies between the label and the contents of the "bottle" (an experience of the author was a bottle labelled "Cobalt Carbonate" that really contained cobalt hydroxide carbonate).

b) Check on Attainment of Equilibrium

The most certain check for true equilibrium conditions is to measure the equilibrium constant from both sides, i.e., with both dissolution and precipitation experiments. Unfortunately, this procedure is not always applicable. Many solids may not precipitate under the particular experimental conditions; some of the Me(II) carbonates cannot be synthesised except under hydrothermal conditions.

Equilibrium may also be checked using temperature variations (SCHINDLER 1963), and a very reliable test can be made using pH variations (see subsection c).

Impurities or very fine or amorphous aggregates may mimic increased solubilities. Therefore, at least one blank dissolution experiment should be performed. In such a blank experiment,

³ This is particularly true for reaction 6 (page 2). Corresponding examples are given in HASELTON & GOLDSMITH 1987 and TAREEN ET AL. 1991.

the same portion of solid is equilibrated sequentially with portions of fresh solution. A series of constant solubilities gives good evidence for the homogeneity of the material.

In many cases experimentalists try to accelerate the attainment of equilibrium by stirring, shaking or by end-over-end rolling. Since reactions at the solid liquid interface are slow, such procedures do not help. Often they lead to supersaturated solutions and scattered results. One may avoid such troubles by circulating the solution very slowly. For this reason, Reinert (SCHINDLER ET AL. 1968) developed a continuously working measurement cell, which was later modified by HEINDL & GAMSJÄGER 1977 for use at elevated temperatures. Another modification permits solubility measurements in the mg range (REITERER ET AL. 1981).

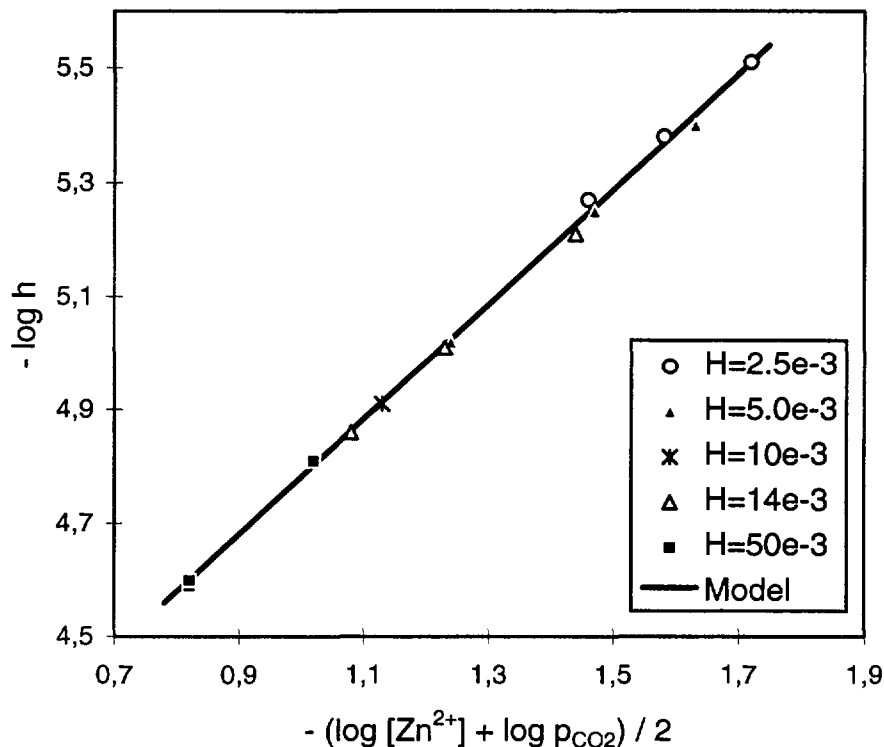
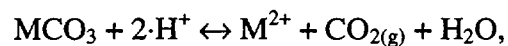


Figure 2 The solubility of zinc carbonate as a function of strong acid (H) additions at different partial pressures of CO₂ (I = 0.2, 25 °C). h: [H⁺] at equilibrium (SCHINDLER ET AL. 1969).

c) Check on Reaction Stoichiometry

Carbonate equilibria are usually measured according to the reaction



where the equilibrium constant is given by

$$^*K_{\text{pso}} = [\text{M}^{2+}] \times p_{\text{CO}_2} \times [\text{H}^+]^{-2} \quad (\text{eq. 1})$$

During the course of the experiment, the partial pressure of CO₂ is fixed, and [H⁺] as well as [M(II)]_{tot} are analysed. Determinations using only one single value for the partial pressure of CO₂ are not reliable, since all the hydroxide and carbonate complexes potentially present in

solution contribute to the result. By varying p_{CO_2} and by adding a well-defined amount of strong acid at the beginning of the experiment, the equilibrium conditions may be varied. Figure 2 exemplifies these types of measurements using $\text{ZnCO}_{3(s)}$ (SCHINDLER ET AL. 1969); experiments performed at five different starting concentrations and at three different partial pressures of CO_2 gave identical results (within the error of chemical analyses). This means that the stoichiometry follows the reaction given above. Hence, $[\text{Zn}^{2+}]$ is equal to $[\text{Zn(II)}]_{\text{tot}}$, because the formation of complexes would otherwise induce a deviation from the straight line in Figure 2.

d) Judgement of Analytical Methods

The various methods for determining the concentration of metals do not permit the formulation of general rules by which to judge them. However, good work describes the methods applied in great detail and gives error limits.

pH measurements are often inadequate; sometimes it is not even clear which definition of pH was used. A correct measurement in solutions with constant ionic strength would yield the concentration of the hydrogen ion $[\text{H}^+]$. Such "correct" measurements are feasible with high accuracy by calibrating a well-suited measurement-chain with concentrations. In addition, diffusion potentials are obtained from the same experimental set up (SCHINDLER 1963, SCHINDLER ET AL. 1964). Relative concentration errors are in the range of $\pm 0.5 \%$.

Unfortunately, scientists are now in the habit of working with combined glass electrodes, calibrated with commercial standard buffer solutions (see for example RUNDE ET AL. 1992). From a methodical point of view this procedure is inaccurate and uncertain⁴. Such measurements include systematic errors due to the lack of consideration of diffusion potentials (note that an uncertainty of 1 mV yields a relative concentration error of 4 %).

