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DIFFERENTIAL THERMAL ANALYSIS OF Mg-BEARING CARBONATES AND SHEET SILICATES

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Abstract

In the present paper the thermal behaviour of Mg-carbonates and -silicates is reviewed and discussed, based on own DTA investigations and data from the literature. Mg-bearing minerals in soils and sediments offer informations about the palaeoenvironment and palaeoclimatology of sediments and soils and – thus – the study of their crystal chemical compositions by means of (differential) thermal analysis informs about environmental conditions of (sedimentary Mg-) mineral (*trans*-) formations. The paper stresses (1) the interrelations between decomposition temperatures of (Mg-) carbonates and substitution processes and is (2) concerned with the interdependence between the dehydroxylation behaviour of Mg-bearing sheet silicates and their crystal chemical composition.

Keywords: carbonates, DTA, sheet silicates, substitution, tropical environment

Introduction

The element magnesium forms one cation, e.g. the divalent Mg^{2+}. Due to its ionic potential (=valency/ionic radius) it belongs to the soluble cations, as the common cations sodium (Na^{+}), potassium (K^{+}), calcium (Ca^{2+}) or iron-II (Fe^{2+}) [1]. That means, in the sedimentary processes of weathering and precipitation from solutions Mg-bearing minerals will only form in environments of low water activity, e.g. in (semi-) aridic soils and sediments. Thus the occurrence of authigenic Mg-bearing minerals in sedimentary profiles or soil profiles points to a milieu of (trans-) formation, which is characterised by the lack of water (by low water activity), it points to a (semi-) aridic period in the palaeoclimatic history of soil (or sediment) development. Although this is also true for other soluble cations, such as K^{+}, Na^{+} or Ca^{2+}, which do not form sedimentary phases in humid environments either, the interrelations between the formation of Mg-bearing carbonates or silicates and palaeoclimatic conditions show to be much clearer, much more striking than the comparable interrelationships envolving K^{+}, Na^{+} or Ca^{2} [2].

Thermal analysis, mainly DTA or DSC, proves to be a very suitable method for the determination of the portion of Mg among the cations in crystal structures (of Mg–Fe–Mn–Ca–silicates or carbonates) [3–5]. This is mainly suitable for sedimentary minerals, such as many sheet silicates or carbonates, in which parts of the primary cations (Fe^{2+}, Ca^{2+}, Al^{3+}) have been replaced by Mg^{2+} during processes of weath-

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ering or diagenesis, thus mirroring a change in the palaeoecological conditions (e.g. the palaeo-temperature). Thus, thermal analysis may help in palaeoclimatic reconstructions during petrogenetic interpretations of soils or sediments.

Thermal analysis of Mg-bearing carbonates

Determination of decomposition temperatures

Only carbonates free of water, Cl, F or OH will be considered here in order to recognise the principles of interrelation. Figure 1 shows the temperatures of decomposition of four simple earth alkaline carbonates *vs.* the ionic radii of the cations. The radii are dependent on the crystal chemical coordination of the cations [1], but in most cases the coordination number 6 occurs, e.g. in octahedra of sheet silicates. The 'classical' values of Goldschmidt [6] have been used, but the slightly different values of other authors show a similar picture, for instance the 'semi-theoretical' values of Pauling [7] or the data of Wedepohl [8] or Evans [9]. The temperatures of decomposition have been obtained from DTA runs made under strictly standardised conditions of preparation and analysis as proposed by Smykatz-Kloss [4, 5]. The resulting diagram (Fig. 1) demonstrates that – at least for the simple carbonates studied, namely magnesite ($MgCO_3$), calcite ($CaCO_3$), strontianite ($SrCO_3$) and witherite ($BaCO_3$) – the temperatures of decomposition increase with increasing size of the cations ($Mg^{2+}< Ca^{2+}< Sr^{2+}< Ba^{2+}$, Fig. 1). Double salts including two different cations among which Mg^{2+} is always found, show a more complex picture (Table 1). The larger cation seems to control the process of decomposition of the carbonate structure: with increasing size of the cation the temperature of decomposition increases as well, e.g. $CaMg_3$< CaMg< BaMg. But apart from the influence of the larger

