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SOME REACTIONS PRODUCED IN CARBONATES BY GRINDING

JOHN C. JAMIESON AND JULIAN R. GOLDSMITH, *University of
Chicago, Chicago 37, Illinois.*

ABSTRACT

Samples of carbonates were ground in a mechanical mortar for periods up to three days, and x-ray powder diffraction patterns were taken at intervals. Calcite was partially converted to aragonite as had been reported by Burns and Bredig. The effect of Mg-substitution in the calcite structure gives an estimate of the local pressures involved in mortar grinding of CaCO_3 to be the order of 20,000 bars. Several mixtures of pure carbonates reacted to form heterogeneous solid solutions which could be roughly related to their phase diagrams. Several pure carbonates decomposed, and in the case of MnCO_3 at least two oxidation states were attained after loss of CO_2 .

INTRODUCTION

Recently, Burns and Bredig (1956) have reported the conversion of aragonite to calcite by prolonged grinding in a laboratory mortar. Acampora *et al.* (1956) have reported formation of heterogeneous solid solutions by grinding a mixture of KCl and KBr, a result similar to that of Vegard and Hauge (1927), who reported that heterogeneous solid solutions of HgCl and HgBr also formed in this manner. Bradley *et al.* (1935) studied the effects of prolonged grinding on dolomite and others have examined the effects produced by grinding clay minerals (Keller, 1955, also see Eitel, 1954, for a partial bibliography). Lea (1893) observed color changes in various salts upon grinding. A ball mill has been described by Roy and Osborn (1952) for grinding at high temperatures and moderate water pressures which is essentially a modified Morey bomb. Its use to date has been to speed up hydrothermal reactions (Roy and Roy, 1955).

We have conducted further experiments of this nature with the thought that prolonged grinding might in a crude sense be related to direct high pressure-high temperature studies on mineral systems. It was determined that an ordinary laboratory power mortar can be roughly "calibrated" in terms of the quasi-hydrostatic pressures and temperatures developed.

EXPERIMENTS

All grinding was done in an ordinary laboratory power mortar, with mullite parts. For quick x-ray analysis of results powder pictures were taken with a North American Philips 57.3 mm. camera using Co or Fe filtered radiation. A 114.59 mm. camera was used when greater resolution was desired.

Since the grinding motion of the mortar is complex, the results ob-

tained as far as quantity and time of appearance of a new phase is concerned are a function of amount of sample and the alignment of the pestle with respect to the mortar. It was soon found that when the pestle was carelessly aligned a large amount of mullite would appear in the mixture early in the grind. This is apparently a danger in using this type of mortar in any work. Careful alignment minimized this as no mullite was apparent in the x -ray patterns in many cases even after 48 hours of grinding. The summary of results appears in Tables 1 and 2.

A. The Calcite-Aragonite Transition

Other than in the length of time required before detection of aragonite our results on the grinding of dry Iceland Spar duplicate those of Burns and Breiding (1956). These authors stated that while the stability of aragonite at high pressures (Jamieson 1953, MacDonald 1956, Clark 1957) may account for its formation during grinding, they felt that more than hydrostatic pressure was involved and postulated that their results could only be accounted for by assuming the presence of a shearing force in addition to the high hydrostatic pressure. This is partially verified by results of Bridgman (1936, 1937). He found that the density of calcite after being sheared at pressures up to 50,000 bars at room temperature was increased to somewhat less than 2.84, presumably due to the formation of aragonite. His samples however were not examined by x -ray diffraction and the identification is uncertain since a portion of this density increase could have been due to material from his pistons being extruded in the sample.

MacDonald (1956) was able to form aragonite from calcite at temperatures as low as 250° C. (\sim 8000 bars) using the "simple squeezer," but again in this device shear is a factor. However shear appears not to be absolutely necessary for the transformation since Clark (1957) using truly hydrostatic pressure definitely formed aragonite from calcite at 575° C. and 12,700 bars.