Editors comment: it seems worthwhile to amplify the former remarks on pH measurements. In Rolf Grauer's opinion pH measurements with combined glass electrodes were inaccurate from a methodical point of view (see also foot note 4).

Most reliable and best reproducible experimental constants are obtained from evaluating a mass action expression which is defined on the basis of concentrations (cf. eq. 1). The thus obtained values are in no way affected by a model (e.g. an activity correction), because they are traceable to a weight procedure in the end.

On the other hand, a pH determination with a combined glass electrode is fundamentally an activity measurement which needs a model M1 for its conversion to the concentration scale. The activity measurement includes contributions from media effects (standard buffer solution / experimental solution) and from the mentioned diffusion potentials (salt bridge / experimental solution). Fundamental inconsistencies are introduced when the constant resulting from evaluating equation 1 is converted to standard conditions with a model differing from M1 (which is usually the case).

The methodical procedure favoured by Grauer does not completely exclude such inconsistencies, but it minimises or even quantifies them.

Similar considerations are necessary when the involved metal is detected with an ion-sensitive electrode. Converting such (activity) readings to concentrations would also require the use of a model.

⁴ "The choice of a pH scale must take into account both the theoretical and the experimental aspects. Unfortunately, no convenient experimental method exists for the routine measurements of pH values on the scales that are most satisfactory in theory. Furthermore, the pH obtained by the convenient experimental techniques has no simple exact meaning", and,

"The operational definition of the practical pH value is an expression of the fact that the experimental pH can never be an exact measure of either the concentration or the activity of hydrogen ion" (BATES 1973).

4 AVAILABLE DATA AND THEIR ORIGIN

4.1 Manganese Carbonate

Early solubility determinations (GAMSIÄGER ET AL. 1970) with freshly precipitated solids give pK_{so} values of 9.4 when evaluating them with current data for the CO_2 - H_2O system. These authors measured the solubility of a very fine precipitate ($A_s = 62.4 \text{ m}^2/\text{g}$) produced under anaerobic conditions and calculated a free energy of formation of $-812.16 \pm 1.47 \text{ kJ/mol}$ with the help of a Carnot cycle. The free energy of formation of α - MnS (alabandine) was identified as the most uncertain entity within this Carnot cycle. When using $\Delta G_f^0(Mn^{2+}) = -228.11 \text{ kJ/mol}$ (WAGMAN ET AL. 1982) a pK_{so} of 9.84 ± 0.25 is obtained at $I = 0$.

The work of GAMSIÄGER ET AL. 1970 revealed that a slightly "surface-oxidised" product dissolves much more easily, even though its specific surface is lower ($A_s = 19.8 \text{ m}^2/\text{g}$). With hydrothermally precipitated manganese carbonate and with natural rhodochrosite ($A_s = 0.6 \text{ m}^2/\text{g}$), equilibrium was not reached, even after several weeks of equilibration time.

In their recent data compilation, NORDSTROM ET AL. 1990 give $pK_{so} = 10.39$ for precipitated manganese carbonate and $pK_{so} = 11.13$ for natural rhodochrosite. These values (which are also included in the PSI database documented in PEARSON ET AL. 1992) are based on solubility experiments performed by GARRELS ET AL. 1960. The original work gives values of 10.32 for the precipitate and 11.05 for rhodochrosite, unfortunately without any error limits. Identical numbers are given in the thermodynamic tables of GARRELS & CHRIST 1965.

The work of GARRELS & CHRIST 1965 suffers from a series of shortcomings. Without exception, all solubility experiments were conducted in a pure CO_2 atmosphere and were not corrected for barometric pressure and for vapor pressure of the water. However, much more serious is their admission: "*Complete equilibrium was seldom achieved*". The pH at equilibrium was extrapolated graphically from time series ($\log(\text{pH})$ vs. $t^{-0.5}$). Most of the experiments had been aborted after 18 hours. The possibility of complex formation is not discussed and, from the remark "*Most experiments were run in duplicate*" it is, conversely, concluded that some of the solubility products reported are based on only a single experiment (in addition to manganese carbonate, eleven other carbonates were investigated in the same study). Finally, raw analytical data are missing and, hence, it has become impossible to do any re-calculations.

Two types of natural rhodochrosite including some 5 mol-% of impurities were investigated: "*Good extrapolation to an equilibrium pH were not easily obtained from either rhodochrosite, so the average result of a number of runs is presented*". This "average result", also given without any error bounds, is $\text{pH} = 5.09$.

Based on experience of GAMSIÄGER ET AL. 1970, that natural and hydrothermally-produced manganese carbonate do not reach equilibrium at $25 \text{ }^\circ\text{C}$, the pK_{so} of 11.13 must be rejected. The reliability of the value for the precipitate (10.32) is uncertain. An estimate of 10.3 ± 0.2 seems appropriate, considering that MORGAN 1967 gave $pK_{so} = 10.4$ for a precipitate which had been measured using a similar experimental methodology.

Single point experiments with a precipitate in de-ionised water and in dilute NaCl solutions were performed by JOHNSON 1982. After three weeks, the final pH values were 6.7. Complex formation with hydrogen carbonate and chloride was included in the solubility calculations and a pK_{so} of 10.60 ± 0.04 was obtained.

However, there are also some reservations about this determination; a constant K_1 of 90 was used for the formation of $MnHCO_3^+$, but according to LESHT & BAUMAN 1978 the value of K_1 is only 18.8.

Two remarkable sentences are found in the work of JOHNSON 1982: "*The ion pair $MnCO_3^0$, while undoubtedly present, does not need to be explicitly considered. The carbonate ion concentration is much less than that of manganese and it will complex an insignificant portion of manganese.*" The principles of mass action were obviously not brought across to the author with sufficient care, which does not increase one's confidence in his work.

From thermochemical data ROBIE ET AL. 1984 calculate $\Delta G_f^0 = -881.13 \pm 0.55$ kJ/mol for natural rhodochrosite. Using $\Delta G_f^0(Mn^{2+}) = -228.11$ kJ/mol leads to a pK_{so} of 10.88 ± 0.10 .

4.2 Iron Carbonate

Various solubility measurements with iron carbonate form a unified picture. Old data from SMITH 1918a, measured on hydrothermally synthesised material, have been re-interpreted several times; the most recent value is $pK_{so} = 10.89$ (NORDSTROM ET AL. 1990).

