

Double carbonate breakdown reactions at high pressures: an experimental study in the system CaO–MgO–FeO–MnO–CO₂

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Abstract The pressure–temperature conditions of the reactions of the double carbonates CaM(CO₃)₂, where *M* = Mg (dolomite), Fe (ankerite) and Mn (kutnohorite), to MCO₃ plus CaCO₃ (aragonite) have been investigated at 5–8 GPa, 600–1,100°C, using multi-anvil apparatus. The reaction dolomite = magnesite + aragonite is in good agreement with the results of Sato and Katsura (Earth Planet Sci 184:529–534, 2001), but in poor agreement with the results of Luth (Contrib Mineral Petrol 141:222–232, 2001). The dolomite is partially disordered at 620°C, and fully disordered at 1,100°C. All ankerite and kutnohorite samples, including the synthetic starting materials, are disordered. The *P–T* slopes of the three reactions increase in the order *M* = Mg, Fe, Mn. The shallower slope for the reaction involving magnesite is due partly to its having a higher compressibility than expected from unit-cell volume considerations. At low pressures there is a preference for partitioning into the double carbonate of Mg > Fe > Mn. At high pressures the partitioning preference is reversed. Using the measured reaction positions, the *P–T* conditions at which dolomite solid solutions will break down on increasing *P* and *T* in subduction zones can be estimated.

Keywords Dolomite · Ankerite · Kutnohorite · High pressure · High temperature · Subduction zones

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Introduction

Carbon is cycled between the Earth's crust and mantle through subduction of carbonate minerals and release of CO₂ in arc volcanism. The CO₂ flux at destructive plate margins has been estimated to be similar to that at convergent plate margins, and CO₂/³He ratios indicate that ~80% of the CO₂ released in arc volcanism is slab-derived (Marty and Tolstikhin 1998). Significantly more carbon, however, appears to be subducted than is released (e.g., Bebout 1995), implying its subduction to depths beyond the source of arc magmas.

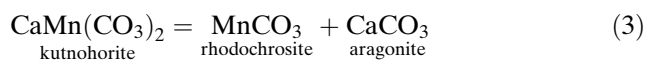
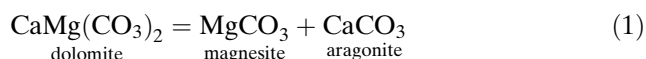
Carbonate minerals may enter subduction zones incorporated in marine sediments and in hydrothermally altered basalt and peridotite. The average CO₂ content of marine sediment entering subduction zones has been estimated at 3.0 wt% (Plank and Langmuir 1998), and the average CO₂ content of metamorphosed mid-ocean ridge basalt is close to this (2.95 wt%, Staudigel et al. 1989). The CO₂ in altered oceanic crust is incorporated through precipitation of Ca, Mg and carbonate from seawater, and its concentration decreases with depth in the crust. The main carbonate minerals entering subduction zones are the Ca,Mg-carbonates: calcite [CaCO₃] and dolomite [CaMg(CO₃)₂].

Evidence for the deep subduction of carbonates comes from ultra-high pressure (UHP) metamorphic rocks, in which, among other parageneses, they have been found coexisting with the high-pressure minerals coesite (e.g., Zhang and Liou 1996) and diamond (e.g., Ogasawara et al. 2000). The deeply subducted carbonates may play an important role in mantle processes at depths beyond the source of arc magmas, such as the genesis of alkaline magmas and carbonatites.

While Ca,Mg-carbonates are the most important compositions entering subduction zones, Fe is also important in basaltic compositions and many sediments, and Mn occurs in appreciable amounts in some pelagic sediments. These will give rise to the Fe-carbonates siderite [FeCO₃] and ankerite [CaFe(CO₃)₂], and the Mn-carbonates rhodochrosite [MnCO₃] and kutnohorite [CaMn(CO₃)₂].

The single carbonates calcite, magnesite, siderite and rhodochrosite are rhombohedral, space group $R\bar{3}c$. The structure comprises layers of triangular CO₃ groups alternating in the *c* direction with layers of octahedrally coordinated cations. Disordered double carbonates are also $R\bar{3}c$, with the two cations randomly occupying the one octahedral site. Upon ordering, the cations occupy alternating layers of larger and smaller cations, leading to the loss of the *c*-glide to give the space group $R\bar{3}$. All structural refinements of natural samples of dolomite–ankerite solid solutions have shown them to be fully ordered, but natural kutnohorite may be partially disordered (Reeder 1983).

