

C–O–H–S fluid composition and oxygen fugacity in graphitic metapelites

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ABSTRACT C–O–H fluid produced by the equilibration of H₂O and excess graphite must maintain the atomic H/O ratio of water, 2:1. This constraint implies that all thermodynamic properties of the fluid are uniquely determined at isobaric–isothermal conditions. The O₂, H₂O and CO₂ fugacities (f_{O_2} , f_{H_2O} and f_{CO_2}) of such fluids have been estimated from equations of state and fit as a function of pressure and temperature. These fugacities can be taken as characteristic for graphitic metamorphic systems in which the dominant fluid source is dehydration, e.g. pelitic lithologies. Because there are no compositional degrees of freedom for graphite-saturated fluids produced entirely by dehydration, the variance of the dehydration process is not increased in comparison with that in non-graphitic systems. Thus, compositional ‘buffering’ of C–O–H fluids by dehydration equilibria, a common petrological model, requires that redox reactions, decarbonation reactions or external, H/O \neq 2, fluid sources perturb the evolution of the metamorphic system. Such perturbations are not likely to be significant in metapelitic environments, but their tendency will be to increase the f_{O_2} of the fluid phase. At high metamorphic grades, pyrite desulphidation reactions may cause a substantial reduction of f_{H_2O} and slight increases in f_{O_2} and f_{CO_2} relative to sulphur-free fluid. At low metamorphic grade, sulphur solubility in H/O \leq 2 fluids is so low that pyrite decomposition must occur by sulphur-conserving reactions that cause iron depletion in silicates, a common feature of sulphidic pelites. With increasing temperature and sulphur solubility, pyrite desulphidation may be driven by dehydration reactions or infiltration of H₂O-rich fluids. The absence of magnetite and the assemblages carbonate + aluminosilicate or pyrite + pyrrhotite + ilmenite from most graphitic metapelites is consistent with an H/O = 2 model for GCOH(S) fluid. For graphitic rocks in which such a model is inapplicable, a phase diagram variable that defines the H/O ratio of GCOH(S) fluid is more useful than the conventional f_{O_2} variable.

Key words: C–O–H–S fluids; desulphidation; devolatilization; graphitic rocks; oxygen fugacity.

INTRODUCTION

Ohmoto & Kerrick (1977) argued that the presence of graphite in rocks undergoing dehydration would cause the composition of coexisting C–O–H fluid to be buffered toward its maximum equilibrium H₂O content. More rigorous arguments presented here show that during simple dehydration, graphite-saturated C–O–H (GCOH) fluids are generated with, rather than buffered toward, the maximum thermodynamic activity of H₂O. This condition corresponds to the fluid composition at which the atomic H/O ratio is that of water, 2:1. To the degree that such a fluid can be regarded as representative of metamorphic fluids, its properties can be used to estimate the fugacities and concentrations of C–O–H species during the metamorphism of graphitic H₂O-dominated systems, a model often appropriate for metapelitic lithologies. A similar approach can be adopted to treat graphite-

saturated C–O–H–S (GCOHS) fluids generated by dehydration and pyrite desulphidation. This communication reports the properties of H/O = 2 C–O–H–S fluids and briefly considers some of their mass-balance and phase-equilibrium implications for dehydration and desulphidation in graphitic metapelites.

FLUID EQUATIONS OF STATE

The speciation of GCOHS fluids was computed at specified H/O ratio and sulphur fugacity assuming the significant fluid species to be H₂O, CO₂, CH₄, CO, H₂ and H₂S (cf. Ohmoto & Kerrick, 1977; Taylor & Green, 1987; Poulson & Ohmoto, 1989). Fugacities of the pure H₂O, CO₂ and CH₄ species were calculated with the HSMRK equation (Jacobs & Kerrick, 1981; Kerrick & Jacobs, 1981). The fugacities of H₂S, H₂ and CO, and the activities of all species, were computed with the MRK equation popular-

ized by Holloway (1977, 1981). At low temperature, the MRK H_2O -dispersion term ($\bar{a}_{\text{H}_2\text{O}}$) used by Holloway is suited only for subcritical pressures. Therefore, for calculations at $T < 738$ K, the expression $\bar{a}_{\text{H}_2\text{O}}$ ($\text{bar cm}^6 \sqrt{\text{K mol}^{-1}}$) = $-0.22894 \times 10^8 + 0.5188369 \times 10^6 T - 0.67665 \times 10^3 T^2 + 0.28623 T^3$ was used. This expression was derived from the data of Burnham *et al.* (1969) for $T = 373$ – 738 K at $P = 2$ kbar. The MRK parameter b_{H_2} ($15.7699 \text{ cm}^3 \text{ mol}^{-1}$) was calculated from H_2 'classical' critical constants (Prausnitz, 1969, p.162), and a_{H_2} ($2.82 \times 10^5 \text{ bar cm}^6 \sqrt{\text{K mol}^{-1}}$) was adjusted to optimize the agreement with the experimentally measured fugacities of Shaw & Wones (1964). The value for the MRK $b_{\text{H}_2\text{S}}$ term ($20.0 \text{ cm}^3 \text{ mol}^{-1}$) given by Holloway (1981) is probably a typographical error; the value used here ($29.94 \text{ cm}^3 \text{ mol}^{-1}$) was derived from H_2S critical properties. A mixed equation-of-state approach was taken because the HSMRK program does not reproduce low- T H_2O - CO_2 - CH_4 phase equilibria, although it does reliably reproduce experimental observations for pure H_2O , CO_2 and CH_4 fluids, and extrapolates well to high pressure. In contrast, activities calculated with the MRK program give a better prediction of the H_2O - CO_2 - CH_4 solvi and mixed-volatile equilibria. Equilibrium constants for the GCOH fluid species equilibria and volumetric data for graphite were taken from Robie *et al.* (1978) and Holland & Powell (1990), respectively. A FORTRAN computer program for these calculations is available upon request; please supply a 3.5" Sun, DOS or Macintosh formatted disk.