BRUNO ET AL. 1992 measured the solubility of a similar product (synthesised at 100 °C; $A_s = 2.2$ m²/g) in 1 M (Na)ClO₄ solution at 25 °C. Their conversion to $I = 0$ using the Specific Ion Interaction Theory (SIT)⁵ gave $pK_{so} = 10.8 \pm 0.2$.

REITERER ET AL. 1981 and REITERER 1980 investigated a material synthesised at 150 °C at 50 °C and $I = 1$. From these solubility data the free energy of formation at 25 °C was calculated to be -669.02 ± 0.46 kJ/mol. When using $\Delta G_f^0(Fe^{2+}) = -78.91$ kJ/mol from WAGMAN ET AL. 1982, a pK_{so} of 10.91 ± 0.08 is obtained.

Finally, SINGER & STUMM 1970 found $pK_{so} = 10.24 \pm 0.17$ for the solubility of "coldly" precipitated iron carbonate and the re-calculation of their value by NORDSTROM ET AL. 1990 leads to $pK_{so} = 10.45$.

There is another point worth mentioning here: the good agreement among the various determinations helps support the presently used, but not very reliable value for the standard potential of Fe/Fe^{2+} (LARSON ET AL. 1968).

4.3 Cobalt Carbonate

Values for the solubility of cobalt carbonate are uncertain. The value of 9.98 given by SMITH & MARTELL 1976 is based on solubility measurements conducted by BUTKEVITSCH 1967, which were performed with a commercial product including oxide impurities. The solution composition was not varied during these experiments and, hence, the stoichiometry cannot be checked. This value is of dubious quality. Presumably, the data given by NAUMOV ET AL. 1971 ($pK_{so} = 10.1$) are based on the same source.

LATIMER 1952 derives $pK_{so} = 12.1$ from data provided by KELLEY & ANDERSON 1935, but the source of these data was not checked (by the author; editors comment).

⁵ Editors comment: the SIT describes the activity coefficient γ_j of a ion j of charge z_j in a solution of ionic strength I_m with

$$\log_{10} \gamma_j = -z_j^2 D + \sum_k \epsilon_{(j,k,l,m)} \cdot m_k, \quad \text{where } D = \frac{A \cdot \sqrt{I_m}}{1 + B \cdot a_j \cdot \sqrt{I_m}}.$$

D is called the Debye-Hückel term (the parameter A is tabulated; the product $B \cdot a_j$ is fixed at 1.5) and the product " $\epsilon \cdot m$ " accounts for a short range, non-electrostatic interaction among the ions in solution. A detailed description and values for various interaction coefficients are given by GRENTHE ET AL. 1992.

4.4 Nickel Carbonate

A tabulated pK_{so} range from 6.8 to 7.1 has been found for $NiCO_3$. This would mean that its solubility is three to four orders of magnitude above the solubility of $FeCO_3$ and $ZnCO_3$. Gamsjäger referred to this inconsistency in 1974 (GAMSJÄGER 1974).

The tabulated range from 6.8 to 7.1 may be traced back to well corresponding solubility measurements performed by AGENO & VALLA 1911 and MÜLLER & LUBER 1930 at 25 °C and 20 °C, respectively. These measurements led to free energies of formation of -611.7 kJ/mol (KELLEY & ANDERSON 1935) and of -613.8 kJ/mol (ROSSINI ET AL. 1952).

Although the good correspondence between the two solubility measurements is clearly recognised, the data seem suspicious. A pure, water free $NiCO_3$ phase can be synthesised only at temperatures above 220 °C (REITERER 1980, see also GMELIN 1966) and the product is virtually inert, even against acids. Attaining solubility equilibria takes several weeks at temperatures not below 70 °C (GMELIN 1966). From this it is concluded that the materials investigated by AGENO & VALLA 1911 and MÜLLER & LUBER 1930 did not consist of nickel carbonate; presumably their compounds consisted of carbonate hydrates⁶. KELLEY & ANDERSON 1935 had a similar suspicion, but obviously this objection has fallen into oblivion in the course of data-diagenesis.

An independent value for the free energy of formation (-631.8 kJ/mol) originates from an inaccessible source (D.E. Wilcox 1962, after GMELIN 1966) and leads to $pK_{so} = 10.3 \pm 0.1$ when using common free energies of formation for Ni^{2+} ($-44.4 / -45.6$ kJ/mol).

Unfortunately, the value $\Delta G_f^0 = -637.6$ kJ/mol has intruded without comment into some data compilations (BAEYENS & MCKINLEY 1989). It was reached using estimates from analogies (SVERJENSKI 1984) and must not be used with such an accuracy.

A figure given in FOUILLAC & CRIAUD 1984 (based on the handbook of NAUMOV ET AL. 1971) gives a pK_{so} value of roughly 9.8 for $NiCO_3$. However, this value is not comprehensible since the pK_{so} would only be 6.8, if directly derived from NAUMOV ET AL. 1971.

4.5 Copper Carbonate

KOTRLÝ & ŠUCHA 1985 give $pK_{so} = 9.63$ for the solubility of copper carbonate. Solubility products of similar orders of magnitude are derived from the free energies of formation quoted by KELLEY & ANDERSON 1935 and ROSSINI ET AL. 1952 (-519.15 and -517.98 kJ/mol, respectively). It is not clear to which solid phase these values refer, since copper carbonate was produced for the first time in 1973 by high pressure synthesis (20 kbar, 500 °C; EHRHARDT ET AL. 1973). Using such a material, REITERER ET AL. 1981 measured the solubility at $I = 0.2$, with variable additions of acid and at different partial pressures of CO_2 . Converting the results to $I = 0$ with the Davies-equation⁷ gives $pK_{so} = 11.45 \pm 0.04$.

⁶ According to GMELIN 1966 it is relatively simple to synthesise the carbonate hydrates of Ni(II). In nature, the hexa-hydrate ($NiCO_3 \cdot 6H_2O$) occurs as "hellyerite" (STRÜBEL & ZIMMER 1991).

⁷ Editors comments: At 25 °C the Davies-equation (DAVIES C.W., Ion association, Washington, D.C., Butterworths 1962) describes the activity coefficient γ_j of a ion j of charge z_j in a solution of ionic strength I_m with

$$\log_{10} \gamma_j = -0.5 \cdot z_j^2 \cdot \left(\frac{\sqrt{I_m}}{1 + \sqrt{I_m}} - 0.3 \cdot I_m \right).$$

A very recent description of the various methods to derive activity coefficients is given in GRENTHE ET AL. 1997.