A knowledge of the stability relations of carbonate minerals at high pressures is clearly important for understanding the fate of CO₂ in subduction zones. We have therefore performed phase-equilibrium experiments to bracket three high-pressure carbonate reactions:



Experiments were done in a multi-anvil apparatus at pressures of 5–8 GPa, in which pressure interval the reactions occur at temperatures between 600 and 1,100°C. These conditions encompass a range of calculated geotherms for subducting slabs, e.g., the low- and high-temperature geotherms for NE and SW Japan, respectively, calculated by Peacock and Wang (1999).

Several studies of reaction (1) have recently been published, using different techniques and giving some conflicting results (Fig. 1). Martinez et al. (1996) used synchrotron X-ray diffraction and a multi-anvil apparatus to determine the equations of state of aragonite and dolomite, and observed the breakdown of dolomite to aragonite plus magnesite at > 5 GPa at 600°C. Using their equations of state, they calculated the position of the equilibrium curve and extrapolated it to

higher and lower temperatures. Recognising the need to place some experimental constraints on their extrapolation, Luth (2001) conducted phase-equilibrium experiments on reaction (1). While his low-temperature bracket (at 627°C) is consistent with the result of Martinez et al., above this temperature the reaction shows a marked curvature, such that by 1,200°C it occurs at almost 9 GPa (Fig. 1). Luth proposed that the curvature is due to increasing disorder in the dolomite with increasing temperature, which stabilises dolomite relative to aragonite plus magnesite and thus increases the reaction pressure.

In the same year as Luth's study was published, Sato and Katsura (2001) also published results of phase-equilibrium experiments on reaction (1) between 600 and 1,200°C. In contrast to Luth's curved reaction, they obtained a straight-line reaction, passing through 5.4 GPa at 600°C, and 1,107°C at 8.5 GPa (Fig. 1). Again, the 600°C bracket is consistent with the result of Martinez et al. (1996), but the slope of the reaction is steeper than their calculation. Sato and Katsura (2001) proposed that this difference is due to uncertainties in the thermodynamic data used in the calculation. They did not, however, discuss the question of dolomite order–disorder. Reaction (1) has also been reversed by Buob et al. (2006) between 5 and 7 GPa, where the reaction position is the same, within error, as determined by Luth (2001).

Luth (2001) compared his experimental curve with that calculated using available thermodynamic data, including the most up-to-date version of Holland and Powell's dataset, Thermocalc v2.7 (Holland and Powell 1998). None of the calculated curves show the same curvature as his experimental curve, and they also underestimate the reaction pressure at 600°C, the only temperature where the three experimental studies described above are in agreement, and where Luth assumes that dolomite is fully ordered. The reaction position calculated using Thermocalc v2.7 is shown in Fig. 1. This calculation incorporates a Landau model of order–disorder in dolomite. A more recent version of the dataset (v3.1), containing small revisions to the carbonates' enthalpies of formation, gives a reaction displaced to slightly lower temperatures (Fig. 1). If the strong curvature in Luth's reaction is due to dolomite's disordering between 600 and 1,200°C, then the difference in shape from the calculated reaction may be due to the onset of disordering occurring at a higher temperature (~800°C) than predicted by Holland and Powell's Landau model. Luth pointed out the problem of applying such a model to a phase-like dolomite that re-orders on quenching. Because of this problem, Antao et al. (2004) investigated the structure of

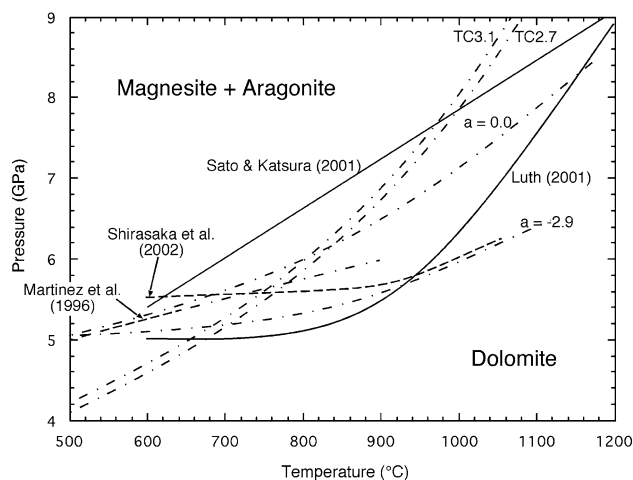


Fig. 1 P–T positions of the reaction dolomite = magnesite + aragonite determined experimentally in previous studies and calculated. *Solid lines* reversed phase-equilibrium experiments; *dashed lines* in situ phase-equilibrium experiments; *dot-dashed lines* calculated reactions: using Thermocalc versions 2.7 (TC2.7) and 3.1 (TC3.1) (Holland and Powell 1998); and from Antao et al. (2004), using an unmodified ($a = 0.0$) and a modified ($a = -2.9$) Bragg-Williams model for order–disorder in dolomite. The experimentally determined reaction position of Buob et al. (2006) is close to that of Luth (2001)

dolomite in situ using synchrotron radiation at 25–1,193°C, 3 GPa. They derived a thermodynamic model for cation disorder in dolomite and then calculated the position of reaction (1), making some thermodynamic assumptions based on Luth’s results. Their calculated curves (Fig. 1) show more curvature than the reaction of Sato and Katsura (2001) but less than that of Luth (2001).

