Low-temperature nucleation of magnesite and dolomite[*]

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with 4 figures and 1 Table

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Abstract: By way of duplicating an experiment described by Liebermann (1967) nucleation of magnesite, huntite and/or dolomite has been attained at temperatures between 313 K and 333 K and under atmospheric pressure. Essential to these experiments are fluctuations in pH value. After interrupting an experiment after 1, 3, 5, or 8 of such fluctuations, the change from one or more metastable phases into the stable phase (magnesite or dolomite) could be followed. A theoretical explanation for these low-temperature syntheses can be found in stability relations. Ostwald's Rule stipulates the nucleation of a metastable phase before that of the stable phase. However fluctuations of sufficient amplitude and duration are capable of crossing the border between the metastable and the stable fields. As a result the stable phase will nucleate together with the metastable phase. Conditions opposing the subsequent growth of the metastable phase (such as the slightly acidic conditions resulting from periodically introducing CO_2 into the solution) will favour the continued growth of the stable phase.

Key words: Magnesite, dolomite, huntite, low-temperature syntheses.

Magnesite

The first time I observed the formation of magnesite was upon duplicating of Exp. No. 57 of Liebermann (1967). In my experiment M-211 0.918 Mol NaCl, 0.0316 Mol $MgCl_2.6\ H_2O$, 0.018 Mol $MgSO_4.7\ H_2O$ and 0.020 Mol KCl (all chemicals are reagent grade) were dissolved in 330 cm^3 distilled water and 2 mMol $CaCO_3$ added later, was dissolved by way of bubbling CO_2 (industrial grade) through the suspension during 12 hours. Titration to pH = 8.00 took place with dilute ammonia. The next phase, the gradual escape of CO_2 from the solution, involved heating the 500 cm^3 Erlenmeyer flask on an electric plate to (in this case) 333 K during 60 hours. As described by Liebermann (1967), the total experiment consists of repeating 14 times the dissolution phase, the titration and the phase of heating and gradual escape of CO_2 . The pH of the solution was measured every time after bubbling CO_2 through it (pH = 5,30 to 6,10 in this particular test), upon titration, and at the end of each 60 hours phase of carbon

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[*] Studies on irreversible geochemical reactions No.7

dioxide escape (pH = 8,34 to 8,85). The experiment lasts 42 days. The precipitate adheres the glass; the Erlenmeyer was washed several times with distilled water and after desiccation (at 303 K) the precipitate was scraped off. In X-ray diffraction (performed on a Philips X-ray diffractometer with Ni filtered Cu-K_α radiation; voltage 40 kV; current 20 mA; scanning speed 1^o per minute.) magnesite together with a small amount of magnesium hydroxide carbonate was found. In order to remove the latter, the precipitate was partly leached in water, through which CO_2 was bubbled during 12 hours. (Before leaching the precipitate weighed 1.5 gr; after leaching 0.4 gr.) The remaining precipitate was found to consist of pure magnesite (Fig. 1).

Based on the 6 strongest lines (Table I) the cell parameters for the sample from experiment M-211 were calculated as a_o = 46.41 nm and c_o = 150.94 nm. These unit cell dimensions may be compared with a_o = 46.33 nm and c_o = 150.15 nm given in JCPDS-ICDD file no. 8-479, as well as with the a_o = 46.41 nm and c_o = 150.93 nm measured for a sample of modern sedimentary magnesite from a salt lake in Turkey (Irion, 1970). When repeating the same experiment with a temperature of 313 K during the 60-hours "escape of CO_2 phase" (my experiment D-211) magnesite plus calcite and dolomite formed. Magnesite was found again after duplicating the same Exp. No. 57 of Liebermann (1967) at 313 K (my experiment M-223), but once more together with a small amount of magnesium hydroxide carbonate (Fig. 2).

In Liebermann's (1967) paper the suggestion is made, that either ammonia or a solution of sodium carbonate can be used for the titration. But when using a sodium carbonate solution, no magnesite forms. Nesquehonite plus Mg-calcite nucleate, when using a solution of sodium carbonate in Exp. No. 57 of Liebermann (1967) at 298 K. When duplicating Liebermann's Exp. No. 57 at 313 K with a concentrated solution of sodium carbonate, magnesium hydroxide carbonate precipitates.

Dolomite

As part of a systematic investigation into the mechanism of dolomite formation all of the known claims on low-temperature synthesis have been duplicated by me. But the experiments yielded precipitates consisting at best of magnesium calcite. Ultimately pure dolomite precipitated in an experiment, which was in fact a variation on the test described by Liebermann (1967). The addition of urea to Liebermann's Exp. No. 57 was found to favour the low-temperature nucleation of dolomite. In my experiment D-222, itself another duplication of Liebermann's Exp. No. 57 but with the addition of 16.65 mMol urea, dolomite *sensu stricto* together with some pure calcite formed (Fig. 3). X-Ray analyses were performed on a Philips X-ray diffractometer with nickel filtered copper radiation (voltage 40 kV; current 20 mA; but at slowed down scanning speed of 1^o per 3.34 min.). The presence of one of the superstructure reflections of dolomite (cf., Goldsmith & Graf, 1958) could be recognized (at 2.54 nm or 35.34^o in Cu-K_α radiation) in this diffractogram (indicated by the arrow in Fig.3). The second superstructure should have been present at 2.06 nm (or 43.84^o in Cu-K_α radiation); but the only undetermined peak of the diffractogram from sample D-222 was found at 43.07^o (or 2.09 nm) and may well belong to calcite.

The use of urea has been inspired on the observations by Mansfield (1980) on the occurrence of pure dolomite as bladder stones in a Dalmatian dog. The catalysis by urea is most probably related to the desorption of chlorine ions and the adsorption of carbonate ions. Chlorine ions (of the $MgCl_2$ used) are known to adsorb onto calcium carbonate surfaces even stronger than hydroxyl or bicarbonate groups (Douglas & Walker, 1950). Another indication as to the rôle of chlorine ions was found in the nucleation of aragonite (not changing during the whole of the experiment), when using only magnesium chloride instead of the mixture of magnesium chloride and magnesium sulfate together with the required amounts of NaCl and KCl in duplicating Exp. No. 57 of Liebermann (1967). Aragonite also precipitates in the same experiment at 313 K or 318 K, when using natural sea water instead of the described solution of sodium chloride, magnesium chloride, magnesium sulfate and potassium chloride.