Copper carbonate crystallises in a monoclinic lattice (SEIDEL ET AL. 1974). Details about a rhombohedral copper carbonate (which should be present in a mixture with other materials) were given by PISTORIUS 1960, but have never been confirmed. However, polymorphism cannot be excluded.

4.6 Zinc Carbonate

SCHINDLER ET AL. 1969 determined the solubility of a hydrothermally prepared zinc carbonate at $I = 0.2$ M and at variable partial pressures of CO_2 . The conversion to $I = 0$, performed with a Carnot cycle by using well established auxiliary data, resulted in $\text{pK}_{\text{so}} = 10.79 \pm 0.04$.

This value agrees very well with earlier determinations: re-evaluating the data from SMITH 1918b, using recent equilibrium constants for the $\text{CO}_2\text{-H}_2\text{O}$ system and applying the Davies ionic strength correction gives $\text{pK}_{\text{so}} = 10.90 \pm 0.04$.

The SMITH 1918b data allow the stoichiometry of the reaction to be checked. It exactly follows the dissolution of ZnCO_3 . Hence, the authors did not investigate a hydroxy carbonate.

From thermochemical data, KELLEY & ANDERSON 1935 derive a free energy of formation which leads to $\text{pK}_{\text{so}} = 9.86$. This value propagates itself through the "critical" compilations of ROSSINI ET AL. 1952 and LATIMER 1952.

4.7 Comparative Measurements on Transition Metal Carbonates

Uncertainties and obvious discrepancies among the transition metal carbonate solubilities gave motivation to measure solubilities in the series from MnCO_3 to ZnCO_3 under uniform conditions. To perform such measurements, REITERER 1980 used well crystallised compounds which had been produced under hydrothermal conditions.

From earlier investigations — for example the investigations by GAMSJÄGER ET AL. 1970 on hydrothermally produced MnCO_3 — it was already known that equilibrium is not reached at $25\text{ }^\circ\text{C}$ (editors comment: the meaning here is "in the time span commonly used for experimental investigations"). Therefore, Reiterer conducted his experiments at $50\text{ }^\circ\text{C}$. To allow for sufficiently large variations of the solution composition (additions of acid, $[\text{M}^{2+}]$, pCO_2) he selected a 1 M $(\text{Na})\text{ClO}_4$ ionic medium.

However, for nickel carbonate an experimental temperature of $50\text{ }^\circ\text{C}$ was still too low to reach equilibrium within a reasonable period of time. Therefore, its solubility was measured at 75 , 85 , and $90\text{ }^\circ\text{C}$, and the equilibrium constant thus obtained was extrapolated to $50\text{ }^\circ\text{C}$ using Arrhenius' law (editors comment: the author most likely mixed up Arrhenius' law with van't Hoff's equation. In the present case van't Hoff's equation is the appropriate formalism for extrapolating to lower temperatures). For $\log^* K_{\text{pso}} = \log ([\text{M}^{2+}] \cdot \text{pCO}_2 \cdot [\text{H}^+]^{-2})$ the following values were obtained at $I = 1$ M and $50\text{ }^\circ\text{C}$:

Carbonate	$\log^* K_{\text{pso}}$
MnCO ₃	7.36 ± 0.06
FeCO ₃	7.61 ± 0.04
CoCO ₃	7.19 ± 0.04
NiCO ₃	7.22 ± 0.10
CuCO ₃	7.16 ± 0.05
ZnCO ₃	7.68 ± 0.04

The value for nickel carbonate, extrapolated to 25 °C is $\log^* K_{\text{pso}} = 7.41 \pm 0.1$ (I = 1 M)

Comparing all these data reveals only slight differences among the solubilities of the transition metal carbonates. It further demonstrates that the solubility products only partially follow the Irving-Williams series (GAMSJÄGER 1974, STUMM 1981). It is fact that a weakly distinct solubility minimum exists for the carbonates of Co, Ni and Cu⁸, but a surprising result is the significantly lower solubility of manganese carbonate if compared to iron carbonate.

The conversion of these data to standard conditions is beset by large uncertainties. However, the charm of these data lies in their intrinsic comparability because of which they form a main connecting thread in judging the quality of literature data.

4.8 Cadmium Carbonate

Common tabulated values for the $\text{p}K_{\text{so}}$ of cadmium carbonate fall into the range from 11.21 (WAGMAN ET AL. 1982) to 13.74 (KOTRLÝ & ŠUCHA 1985). Using a carefully reconstructed genealogical tree, STIPP ET AL. 1993 have recently demonstrated that the heat of formation of cadmium carbonate determined in 1883 forms the master datum for the wide spectrum of solubility constants. The use of differing auxiliary data through the years led to this unpleasant situation. The very nice case study by STIPP ET AL. 1993 substantiates the law of mythical numbers (*An expert opinion, once referenced, becomes fact despite evidence of the contrary*: SINGER 1990) and shatters one's confidence in "critical" data compilations.

It seems that GAMSJÄGER ET AL. 1965 were the first who made an experimental determination of the solubility of cadmium carbonate. The experiments were conducted at variable partial pressure of CO₂ and at high ionic strength (I = 3 M). The conversion to I = 0 was performed with a Carnot cycle, including the experimentally accessible standard potential of Cd/Cd²⁺ (at I = 3 M) as the critical parameter.

A $\text{p}K_{\text{so}}$ of 12.00 ± 0.05 is obtained from measurements on two different products with slightly different solubilities ($\Delta\log K = 0.06$). Two recent studies confirm this result (RAI ET AL. 1991: $12.2(4) \pm 0.1$; STIPP ET AL. 1993: 12.1 ± 0.1). A $\text{p}K_{\text{so}}$ value of 11.3 from DAVIS ET AL. 1987 is questioned by RAI ET AL. 1991 on the basis of potential artefacts.

⁸ Copper carbonate crystallises in a monoclinic lattice and so differs from all the other representatives of this series, which crystallise in the calcite lattice. In comparing the constants, an unknown "structural contribution" needs therefore to be considered for copper carbonate.

4.9 Lead Carbonate

Lead carbonate crystallises in the aragonite-type lattice. Details on its solubility are meagre. According to an elderly and not documented table from SEEL 1955 its pK_{so} is 13.48.

BILINSKI & SCHINDLER 1982 investigated the solubility of a commercial product at $I = 0.3$ M and at variable partial pressure of CO_2 . Converting their pK_{so} (12.15 ± 0.05 at $I = 0.3$ M) to $I = 0$ using the Davies-equation yields $pK_{so} = 13.2(3)$.