Another in situ synchrotron study of reaction (1) was carried out by Shirasaka et al. (2002), who determined the locations of dolomite decomposition on increasing pressure, and of dolomite synthesis on decreasing pressure. The reaction positions coincide at high temperatures, but diverge at low temperatures due to the reaction being kinetically hindered. The authors proposed that the equilibrium boundary is close to their dolomite decomposition reaction (Fig. 1).

There have been far fewer previous experimental studies on the Fe- and Mn-carbonates than the Mg-carbonates. Ankerite and siderite are included in Thermocalc, enabling reaction (2) to be calculated (Fig. 4). However, the enthalpy of formation of ankerite relies on exchange equilibria with dolomite, and some other thermodynamic properties are estimated. There are no data for kutnohorite in Holland and Powell’s dataset, but there are for rhodochrosite, including an enthalpy of formation derived from phase-equilibrium experiments. The thermodynamic

data for ankerite must be treated with caution, since ordered endmember ankerite has neither been found nor synthesised. A maximum of ~70% substitution of Fe for Mg has been found to occur in natural ordered dolomite–ankerite samples (Reeder and Dollase 1989), while a similar limit has been observed in phase-equilibrium experiments (Goldsmith et al. 1962; Rosenberg 1967). Disordered $\text{CaFe}(\text{CO}_3)_2$ can, however, be synthesised (e.g., Davidson et al. 1994). These authors predicted from phase-equilibrium data that ordered $\text{CaFe}(\text{CO}_3)_2$ would be stable only below ~450°C, and from cell volume data they observed a negative volume of disordering, which would tend to stabilise the disordered phase at high pressure. Kutnohorite also has a relatively low disordering temperature interval, beginning at ~450°C (Goldsmith and Graf 1960). These low temperatures contrast with the high temperature of dolomite disorder, indicating a rough correlation between the thermal stability of the ordered structure and the difference in size between the two cations involved (Reeder 1983). The relatively small difference between the sizes of Ca and Mn also enables greater substitution of one cation for the other within the ordered structure.

Experimental procedure

The starting materials used for the experiments were natural aragonite, magnesite, dolomite, siderite and rhodochrosite, and synthetic ankerite and kutnohorite. Their compositions are shown in Table 1. The synthetic samples were synthesised in a piston-cylinder apparatus from stoichiometric mixtures of the appropriate natural minerals: ankerite from aragonite and siderite at 1.5 GPa, 850°C for 24–48 h, and kutnohorite from aragonite and rhodochrosite at 1.7–1.8 GPa, 950°C for 24 h. The ankerite was synthesised in a graphite capsule, and the kutnohorite in a gold capsule. Powder X-ray diffraction (XRD) of both samples showed no traces of impurity or unreacted material. Table 1 shows that, while the cation contents of the natural samples are all within 5% of ideal, the synthetic samples are relatively enriched in Ca. The effect of starting composition on measured reaction positions will be considered in the next section.

The degree of order in the double carbonates was investigated using powder XRD. Diffraction patterns were obtained on a Philips diffractometer with a copper filament, operated at 40 kV and 20 mA, with step sizes and times of 0.02° and 1 s, respectively. For dolomite, the degree of order was measured using the

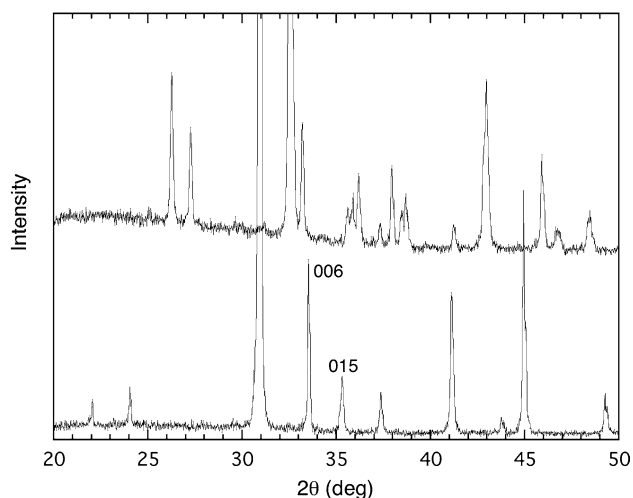


Fig. 2 X-ray diffraction patterns of DAM5 (*lower pattern* dolomite) and DAM9 (*upper pattern* magnesite + aragonite). The dolomite reflections used to determine the order parameter are shown