With the assumptions of ideal mixing, of no Mg in the aragonite structure, and using various thermodynamic data (cf. Jamieson, 1953), it is possible to show that the calcite-aragonite equilibrium point (about 16,000 bars) is raised about 3000 bars at 1000° K. by the addition of 7% Mg to the calcite structure and about 6000 bars by the addition of 13% Mg. The (P, T) extension of these curves parallels that of the pure calcite-aragonite curve (Clark 1957, Jamieson 1953). It should be mentioned in passing that an extension of this type of calculation gives excellent agreement with unpublished data of one of the authors (J.R.G.) on the (P, T) equilibrium curve for the triple point calcite-aragonite-dolomite.

The pressures (stresses) and temperatures developed in a grinding ex-

TABLE 1. SINGLE SUBSTANCES GROUND

Sample Number	Initial Material	Time	*Observations from <i>x</i> -Ray Pattern
1	Iceland Spar	6 hr. 24 hr. 48 hr.	No significant change Some aragonite formed More aragonite formed
2	Iceland Spar ground under distilled H ₂ O	22 hr. 46 hr.	Some aragonite formed No significant further alteration
3	Iceland Spar ground under ethyl alcohol	15 hr. 22 hr.	Little aragonite present More aragonite present
5	Natural aragonite crystals	18 hr. 39 hr.	No significant change No significant change
24	Synthetic CdCO ₃	5 hr. 22 hr.	No significant change Sample yellow, some CdO present
13	Siderite (Roxbury)	¼ hr. 3 hr. 6 hr. 24 hr. 46 hr.	Sample began to darken. No change (<i>x</i> -ray) Sample darker, no change (<i>x</i> -ray) Sample darker, trace Fe ₂ O ₃ present All Fe ₂ O ₃ , no FeCO ₃ visible on pattern All Fe ₂ O ₃ , no FeCO ₃ visible on pattern
11	Synthetic MgCO ₃	67 hr.	General structural degradation but no formation of MgO
19	"MgCO ₃ ," Mallinkrodt's An. Reag. †	23 hr.	No trace of anything other than mullite (amorphous to <i>x</i> -rays)
12	Brucite (natural)	25 hr. 48 hr.	Very badly degraded <i>x</i> -ray patterns—still Mg(OH) ₂ No trace Mg(OH) ₂ (amorphous to <i>x</i> -rays), trace of mullite
10	Rhodochrosite	19 hr. 42 hr. 88 hr.	Large amount of hausmanite (Mn ₂ O ₄) Only bixbyite (Mn ₂ O ₃) Bixbyite
9	Synthetic MnCO ₃	17 hr.	Largely bixbyite
8	Smithsonite (Saurium, Greece)	23 hr.	Largely ZnO
16	BaCO ₃ —An. Reagent	21 hr.	No significant change
6	Calcareous Algae ‡ 13% Mg	19 hr. 40 hr.	Mullite appears, no aragonite Mostly mullite, no aragonite
7	Coral Spicules ‡ 17% Mg	43 hr.	No significant change, no aragonite
21	Echinoid plates ‡ 6% Mg	70 hr. 90 hr.	Some aragonite formed
23	Dolomite, Lee Mass.	24 hr.	Significant structural degradation

* The general pattern degradation, characteristic of ground materials is only reported when it seems somewhat excessive for a given substance.

† Basic magnesium carbonate.

