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Enthalpies of formation of dolomite and of magnesian calcites

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ABSTRACT

(Ca,Mg) carbonates have been studied by solution calorimetry at 85°C in an acid solvent (1*M* HCl) that was saturated at room temperature with NaCl and contained 0.75*M* $CaCl_2$ and 0.25*M* $MgCl_2$. The enthalpy of formation of ordered dolomite from calcite and magnesite at 85°C is -5.74 ± 0.25 kJ/mol, for a formula unit of dolomite containing 1 mol of cations. A synthetically disordered dolomite has an enthalpy of formation of $+1.23 \pm 0.32$ kJ/mol. At 85°C, four synthetic magnesian calcites with mole fraction, X, of $MgCO_3$ between 0.01 and 0.13 show exothermic heats of mixing relative to $CaCO_3$ and $MgCO_3$. Combined with positive excess free energies of mixing, the enthalpy data suggest substantial negative excess entropies of mixing in the synthetic magnesian calcites. It is possible that considerable local order, perhaps clustering of Mg into randomly spaced Mg-rich cation layers, exists in synthetic magnesian calcites equilibrated near 700°C. The thermodynamic behavior of synthetic magnesian calcites may differ from that of biogenic samples.

INTRODUCTION

The system $CaCO_3$-$MgCO_3$ is the geologically most important carbonate system. Calcite ($CaCO_3$, sometimes containing some $MgCO_3$), dolomite (ordered phases near $CaMg(CO_3)_2$ in composition), and, to a far smaller extent, magnesite ($MgCO_3$) occur in sedimentary, metamorphic, and even igneous settings. The disordered substitutional rhombohedral $CaCO_3$-$MgCO_3$ solid solution is interrupted by a large phase field for the ordered dolomite phase (Goldsmith and Heard, 1961; Graf and Goldsmith, 1955; MacKenzie et al., 1983; Walter and Morse, 1984). At temperatures of 1100–1200°C (under appropriate CO_2 pressure), dolomite undergoes a cation-disordering reaction (Goldsmith and Heard, 1961; Reeder and Wenk, 1983) to a calcite-like phase. Mg-rich calcites occur in low-temperature environments and are of both inorganic and biogenic origin. The biogenic materials may differ somewhat in crystallographic parameters and vibrational spectra from synthetic materials of the same composition (Bischoff et al., 1983, 1985).

Yet despite the common occurrence of calcites and dolomites, the thermodynamic behavior of the $CaCO_3$-$MgCO_3$ system is not fully known. We have recently developed new solution calorimetric techniques for the study of carbonates and applied them to the $MnCO_3$-$CaCO_3$ system (Capobianco and Navrotsky, 1987) and to the $CdMg(CO_3)_2$ phase (Capobianco et al., 1987). The present study reports new enthalpy data for dolomite ($CaMg(CO_3)_2$), for a (partially) disordered dolomite, and for the terminal solid solution of $MgCO_3$ in $CaCO_3$ (magnesian calcite).

EXPERIMENTAL METHODS

Sample synthesis and characterization

The dolomite used in this study was a natural, optically clear, and virtually stoichiometric material from the metamorphic complex of Eugui, Spain. It was kindly supplied by Richard Reeder of the State University of New York at Stony Brook. Previous investigations of similar material have found it to be compositionally homogeneous (Reeder and Wenk, 1983) with very few microstructural defects (Barber et al., 1981). The composition determined by electron-microprobe analysis corresponds with published data and is low in Fe and Mn (CaO 30.65 wt%; MgO 21.70 wt%; MnO 0.08 wt%; FeO 0.41 wt%).

A disordered sample of Eugui dolomite was obtained by annealing approximately 200 mg of coarsely crystalline powder in closed Pt capsules at 1250°C for 20 min at 15 kbar in a piston-cylinder apparatus. For the quenched sample, no ordering reflections were observed by either X-ray powder diffractometry or single-crystal precession techniques. Reeder and Wenk (1983) refined the structures of single crystals of annealed Eugui dolomite and found significant reordering during quench. Our sample may also have been locally ordered, but X-ray diffraction indicated that no long-range order persisted. Without more detailed structural work, it is difficult to determine the exact state of order of this quenched material.