All too often the low-temperature formation of dolomite is explained by way of a conversion of pre-existing calcium carbonate deposits (= "dolomitization" according to Von Morlot, 1847). But there is an obvious impossibility for "dolomitization" theories to explain the occurrence of dolomite in soils (Sherman et al., 1962), in coal (Gothan & Benade, 1932), in rivers (Barnes & O'Neil, 1971), in lakes (DeDecker & Last, 1988), in pearls (Tanaka et al., 1960), or in sea floor concretions (Brown & Farrow, 1978).

The close association between magnesite and dolomite (forming even in one and the same experiment) may seem surprising at first look. But as early as 1894 Pfaff has described mixed crystals with a composition in between that of dolomite and magnesite. In my experiment D-163 (conducted at 316 K) such "calcium magnesites" originated. The mixed crystals with a composition in between that of calcite and magnesite (the magnesium calcites) are relatively well known. In other experiments huntite formed (in experiments M-224 at 333 K and in M-226 at 303 K).

Dissolution and precipitation

The 14 different cycles typical of Liebermann's (1967) experiment involve amongst other things saturating the solution with carbon dioxide. These dissolution phases are to be repeated 14 times, and I have observed how each time much of the precipitate would dissolve again when bubbling CO_2 through the solution. Up to now no reproducible low-temperature syntheses of magnesite have become known, and perhaps the alternations between precipitation and dissolution phases do play a rôle. Static control experiments confirm this observation. When adding the total amount of the ammonia solution used in the 14 different titrations in one time, the precipitate consists of magnesium hydroxide carbonate at 333 K (and of an X-ray amorphous precipitate when conducting the same experiment at 313 K).

An attempt was made to study the reaction taking place by way of interrupting Liebermann's (1967) experiment. By way of performing a series of experiments under identical conditions, but ending the experiment after 1, 3, 5, or 8 cycles (1 cycle = 12 hours of CO_2 bubbling; titration + 60 hours of CO_2 escape), precipitates were obtained, that should represent subsequent stages in an overall reaction. In order to minimize possible variations in the composition of the artificial brine, 6.6 dm^3 of the solution used by Liebermann (1967) in his experiment No. 57 were prepared in advance. Each new experiment started out with adding 2 mMol $CaCO_3$ (p.A., MERCK art. 2066) to 330 cm^3 of the stock solution of artificial brine. Usually 12 hours of bubbling CO_2 through the brine would suffice to completely dissolve all of the $CaCO_3$. Step-wise interruption was used in duplications of Liebermann's Exp. No. 57 at 333 (= exp. M-227) and 313 K (exp. D-228). The precipitates from each experiment were X-rayed in one uninterrupted session with identical instrument setting and calibration of the diffractometer. In exp. M-227 the initial precipitate consisted mainly of aragonite, little calcite and a trace of magnesium calcite (with its main diffraction peak at 28.7 nm) (Fig.4 A). After 3 cycles it had changed into aragonite, with a little dolomite and a trace of magnesite (Fig.4 B). After 5 cycles mainly aragonite was present, but magnesite had been clearly developed, with some dolomite remaining (Fig.4 C). After 8 cycles only pure magnesite was found in X-ray diffraction, with its main peak at 27.8 nm (instead of the usual 27.42 nm) (Fig.4 D). When conducting the same series of tests at 313 K (exp. D-228) calcite, some aragonite and a small amount of magnesium calcite (main peak at 29.0 nm) precipitated after 1 cycle. The precipitate changed into aragonite and magnesium calcite (with its main peak at 28.8 nm) after 3 cycles. After 5 cycles only small amounts of aragonite and calcite remained together with magnesium calcite (with a rather broad diffraction peak from 29.4 to 27.8 nm, but with its main peak at 28.8 nm). After 8 cycles aragonite and magnesium calcite with a rather broad diffraction peak was found, but this time the main peak of magnesite (at 2.74 nm) was present as well. After the complete set of 14 cycles the precipitate consisted of magnesite.

The dissolution phases appear to form an essential element in the low-temperature formation of magnesite, dolomite and huntite. In the case of dolomite the rôle of dissolution has long been recognized, and has given rise to a theory of "replacement" of pre-existing limestones (Bischoff, 1855). The present experiments confirm at least this aspect of the formation of dolomite. In the absence of any analyses made with the electron microscope, no conclusions can be reached at this moment concerning the exact mechanism of nucleation and growth. Nevertheless a fundamental theory to explain the nucleation and subsequent growth of magnesite, dolomite or huntite in one and the same experiment, can be outlined.

Breaking Ostwald's Rule

In Ostwald's original definition of the concept of a metastable state and a stable state, the boundary between these two states consists of a certain amount of energy to be supplied before the stable state can be reached (Ostwald, 1893). In a subsequent paper on crystallization during supersaturation (or undercooling) Ostwald (1897) claimed as a universal principle, that a metastable phase would appear **before** the stable phase. However this claim is contradicted by observations on the *simultaneous* appearance at a particular temperature of 2 (or even 3) polymorphs of one and the same compound, as made by various authors (among them Tammann, 1898, 1903; Schaum, 1898; Schaum & Schoenbeck, 1902; De Coppet, 1907; Othmer, 1915). Such observations should have cast some doubt on the possible universal application of Ostwald's Rule.