method of Schultz-Güttler (1986), which involved comparing the intensity of the most intense ordering reflection (015) with the intensity of a reflection common to both $R\bar{3}$ and $R\bar{3}c$ structures (006). For a completely ordered sample, the intensity ratio, $I_{015/006}$, is equal to 1, corresponding to a value for the order parameter, S , of 1. The dolomite used in this study was found to be partially disordered, with $I_{015/006} = 0.35$. The implied low value of S is considered unlikely,

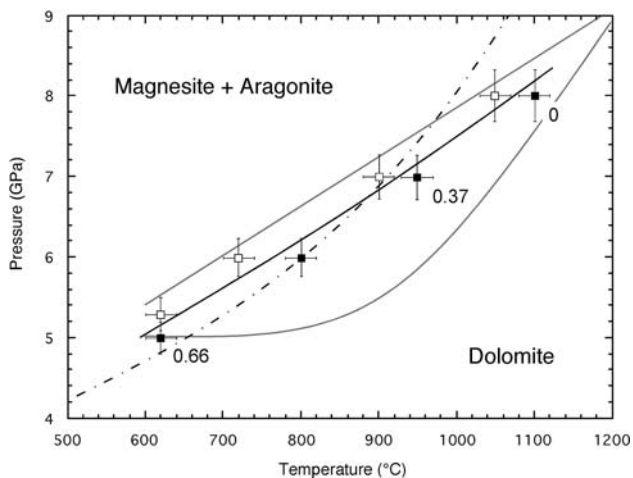


Fig. 3 Results of experiments on reaction (1), dolomite = magnesite + aragonite. *Filled squares* growth of dolomite; *open squares* growth of magnesite + aragonite. The *numbers* beside three of the points are the values of $I_{015/006}$ for the dolomite in those experiments. The curve has been fitted by eye. *Dot-dashed line* reaction calculated using Thermocalc v3.1 (Holland and Powell 1998); *solid grey lines* experimentally determined curves of Luth (2001) and Sato and Katsura (2001)

given the high critical temperature for the order–disorder transition ($\sim 1,150^\circ\text{C}$, Reeder and Wenk 1983). However, this method for determining S is only semi-quantitative, as some preferred orientation may exist in the XRD patterns, peak intensities may be affected by compositional variation away from the ideal composition, and intensities of the ordering reflections are low so that accurate measurement is difficult.

X-ray diffraction patterns of the synthetic ankerite and kutnohorite show no ordering reflections. Synthesis of disordered structures is consistent with previous studies on both compositions (e.g., Davidson et al. 1994; Goldsmith and Graf 1957).

Experiments on the three reactions used stoichiometric mixes of reactants and products (i.e., 50 mol% dolomite, 25% aragonite and 25% magnesite), dried at 110°C before sealing in Pt capsules (reactions 1 and 3) or placing in graphite capsules (reaction 2). Graphite was used for both the ankerite synthesis and the experiments on reaction (2) to maintain a low oxygen fugacity and to avoid any danger of Fe alloying with a Pt capsule. Experiments were run in a multi-anvil apparatus, details of which are presented elsewhere (Bromiley and Pawley 2002; Pawley 2003). Briefly, the anvils were 1 in. tungsten carbide cubes with 12 mm truncation edge lengths, and the pressure medium was a castable MgO ceramic octahedron containing a cylindrical graphite furnace in which the 2 mm-diameter \times 3 mm-long Pt or 3.5 mm-diameter \times 3.5 mm-long graphite capsule was centrally placed.

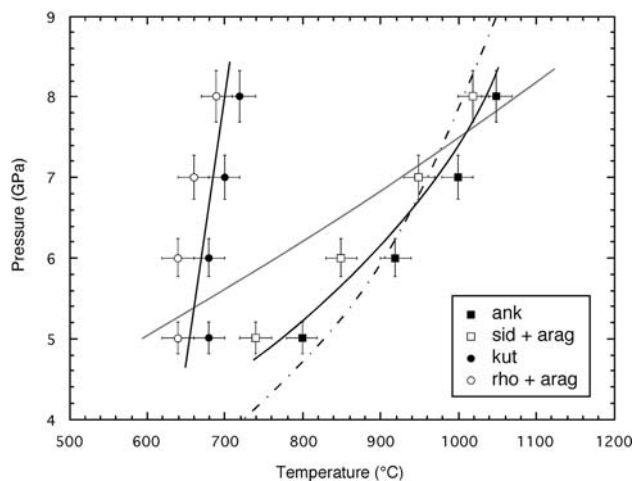


Fig. 4 Results of experiments on reactions (2), ankerite = siderite + aragonite, and (3), kutnohorite = rhodochrosite + aragonite. *Solid black lines* are visual fits to the experimental data; *dot-dashed line* position of reaction (2) calculated using Thermocalc v3.1 (Holland and Powell 1998); *solid grey line* position of reaction (1) determined in this study. Abbreviations are as in Table 2