‡ Metastable magnesian-calcites.

periment of this nature are actually spectrums of values over the area of grinding action at any instant. With this in mind the data from organically produced carbonates as seen in Table 1 would seem to indicate that the quasihydrostatic pressures and temperatures developed with CaCO₃ lie along a (P, T) curve given roughly by a band passing though 1000° K. and 19,000–22,000 bars parallel to the calcite-aragonite equilibrium curve. However the lack of aragonite formation in calcites containing

TABLE 2. MIXTURES GROUND

Sample Number	Initial Material *	Time	*Observations from x-Ray Pattern
14	Synthetic MgCO ₃ and MnCO ₃	17 hr.	Uninterrupted Solid Solution Bands Tr. Mn ₃ O ₄
		35 hr.	Mostly Mn ₃ O ₄ plus MgCO ₃
15	Synthetic MnCO ₃ and Iceland Spar	4 hr.	No significant change
		21 hr., 44 hr., and 64 hr.	Heterogeneous solid solution bands. Line broadening of CaCO greater than that of MnCO ₃ . Bands increase width with time. No oxidation apparent
18	Synthetic MgCO ₃ and Iceland Spar	21 hr.	Aragonite formed, possible dolomite or protodolomite
		45 hr.	Pattern more degraded. Possible dolomite reflection no longer visible. No solid solution effects
25	Synthetic MgCO ₃ and Synthetic CdCO ₃	6 hr.	CdCO ₃ reflection broadened toward MgCO ₃
		23 hr.	CdCO ₃ reflections broadened toward MgCO ₃ and displaced
		41 hr.	No further significant alteration

* The general pattern degradation, characteristic of ground materials is only reported when it seems somewhat excessive for a given substance.

more than 7% Mg may be due only to the rate of the required processes of forming a calcite richer in Mg than the starting materials along with the pure Ca-aragonite. The failure to develop calcite in grinds of aragonite as the starting material would indicate that local temperatures in excess of ~700° K. were only reached (in any significant amount of material) when the pressures were above those for the pure calcite-aragonite equilibrium. If this were not true some calcite should have formed from aragonite, for the conversion is well known to take place rapidly at temperatures above 425° C.

The actual local physical conditions in the present set of experiments must be regarded as ill-defined; it is however of some interest to discuss them qualitatively. That stresses in the tens of kilobars range are available seems obvious since even one gram of force applied to a square micron of area (10^{-8} cm²) gives a pressure of 10^5 kilograms/cm². The principal unknown factors are the number (and area) of particles supporting the stress, whether the particles themselves are supported by neighbors, or whether they are generally free to roll or move about. If it is assumed that at least a few particles are trapped in such high stress environments by the moving pestle, then the stress developed depends on their ability to undergo plastic flow (Bowden and Tabor (1950)). If the onset of plastic flow in the material is instantaneous then the limiting "pressures" and hence temperatures are given by the yield pressure of the material. The yield pressure is a fairly strong function of the total confining pressure, and indeed, King and Tabor (1954) have found a factor of seven between the bulk shear strength and the specific shear strength of NaCl calculated from sliding experiments. A factor of twenty-four was found for sapphire. It does not seem unreasonable to assume that CaCO₃ possesses a "frictional" shear strength in the 10,000 bar range and thus can maintain higher stresses for short periods of time. In the presence of such stresses, frictional heating to several hundred degrees centigrade occurs (see for example Bowden and Thomas (1954)). In the case of calcite-aragonite another temperature factor enters in, namely, the change in temperature due to inversion. If the inversion takes place throughout the whole of a small particle, at constant pressure, in an adiabatic fashion we have $\Delta T = T\Delta S/C_p$ where ΔS is the molal entropy change in calcite transforming to aragonite and C_p is the average molal specific heat of the two phases. This gives $\Delta T \cong .04T$ or $\Delta T \cong 40^\circ$ at 1000° K. for the rough values of the thermodynamic parameters of CaCO₃ in this range. The adiabatic assumption makes this a maximum estimate of the temperature effect from this source. (It should be noted that this is a temperature decrease for calcite→aragonite at constant stress). In any case, the local temperatures from ordinary frictional heating should dominate the latent heat effect. However, it is probable that the presence of a polymorphic transition in a substance undergoing frictional heating will limit the temperature rise, since the coefficient of friction may become very low for a surface which is in a process of change. A possible analogue has been described by Bowden and Tabor (1950), who report that the rise in temperature of a sliding metal is limited by its melting point. Bowden and Thomas (1954) have also described the converse effect, namely the much greater temperature increase obtained in

local hot spots when an easily oxidizable metal is heated by friction to the point where it reacts readily with air.