Fluctuations in concentration, temperature or pressure on a local scale in a solution are, as Volmer (1939) pointed out, crucial in nucleation processes. Fluctuations will lead to "overstepping phenomena" (the "*Ueberschreitungserscheinungen*" of Kornfeld, 1916 and Haber, 1922): locally, i.e., there where the concentration is the highest, the boundary between Ostwald's metastable and labile fields will be surpassed. The nucleation of the metastable phase, taking place only locally at first, will influence the whole of the solution. Crystallization can take place long before the averaged values, given by the supersaturation limit, have been reached. Hence Volmer (1939) concluded, that the stability of the metastable phase does not depend as much on average values described in the macroscopic parameters of concentration, temperature and pressure, but much more on local crossings of the supersaturation limit. As a result the stability of a metastable solution as a whole depends on the amplitude and duration of such fluctuations.

At present Volmer's theory can be extended to include the boundary between the metastable state and the stable state. Fluctuations in free energy of sufficient amplitude and duration will be able to cross the stable boundary and so initiate the nucleation of the stable phase rather than the metastable phase. But perhaps a distinction must be made between nucleation and subsequent growth. Possibly more effective in creating measurable quantities of the stable phase are fluctuations of a distinctly different magnitude; fluctuations responsible for periodically recurring conditions averse to the growth of the metastable phase. Or as Schaum & Schoenbeck (1902) have expressed it: crystallization of the stable phase instead of the metastable will be favoured by conditions counteracting the metastable phase. If only the rate of dissolution of the metastable phase during the dissolution stage of such a periodical alternation surpasses that of the stable phase, the amount of the stable phase will, after a number of such alternations, surpass that of the metastable phase.

Breaking Ostwald's Law must be responsible for the low-temperature formation of magnesite instead of metastable magnesium hydroxide carbonate or of dolomite instead of the metastable phases aragonite or magnesium calcite. The described syntheses of magnesite and dolomite ultimately decide in favour of Nernst's criticism on Ostwald's "Step Rule". In a section on *irreversible reactions* of his textbook on theoretical chemistry Nernst (1921) remarked, that because so little was known (at that time at least) concerning these reactions, there was no need at all to postulate anything like a "Step Rule". Chemical systems far from the stable state would, according to Nernst (1921) , often show a marked increase in reaction rate with an increase in temperature. Irreversible reactions would be essentially different from phenomena of dissociation, and would be governed by a difference in reaction rate compared to that of the reaction leading to the metastable state.

At first sight the formation of magnesite, huntite and dolomite seemed to be related to the temperature, at which the solution is kept during the "escape of CO_2" phase. But when repeating my own experiments (in order to establish their reproducibility), the result was not the same in every experiment. For example when repeating exp. M-211 (in which magnesite had been formed at 333 K) at the same temperature (= exp. M-224), mainly huntite (along with some magnesite) formed. It must be admitted, that factors such as pCO_2 , amount of NH_4OH and salinity were not measured (thereby in a way facilitating duplication by others). It is surprising to note, how such variability in the final results of nucleation experiments has also been found by Tammann (1903), Othmer (1915) and Kornfeld (1916). The statistics typical of the atomistic approach not only explain the observations made, but also predict how an increase in the number of nucleation experiments would decrease the spread among the results.

The mechanism proposed here is different from what is known as "Ostwald Ripening" (Liesegang, 1911; Kolthoff, 1936), for that process consists of grain coarsening by way of recrystallization. Whereas Ostwald's Rule predicts the sequence of phases formed during nucleation, the sequence of precipitation 1) metastable and 2) stable phase can be forced to change by way of periods of dissolution alternating with periods of precipitation. By definition the metastable phases grow fastest, and therefore will be dissolved fastest. Breaking Ostwald's Rule is based on intervals during which the metastable phase will be largely leached out, and in this way the stable phase is ultimately favoured.

Irreversible geochemical reactions

In the past I have shown, that fluctuations are essential in the low-temperature synthesis of anatase TiO_2 (Deelman, 1979) and that of eitelite $Na_2CO_3.MgCO_3$ (Deelman, 1984). In those experiments not fluctuations in pH, but in concentration were involved. In my view the various low-temperature syntheses of minerals known to possess a minimum temperature in "classical" laboratory tests, illustrate the theory of Volmer (1939) on the active rôle played by fluctuations in pressure, temperature or concentration. On the basis of the practical results gained thus far, I feel free to claim, that "Breaking Ostwald's Rule" may well provide the theoretical basis for a number of *irreversible geochemical reactions* such as for example the low-temperature nucleation of magnesite, huntite and dolomite. The required alternations in pH conditions can be found in natural settings at different frequencies (seasonal changes in water chemistry; daily changes caused by the photosynthesis of for example algae; tidal flooding by water rich in CO_2). The present theory explains at the same time, why up to now no (reproducible) syntheses of magnesite and dolomite under conditions of room temperature and atmospheric pressure have become known. Only in dynamic experiments involving the required fluctuations, these stable phases can be synthesized. In static experiments invariably the metastable equivalents are formed.

Various minerals still await low-temperature synthesis. In nature the mineral known as the stable phase does in fact precipitate (although at very slow rates). In many instances this stable phase known from nature, has not yet been precipitated in the static laboratory experiments conducted at room temperature and under atmospheric pressure. Fluctuations in p, T, or x capable of breaking Ostwald's Rule, will be required to enable the low-temperature synthesis of minerals such as quartz, hematite, apatite, kaolinite, and zeolites.

In the case of kaolinite the significance of fluctuations in fact has been documented. The low-temperature synthesis of kaolinite as described by DeKimpe, Gastuche & Bradley (1964) involved *daily additions* of alumina (as $AlCl_3.6\ H_2O$) and silica (in the form of ethyl silicate) during at least 60 days. In addition daily adjustments of the pH took place by way of adding either NaOH or HCl. The significance of fluctuations can now be deduced even from field observations: the soil overlying a weathered basalt of Kivu Province (Zaire) contains kaolinite only there, where distinct alternations between wet and dry conditions exist. In those parts of the same soil that lack good drainage, halloysite is found (Gastuche & DeKimpe, 1962). The metastable equivalent of the stable phase kaolinite must be halloysite. In the case of the low-temperature nucleation of anatase comparable indications were found. In the titaniferous ferruginous latosols of Hawaii anatase is present only, if definite alternations between wet and dry seasons exist (Walker et al., 1969). Those parts of the same soil that are perennially moist contain X-ray amorphous hydrated titanium and iron oxides. The presence of even "... rather large crystals" of α-quartz was the more surprising, because the parent rock here did not contain any free silica. Quartz was found only in the upper parts of bare profiles, and not in the vegetation-covered profiles of the same soil (Walker et al., 1969).