The Pt/Pt10Rh thermocouple tip was in contact with one end of the capsule, with the wires exiting radially, through holes in the furnace. Short lengths of stainless steel capillary tubing protected the thermocouple wires where they exited the octahedron through opposite corners. Pressure and temperature uncertainties, ignoring the effect of temperature on thermocouple emf, are estimated to be $\pm 4\%$ and $\pm 20^\circ\text{C}$, respectively (Bromiley and Pawley 2002).

Run products were recovered as powders which were examined by XRD. Reaction direction was determined by comparing the XRD patterns of the starting material and run products. In all experiments except one, reaction was unambiguous, with a relative peak height change averaging more than 70%. In the experiment which showed no reaction (DAM4, Table 1), the 12 h-run duration evidently was too short for noticeable reaction to occur. Repeating the experiment for 48 h (DAM5) produced significant reaction. Examples of diffraction patterns of samples from both sides of the reaction are shown in Fig. 2. Owing to the fine grain size of run products, attempts to analyse their compositions using the electron microprobe proved unsuccessful.

Results and discussion

Reaction (1)

The results (Table 2; Fig. 3) show that reaction (1) has been constrained by four brackets between 5.0 and 8.0 GPa. The outer brackets are similar to those of

Table 1 Compositions of phases used in the experiments on reactions (1), (2) and (3), measured using a JEOL 6400 scanning electron microprobe

	1	2	3	4	5	6	7
FeO	0.00	0.74	0.25	59.35	25.93	0.84	0.26
MnO	0.04	0.61	0.00	0.43	0.41	58.90	22.64
MgO	0.01	59.64	20.87	0.20	0.20	0.72	0.16
CaO	55.01	0.43	31.52	0.18	27.59	0.60	29.46
CO ₂	44.94	38.58	47.36	39.84	45.87	38.44	47.48
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Number of ions on the basis of six O							
Fe ²⁺	0.000	0.014	0.006	1.966	0.836	0.023	0.008
Mn	0.001	0.011	0.000	0.014	0.013	1.908	0.749
Mg	0.001	1.965	0.956	0.012	0.011	0.041	0.009
Ca	1.998	0.010	1.038	0.008	1.139	0.025	1.233

CO₂ was calculated by difference

1 aragonite, natural, Morocco; 2 magnesite, natural, UK; 3 dolomite, natural, UK; 4 siderite, natural, UK; 5 ankerite, synthetic; 6 rhodochrosite, natural, Morocco; 7 kutnohorite, synthetic

Luth (2001) and of Sato and Katsura (2001), but between these the reaction position is much closer to that determined by Sato and Katsura (2001). Experiment DAM11 was conducted to determine whether the reaction position might be misjudged because of kinetic problems, in the same way as investigated by Luth (2001). He considered the fact that the equilibrium compositions of aragonite and magnesite will not be the pure endmembers under the high *P* and *T* conditions of reaction (1). Therefore, even at temperatures within the stability field of aragonite plus magnesite, it might be kinetically more favourable for the pure aragonite and magnesite in the starting material to react to dolomite than to the stable solid solution compositions. This experiment was therefore run for 24 h at 900°C at 7.0 GPa, conditions which experiment DAM9 had shown to give strong reaction to aragonite plus magnesite, followed by 48 h at 950°C. The final product showed strong reaction to dolomite, confirming the result of DAM10, which also produced dolomite at 7.0 GPa, 950°C.

The state of order in the dolomite along reaction (1) was measured from the intensity of ordering reflections in XRD patterns, using the same method as for the starting materials. This is also the method used by Luth (2001). Values of $I_{015/006}$ are shown on Fig. 3 for the three run products for which measurement was possible. The starting material has $I_{015/006} = 0.35$. The almost doubling of $I_{015/006}$ in the experiment at 5 GPa and 620°C (DAM5) indicates that the degree of order in the new dolomite in this experiment is not determined by that of the starting material: either the starting dolomite maintains its low value of *S* and the crystallising dolomite is close to fully ordered, leading to an average value of $S = 0.66$, or the starting dolomite partially orders to the same value of *S* as the new dolomite. The latter is considered more likely, as this value of $I_{015/006}$ is very close to that observed at 627°C by Luth (2001), who used a very well-ordered dolomite as the starting material.