Lattice parameters for the fully ordered and apparently disordered dolomites are given in Table 1. These were obtained from least-squares refinements of at least 10 reflections using a Guinier camera with Si as an internal standard.

Samples of magnesian calcites with compositions between calcite and the limb of the Ca-rich solvus were prepared initially by precipitation from aqueous mixtures of 4*M* $CaCl_2$ and 4*M* $MgCl_2$ by adding excess concentrated K_2CO_3 solution. The curdy precipitate was filtered and washed with distilled H_2O and dried

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TABLE 1. Compositions, lattice parameters (hexagonal all), and enthalpies of solution of (Ca,Mg)CO_3 phases

Composition, X_{MgCO_3}		Lattice parameters		Enthalpy of solution (kJ/mol $Mg_xCa_{1-x}CO_3$)	
Micro-probe analysis	Wet-chemical analysis	*a* (Å)	*c* (Å)	Solid solution or compund	Mechanical mixture‡
0.500*		4.8066(11)	16.0016(10)	+5.68(8)	−0.06(24)
0.500**		4.8037(15)	16.0721(12)	−1.29(21)	−0.06(24)
0.0174(4)	0.0141(4)	4.9844(16)	17.0382(16)	+10.17(32)	+10.04(38)
0.0464(8)	0.0425(37)	4.9722(8)	16.9827(6)	+10.47(34)	8.92§
0.0604†		4.9663(7)	16.9489(7)	+9.34(32)	7.99(13)
0.0835(16)	0.0895(28)	4.9572(12)	16.9098(10)	—	—
0.1241(44)	0.1231(5)	4.9423(20)	16.8432(20)	+7.30(46)	6.35(18)
0†		4.9902(17)	17.0625(15)	—	—

Note: Number in parentheses is standard deviation of value in last decimal place.

* Eugui dolomite.

** Heat-treated (disordered) Eugui dolomite.

† Estimated from our data shown in Fig. 2.

‡ Mechanical mixture of composition given by wet-chemical analysis when available; otherwise of only composition listed.

§ ΔH_{sol} for mechanical mixture is an estimated value.

at 110°C. This became the starting material for recrystallization in a hydrothermal apparatus at 700°C under 1-kbar CO_2 pressure for at least 2 d. The products of this preparation invariably yielded very sharp X-ray powder reflections. In many runs the strongest peak for dolomite, $(104)_{hex}$, was detectable above background. Since the bulk composition of the starting material was within the single-phase region of the phase diagram at 700°C, it is suspected that the trace quantities of dolomite were acquired during quench or that local compositional heterogeneity led to some small regions of the sample being in the two-phase field. Such samples were discarded, and all calorimetric data reported pertain to samples with no detectable dolomite. Recrystallized samples showed crystals from 10 to 30 μm in diameter. The samples were analyzed by electron microprobe following the suggestions of Essene (1983). Stoichiometry with respect to M^{2+}/CO_3^{2-} ratio was assumed. In addition, wet-chemical analysis, based on EDTA titration (Flaschka, 1953; Capobianco, 1986) was used as a second independent method. The results of the two methods, which are in essential agreement, are shown in Table 1. The microprobe analyses did not detect any heterogeneities in Ca/Mg ratio in the magnesian calcites.

Lattice parameters for magnesian calcites are given in Table 1. They were obtained by methods described above for dolomite.

Mechanical mixtures provided reference enthalpies of solution in the calorimetric solvent and were prepared from reagent-grade $CaCO_3$ and $MgCO_3$ that were separately recrystallized at 700°C and 1-kbar CO_2 pressure in open Pt capsules.

Enthalpy of solution measurements

After preliminary experiments with several aqueous and molten salt solvents at 80–350°C, an aqueous solvent saturated in NaCl and containing 1.0*M* HCl, 0.75*M* $CaCl_2$, 0.25*M* $MgCl_2$ at room temperature was adopted. This acid brine of high ionic strength has a low vapor pressure and low CO_2 solubility, and it dissolves carbonates rapidly and reproducibly at 85°C. Heats of solution were obtained in this solvent using a Tian-Calvet calorimeter operating at 85°C. All samples used for calorimetry were powders of grain size <150 μm. Prior to dissolution, samples were encapsulated in thin-walled Pyrex tubes to prevent prereaction with the corrosive solvent. After thermal equilibrium was attained in the calorimeter, runs were initiated by crushing the Pyrex sample tube. The dissolution was completed within 30 s, but the resulting calorimetric peak lasted between 1 and 2 h because of the long time constant of the large-volume calorimeter used. Further details of the experimental method are found in Capobianco (1986).