NÄSÄNEN ET AL. 1961 calculated the solubility of commercial products on the basis of pH measurements without varying the CO_2 partial pressure. A pK_{so} of 13.13 from this work is found in recent tables (KORTLÝ & ŠUCHA 1985).

5 DATA JUDGEMENT AND RECOMMENDED VALUES

5.1 Manganese Carbonate

The solubility data of manganese carbonate are contradictory in part and, as discussed in section 4.1, are of limited reliability.

From an experimental point of view, only the measurements of REITERER 1980 (measured on hydrothermally produced material at 50 °C; $I = 1$ M) and GAMSJÄGER ET AL. 1970 (obtained with a fine-grained $MnCO_3$ at 25 °C; $I = 3$ M) appear reliable. However, even these determinations are not free from contradictions.

a) Crystalline Materials and Rhodochrosite

Starting from the assumption that the solubilities of transition metal carbonates follow the Irving-Williams series (or at least depend on the ionic radii), one would expect that manganese carbonate would be more soluble than iron carbonate at 50 °C. This is not the case, but with $\Delta \log K = 0.25$, the difference is not grave.

The auxiliary data required to rigorously convert Reiterer's solubility data to standard conditions are missing, but a sound estimate seems to offer a practical way. In addition to the 50 °C data, trustworthy constants at standard conditions are available for some of the carbonates. A comparison reveals that the difference

$$\Delta \log K(I, T) = \log^* K_{ps0}(I = 1 \text{ M}, 50 \text{ °C}) - \log^* K_{ps0}(I = 0, 50 \text{ °C})$$

shows little variation:

Solid	I (M)	$\Delta \log K(I, T)$	Reference
CaCO ₃	1	+ 0.33	REITERER 1980
	3	+ 0.33	RIESEN 1970
ZnCO ₃	1	+ 0.33	REITERER 1980; SCHINDLER ET AL. 1969
FeCO ₃	1	+ 0.36	REITERER 1980
	1	+ 0.26	REITERER 1980; BRUNO ET AL. 1992
CuCO ₃	1	+ 0.46	REITERER 1980

These results are not surprising since the compounds have similar solubilities and similar thermochemical properties. However, for copper carbonate which is not iso-structural such agreement is less understandable.

Using the correction $\Delta \log K(I,T) = 0.33$ one obtains $\log^* K_{\text{pso}} = 7.0(3)$ for crystalline MnCO_3 at $I = 0$, and from this $\text{p}K_{\text{so}} = 11.1^9$. A comparable value of $\text{p}K_{\text{so}} = 10.88 \pm 0.10$ is calculated from the thermochemical data of ROBIE ET AL. 1980.

Having suitable reservations about the extrapolation method and maintaining one's suspicion about the thermochemical data, a provisional value of $\text{p}K_{\text{so}} = 11.0 \pm 0.2$ is proposed for crystalline MnCO_3 as well as for rhodochrosite.

b) Fine Grained Precipitates

The measurements performed by GAMSJÄGER ET AL. 1970 at $I = 3$ M seem to be reliable and so we judge their $\log^* K_{\text{pso}}$ of 7.97 ± 0.04 ($I = 3$ M; 25 °C). The conversion to $I = 0$ gives $\log^* K_{\text{pso}} = 8.31 \pm 0.25$ ($I = 0$; 25 °C). There are some doubts about this value because it leads to a higher solubility at $I = 0$ than at $I = 3$ M. This is not only contradictory to sound chemical feelings, but also is not consistent with a majority of experimental results.

Usually, the difference

$$\Delta \log K(I) = \log^* K_{\text{pso}}(I) - \log^* K_{\text{pso}}(I=0)$$

is positive, but in the latter case it is negative:

Solid	I (M)	$\Delta \log K(I)$	Reference
MgCO_3	3	+ 0.18	KÖNIGSBERGER ET AL. 1992
CdCO_3	3	+ 0.33	GAMSJÄGER ET AL. 1965
CaCO_3	3	+ 0.50	RIESEN 1970
FeCO_3	1	+ 0.24	BRUNO ET AL. 1992
MnCO_3	3	- 0.35 !!	GAMSJÄGER ET AL. 1970

Two weak points are recognised in the conversion of the solubility constant for MnCO_3 :

- the Carnot cycle used to calculate the free energy of formation (GAMSJÄGER ET AL. 1970), and
- the standard electrochemical potential Mn/Mn^{2+} (see reaction 3 on page 2).

Assuming that $\Delta \log K(I)$ is in the range + 0.2 to + 0.5 one can be courageous and derive $\log^* K_{\text{pso}} = 7.6(5)$ and $\text{p}K_{\text{so}} = 10.5 \pm 0.3$.

The values from JOHNSON 1982 and from GARRELS ET AL. 1960, although not completely reliable, fall into the same range. With $\text{p}K_{\text{so}} = 10.5 \pm 0.3$, therefore, we provide only a provisional value for precipitated manganese carbonate.

⁹ The relationship $K_{\text{so}} \leftrightarrow ^*K_{\text{pso}}$ is given by $K_{\text{so}} = ^*K_{\text{pso}} \cdot K_{\text{H}} \cdot K_{\text{a1}} \cdot K_{\text{a2}}$. Using the equilibrium constants for the $\text{CO}_2/\text{H}_2\text{O}$ system given by NORDSTROM ET AL. 1990 ($\log K_{\text{H}} = -1.47$; $\log K_{\text{a1}} = -6.35$; $\log K_{\text{a2}} = -10.33$), the numerical relationship is $\log K_{\text{so}} = \log^* K_{\text{pso}} - 18.15$.

c) Recommended Values

Solubility constants for manganese carbonate can only be given with some reservations. As provisional values we recommend

$$pK_{so} = 11.0 \pm 0.2$$

for crystalline $MnCO_3$ and rhodochrosite, and

$$pK_{so} = 10.5 \pm 0.3$$

for precipitates.

Presumably these solubility differences are based to a limited extent on particle size effects. The water content always associated with precipitates should contribute to this difference as well. Much more trustworthy solubility products for manganese carbonate will be available only when further thorough experimental investigations have been conducted. Simple cosmetic operations performed on available data will never improve the present knowledge.