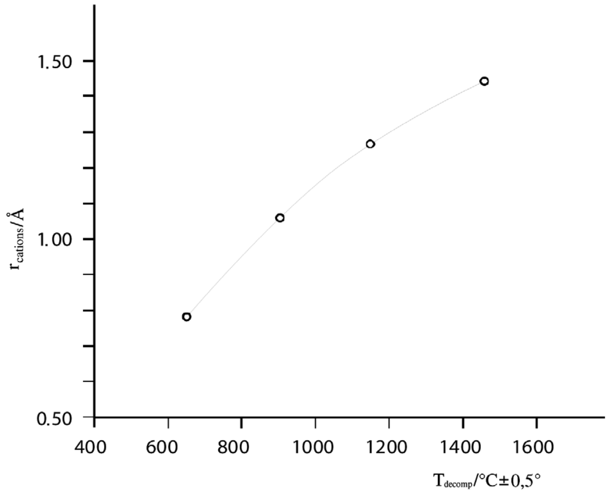

Fig. 1 Relationships between ionic radii and decompositionic temperatures for simple earth alkaline carbonates free of water (from standadized DTA runs – 100 mg, 10 K min^{-1})

cation (Ca, Ba) the ratio of both cations seems to have some influence on the temperature of decomposition, too (e.g. huntite, Ca:Mg=1:3, and dolomite, Ca:Mg=1:1). Studies of other authors – who generally did not specify all conditions of analysis – show analogous results [3, 10–12].The temperature of decomposition of the $MgCO_3$-portion occurs between 613 and 645°C – except in the minerals ankerite and dolomite. These seem to be characterised by more compact crystal structures and stronger bonding energies between Mg^{2+} and the coordinating ions [13].

Table 1 Standardised decomposition temperatures of double salts (X–Mg carbonates, X=Ca, Fe^{2+}, Ba)

Mineral	Formula	T_{decomp}/°C ($MgCO_3$)	T_{decomp}/°C (XCO_3)	Reference
Huntite	$CaMg_3(CO_3)_4$	635	895	[12]
	$Ca(Mg,Fe)_3(CO_3)_4$	613	826	[4]
Breunnerite	$Ca(Mg_{0.45}Fe_{0.55})(CO_3)_2$	645		[4]
Ankerite	$Ca(Fe,Mg)(CO_3)_2$	762	898	[4]
	$Ca(Fe,Mg)(CO_3)_2$	773	882	[4]
Dolomite	$CaMg(CO_3)_2$	807	901	[4]
	$CaMg(CO_3)_2$	795	960	[11]
Norsethite	$BaMg(CO_3)_2$	628	1174	[4]

The influence of crystal chemical substitutions on the temperature of decomposition of carbonates

Generally, each replacement of the original cations of a crystal structure by substituting ions creates physical disorder. Increasing structural disorders (by increasing substitutions) means decreasing bonding energies between the constituents of the crystal structure. For the temperature of decomposition this means increasing crystal chemical disorder lowers the temperatures of decomposition.

Sub-recent marine organisms from tropical and subtropical environments quite often exhibit calcitic or aragonitc shells which include up to 25 mol% of $MgCO_3$ (Table 2). The lowering of the temperatures of decomposition in Mg-calcites caused by the Mg→Ca substitution can be used as a tool for the determination of the Mg-content of Mg-calcites, $(Ca, Mg)CO_3$ (Fig. 2).

Dolomites, $CaMg(CO_3)_2$, quite often show substitutions of the Mg^{2+} by Fe^{2+}, Mn^{2+}, Zn^{2+}, and/or Ni^{2+}. The decomposition of the (Fe^{2+}, Mn^{2+}) CO_3 – component causes an additional endothermic peak, or at least a shoulder on the lower side of the $MgCO_3$-decomposition peak. This peak tends towards the lower temperature of siderite ($FeCO_3$) decomposition with increasing amounts of the substituent Fe^{2+} (Fig. 3).

For the exact determination of small amounts of incorporated Fe^{2+} the equipment used should be calibrated by heating samples with known iron contents and under standardized conditions: 100 mg sample amount, Pt_{90}/Rh_{10} thermocouples, 10 K min^{-1} heating rate, 100 mg of Al_2O_3 for inert comparison, crucibles of Al_2O_3, standing air as furnace atmosphere.

Table 2 MgO contents and decomposition temperature of Mg-calcites (150 mg of sample amount)

Sample	Locality	MgO/mol%	$T_{decompos}$/°C±0.5°	d_{1014}/Å
Calcite, pure	Harz, Germany	0	925	3.035
Mg-calcite (shell fragments)	Bermudas (1)	5.9	898	3.018
Mg-calcite (shell fragments)	Bermudas (2)	8.7	893	3.005
Calcitic algae	Saõ Thomé	18.1	889	2.974
Calcitic algae	Saõ Vicente	19.0	889	2.972
Calcitic algae	Bioco	21.0	887	2.966

The last value of Table 2 represents the corresponding *d*-value for the main interference in the X-ray diffractogram (d_{1014} in Å)