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M-211 line	two theta	d entered	h k l	d calculated
1)	32.50 =	27.55	1 0 4	27.550
2)	35.71 =	25.15	0 0 6	25.153
3)	38.55 =	23.36	1 1 0	23.352
4)	42.84 =	21.10	1 1 3	21.121
5)	46.70 =	19.45	2 0 2	19.450
6)	51.43 =	17.77	0 2 4	17.770
7)	53.70 =	17.07	1 1 6	17.050
calculated	a = 46.415 nm		c = 150.944 nm	

JCPDS 8-479 line	two theta	d entered	h k l	d calculated
1)	32.63 =	27.42	1 0 4	27.420
2)	35.84 =	25.03	0 0 6	25.030
3)	38.82 =	23.18	1 1 0	23.178
4)	42.99 =	21.02	1 1 3	21.024
5)	46.81 =	19.39	2 0 2	19.390
6)	51.62 =	17.69	0 2 4	17.690
7)	53.88 =	17.00	1 1 6	16.997
calculated	a = 46.353 nm		c = 150.181 nm	

Table I. Calculation of cell constants for magnesite synthesized in experiment M-211 and for sample from JCPDS-ICDD 8-479.

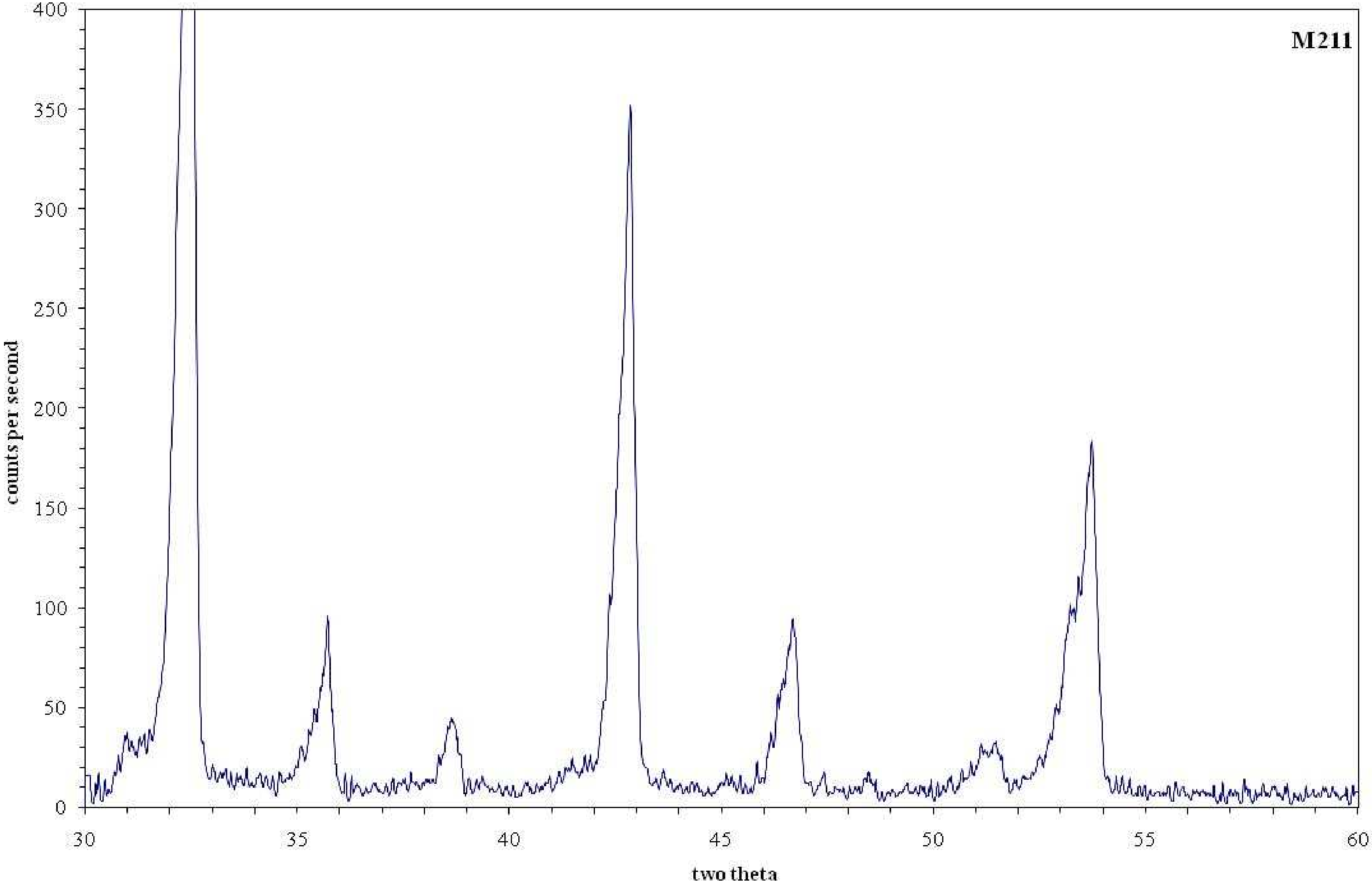

Fig. 1 - Magnesite synthesized at 333 K (original X-ray diffractogram).