Aragonite ordinarily occurs in nature only as a metastable form, and it might be supposed that in the grinding experiments it is also produced metastably, perhaps due to precipitation from a solution. In the dry grinds the only solution phase available for aragonite "precipitation" is the water (and gas) absorbed on the grain surfaces. It is felt that this mechanism does not operate in this case since all experiments with calcite, whether ground dry, or with distilled water or alcohol covering the sample, produced aragonite. It is known that (1) precipitation of CaCO_3 from a saturated solution by release of high pressure at room temperature gives both aragonite and vaterite (Jamieson, 1953), and (2) alcohol inhibits the formation of aragonite in precipitation from chemical reactions (Favre, 1946). However since the conditions for the metastable formation of aragonite are not known at present this argument can not be deemed conclusive.

B. Carbonate Solid Solutions

A mixture of CaCO_3 and MgCO_3 (synthetic) after 21 hours of grinding was found to contain much aragonite in addition to a calcite phase. A very faint line on the x-ray pattern could conceivably be the strongest reflection from dolomite, or more likely, a protodolomite-like material. 19 hour exposures in the 114.59 mm. camera using filtered Cu radiation verified the existence of this line. The amount of solid solution to be expected in this system is very small for the apparent working conditions of the mortar. For example, the solubility of Mg in CaCO_3 is $\sim 8\%$ at 900°K . (Graf and Goldsmith, 1958). Unreported work of one of the authors (J.R.G.) shows the effect of pressure on this solubility to be small.

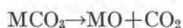
In grinding CaCO_3 and synthetic MnCO_3 the diffraction lines became "bands," CaCO_3 lines progressively widening toward the corresponding MnCO_3 lines and vice-versa. This indicates that heterogeneous solid solutions were formed. At no time was there a complete linkage nor was there a formation of sharp line corresponding to a unique homogeneous solid solution even with 64 hours of grinding. The broadening of CaCO_3 lines was greater than those of MnCO_3 . This is in accord with the phase diagram obtained by Goldsmith and Graf (1957) which displays a greater solubility of Mn in CaCO_3 than vice-versa. The effect of pressure on this system is unknown, but if it is negligible we see again that the local temperatures can not have exceeded 525°C . and must presumably have been below 475°C . to show the large immiscibility gap illustrated by the patterns.

After 17 hours of grinding, the mixture of synthetic MgCO_3 and synthetic MnCO_3 gave a diffraction pattern showing uninterrupted heterogeneous, solid solution "bands" between the positions of corresponding lines of MgCO_2 and MnCO_3 . Recent work of Goldsmith and Graf (1960) has shown that solid solubility is complete in this system at 450°C ., the lowest temperature at which equilibrium reaction could be carried out.

The MgCO_3 - CdCO_3 grind gave still different behavior in that, not only did the CdCO_3 lines broaden in the direction of those of MgCO_3 (which remained moderately sharp) but they shifted their peak of maximum intensity also toward MgCO_3 indicating a fairly "complete" reaction. No CdO was discerned in the x -ray patterns.

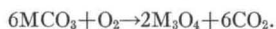
C. Decomposition of Carbonates by Grinding