No attempt was made to correct for the total dissolved impurities in the natural dolomite sample, which amount to less than 0.5 wt% oxides. The quoted errors on the enthalpies are based on the standard deviations of the means of at least six calorimetric measurements at each composition. The data are shown in Table 1.

As discussed previously (Capobianco, 1986; Capobianco and Havrotsky, 1987; Capobianco et al., 1987), the calorimetric technique used here offers certain simplifications over previous calorimetric cycles used for carbonates. An advantage of this calorimetric solvent is the relatively small magnitude (<30 kJ/mol) of the experimental heats of solution. A potential disadvantage is the complexity of ionic interactions in this multicomponent, hot aqueous solution, to which the laws of dilute solution may not apply. To permit unequivocal interpretation of the enthalpies of solution, several precautions were taken. The excess enthalpy of the (partially) disordered sample was found by the difference in heats of solution between that sample and the fully ordered dolomite. Similarly, the enthalpy of mixing in the magnesian calcites and in dolomite was found as the difference between the enthalpies of solution of the sample and of a mechanical mixture of $CaCO_3$ and $MgCO_3$ at the same composition. In all cases, the volume of solvent and the mass of all samples dissolved were held strictly constant for all runs (40.0-mg samples were dissolved in 10.0 mL of solvent). This procedure made it unnecessary to correct for the work done in CO_2 evolution or to unravel the complex chemical interactions with the solvent, since the dissolution process was the same for reactants and products. Furthermore, the rapid dissolution process and small size of the sample assured a fast and complete reaction. The reproducibility of the data supports the reproducibility of the final state.

We believe that the rates of solution of all samples used were similar (complete dissolution in a few seconds) as long as material of similar fine grain size was used. Coarse material tended to give less-reproducible results, perhaps because of irregularities of CO_2 evolution. One might be concerned whether any H_2O may be carried away with the vaporizing CO_2, having an unknown effect on the measured enthalpy of reaction. Once more, the strict control of experimental conditions (constant sample size, amount of solvent, ampoule geometry, fine powdered samples) would tend to make any such effect constant if it were present at all. Such an effect would then cancel between reactants and products and not affect the heats of formation. We note (Capobianco, 1986) that this method successfully reproduced the enthalpy of the calcite-aragonite transition. For the above reasons we think that differences, discussed below, between our values and earlier estimates of the enthalpy of formation of dolomite cannot be explained by any problems of controlling gas evolution in our work.

RESULTS AND DISCUSSION

Dolomite

The enthalpy of formation of dolomite from calcite and magnesite is expressed by (per 1 mol carbonate)

$$0.5CaCO_3 + 0.5MgCO_3 = Ca_{0.5}Mg_{0.5}CO_3. \qquad (1)$$

For ordered Eugui dolomite, the enthalpy of Reaction 1 is -5.74 ± 0.25 kJ/mol. This value compares favorably with an earlier estimate of -6.07 kJ/mol (Stout and Robie, 1963) derived from consideration of decomposition phase equilibria. It is, however, in marked contrast to the value one calculates from the tabulated data of Robie et al. (1978), which give only -1.88 kJ/mol. This latter value is based in part on unpublished solution calorimetric data in combination with decomposition phase equilibria for $MgCO_3$ (Bruce Hemingway, USGS, Reston, Virginia, pers. comm., 1984). Hemingway has suggested that the source of the discrepancy might arise from imprecisely known P-T points for $MgCO_3 = MgO + CO_2$. We recommend our new value since it was obtained directly by comparison of the heat of solution of dolomite with that of an equal amount of an isocompositional mechanical mixture of $MgCO_3$ plus $CaCO_3$. Thus in our work, the heats of solution for both sides of Reaction 1 have been measured and compared directly. We cannot compare our calorimetric technique and samples to those used in previous solution calorimetry since the details of that work have not been published.

