

Immiscible fluids in metamorphism: Implications of two-phase flow for reaction history

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ABSTRACT

Fluid immiscibility between a CO₂-rich fluid and brine has been described from several medium- to high-grade marbles and calc-silicates. Here we also report evidence for CH₄-H₂O immiscibility in low-grade metamorphic rocks from Wales and suggest that the flow of such immiscible fluids may be comparable to that of water-oil or water-gas mixtures in petroleum reservoirs. This analogy implies that where one fluid is being produced by reaction it will flow out of the rock while the other remains immobile, except insofar as it is soluble in the more abundant fluid phase. Hence, extensive reaction may take place in the presence of coexisting immiscible fluids, each having high activities. It is proposed that this type of flow behavior not only accounts for the development of salt-saturated fluids in marbles but also may be responsible for the elimination of carbonate and extensive loss of graphite from pelites in the lower part of the greenschist facies.

INTRODUCTION

In many studies of the role of fluids in metamorphic processes, it has been assumed that any fluid present occurs as a single phase only, irrespective of compositions. This is a reasonable assumption where one fluid species dominates (as is commonly the case); however, fluids with significant fractions of both water and a nonpolar species (CO₂, CH₄, or N₂) may display immiscibility under subgreenschist facies conditions. Furthermore, microthermometric analysis of metamorphic fluid inclusions almost invariably demonstrates the presence of dissolved salts in aqueous fluids that extend the immiscibility between CO₂ and H₂O to higher temperatures (Gehrig et al., 1979).

The implications of CO₂-H₂O immiscibility for phase equilibria in carbonate rocks have been explored by Bowers and Helgeson (1983a) and Skippen and Trommsdorff (1986); we show here, however, that when the physical flow characteristics of two-phase fluids are also taken into account, it is apparent that the progress of metamorphism in rocks with two fluids may be very different from that predicted by single-fluid models. Trommsdorff and Skippen (1986) have suggested that separation of a CO₂-rich vapor plays an essential part in the formation of salt-bearing tremolite marbles, and they considered that low density and viscosity cause the CO₂ to "boil off." Our approach is to apply the semiempirical principles developed for petroleum reservoir engineering, which allow general prediction of two-phase flow behavior, and to show, for example, that the type of behavior opposite to that described by Trommsdorff and Skippen is also possible.

EVIDENCE FOR IMMISCIBLE METAMORPHIC FLUIDS

The main evidence for fluid immiscibility in metamorphism comes from fluid-inclusion studies. At medium to high grades, examples are mostly from calc-silicates and marbles (Crawford et al., 1979; Sisson et al., 1981; Mercolli, 1982; Trommsdorff et al., 1985). This is presumably because the high salinities necessary for fluid immiscibility at these

temperatures are only likely to be brought about by reactions that consume H₂O, causing an increase in the salinity of the residual fluid, and these are only common in carbonate-bearing rocks at medium to high grade.

Some reports of fluid immiscibility in calc-silicates are ambiguous and merely demonstrate that different fluids were trapped at the same *P-T* conditions. Given that inclusions are trapped instantaneously—relative to the duration of metamorphism—this does not preclude the possibility that different fluids in separate inclusions, although trapped under the same conditions, may never have coexisted (Yardley, 1983). Ramboz et al. (1982) have established rigorous criteria to determine if distinct inclusion fluids once coexisted immiscibly. The most important of these criteria is that each fluid should homogenize at the same temperature, close to that of original trapping. This is because where two fluids coexisted but were trapped separately, the composition of each lies on the solvus at the trapping temperature. Each fluid-inclusion population will unmix into two phases on cooling and must be restored to the trapping temperature before it can revert to a single phase. When two types of fluid inclusion containing the same fluid phases in different proportions yield almost identical homogenization temperatures, this constitutes powerful evidence for an originally immiscible pair of fluids.

This criterion is met by the samples studied by Trommsdorff et al. (1985), Mercolli (1982), and Pecher (1979), and by the samples described below, but not by the samples studied by Sisson et al. (1981). Nevertheless, Sisson et al. clearly showed the existence of hypersaline metamorphic brines that would have been immiscible with CO₂, and it is possible that the compositions of original immiscible fluids were merely modified during transport before trapping.