GCOH FLUIDS

The properties of GCOH $\text{H}/\text{O} = 2$ fluid were calculated over a P - T range of 250–1000°C and 0.5–30 kbar at 10°C and 200 bar intervals. The resulting molar fractions of the major species H_2O , CO_2 and CH_4 , designated $X_{\text{H}_2\text{O}}^m$, $X_{\text{CO}_2}^m$ and $X_{\text{CH}_4}^m$, respectively (the superscript m denotes $\text{H}/\text{O} = 2$ GCOH fluid speciation), are contoured in Fig. 1. The fugacities of O_2 , H_2O and CO_2 ($f_{\text{O}_2}^m$, $f_{\text{H}_2\text{O}}^m$ and $f_{\text{CO}_2}^m$) obtained from the calculations were fit as functions of pressure and temperature, the coefficients of which are presented in Table 1. Figure 1(a) shows $f_{\text{O}_2}^m$ and the difference between $f_{\text{O}_2}^m$ and the f_{O_2} of the quartz-fayalite-magnetite (QFM) equilibrium. At low temperature, the QFM equilibrium is more reducing than $f_{\text{O}_2}^m$ and at high temperature ($T > 425^\circ\text{C}$) is more oxidizing. Although the discrepancy may appear minor, these differences are significant because H_2O is the dominant GCOH species only within about $\pm 0.9 \log_{10}$ units of $f_{\text{O}_2}^m$. The values of $X_{\text{H}_2\text{O}}^m$ calculated here (Fig. 1b) are higher than those estimated by Ohmoto & Kerrick (1977), particularly at low temperature. This difference is primarily due to the their assumption of ideal mixing. At $T = 400^\circ\text{C}$ and $P = 1$ kbar the speciation calculated assuming ideal mixing is $X_{\text{H}_2\text{O}}^m = 0.848$, $X_{\text{CO}_2}^m = 0.075$ and $X_{\text{CH}_4}^m = 0.074$; if non-ideality is taken into account, the speciation is $X_{\text{H}_2\text{O}}^m = 0.962$, $X_{\text{CO}_2}^m = 0.019$ and $X_{\text{CH}_4}^m = 0.019$. Because C-O-H fluids have solvi at low temperature, the assumption of ideal mixing cannot be valid and results in