The Eugui dolomite, which had been quenched from 1250°C and which showed no ordering reflections, has an enthalpy of formation of $+1.23 \pm 0.32$ kJ/mol. Thus the formation of the ordered phase from $CaCO_3$ and $MgCO_3$ is exothermic, that of the apparently disordered phase is endothermic, and the difference between the heats of solution of ordered and disordered phases, namely the enthalpy of disordering, is 6.97 ± 0.22 kJ/mol. However, because the dolomite samples may have acquired some short-range order during quench and because other studies (Reeder and Wenk, 1983) could not quench crystals without ordering reflections (as we seem to have done), we regard this value as a lower limit to the disordering enthalpy. The present data confirm that the degree of cation order has a very significant influence on the energetics.

The fact that the ordered phase has a negative heat of mixing from the end members, whereas the disordered phase has a positive heat of mixing, is important for developing models of the order-disorder reaction. A simple Bragg-Williams model is ruled out by the positive enthalpy of mixing in the disordered phase (Burton, 1987; Capobianco et al., 1987) because such a model, with only one energy parameter, can account only for negative heats of mixing that lead to ordering. Dolomite has an analogue in the Cd compound, $CdMg(CO_3)_2$, for which, for the reaction

$$0.5CdCO_3 + 0.5MgCO_3 = Cd_{0.5}Mg_{0.5}CO_3, \qquad (2)$$

$\Delta H = -2.82$ kJ/mol for the ordered phase and $+4.06$ kJ/mol for the disordered phase (Capobianco et al., 1987). In $Cd_{0.5}Mg_{0.5}CO_3$ the critical temperature for disordering is 800–850°C (Goldsmith, 1972), quenching of cation distribution does not seem to be a problem, and phases of intermediate states of order have been studied by X-ray diffraction and calorimetry (Capobianco et al., 1987). The phase diagram, order parameter, and heats of mixing could be qualitatively explained by models based on the generalized point approximation of the Bragg-Williams type or on the tetrahedron approximation of the cluster-variation method. In such models, negative interlayer interactions are balanced by positive intralayer interactions (Burton, 1987; Capobianco et al., 1987). However, the details of the enthalpy and order-parameter behavior could not be accounted for quantitatively by the models used. For $CaMg(CO_3)_2$, the exact site occupancies of the apparently disordered phase remain uncertain, and we do not attempt further model calculations. Nevertheless, the similarity between $CaMg(CO_3)_2$ and $CdMg(CO_3)_2$, first noted by Goldsmith (1972), is supported by these data. Both systems show negative heats of formation of ordered phases and positive heats of formation of disordered phases at $X = 0.5$.

Magnesian calcites

The data, given in Tables 1 and 2 and Figure 1, can be fit by a one-parameter or a two-parameter equation:

$$\Delta H^{mix} = X(1 - X)(-20.37 \pm 13.39) \qquad (3)$$

or

$$\Delta H^{mix} = X(1 - X)[-25.65 \pm 5.94 + (88.49 \pm 49.71)X], \qquad (4)$$

where X is the mole fraction of $MgCO_3$ and ΔH^{mix} is in kilojoules per mole of $Ca_{1-X}Mg_XCO_3$. The errors given were obtained by a Monte Carlo method after Anderson (1976) and are fairly large. There is no significant statistical difference in quality of fit between the two equations. Both equations imply that (1) the system $MgCO_3$-$CaCO_3$ shows exothermic heats of mixing at compositions $0.01 < X < 0.13$ and (2) this exothermic behavior is beyond the uncertainty of the measurements. For dolomite compo-

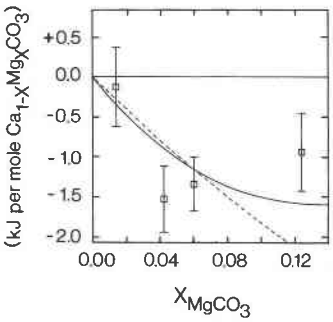

Fig. 1. Enthalpy of mixing (kJ/mol of $Mg_xCa_{1-x}CO_3$) in magnesian calcites. Solid line represents ideal mixing; solid curve represents data fit by Eq. 3; dashed curve represents data fit by Eq. 4.