Fluid immiscibility might be expected to be more common at very low metamorphic grades because CO₂ and H₂O are immiscible below about 300 °C even in the absence of salt (Takenouchi and Kennedy, 1964). Synmetamorphic quartz veins in prehnite-pumpellyite-grade sandstones and quartzites of the Harlech Dome, Wales (Matley and Wilson, 1943), primarily contain H₂O fluid inclusions, but in the graphitic lithologies there are also CH₄-bearing fluids (Bottrell, 1986) that show evidence of immiscibility. The aqueous fluid in these mixed inclusions is moderately saline (equivalent salinity 3–14 wt%). Coexisting CH₄-rich and H₂O-rich fluids are found in both synmetamorphic quartz veins and late-metamorphic mineralized quartz veins of the Dolgellau gold belt; results from both types of sample are summarized in Table 1. Within any one sample, both CH₄-rich and H₂O-rich inclusions yield similar temperatures of final homogenization (*T_h*), although H₂O-rich inclusions usually show a greater spread to lower *T_h* values, perhaps reflecting easier resetting. The upper values of *T_h* from the metamorphic veins are in good agreement with values for prehnite-pumpellyite facies metamorphism as required by the criteria of Ramboz et al. (1982). There are considerable differences between samples of mineralized veins, but in each the *T_h* values of CH₄-rich and H₂O-rich inclusions are similar; the variability may result from temperature differences between wall rocks and the incoming mineralizing fluid (Bottrell, 1986).

TABLE 1. SUMMARY OF DATA ON MIXED CH₄-H₂O FLUIDS IN QUARTZ VEINS FROM THE GRAPHITIC CLOGAU SHALES, NORTH WALES

Sample number	CH ₄ -rich inclusions*		H ₂ O-rich inclusions†		Bulk fluid compositions#			
	No. measured	T _h range (°C)	No. measured	T _h range (°C)	H ₂ O	CO ₂	CH ₄	N ₂
Metamorphic veins								
19C	0	--	23	209 - 335	97.2	0.24	2.12	0.34
46H	5	305 - 365	5	252 - 358	98.8	0.18	0.84	0.14
Mineralized veins**								
80.7	2	314 - 319	3	309 - 327	98.2	0.32	0.80	0.64
128C	3	247 - 260	11	225 - 275	97.0	0.36	2.07	0.41
128TE	6	300 - 324	4	295 - 320	95.2	0.20	3.09	1.04
128D:UM	0	-	10	232 - 285	97.8	0.45	1.03	0.65
128H	2	254 - 270	10	216 - 273	96.5	0.57	1.61	0.99
125C	7	287 - 342	14	259 - 340	97.8	0.15	1.75	0.28
130B	3	271 - 284	6	261 - 280	98.1	0.24	1.26	0.35

Note: Scarcity of data on metamorphic veins is because such veins are extremely rare in graphitic lithologies.

* Typically 80% CH₄ at 25 °C.

† Typically 5-15% CH₄ at 25 °C.

Includes all fluid-inclusion generations, determined by decrepitation and mass spectrometry.

** Samples 80.7, 128C, 128TE, 128D:UM, and 128H are from Clogau-St. Davids mine; sample 125C is from Nantgoch mine; sample 130B is from North Figra mine.

The homogenization temperatures presented in Table 1 provide clear evidence for the occurrence of immiscible CH₄- and H₂O-rich fluids in low-grade graphitic rocks during both regional metamorphism and subsequent mineralization. Data on other nongraphitic lithologies suggest that they were dominated by an aqueous fluid during metamorphism. Where reactions involving carbonate minerals are important, H₂O-CO₂ immiscible fluids might also be expected at low metamorphic grades.

It is evident from our own work and previous studies that fluid immiscibility may be a fairly common phenomenon in low-grade metamorphism and may persist to high grades, especially in calc-silicates and marbles.