The thermal analytical study of Mg-bearing sheet silicates

For Mg-bearing silicate minerals which include hydroxyl anions (e.g. all Mg-bearing layer silicates, clay minerals such as chlorites, tri-octahedral illites, smectites etc.) the dehydroxylation effect could be used for crystal chemical determinations. The layer structures of clay minerals contain the (OH) at the corners of the octahedra, directly bound to the central cation of the octahedra (Al^{3+}, Mg^{2+}, $Fe^{2+, 3+}$). For detailed clay mineral structures see e.g. [14–16]. That means, the bonding strength between this

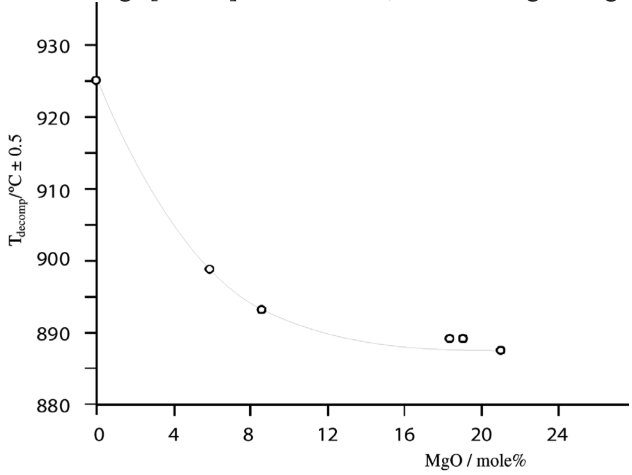

Fig. 2 MgO contents and decomposition temperatures of Mg-calcites (150 mg of sample amount)

central cation and the (OH) will control the temperature of the dehydroxylation. The strength of the bonding is dependent (a) on the type of the cation bound to the (OH), and (b) on the type of the structure. Different crystal structures will show different temperature ranges for the process of dehydroxylation, and different cations occupying the octahedral central positions of the same mineral will show different temperatures of dehydroxylation. This enables crystal chemical determinations by measuring the peak temperatures and the peak areas of the dehydroxylation effects. For example it enables the determination of the portions of the octahedral Fe, Mg and Al in smectites, chlorites or other clay minerals. DTA curves of Mg-bearing sheet silicates were previously described [4, 17–23].

The minerals pyrophyllite and talc exhibit identical crystal structures (‘isostructural’). Both are simple 3-layer silicates and differ only in the occupation of the central octahedral position by Al or Mg, respectively, [6], as follows, pyrophyllite, $Al_2^{[6]}$ $[(OH)_2\ Si_4\ O_{10}]$ and talc, $Mg_3^{[6]}$ $[(OH)_2\ Si_4\ O_{10}]$.

Talc includes the larger octahedral cation Mg^{2+} (r, radius=0.78 Å) whereas pyrophyllite includes Al^{3+} (r=0.57 Å). Nearly equal distances between (OH) and the core of the central cation (‘bonding lengths’) indicate that the M–OH bonding strength in talc (Mg–OH) is stronger than in pyrophyllite (Al–OH). Consequently, the dehydroxylation of the tri-octahedral talc needs more energy supply (=higher temperatures in DTA) than that of the analogous di-octahedral Al-silicate pyrophyllite. This means that pyrophyllite dehydroxylates at lower temperatures than talc (compare Table 3). The same interrelation occurs in smectites, chlorites, kaolinite/serpentine (Table 3).

Table 3 Temperatures of dehydroxylation [°C] of Al-and Mg-sheet silicates

Mineral	Formula	Structural type	Temp. of dehydrox.
kaolinite	$Al_2[(OH)_4Si_2O_5]$	1:1, *T-O*	550–600
serpentine	$Mg_3[(OH)_4Si_2O_5]$	1:1, *T-O*	650–720
pyrophyllite	$Al_2[(OH)_2Si_4O_{10}]$	2:1, *T-O-T*	745
talc	$Mg_3[(OH)_2Si_4O_{10}]$	2:1, *T-O-T*	~ 940
Al-smectite (montmorillonite) Mg-smectite (saponite)	form. see below	2:1 + water *T-O-T*	670–725 840
Al-chlorite (sudoite)	$Al_4[(OH)_8Si_4O_{10}]$	2:1:1 *T-O-T-O*	495–525
Mg-chlorite	$Mg_6[(OH)_8Si_4O_{10}]$	*T-O-T-O*	825–860

T – tetrahedral, *O* – octahedral layer, montmorillonite: $Al_{1.7}Mg_{0.3}[(OH)_2Si_4O_{10}]\cdot 0.3Na+nH_2O$,
saponite: $Mg_3[(OH)_2Si_{3.7}Al_{0.3}O_{10}]\cdot 0.3Na+nH_2O$,

The dehydroxylation of the dioctahedral Al-bearing sheet silicates always happens at lower temperatures than that of the trioctahedral Mg-bearing species.