There is the potential for dolomite samples quenched from high temperature to partially re-order on quench, but this does not appear to have occurred in this study, as the sample quenched from 8 GPa and 1,100°C (DAM15) contains no ordering reflections in its XRD pattern. The same was true of the sample run under the same conditions by Luth (2001).

The order parameters determined in this study are significantly less than measured in the in situ experiments of Antao et al. (2004), suggesting either that the method of Schultz-Güttler underestimates *S* (as suggested by Luth 2001), or that the samples synthesised in our phase-equilibrium experiments are more

Table 2 Experimental conditions and results

Experiment	Pressure (GPa)	Temperature (°C)	Duration (h)	Run products
Reaction (1)				
DAM4	5.0	620	12	dol + arag + mag
DAM5	5.0	620	48	dol
DAM12	5.3	620a	48	arag + mag
DAM6	6.0	720	24	arag + mag
DAM7	6.0	800	24	dol
DAM9	7.0	900	24	arag + mag
DAM10	7.0	950	24	dol
DAM11 ^a	7.0	900–950	24–48	arag + mag → dol
DAM14	8.0	1050	24	arag + mag
DAM15	8.0	1100	24	dol
Reaction (2)				
AAS2	5.0	740	24	arag + sid
AAS4	5.0	800	24	ank
AAS5	6.0	850	24	arag + sid
AAS6	6.0	920	24	ank
AAS9	7.0	950	24	arag + sid
AAS10	7.0	1000	24	ank
AAS11	8.0	1020	24	arag + sid
AAS13	8.0	1050	24	ank
Reaction (3)				
KAR4	5.0	640	24	arag + rho
KAR3	5.0	680	24	kut
KAR1	5.0	740	24	kut
KAR7	6.0	640	24	arag + rho
KAR6	6.0	680	24	kut
KAR5	6.0	740	24	kut
KAR10	7.0	660	24	arag + rho
KAR9	7.0	700	24	kut
KAR13	8.0	690	24	arag + rho
KAR12	8.0	720	24	kut

ank ankerite, *arag* aragonite,
dol dolomite, *kut* kutnohorite,
mag magnesite, *rho*
 rhodochrosite

^aTwo-stage experiment

disordered at the same temperature than the natural sample used in the heating experiment of Antao et al. (2004).

The observation, that the degree of order of our phase-equilibrium samples is not affected by the starting dolomite's degree of order, suggests that their compositions are also not determined by the degree of order of the starting dolomite. This shows a small Ca-enrichment (Table 1). Instead the compositions should be determined purely by the P – T conditions of the experiments. In the system CaCO_3 – MgCO_3 , the equilibrium between dolomite, aragonite and magnesite is univariant, and there are no compositional degrees of freedom if T (or P) is specified. The equilibrium composition of dolomite on the reaction boundary need not correspond exactly to stoichiometric $\text{CaMg}(\text{CO}_3)_2$, and in fact Luth (2001) observed an assemblage at 8 GPa, 1,100°C that implied that stoichiometric dolomite was metastable with respect to Ca-enriched dolomite at these conditions.

Since under equilibrium conditions, the compositions of the phases coexisting along univariant reaction (1), their state of order and the P – T position of the

reaction are fixed, the reaction position determined in our study and the studies of Sato and Katsura (2001) and Luth (2001) should coincide. This assumes that the experimental bulk compositions lie close to the binary join CaCO_3 – MgCO_3 , as otherwise substitution of other elements could occur and lower the activities of the Ca,Mg-carbonates. All of the bulk compositions used in these three studies contained minor amounts of Fe and Mn, but in no case do their mole fractions exceed 0.01 (expressed on the basis of six oxygens).

The difference between our results and those of Luth (2001) suggests that one or both studies have determined a metastable reaction position. We can rule out erroneous multi-anvil calibration in one or the other study as the cause of the discrepancy, as they agree at 620°C and ~1,200°C, respectively. It is only in the intervening temperature interval that our reaction occurs at a higher pressure than Luth's. Our two-stage experiment at 7 GPa (DAM11) confirmed that the reaction temperature here is not underestimated due to kinetic reasons, and so there must be another explanation for the difference. Our XRD estimation of the order parameter also produced the same results at 620

and 1,100°C as Luth. However, at 950°C, his product dolomite showed a significantly higher degree of order (average $I_{015/006} = 0.71$). Our measurement of 0.37 is for a higher-pressure sample (7 GPa) than his (5–6 GPa), but although Luth suggested a decrease in disordering temperature with increasing pressure, the magnitude of the pressure effect is likely to be much smaller than the observed difference. Thus, our dolomite appears to have a lower temperature of disordering. This might explain the discrepancy between the two studies, with one or both determining a metastable reaction position. For example, in Luth's study it may be that relatively well-ordered dolomite broke down to the less unstable aragonite + magnesite rather than reacting to a stable disordered dolomite + magnesite. If this is the case, it suggests that Sato and Katsura (2001), whose reaction position is close to ours, also located the position of reaction of more disordered dolomite.