FLOW BEHAVIOR IN IMMISCIBLE FLUIDS

Immiscibility has a profound effect on the flow of fluids through rocks because each fluid phase tends to behave independently. If one fluid is much less abundant, it occurs as isolated globules suspended within the other or adhering to grain surfaces, according to its wetting characteristics. The minor fluid phase occupies isolated volumes within the dominant fluid that are not interconnected, and so the rock is effectively impermeable with respect to that phase, provided the interconnections of the pores in the rock are not much larger than individual fluid globules. To use the terminology of the petroleum engineering literature (e.g., Langnes et al., 1972; Archer and Wall, 1986), effective impermeability is attained when the saturation (*S*) of the pore or crack space with respect to a fluid *i* (defined as the fraction of pore space occupied by *i*) is at or below an irreducible saturation level (*S*_{*i*, irr}). Values of *S*_{*i*, irr} are typically about 0.2, somewhat higher in the case of the wetting phase. If a fluid forms a continuous film through the pore and crack space, it can flow in response to pressure gradients, but the presence of another immiscible phase effectively constricts the apertures available for it to pass through, reducing effective permeability. For example, when it is the nonwetting phase that is the less abundant, individual droplets appear to be held back by constrictions in the pore network while the enveloping fluid flows around them at a reduced rate.

The flux of fluid through a rock in response to a given pressure gradient is a function of the permeability of the rock (*k*) and the kinematic

viscosity of the fluid. The effect of a second fluid on the flux of *i* can be described in terms of the relative permeability of the rock with respect to *i*: *k*_{*r,i*}. The relative permeability (*k*_{*r*}) is defined as

$$k_{r,i} = k_i/k,$$

where *k*_{*i*} is the effective permeability of the rock with respect to *i*. As *S*_{*i*} → 1, so *k*_{*i*} → *k* and *k*_{*r,i*} → 1; however, as *S*_{*i*} → *S*_{*i*, irr}, so *k*_{*i*} and *k*_{*r,i*} → 0.

Although this treatment was developed for mixtures of oil, gas, and water at temperatures to 250 °C, its simple physical basis means that it will be generally applicable to a wide range of geologic settings. In particular, our metamorphic interpretations are based on the observation that a fluid phase becomes immobile when its saturation level falls below the irreducible saturation value. Because *k*_{*i*} = 0 in this condition and no flow occurs, variable contrasts in viscosity between fluids will not influence the conclusions.

IMPLICATIONS OF TWO-PHASE FLOW FOR REACTION PATHWAYS

When two fluid components occur as two immiscible fluids, the activity of each is higher than if only a single mixed fluid were present, and this influences phase equilibria involving solids. Furthermore, the addition of an extra phase means that divariant reactions may become univariant, producing a distinct isograd. In this section we explore two possible situations where extensive reaction can take place in the presence of an immiscible fluid pair because of the immobility of the minor fluid phase. In addition, direct production of an immiscible pair of fluids by a single reaction would also allow extensive reaction with two fluids present.

Decarbonation in the Presence of H₂O

Figure 1 illustrates the progression of an internally buffered decarbonation reaction in a rock with an initially water-rich fluid, *A*, under conditions where CO₂ and H₂O are immiscible. Fluid leaves the system as the decarbonation reaction takes place. Reaction commences at *T*_{*A*} in the presence of a single fluid phase and continues with rising temperature to *T*_{*B*}. At *T*_{*B*} the fluid separates into a CO₂-rich "vapor" phase and an

H₂O-rich "liquid" phase (terminology of Skippen and Trommsdorff, 1986). Reaction will continue at T_B so long as a discrete liquid phase remains. Initially, both fluids will flow out of the rock at T_B , but as the CO₂-rich phase becomes volumetrically more abundant due to reaction, so S_{H_2O} falls to the irreducible value. The aqueous phase is then immobile, and water is further removed only by solution in the CO₂-phase, which may be an inefficient process.