Several experiments on pure carbonates resulted in decomposition to the oxides. It is rather difficult to obtain any quantitative information from these decompositions since neither the CO_2 pressure or O_2 pressure is well defined for a particle during grinding. It is not sufficient to assume that atmospheric partial gas pressures prevail since the actual partial pressures at the stressed surface of a particle are dependent on the ease with which a released gas may escape in the case of CO_2 , or the partial pressure of a confined gas, possibly trapped and compressed by surrounding particles in the case of O_2 . If the local partial pressure of CO_2 in these experiments were truly atmospheric, all the pure carbonates that were ground would have decomposed, with the possible exception of BaCO_3 . Actually the decompositions seem to fall into two classes. The first class being reactions of the type



in which the oxygen is supplied by the carbonate itself and hence the reaction is essentially independent of oxygen partial pressures and dependent only on the CO_2 content of the trapped gas. If we assume a nominal partial pressure of .01 atmosphere for CO_2 in the normal atmosphere, and if the reasoning earlier on solids is correct, in compression of any included atmosphere a maximum CO_2 pressure (from atmospheric CO_2) of 200 atmospheres could be reached. The decomposition of smithsonite to ZnO behaved in this fashion. A rough extrapolation of the data of Harker and Hutta (1956) indicate that ZnCO_3 is almost unstable under natural conditions at the earth's surface, so with the application of the stresses and temperatures of grinding it is not surprising that ZnCO_3 decomposes. In addition, the oxidation relations of ZnO are simple. Apparently the decomposition of CdCO_3 falls in this class also.

The second class of decomposition may be exemplified by



Now the oxygen pressure (assuming 20% normal) can be as high as 4000 atmospheres by the above argument, certainly highly oxidizing conditions. Due to the uncertainty of local O_2 and CO_2 pressures as mentioned in the beginning of this section, it would take much more experimental work to actually know what the various physical processes occurring in the case of FeCO_3 and MnCO_3 are. Kissinger *et al.* (1956) report that FeCO_3 decomposes and oxidizes in air to Fe_2O_3 , the change being essentially complete at 500°C . This is analogous to our results. Keller (1955) has also reported the oxidation of iron in montmorillonite by grinding. Kissinger *et al.* (1956) report that on heating MnCO_3 in air Mn_2O_3 appears at 600°C . while if MnCO_3 is heated in CO_2 , MnO and Mn_3O_4 appear, the MnO disappearing by the time a temperature of 600°C . was reached. In our grind of a natural sample, the greenish color suggest the formation of MnO , but this was not detected by x -ray diffraction. A comparison of the grinding results with those of Kissinger *et al.* (1956) would suggest that our partial pressures of CO_2 were greater than that in normal air. The apparent direct transition of synthetic MnCO_3 to Mn_2O_3 indicates the delicate balance of physical parameters involved since the same material when mixed with MgCO_3 , formed a heterogeneous solid solution which then decomposed, the oxide formed being Mn_3O_4 . Again the same material mixed with CaCO_3 formed only a heterogeneous solid solution and no decomposition occurred. And again, the addition of MgCO_3 to CdCO_3 apparently prevented decomposition. These results suggest that the rate of solid solution formation is great enough to at least "armor" the surface, and inhibit oxidation or decomposition for the materials studied.

D. Miscellany

In some grindings, especially after two or more days, mullite lines from the mortar and pestle became obvious in the x -ray diffraction patterns. These were readily "discarded" in analyzing the results, but they do point out that prolonged grinding may produce a degree of contamination detrimental to experimental accuracy in various other work; mullite is of course present before it develops in amounts sufficient for x -ray detection. The oxidation reactions found, produced apparently by high local O_2 pressures, may very well also occur in the grinding of certain silicates prior to calorimetric studies. In these cases, an uncertainty is

introduced into the experimental data. The same may be said for structural degradation during grinding.

CONCLUSIONS

Prolonged grinding does to a partial extent duplicate the results of high pressure experimentation, however its use for this purpose at least with ordinary laboratory equipment is somewhat ambiguous. Heterogeneous solid solutions of various carbonates may be formed by grinding. A systematic study of carbonate decompositions and oxidations could give information on local gas pressures during grinding as the equilibrium diagrams for carbonate systems are becoming known. The grinding of mixtures can be used in a rough way to amplify our knowledge of miscibility in some solid systems in which no experimental work has been performed. Finely ground materials used for solution calorimetry etc., should be carefully examined for phase changes and degradation effects.

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