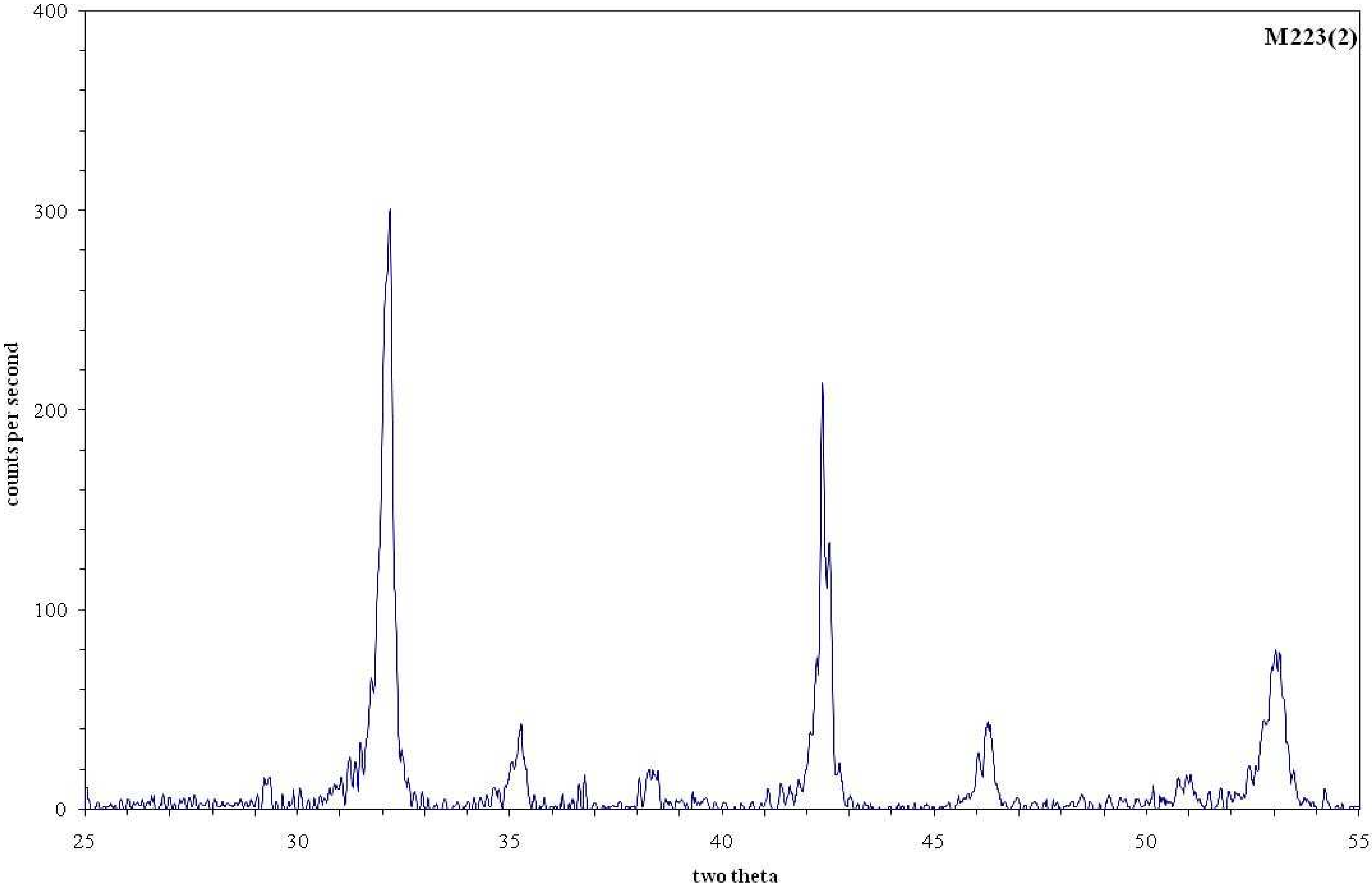

Fig. 2 - Magnesite synthesized at 313 K (after digital processing).