sition, Equation 3 gives an exothermic heat of mixing of −5.1 kJ/mol, whereas Equation 4 gives an endothermic +4.6 kJ/mol. The apparently disordered dolomite studied shows an endothermic heat of mixing of +1.2 kJ/mol; ordered dolomite shows a heat of mixing of −5.8 kJ/mol. Should the magnesian calcites in this study be regarded as disordered solid solutions with random substitution of Mg into all Ca layers? If so, then Equation 4 may be a better description of their energetics, since it is consistent with positive heats of mixing at higher Mg contents. But then the negative heats of mixing observed for $X < 0.12$ would have no ready explanation, since size mismatch between Ca and Mg would be expected to lead to destabilization and positive heats of mixing [see Newton and Wood (1980) and Davies and Navrotsky (1983) for discussions of systematic trends in solid-solution energetics].

Positive deviations from ideal activity-composition relations have been suggested for magnesian calcites (Gordon and Greenwood, 1970). Negative heats of mixing coupled with positive or ideal excess free energies imply negative excess entropies of mixing. Such behavior, suggestive of substantial short-range order or structural complexity in solid solutions, has been observed in NiO-MgO (Davies and Navrotsky, 1981) and in $MgAl_2O_4$-$Al_{8/3}O_4$ defect-spinel solid solutions (Navrotsky et al., 1986). Perhaps some analogous complexity exists in these synthetic magnesian calcites.

Further evidence comes from two sources: an estimate of entropies of mixing and the variation of lattice parameters with composition. Gordon and Greenwood (1970) studied the reaction dolomite + quartz + water = talc + calcite + carbon dioxide. To characterize the thermodynamics of the Mg-containing calcite phase, they analyzed the carbonate-decomposition data of previous workers. They obtained a two-parameter equation for ln γ_{MgCO_3} that showed no temperature dependence (with rather large scatter in the data) in the range 600–800°C at compositions $X \leq 0.18$. The expression for the integral excess free energy of mixing consistent with their equations is

$$\Delta G^{ex,mix} = RT[X(1 - X)(2.172 - 0.948X)]. \quad (5)$$

TABLE 2. Mixing parameters for magnesian calcites, $Mg_xCa_{1-x}CO_3$

X_{MgCO_3}	Enthalpy of mixing* (kJ/mol $Mg_xCa_{1-x}CO_3$)	Estimated entropy of mixing§ ($J \cdot K^{-1} \cdot mol^{-1}$)	
		Excess	Total
0.0141	−0.13(50)**	−0.38	+0.23
0.0425	−1.50(50)**	−2.26	−0.80
0.0604	−1.35(35)**	−2.39	−0.49
0.1241	−0.95(49)**	−2.83	+0.28
0.500	−5.74(25)†	—	—
0.500	+1.23(32)‡	—	—

* Number in parentheses is standard deviation of value in last decimal place.

** Magnesian calcite.

† Eugui dolomite.

‡ Heat-treated Eugui dolomite.

§ Calculated as described in text. Uncertainty is about ±1 $J \cdot K^{-1}$.

Assuming that this equation applies to our carbonates at their synthesis temperature, we can estimate entropies of mixing as follows:

$$\Delta S^{ex,mix} = \frac{\Delta H^{mix} - \Delta G^{ex,mix}}{T} \quad (6)$$

and

$$\Delta S^{mix} = \Delta S^{ex,mix} - R[X \ln X + (1 - X)\ln(1 - X)]. \quad (7)$$

The results are shown in Table 2, where our actual heats of mixing (not values from either polynomial fit) were used in Equation 6. The uncertainties in the calculated entropies are hard to judge, since the systematic and statistical errors in Equation 5, which represents a fit to polythermal data, cannot be evaluated readily. On the basis of uncertainties in ΔH alone, the uncertainties in ΔS are on the order of ±1 $J \cdot K^{-1}$. Despite these uncertainties, the data support significantly negative excess entropies of mixing. The total entropies of mixing (formation of magnesian calcites from $MgCO_3$ and $CaCO_3$) are zero within experimental error. This result argues either for a large negative excess vibrational entropy or for a much diminished configurational contribution.