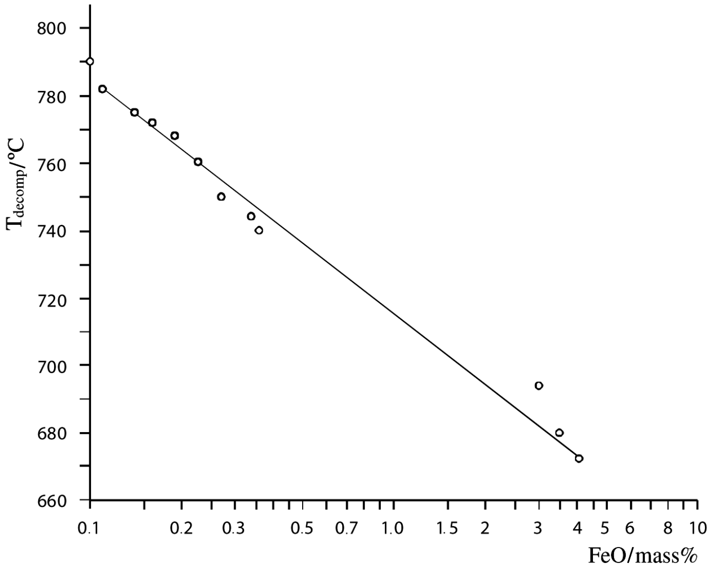

Fig. 3 Decomposition temperatures of Fe-bearing dolomites

Al-chlorites, however, are very rare minerals. Usually these chlorites form mixed crystals (solid solutions) of the Mg-end member, Mg_6 $[(OH)_8Si_4O_{10}]$, with an iron end member. Due to the partly oxidised iron (Fe^{3+}) in addition to the Fe^{2+} in the same crystal structure, iron-bearing clay minerals are characterised by a remarkable degree of disorder. Consequently, the dehydroxylation of (Fe–OH) occurs at comparably low temperatures. For example, the dehydroxylation of Fe–OH in chlorites or smectites occurs already at 470–530°C.

As shown in earlier publications [4, 5, 24], the MgO/Fe_2O_3 ratio in chlorites can be determined accurately in standardised DTA runs, using this interdependence of

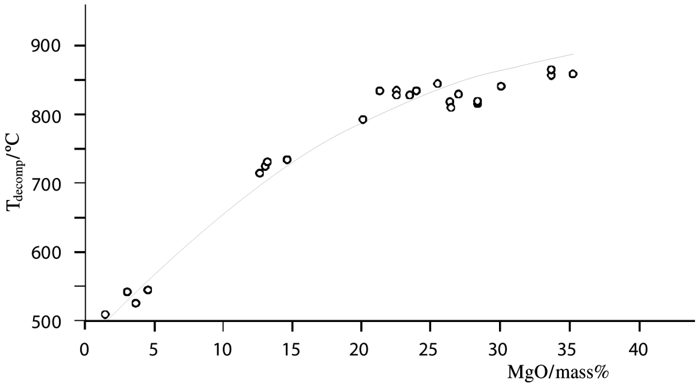

Fig. 4 Dependence of decomposition temperatures on MgO contents in chlorite mixed crystals

crystal chemical composition of the octahedral layers and the temperatures of the dehydroxylation (Fig. 4).

The crystal chemistry of smectites seems to be even more complex than that of chlorites. Quite often smectites form solid solutions between three or more end members. Mostly the mixed crystals of this group contain Al^{3+}, Mg^{2+} and $Fe^{2+/3+}$ as octahedral central cations. This is mirrored in three endothermic dehydroxylation effects around 500°C (=Fe–OH), 700°C (=Al–OH) and 850°C (=Mg–OH). Most smectites show a great degree of disorder. Crystal physical disorder lowers the temperatures of dehydroxylation as well. Therefore, for smectites it is difficult to find the exact interrelation between MgO- or Al_2O_3 content and temperatures of dehydroxylation. But a rough estimation of the portions of Mg, Fe, Al in the octahedral layers is still possible by comparing the peak areas of the three mentioned endothermic dehydroxylation effects.

The DTA curves of the studied magnesium carbonates and silicates can be found in many publications [for detailed references see 3, 4, 25, 26].