Our experimentally determined position of reaction (1) is in good agreement with that calculated using Thermocalc v3.1 (Holland and Powell 1998) between 600 and 950°C, the two curves being within 0.5 GPa of each other over this temperature interval (Fig. 3). However, at higher temperatures, the steeper dP/dT slope of the calculated curve means it diverges from the experimental curve above ~900°C. This is hardly surprising, given that thermodynamic properties of the minerals involved in the reaction have, for the most part, not been measured at these high pressures and temperatures, but have been extrapolated from lower P and T measurements. The different degree of order in our samples compared to the calculated values will also contribute to the difference in reaction positions. For example, our sample has $S = 0.37$ at 7 GPa, 950°C, and is completely disordered at 8 GPa, 1,100°C. Calculations of S using the parameters in Thermocalc (which include the transition temperature at 1 bar, $T = 1,100^\circ\text{C}$, and a pressure dependence of the transition temperature) give $S = 0.63$ and 0.50 at these two P – T conditions, respectively.

Reactions (2) and (3)

The results of the experiments on reactions (2) and (3) are shown in Table 2 and Fig. 4. All run products showed strong reaction. No ordering reflections were observed in any of the ankerite or kutnohorite run products, and so, like the starting materials, they are inferred to be completely disordered along the reactions. This is to be expected, if disordering begins at approximately 450°C at ambient pressure for both minerals, and if ordered ankerite is destabilised with

increasing pressure, as predicted by Davidson et al. (1994).

In the same way as the P – T position of reaction (1) has been shown to be independent of the compositions of the starting materials, the positions of reactions (2) and (3) should not be affected by the fact that the synthetic ankerite and kutnohorite are significantly Ca-enriched with respect to the ideal composition.

The agreement between the experimental reaction (2) and that calculated using Thermocalc (Fig. 4) is perhaps surprising, considering the number of estimated thermodynamic parameters for ankerite in the dataset, and that the calculation assumes that ankerite will be only partially disordered at low temperature and become more disordered with increasing temperature along the reaction, rather than being completely disordered at all temperatures.

Comparisons between the three reactions

Comparisons between our experimental positions of reactions (1), (2) and (3) allow some interesting observations to be made about the relative stabilities of the phases involved. Firstly, we can compare the P – T slopes of the reactions. These are steeper for reactions (2) and (3) than reaction (1), (Fig. 4), with reaction (3) having the steepest slope, at $15^\circ\text{C GPa}^{-1}$. Thus the stability of kutnohorite is relatively insensitive to pressure, while that of dolomite is very much pressure-dependent. The P – T slopes of the reactions depend on entropy and volume changes, according to the Clapeyron equation $dP/dT = \Delta S/\Delta V$. A rigorous comparison of ΔS for the three reactions is not possible here, as insufficient thermodynamic data exist for ankerite and kutnohorite. Moreover, whilst we might expect that the increasing disorder in dolomite along reaction (1) would cause sufficient increase in ΔS for the reaction to show a marked curvature, this is not observed. Instead, the only reaction showing significant curvature is reaction (2), in which the ankerite is disordered along the entire length of the reaction. Thus the relationships between ΔS for the three reactions remain unresolved. However, we can make simple comparisons of ΔV , since sufficient volume data exist for all of the phases for us to consider their effects on the reaction slopes. All three reactions involve aragonite, and therefore only the rhombohedral carbonates' volumes need be compared. ΔV is a function of the relative compressibilities and thermal expansivities of the reactants and products. Compressibilities of all the rhombohedral carbonates involved here have been measured (MgCO₃, FeCO₃, MnCO₃; Zhang and Reeder 1999; dolomite, ankerite: Ross and Reeder 1992; kutnohorite: A. Pawley, unpublished data). Apart from

MgCO₃, they all show an inverse linear correlation between bulk modulus and unit cell volume, as described for $R\bar{3}c$ carbonates by Zhang and Reeder (1999). The bulk modulus of MgCO₃, however, lies well above the trend. Fewer thermal expansivity measurements on these minerals have been made, with only magnesite and dolomite measured at ambient pressure (Markgraf and Reeder 1985; Reeder and Markgraf 1986), while siderite's volume has been measured at simultaneous high pressure and high temperature (Zhang et al. 1998). These data indicate that differences in thermal expansivity are small compared to differences in compressibility. Therefore, we can explain the steep slopes of reactions (2) and (3) as being partly due to the much higher compressibilities of ankerite and kutnohorite than of siderite and rhodochrosite, respectively. In contrast, magnesite's higher compressibility than that expected contributes towards a shallower slope for reaction (1).