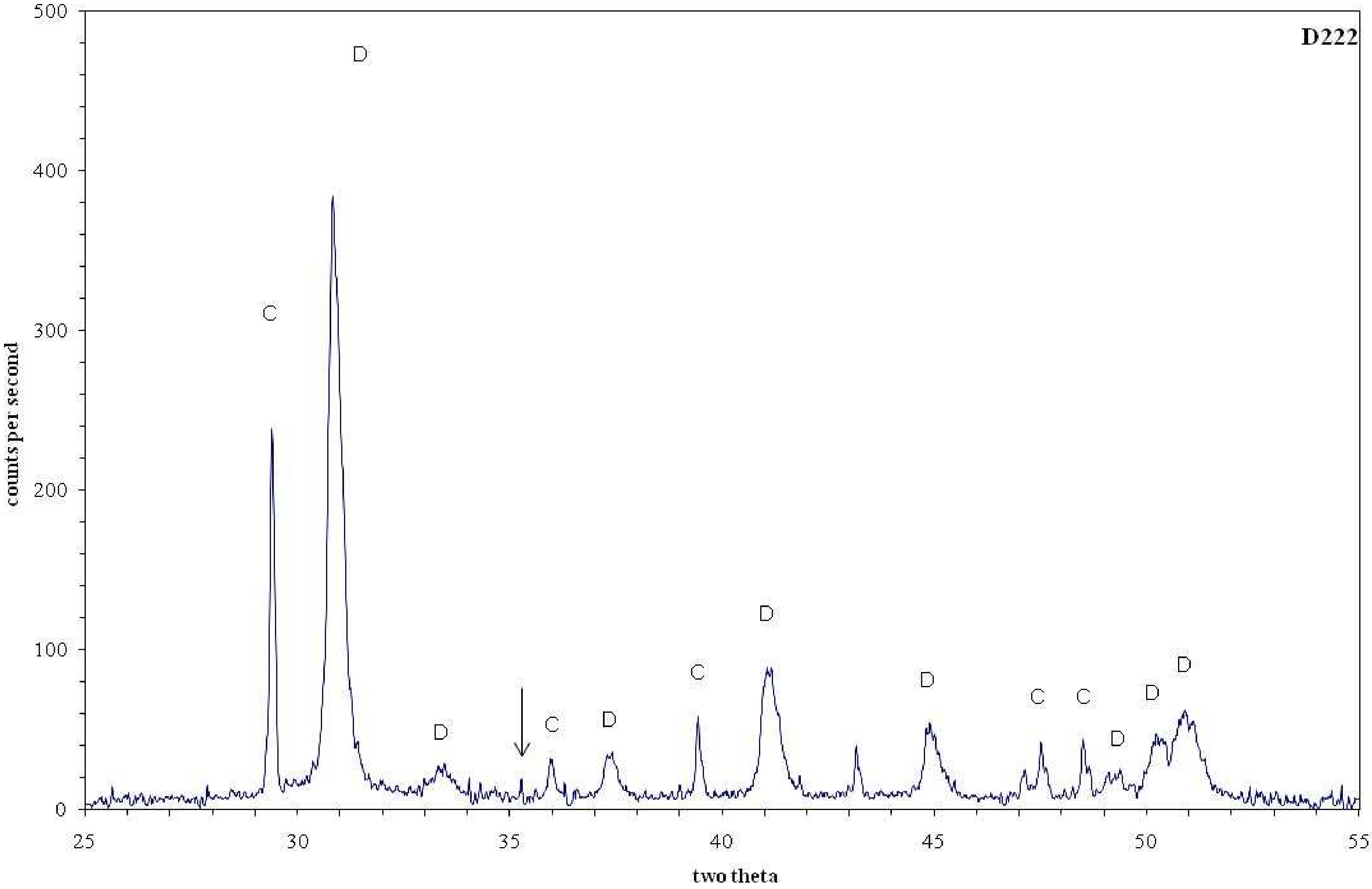

Fig. 3 - Dolomite synthesized at 312 K (original X-ray diffractogram).

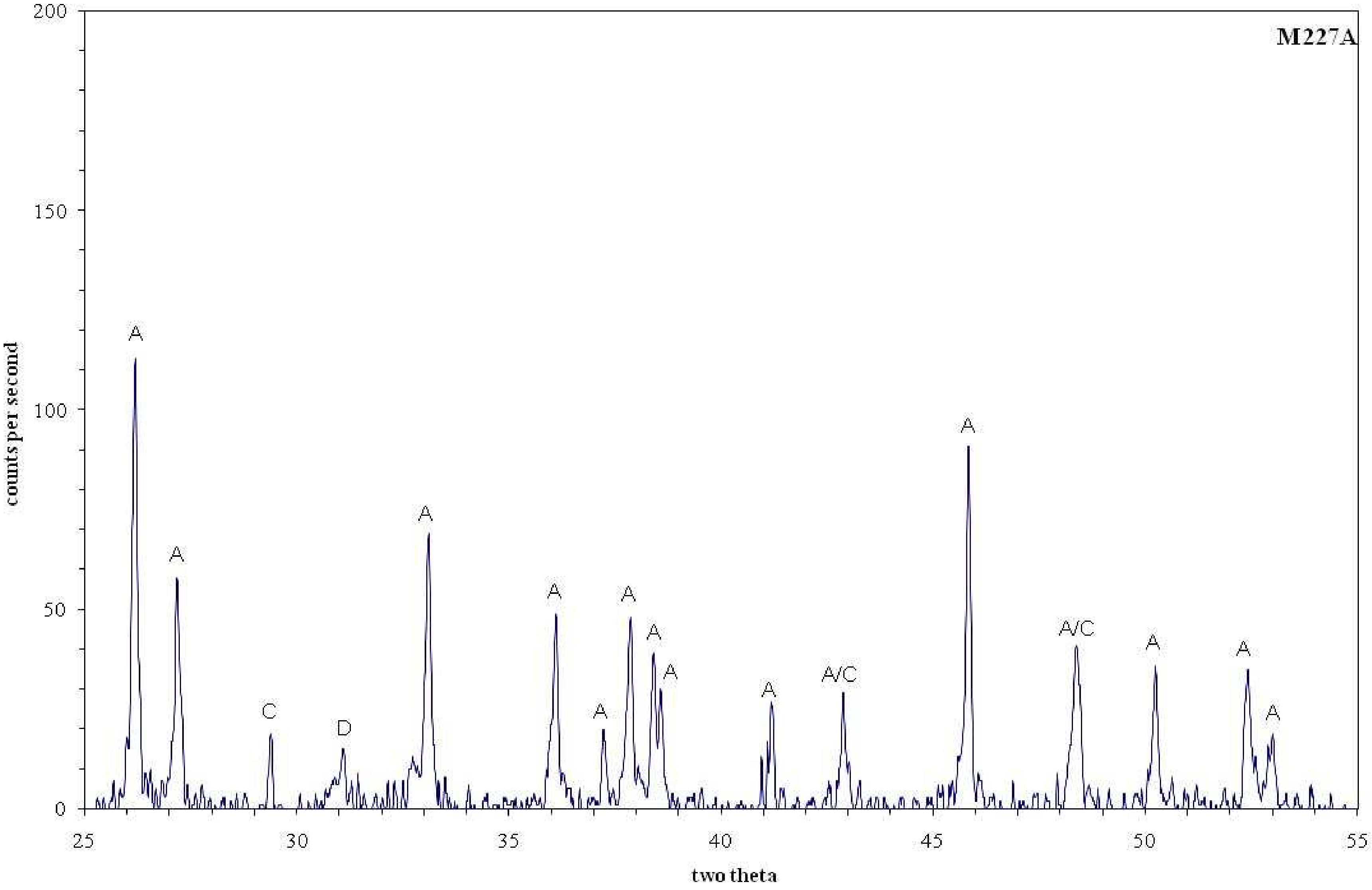

Fig. 4 A - Mineralogical changes upon duplicating Liebermann's Exp. No. 57 at 333 K after 1 "cycle"
(A = aragonite, C = calcite, D = dolomite).