Figure 1 is simplified; it cannot show the effect of the salinity of the aqueous phase, which may increase if H₂O is dissolved preferentially into the vapor, thereby enlarging the miscibility gap. We have also carried out a numerical model based on the H₂O-CO₂ solvus of Bowers and Helgeson (1983b) for NaCl-bearing systems. We set the ratio NaCl/H₂O equal in both vapor and liquid, in the absence of other constraints, and chose $S_{CO_2, irr} = 0.2$, and $S_{H_2O, irr} = 0.4$. We then modeled a progressive decarbonation reaction by setting the initial pore volume = 1 and allowing the volume to expand by a fraction x until an episode of fluid loss occurred, when the pore space deflated back to the initial value. As a simplification, we assumed that whichever fluid phase had the greater value of $k_{r,i}$ would flow exclusively, an assumption that minimizes the effect we seek to demonstrate. For conditions of $P = 2$ kbar, or $T = 350$ °C, we have calculated the volume of CO₂ released by reaction in the presence of a liquid, water-rich phase, relative to the initial pore volume. Results at two initial salinities and for a range of values of x are shown in Table 2.

We lack the information to judge which, if any, of our model parameters have the most realistic values. In particular, the porosity of a rock undergoing metamorphism is not known. Very small values are probably unrealistic because rocks must achieve appreciable porosity in order to be sufficiently permeable for fluid to escape as it is released by reaction. Yardley (1986) estimated a permeability value of about $10^{-19} m^2$. A porosity of about 1% is probably realistic; it is clear from Table 2 that, depending on the appropriate value of x , appreciable volumes of CO₂ may be produced in the presence of two fluid phases. Much more work needs to be done, however, before these calculations can be made reliable.

Open System Hydration-Decarbonation

Infiltration of saline H₂O and release of CO₂ due to a hydration-decarbonation reaction can continue indefinitely under two-phase conditions, provided that the rate of inflow of H₂O is slow and is the

rate-limiting step for the reaction. Otherwise, excess water prevents sufficiently high salinities being attained for immiscibility; in either case, reaction continues until infiltration ceases or all reactants are consumed. However, carbonation-dehydration reactions, even if they commence with two fluids present, will rapidly dilute the salt content of the aqueous phase and eliminate the miscibility gap, unless temperatures are below the solvus in the salt-absent system.

A TEST FOR THE MODEL

We have proposed that, where two immiscible fluids coexist, whichever is being produced by reaction will tend to move out of the rock and leave the other behind. Alternatively, if fluids are expelled in response to recrystallization or deformation, the more abundant will probably move independently of the minor phase. Secondary planes of fluid inclusions contain fluids that were trapped as they moved and should therefore normally contain only one of the fluids of the immiscible pair. This is observed in most cases, and it is implicit that this is so in the criteria for recognizing fluid immiscibility developed by Ramboz et al. (1982), used successfully here. If some of the CH₄-H₂O inclusions whose homogenization temperatures are summarized in Table 1 had been trapped as two-phase inclusions, then there would be a broad spectrum of homogenization temperatures above those of trapping up to the crest of the solvus. Whereas such intermediate inclusions sometimes occur (Pecher, 1979), and would be anticipated if for both phases $S > S_{irr}$, their extreme rarity shows that, in general, immiscible fluids move separately. Bodnar et al. (1985) found that, over a few millimetres in an experimental capsule, two-phase fluids were able to separate very effectively.

EXAMPLES OF THE INFLUENCE OF TWO-PHASE FLOW ON THE DEVELOPMENT OF METAMORPHIC ROCKS

The only example of the importance of two-phase flow for the development of metamorphic rocks considered to date is in the formation of salt-bearing tremolite in marble, discussed by Trommsdorff and Skippen (1986). Dolomite and quartz, present originally, reacted with infiltrating water to produce tremolite and CO₂, which moved away preferentially. In the light of our analysis, it is clear that this process must be more complex than they envisaged, because if CO₂ is the abundant phase and is moving out of the rock preferentially, H₂O is effectively immobile. However, infiltration of H₂O is a prerequisite for the reaction to take place. Reaction may have occurred in spurts, with infiltration along cracks of H₂O from a