A second observation can be made about the three reaction positions if we extrapolate them to lower pressures. At ~4 GPa, reactions (2) and (3) will cross each other, so that at lower pressures the three reactions occur in the order (1), (2), (3) with increasing temperature. At high pressures, because of their different slopes, the order is reversed. These three reactions are univariant, but between them continuous reactions will occur. Thus, with increasing temperature at low pressures, on crossing reaction (1) Fe- and Mn-free dolomite is initially the only stable double carbonate. On increasing temperature, its solid solution field expands towards ankerite and kutnohorite, with the latter phase being the last endmember to become stable. Thus, there is a preference for partitioning into the double carbonate of Mg > Fe > Mn, i.e., the smaller the cation the more it prefers to enter the dolomite structure. This is consistent with the greater tendency for ordering in structures with a greater cation size difference, already observed from previous studies, which will further stabilise the double carbonate structure. At high pressures, the partitioning preference is reversed. Here, there is a preference for the smaller cation to enter the single carbonate, so that there are fewer mismatches between the cation sizes in the double carbonate. This is to be expected, since cation size mismatches will become increasingly energetically unfavourable as pressure increases.

One factor that we have not considered in comparing the three reaction positions is the extent of solid solution between aragonite and the single carbonate. This should become more favourable as the difference in cation size decreases (Mn occurs more commonly in natural aragonites than do Fe and Mg, Speer 1983), so that the greatest solid solution should occur between

rhodochrosite and aragonite. This would then have a stabilising effect on the assemblage rhodochrosite + aragonite with respect to kutnohorite. However, the fine grain size of our run products meant that we could not quantify this effect.

Implications for carbonate stability in subduction zones

The reaction positions determined in this study lie within the range of modelled P – T paths for subduction zones. For example, Peacock and Wang (1999) present models for cool and warm subduction zones in NE and SW Japan, respectively, which pass through 5 GPa at ~590 and 900°C, respectively. These temperatures are for the top of the subducting crust, which will be the location of the highest concentrations of carbonates, in metasediments and hydrothermally altered oceanic crust. Therefore, the positions of reactions (1), (2) and (3) determined in this study can be used qualitatively to determine the P – T positions at which dolomite solid solutions will break down on increasing pressure in subduction zones. The reactions can also be compared with results of experiments on natural systems. Experimental studies of carbonated metabasalt under conditions relevant to subduction zones have recently been undertaken by Molina and Poli (2000) and Hammouda (2003), at pressures up to 2.0 and 10 GPa, respectively. In both studies, dolomite was observed to take over from calcite/aragonite as the main carbonate phase on increasing pressure. As there was Fe in the starting materials used in both studies, the dolomite was a dolomite–ankerite solid solution. Hammouda does not report its composition. Molina and Poli, on the other hand, who used three representative basalt compositions with different Mg numbers, report that the dolomite in their high-Fe basalt (at 2.0 GPa, 730°C) had an Fe content of 0.24 pfu, which is almost as much as the Mg content. Hammouda observed that the dolomite broke down to magnesite plus aragonite at between 900 and 950°C at 7 GPa. His reaction position is in good agreement with ours: at 7 GPa, our positions of reactions (1) and (2) are close to each other and to his reaction position.

The P – T position of the dolomite solid solution breakdown reaction in subducting oceanic crust will have little effect on the position of decarbonation or melting reactions, since the dolomite reaction is CO₂-conservative. Thus, Hammouda (2003) observed negligible change in slope of the carbonated eclogite melting reaction on crossing the dolomite reaction. Nevertheless, there will be consequences for mantle processes on crossing the reaction, due, for example, to changing

physical properties or trace element partitioning. The reaction has also been proposed as a geobarometer, by Sato and Katsura (2001). They pointed out the fact that in diamond-bearing UHP metamorphic rocks, the graphite/diamond phase boundary may be the only available barometer, and it will only provide a minimum pressure of metamorphism. The presence of dolomite will allow a maximum pressure to be constrained, while the occurrence of magnesite and calcite after aragonite would indicate that metamorphism had occurred at a pressure above the dolomite breakdown reaction. Sato and Katsura's barometer is based on the reaction in the system CaO-MgO-CO_2 . Our results allow it to be extended into the system $\text{CaO-MgO-FeO-MnO-CO}_2$.

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