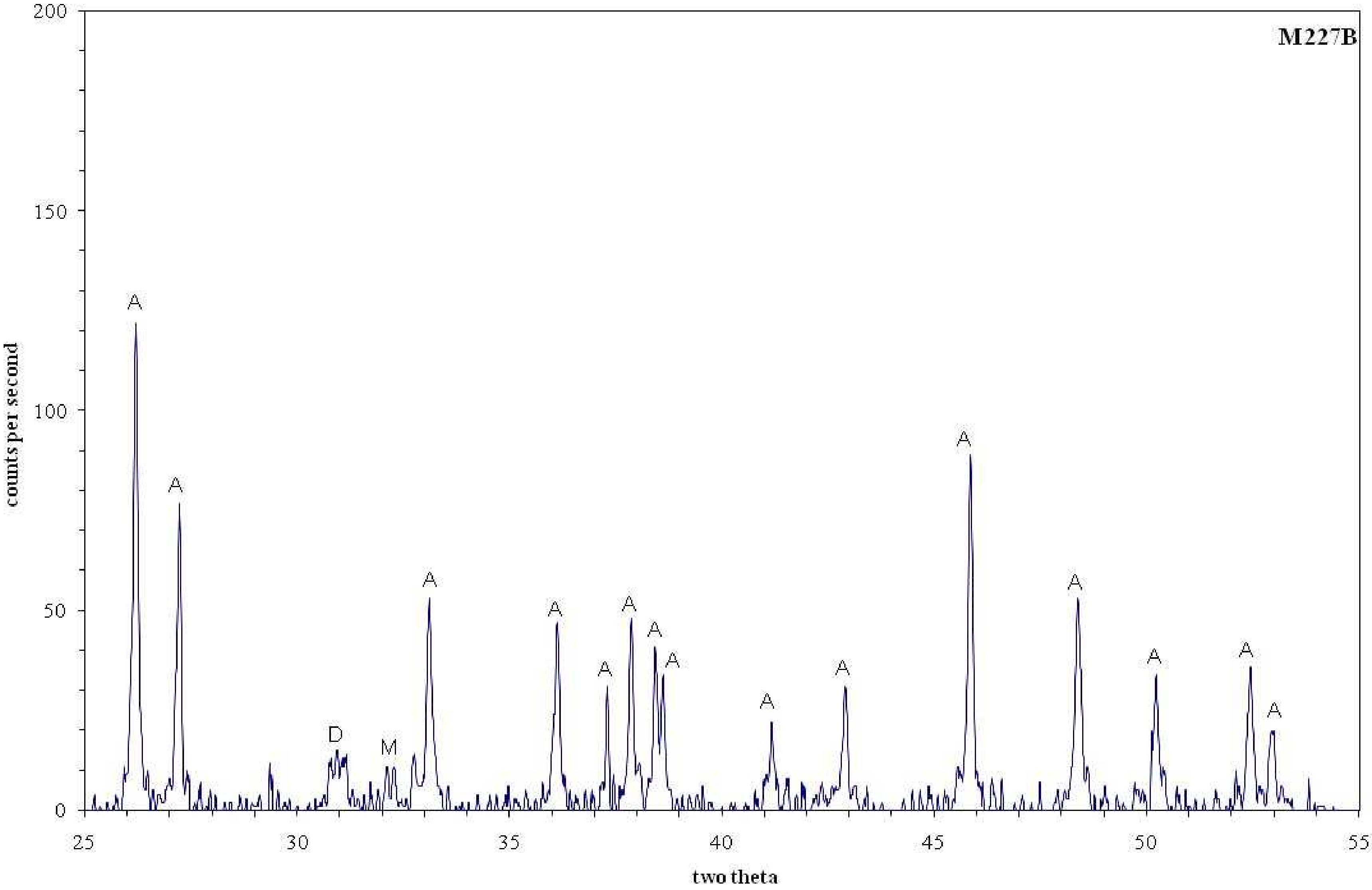

Fig. 4 B - Mineralogical changes upon duplicating Liebermann's Exp. No. 57 at 333 K after 3 "cycles" (A = aragonite, D = dolomite, M = magnesite).