Conclusions

- Soluble cations due to their ionic potential and incorporation into the crystal structures of sedimentary or soil minerals are indicators for mineral formations and transformations in aridic and semi aridic environments.
- Mainly the soluble cation Mg^{2+} shows clear interrelations to palaeoecologic mineral formations and transformations.
- Differential thermal analysis showed to be a suitable method to determine (a) the interrelation between the decomposition temperature of carbonates and the degree of substitution of the primary cation (Ca^{2+}, Al^{3+}) by Mg^{2+}, Fe^{2+}, Sr^{2+}; (b) the interdependence between dehydroxylation temperatures of Mg-bearing sheet silicates and the crystal chemical composition of the octahedral sites of these mineralmination of the MgO-contents in chlorites, the $MgO/Fe_2O_3/Al_2O_3$ ratio in smectitess.
- Thus standardised differential thermal analysis enables the deter and the types of the sheet silicates whether they are di- or trioctahedral clay minerals.

* * *

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References

1 P. Möller, Anorganische Geochemie, Springer, Berlin-Heidelberg-New York- Tokyo 1986.
2 W. Smykatz-Kloss, B. Smykatz-Kloss, N. Naguib and L. Zöller, in: W. Smykatz-Kloss and P. Felix-Henningsen, (Eds) Palaeoecology of Quaternary Drylands., Springer-Verlag, Heidelberg–Berlin–New York (2002 in print).
3 T. L. Webb and J. E Krüger, Carbonates, Chapter 10 of, R. C. Mackenzie. (Ed.), Differential Thermal Analysis, 1 (1970) 303.
4 W. Smykatz-Kloss, Differential Thermal Analysis Application and Results in Mineralogy, Springer-Verlag Heidelberg–Berlin–New York 1974.
5 W. Smykatz-Kloss, J. Thermal Anal., 23 (1982) 15.
6 V. M. Goldschmidt, Geochemistry, Oxford Univ. Press, London 1958.
7 L. Pauling, J. Amer. Chem. Soc., 49 (1927) 765.
8 K. H. Wedepohl, Geochemie, de Gruyter/Göschen, Berlin 1967.
9 R. C. Evans, Einführung in die Kristallchemie, de Gruyter, Berlin-New York 1976.
10 C. W. Beck, Am. Mineralogist, 35 (1950) 985.
11 P. Murray and J. White, Trans. Brit. Ceram. Soc., 48 (1949) 187.
12 G. T. Faust, Am. Miner., 38 (1953) 4.
13 F. Lippmann, Sedimentary Carbonate Minerals, Springer-Verlag, Heidelberg–Berlin–New York 1973.
14 C. W. Correns, Einführung in die Mineralogie, Springer-Verlag, Heidelberg–Berlin–New York 1968.
15 G. W. Brindley and G. Brown, Crystal Structures of Clay Minerals and Their X-ray Identification, Min. Soc., London 1980.
16 B. Velde, Clay Minerals. Developments in Sedimentology 40, Elsevier 1985.
17 S. Caillère, Bull. Soc. Franç. Mineral. Cryst., 59 (1936) 163.
18 R. C. Mackenzie, The Differential Thermal Investigation of Clays., Mineral. Soc., London 1957.
19 J. L. M. Vivaldi and P. F. Hach-Ali, Palygorskites and Sepiolites, Chapter 20 of, R. C. Mackenzie, (Ed.), Differential Thermal Analysis, 1 (1970) 553.
20 M.Müller-Vonmoos and C. Schindler, Schweiz. Mineral. Petrogr. Mitt., 53 (1973) 395.
21 G. Liptay, Atlas of Thermoanalytical Curves, vol. 1-5, Akadémiai Kiadó, Budapest 1973-1985.
22 U. Shuali, M. Steinberg, S. Yariv, M. Müller-Vonmoos, G. Kahr and A. Rub, Clay Mins., 25 (1990) 107.
23 Ch. Earnest, in: W Smykatz-Kloss and S. St. J.Warne, (Eds) Thermal Analysis in the Geosciences, Springer, Heidelberg–Berlin–New York 1991, p. 288
24 W. Smykatz-Kloss, Determination of Impurities in Minerals by Means of Standardized Differential Thermal Analysis, R.L. Blaine and C. K. Schoff (Eds.): Purity Determinations by Thermal Methods, ASTM-STP 838 1984, p. 121
25 K. Heide, Dynamische thermische Analysenmethoden, VEB Dt. Verlag für Grundstoff-Industrie, Leipzig 1982.
26 W. Smykatz-Kloss and K. Heide, Application of Thermal Analysis Methods in the Geosciences., In: Gallagher, P.K. (Ed.), Handbook of Thermal Analysis, Elsevier, Amsterdam 2003, in print.