5.2 Iron Carbonate

The reported solubility products of crystalline iron carbonate remained conspicuously constant in the course of the years (SMITH 1918a, REITERER ET AL. 1981, BRUNO ET AL. 1992), and all the referenced reports appear credible. The value provided by BRUNO ET AL. 1992 covers most of the reported ranges and it is recommended that

$$pK_{so} = 10.8 \pm 0.2$$

be used for crystalline iron carbonate.

5.3 Cobalt- and Nickel Carbonate

Common tabulated values for the solubility of $CoCO_3$ are of doubtful quality, and those for $NiCO_3$ are grossly wrong. From recent hydrothermal data pK_{so} values of 13.1 and 9.8 are obtained for $CoCO_3$ and $NiCO_3$, respectively (TAREEN ET AL. 1991), but this work appears to be less trustworthy (see also footnote on page 3).

The only reliable data are the measurements from REITERER 1980 for the temperature range 50 to 90 °C at ionic strength 1 M. These data demonstrate negligible solubility differences between the two carbonates and show that their solubility constant is 0.4(1) log units below that for iron carbonate. Presuming that this difference is also valid at 25 °C, and using the recommended value for iron carbonate at standard conditions ($pK_{so} = 10.8 \pm 0.2$), $pK_{so} = 11.2 \pm 0.2$ is obtained for cobalt- and nickel carbonate.

REITERER 1980 gives a solubility constant at $I = 1$ M, extrapolated to 25 °C ($\log^*K_{pso} = 7.4(1) \pm 0.1$). Using the ionic strength correction for iron carbonate as proposed by BRUNO ET AL. 1992 ($\log^*K_{pso}(I=1 \text{ M}) - \log^*K_{pso}(I=0) = 0.24$), $\log^*K_{pso}(NiCO_{3(s)})$ becomes 7.17 ($I = 0$; 25 °C) and, hence, $pK_{so} = 11.0 \pm 0.2$. Comparing the two (I, T) - corrections, a larger importance was attached to the relative solubility difference measured at 50 °C. The extrapolation of the "75 to 90 °C \log^*K_{pso} " values down to 25 °C leads to a less accurate result. Within the work of BRUNO ET AL. 1992 the ionic strength correction led to a doubling of the error limits.

The recommended value for both, $CoCO_3$ and $NiCO_3$ is

$$pK_{so} = 11.2 \pm 0.2.$$

5.4 Copper Carbonate

Common tabulated solubility products refer to an unknown solid phase; all of them should be rejected without exception. Only one determination was performed with a characterised copper carbonate at 25 °C (REITERER 1980, REITERER ET AL. 1981). This determination is judged to be reliable and the recommended value (including enlarged error limits) is

$$pK_{so} = 11.45 \pm 0.10.$$

5.5 Zinc Carbonate

The value from SCHINDLER ET AL. 1969 is recommended without any reservations:

$$pK_{so} = 10.80 \pm 0.10.$$

Their ionic strength correction, based on a Carnot cycle, is very trustworthy. Direct support for the solubility product is found in older work; indirect support is given by REITERER'S 1980 measurement at 50 °C.

5.6 Cadmium Carbonate

As shown by STIPP ET AL. 1993, all values from older compilations must be rejected. Three independent, high quality publications agreeing well with one another are available for deriving a solubility product (GAMJSJÄGER ET AL. 1965, RAI ET AL. 1991, STIPP ET AL. 1993). Without giving preference to a single publication

$$pK_{so} = 12.1 \pm 0.2$$

is recommended.

5.7 Lead Carbonate

In our opinion, based on the methodology employed, the work of BILINSKI & SCHINDLER 1982 appears more reliable than the single-point experiments performed by NÄSÄNEN ET AL. 1961. However, at $I = 0.3$ M the Davies ionic strength correction reaches its limitations. The recommendation

$$pK_{so} = 13.2 \pm 0.2$$

takes this fact into account and includes the values provided by NÄSÄNEN ET AL. 1961. Due to the somewhat uncertain extrapolation it is necessary to state that the basic values used to derive the recommendation were $\log^*K_{ps0} = 5.20 \pm 0.03$ ($I = 0.3$ M) and $pK_{so} = 12.15 \pm 0.05$ ($I = 0.3$ M).

5.8 Summary

Table 1 is a compilation of the recommended pK_{so} values. The figures for manganese carbonate should be considered provisional. Agreement with the compilation of SMITH & MARTELL 1976 is restricted to $FeCO_3$ and $PbCO_3$. The tables compiled by LATIMER 1952 scored only one hit ($FeCO_3$).

Figure 3 repeats the representation of pK_{so} values as a function of the atomic numbers shown in Figure 1. The picture has changed and now shows a consistent relationship among the transition metal carbonates from manganese to zinc.

Table 1 Summary of recommended solubility products of transition metal carbonates, given as pK_{so} values and compared with former compilations (25 °C, $I = 0$).

	Recommended Values	SMITH & MARTELL 1976	LATIMER 1952	
MnCO ₃	11.0 ± 0.2 10.5 ± 0.3	9.30	10.06	Rhodochrosite Precipitate
FeCO ₃	10.8 ± 0.2	10.68	10.68	
CoCO ₃	11.2 ± 0.3	9.98	12.1	
NiCO ₃	11.2 ± 0.3	6.87	6.87	
CuCO ₃	11.45 ± 0.10	9.63	9.6	
ZnCO ₃	10.80 ± 0.10	10.00	9.7	
CdCO ₃	12.1 ± 0.2	13.74	11.28	
PbCO ₃	13.2 ± 0.2	13.13	12.82	