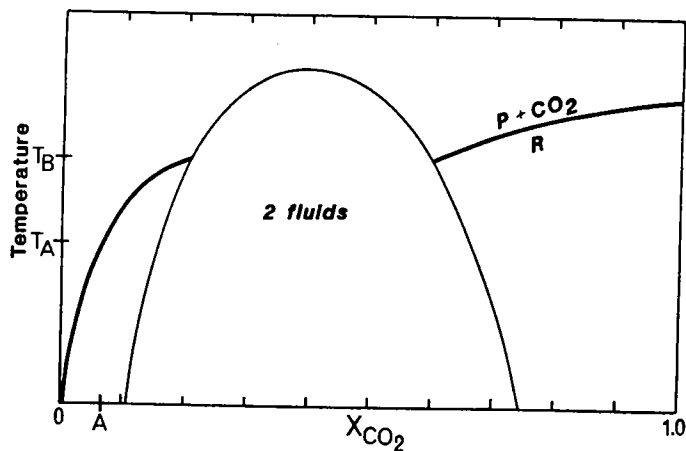


Figure 1. Schematic T - X_{CO_2} diagram to illustrate progression of decarbonation reaction with heating under conditions of CO₂-H₂O immiscibility. Reaction $R \rightarrow P + CO_2$ commences at temperature T_A for initial fluid composition A. At T_B , fluid splits into two immiscible phases.

TABLE 2. VOLUMES OF CO₂ PRODUCED UNDER TWO-PHASE CONDITIONS, NORMALIZED TO INITIAL PORE VOLUME

pore size increment (x)*	Initial fluid (weight ratios)	
	$\frac{NaCl}{H_2O + NaCl} = 0.06$	$\frac{NaCl}{H_2O + NaCl} = 0.12$
0.10	1.00	0.70
0.25	1.50	1.25
0.50	2.00	2.50
0.75	2.25	2.25
1.00	3.00	3.00
1.25	2.50	6.25
1.50	4.50	6.00

*x = fraction by which initial pore volume expands prior to an episode of fluid loss.

reservoir at fairly constant fluid pressure leading to reaction and "blow-back" of CO₂ down the cracks as it was rapidly produced. Once an increment of H₂O was consumed and the reaction stopped, a further incremental infiltration of H₂O would be possible.

Another possible example may be in the elimination of graphite and carbonate from many rock types in the lower part of the greenschist facies. Ferry (1984) pointed out that below the biotite isograd many pelites contain appreciable amounts of carbonates, but these carbonates are absent at higher grade. Hence, many pelites undergo decarbonation without dehydration near this isograd, and the mineral assemblages require a high value for water activity (a_{H_2O}). Ferry interpreted his results as indicating that the decarbonation was a consequence of the influx of large amounts of externally derived H₂O-rich fluid, but fluid immiscibility allows an alternative explanation. If immiscible fluids were present in the chlorite zone, then CO₂ generated by decarbonation reactions near the biotite isograd could have left the rock while a small amount of an H₂O-rich fluid remained immobile so that a_{H_2O} was high and dehydration was inhibited. At the low temperature involved, dissolution of H₂O in CO₂ would be strongly inhibited once the salinity of the aqueous phase began to rise. How likely is it that immiscible fluids would have developed in these rocks? Gehrig et al. (1979) reported that only 6 wt% NaCl extends the CO₂-H₂O solvus to 380 °C at 2 kbar, and this compares with values of 3–14 equivalent wt% NaCl from the veins we have studied in the Harlech Dome. Other fluid components such as N₂ and CH₄ would also extend immiscibility. Furthermore, Ferry reported that the net reactions at the biotite isograd actually involve hydration as well as decarbonation, and as we have shown above, this provides optimum conditions for immiscible fluids to develop.

Although precise data are hard to come by, fluid immiscibility may also play a role in the marked reduction of the amount of graphite in metasedimentary rock in the greenschist facies. Graphite is found in a wide range of rock types in the chlorite zone of the Dalradian series of Scotland and Ireland, but it appears to be much more restricted in the amphibolite facies. Hence, extensive low-grade dewatering as clays recrystallized to chlorite and muscovite was not accompanied by major breakdown of graphite, whereas dewatering at higher grades led to extensive loss of graphite. This could be explained by the persistence of a separate CH₄-rich phase in the low-grade rocks, inhibiting breakdown of graphite; once the metamorphic fluid became single phase at higher temperatures, dewatering would be accompanied by loss of carbon as methane.

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