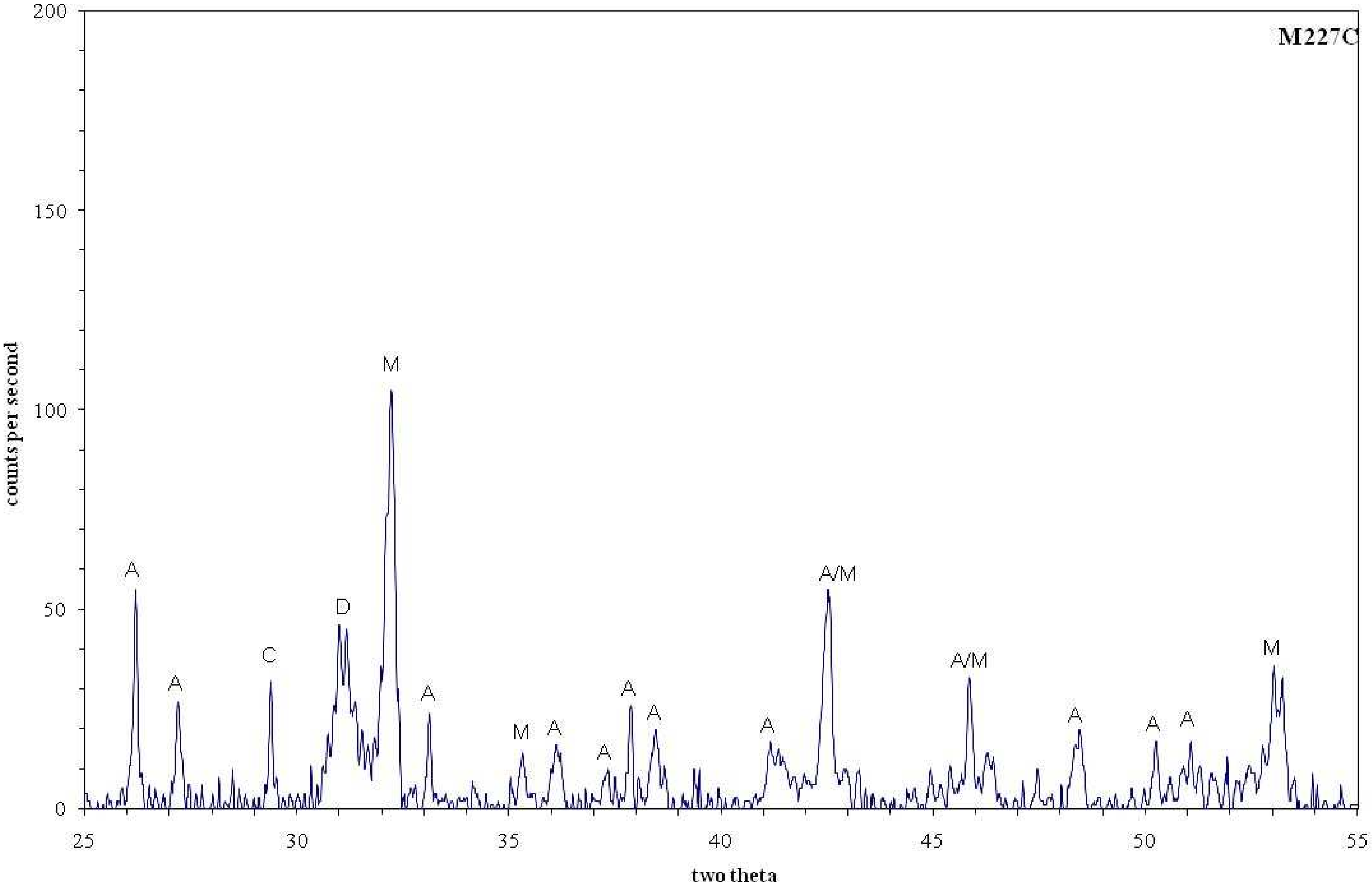

Fig. 4 C - Mineralogical changes upon duplicating Liebermann's Exp. No. 57 at 333 K after 5 "cycles"
(A = aragonite, C = calcite, D = dolomite, M = magnesite).

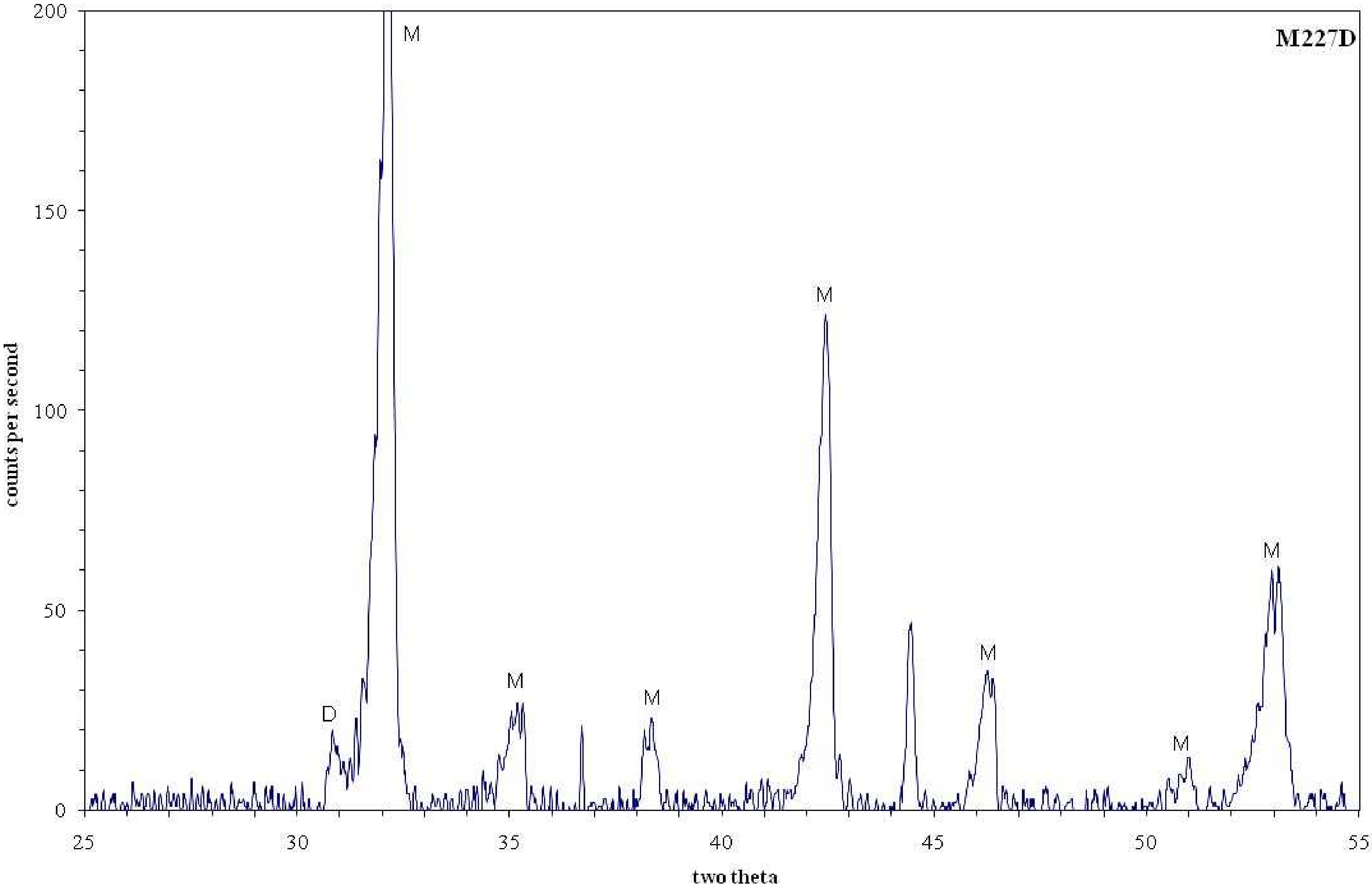

Fig. 4 D - Mineralogical changes upon duplicating Liebermann's Exp. No. 57 at 333 K after 8 "cycles" (D = dolomite, M = magnesite).