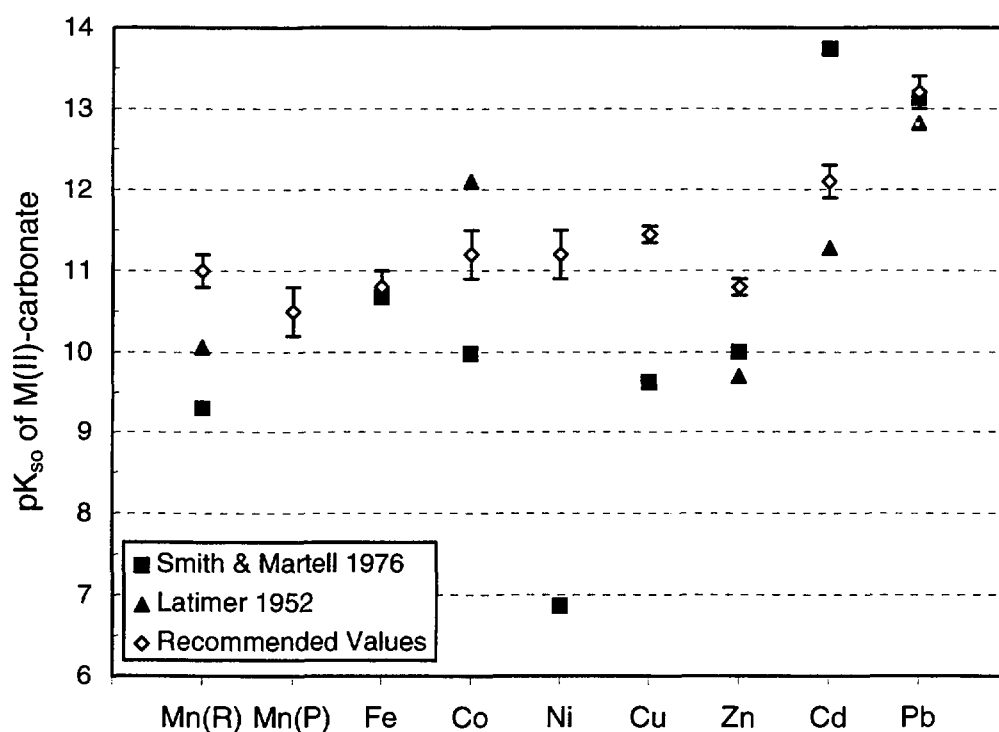


Figure 3 Solubility data of heavy metal carbonates with the composition M(II)CO₃, taken from SMITH & MARTELL 1976 and LATIMER 1952, as compared to the resolved recommendations from the present work.

6 GEOCHEMICAL RELEVANCE OF HEAVY-METAL CARBONATES

6.1 Conditions of Synthesis

The carbonates of manganese and iron may be synthesised under reasonably mild conditions, but carbonates of succeeding elements cause difficulties which increase with the atomic number; REITERER 1980 could not produce pure, water free CoCO_3 below 160 to 170 °C, and to obtain pure NiCO_3 , a temperature of 220 °C was necessary. Hydroxy carbonates were formed at lower temperatures. Up to now, CuCO_3 has only been produced through high pressure synthesis (20 kbar, 500 °C; EHRHARDT ET AL. 1973).

On the other hand, it is well known that the synthesis of zinc and lead carbonate becomes simpler. Finally, the formation of cadmium carbonate can be carried out without any problems; it forms as a pure phase even as a corrosion product at ambient temperature (GRAUER 1980).

The formation of water-free carbonates includes dehydration of the cation. The pattern of the energies of hydration indicates that this dehydration becomes more and more difficult with increasing atomic number in the series from manganese to copper. In parallel to these findings the energy of activation of water exchange also increases (COTTON & WILKINSON 1982). With these facts and from a qualitative point of view it becomes comprehensible that for example the synthesis of MgCO_3 is not possible without pressure. Further, it is not astonishing that carbonate hydrates are formed under too mild conditions. One simply succeeds in forming the hexa hydrates of CoCO_3 and NiCO_3 .

Under mild conditions (i.e. precipitation at ambient temperature) manganese and iron form carbonates, but without exception cobalt, nickel and copper form hydroxy carbonates. Hydroxy carbonates are also the common precipitates of zinc.

6.2 Natural Carbonate Minerals

Knowing the conditions of synthesis one understands why CuCO_3 has never been found in natural systems. Most likely, this is also true for a pure NiCO_3 . The rarely occurring gaspeite, which has the composition $(\text{Ni},\text{Mg},\text{Fe})\text{CO}_3$, is a berthollide (STRÜBEL & ZIMMER 1991). It further becomes understandable why $\text{NiCO}_3 \cdot 6\text{H}_2\text{O}$ is found (as rarely as is gaspeite) in the form of hellyerite; according to the prevailing conditions one expects the formation of hydroxy carbonates. A natural representative of this group is the mineral nullagite ($\text{Ni}_2(\text{OH})_2\text{CO}_3$), but solubility data for this compound are lacking.

CoCO_3 , which is easier to prepare than NiCO_3 occurs as the natural mineral sphero-cobaltite (STRÜBEL & ZIMMER 1991). It is supposed that this compound is a mixed phase (a calcite including cobalt is named cobalto-calcite, but this name also serves as a synonym for sphero-cobaltite; STRÜBEL & ZIMMER 1991). However, usually the hydroxy carbonates are found in nature.

Natural carbonates of copper are malachite (a common corrosion product of copper; GRAUER 1980) and the less abundant azurite. The solubilities of these compounds were investigated by SCHINDLER ET AL. 1968 (see also Figure 4).

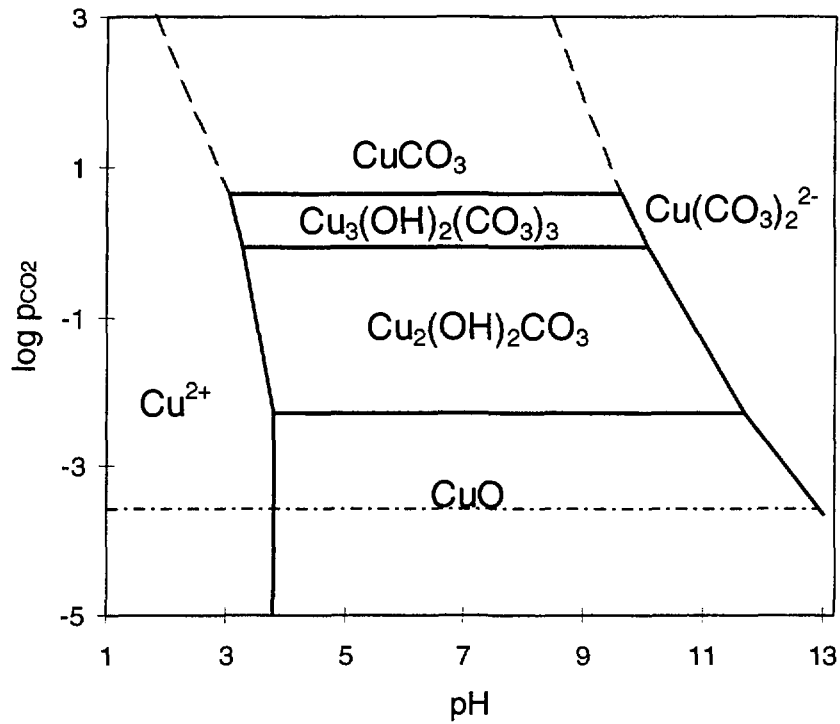


Figure 4 Stability diagram for the system Cu^{2+} - H_2O - CO_2 ($I = 0$, 25°C) according to REITERER ET AL. 1981. Activities of dissolved species are assumed to be unity.