There have also been a number of attempts to deduce magnesian calcite stabilities from their dissolution in aqueous solution in both equilibrium and kinetics experiments [for reviews, see Mackenzie et al. (1983) and Walter and Morse (1984)]. We believe that the activities derived from these studies are generally more uncertain than those obtained from the high-temperature studies (Gordon and Greenwood, 1970) and have not used them to compute entropies. Since these aqueous-solution data also generally suggest positive deviations from Raoult's law in the system $CaCO_3$-$MgCO_3$, they qualitatively support the negative excess entropies derived above.

The crystallographic data are also suggestive (see Fig. 2). Our data for magnesian calcites show negative volumes of mixing with respect to calcite and magnesite (dashed line) but virtually ideal volumes of mixing with

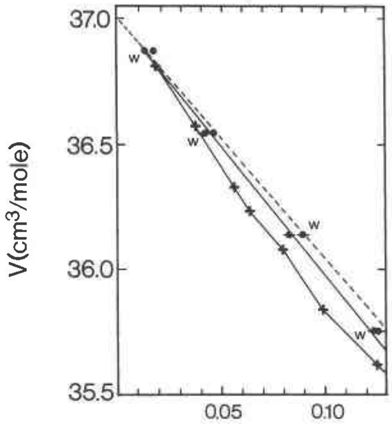

Fig. 2. Molar volumes of magnesian calcites vs. mole fraction $MgCO_3$. Crosses and jagged line represent data of Bischoff et al. (1983). Solid circles represent present data; those marked with "w" are based on wet-chemical analysis; those not marked are based on microprobe analysis (see Table 1). Horizontal bar through symbol indicates that computational uncertainty is greater than symbol size. Dashed line represents ideal volume of mixing between calcite and magnesite; solid line represents ideal volume of mixing between calcite and dolomite.

respect to calcite and dolomite (solid line). Bischoff et al. (1983) have reported even more negative volumes of mixing than our data suggest. The reason for this difference is unclear.

The following hypothesis would explain the enthalpy, entropy, and volume data for the magnesian calcites but is, we stress, unsupported by any direct structural work. If Mg clustered mainly into selected cation layers rather than substituting randomly for Ca, a structure more closely related to dolomite than to calcite could form. This structure would have Ca layers randomly interspersed with Mg-rich layers. For $X = 0.1$, for example, one layer in nine, on the average, would be a Mg-rich layer. We emphasize that such Mg-rich layers would occur at random in the stacking sequence. Some stabilization energy, arising from the dolomite-like arrangement of this Mg-rich layer and its two neighboring Ca layers, could lead to a negative heat of mixing. The entropy of mixing would be negligible, since the mixing of layers would represent a nearly two-dimensional rather than a three-dimensional problem. The volumes would fall near the weighted average for calcite and dolomite.

Bischoff et al. (1983, 1985) studied several series of synthetic and biogenic magnesian calcites, finding significant differences in lattice parameters and vibrational spectra between these two groups of materials. Mackenzie et al. (1983) have referred to unpublished calorimetric data of Wollast and Loijens that suggest positive enthalpies of mixing in biogenic magnesian calcites. The differences between biogenic materials precipitated near room temperature and synthetic materials annealed above 500°C could reflect differences in local order, with the biogenic materials having greater (Ca,Mg) disorder. However, the differences in calorimetric results could also reflect differences in sample purity, grain size, or calorimetric technique. Because only the data from calorimetric studies on biogenic calcites have been quoted (Mackenzie et al., 1983) but the details of sample characterization and calorimetric procedure have not been published, it is inappropriate to speculate further on possible reasons for the different results. Further study is needed.

Our data tentatively suggest that the energetically stable way of putting Mg into calcite is by introducing random stacking of Mg-rich layers between Ca layers rather than random substitution of Mg for Ca. The biogenic materials may be metastable relative to this layered structure. The latter could well be stable at the temperature of synthesis (700°C), although we cannot rule out its being a quench product.

High-resolution electron microscopy of natural calcites and dolomites reveals a wealth of microstructures, dislocations, and modulated structures (see Wenk et al., 1983, for a summary). In calcian dolomites, extra reflections in diffraction patterns may be associated both with cation ordering within a basal layer and with periodic stacking of extra Ca-rich basal layers to accommodate the nonstoichiometry (Van Tendeloo et al., 1985). The model we propose for synthetic magnesian calcites would be analogous to the latter.

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