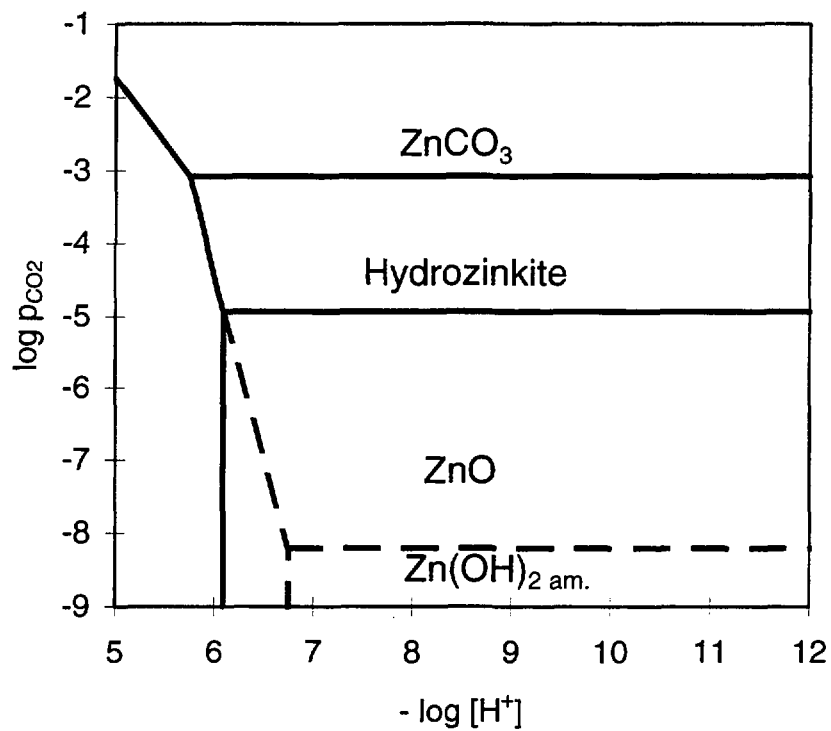


Figure 5 Stability diagram for the system Zn^{2+} - H_2O - CO_2 ($I = 0$, 25°C), with $[\text{Zn}^{2+}] = 0.1\text{ M}$ (GRAUER 1980). Dashed lines represent metastable equilibria of amorphous $\text{Zn}(\text{OH})_2$ and hydrozinkite.

Based on the very mild conditions, smithsonite (ZnCO_3) is very common in nature. It often includes other divalent cations as impurities. By inspecting the stability diagram in Figure 5 it becomes understandable why smithsonite weathers to hydrozinkite ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$) under atmospheric conditions. Dis-ordered hydrozinkite is the common corrosion product of zinc under atmospheric and natural water conditions.

Similar conditions are found for lead as are for zinc: cerussite (PbCO_3) is an important ore mineral in local environments, but usually the hydroxy carbonates are very abundant. Analysis of corrosion products, indicating that the carbonate and the hydroxy carbonate occur together (GRAUER 1980), gives a similar picture. The solubility of hydro-cerussite has been determined by BILINSKI & SCHINDLER 1982.

According to the geochemical abundance of the elements and based on their mild formation conditions, siderite (FeCO_3) and rhodochrosite (MnCO_3) are not only important as ore minerals but also as secondary sedimentary minerals.

Isomorphic substitutions in the crystal lattice are very common. Usually, siderite includes magnesium and manganese and STRÜBEL & ZIMMER 1991 describe cobalto-sphero-siderite as a (Fe,Mg,Mn,Co)-carbonate with a cation ratio of about 2:1:1:1. On the other hand, iron carbonate forming in low temperature sediments is usually very pure (see literature in BRUNO ET AL. 1992 and WERSIN ET AL. 1989). Including sedimentary formations, much higher impurities are common for rhodochrosite which preferentially incorporates magnesium and calcium (PEDERSON & PRICE 1982, SUESS 1979).

Only minor amounts of otavite (CdCO_3) have been found in zinc deposits (see literature in STIPP ET AL. 1993). Based on the geochemical rareness of the element as well as on the similarity of the ionic radii of Cd^{2+} and Ca^{2+} it is supposed that cadmium occurs in natural systems as a (Ca,M(II),Cd) CO_3 - mixed phase (DAVIS ET AL. 1987, KÖNIGSBERGER ET AL. 1991).

6.3 Summary

From a geochemical point of view the pure carbonates of copper, nickel and cobalt are irrelevant. On the other hand, their hydroxy carbonates are important, although solubility data are available solely for malachite and azurite (SCHINDLER ET AL. 1968).

In the case of zinc and lead the carbonates and the hydroxy carbonates are of comparable importance. Reliable solubility data are available for hydrozinkite (SCHINDLER ET AL. 1969) and for hydro-cerussite (BILINSKI & SCHINDLER 1982).

In the geosphere, the carbonates of manganese and iron (rhodochrosite and siderite, respectively) are important as ore minerals and as secondary sediments. For manganese carbonate the formation of mixed phases seems considered normal.

Based on the geochemical rareness of the element, pure CdCO_3 (otavite) is an exception. The formation of mixed phases with calcite is considered to be the rule.

All the above considerations concentrated on carbonate phases. One should, however, remember that under anoxic conditions the sulphides form the relevant phases for most of the elements discussed so far. For this class of compounds the "data-situation" is even worse than for the carbonates (Editors comments: although work on this topic is becoming increasingly important, see for example THOENEN 1999). Further, one should not forget that nature does not only form hydroxy carbonates, but also hydroxy salts with chloride and sulphate. Only single point measurements of this class of compounds, rich in variants, are known.

EDITOR'S ACKNOWLEDGEMENTS

I would like to express my gratitude to Dr. J. Pearson for his substantial contributions to the improvement of the choice of words in the present translation. To a non-native speaker of a foreign language it is sometimes difficult to find the precise word, even with the help of a large and comprehensive dictionary. I think that the style would have suffered from some more awkwardness without Joe's help.

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