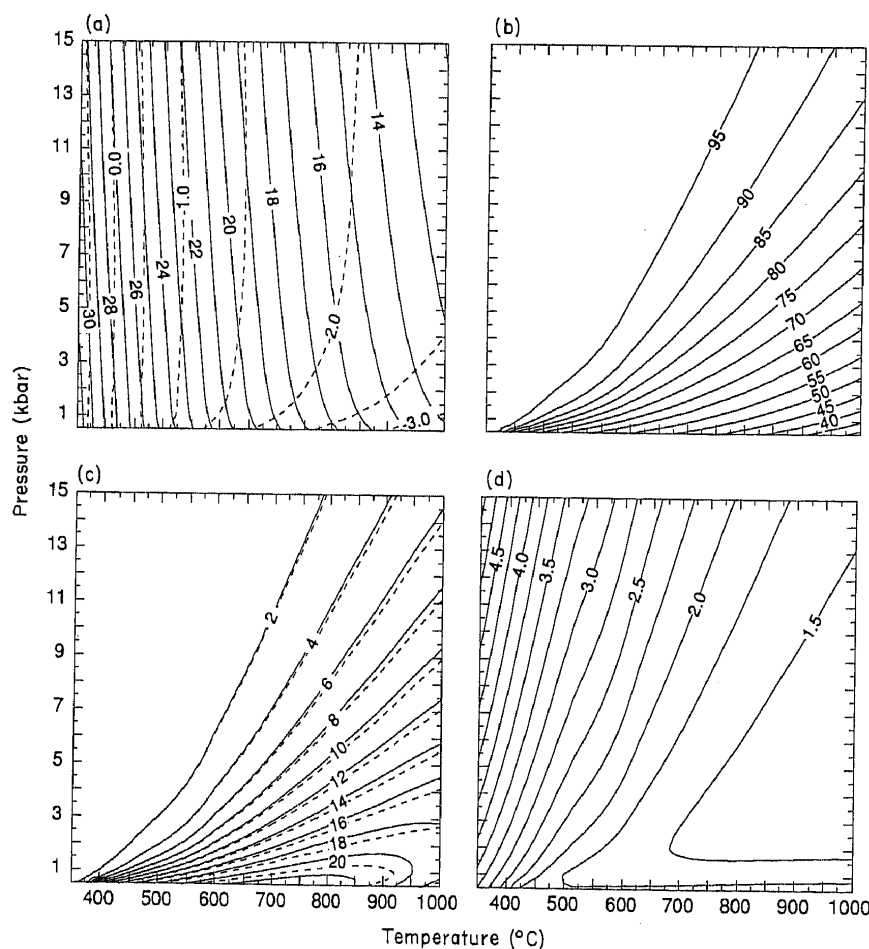


Fig. 1. $\text{H}/\text{O} = 2$ GCOH fluid properties: (a) $-\log_{10}(f_{\text{O}_2}^m)$ contoured at unit intervals (solid curves) and the difference $\log_{10}(f_{\text{O}_2}^m) - \log_{10}(f_{\text{O}_2}^{\text{qfm}})$ contoured at 0.5-unit intervals (dashed curves); $f_{\text{O}_2}^{\text{qfm}}$ is the quartz-fayalite-magnetite equilibrium f_{O_2} ; (b) $X_{\text{H}_2\text{O}}^m$ contoured at 5-mol% intervals; (c) $X_{\text{CO}_2}^m$ (solid curves) and $X_{\text{CH}_4}^m$ (dashed curves) contoured at 2-mol% intervals; (d) log of the molar volumetric ratio of GCOH fluid to graphite, contoured at 0.25- \log_{10} unit intervals; this ratio is a measure of the buffering capacity of graphite during dehydration.

Table 1. Coefficients for fits to $f_{\text{O}_2}^m$, $f_{\text{H}_2\text{O}}^m$ and $f_{\text{CO}_2}^m$ by the P (bar)– T (K) function:

$\log_{10} f_i^m = a + bT + cP$	a	-674.864	-73.0913	-375.522
$+ dT^{-2} + ePT + fP^2 + gT^2$	b	-0.206785	-0.369956×10^{-1}	-0.155513
$+ h\sqrt{(PT)} + iT^3 + jP^3$	c	0.583046×10^{-2}	0.606934×10^{-2}	0.581154×10^{-2}
$+ kPT^{-2} + l \log_{10} T$	d	406602.0	-72109.1	0.220387×10^7
$+ m \log_{10} P + nP^{-2}$	e	0.263925×10^{-6}	0.223397×10^{-6}	0.262886×10^{-6}
$+ oP^2/T + pP/T$	f	0.108173×10^{-8}	0.371819×10^{-8}	0.108199×10^{-8}
$+ qT/P + rT^2/P$	g	0.739942×10^{-4}	0.139508×10^{-4}	0.599467×10^{-4}
$+ sT \log_{10} T + tP \log_{10} T$	h	0.399737×10^{-4}	0.176319×10^{-2}	0.399954×10^{-4}
	i	-0.135130×10^{-7}	-0.271504×10^{-8}	-0.114832×10^{-7}
	j	0.369351×10^{-14}	$-0.214252 \times 10^{-13}$	0.368917×10^{-14}
	k	115.579	129.166	115.256
	l	267.058	35.4064	160.486
	m	-1.35639	-2.20143	-1.35642
	n	11868.4	104986.0	11861.9
	o	-0.136921×10^{-5}	-0.135958×10^{-5}	-0.140576×10^{-5}
	p	-0.615369	-0.673873	-0.587710
	q	-0.215566	-1.43161	-0.215532
	r	0.850931×10^{-4}	0.668271×10^{-3}	0.850944×10^{-4}
	s	0.178698×10^{-2}	0.329498×10^{-3}	0.178706×10^{-2}
	t	-0.183858×10^{-2}	-0.196159×10^{-2}	-0.183234×10^{-2}
	r_{ave}	0.00551	0.00259	0.00551
	r_{max}	0.0451	0.0269	0.0451
$\log_{10} f_i^m$ at 1000 bar and 873 K		-21.3922	2.63917	2.31002

Fugacities are relative to an ideal gas standard state at 1 bar and the temperature of interest and were fit in the range 523–1273 K and 0.5–30 kbar. r_{ave} and r_{max} are the mean and maximum absolute log unit deviations of the fits. Residual statistics are a measure of the precision of the fits, but the accuracy of the fugacities is dependent on a number of factors that cannot be assessed. In particular, it should be noted that the properties of H_2O , CO_2 and CH_4 are extrapolated to high pressure, and that the properties of mixtures are based on an interpolative equation of state.

underestimation of H_2O fugacity and concentration. The predicted consolute point of the H_2O – CH_4 solvus ($T = 366^\circ\text{C}$ and $X_{\text{H}_2\text{O}} = 0.82$ at $P = 1$ kbar) is in excellent agreement with experimental determinations ($T \approx 360^\circ\text{C}$ and $X_{\text{H}_2\text{O}} \approx 0.80$; Larsen & Prausnitz, 1984). However, the consolute point of the H_2O – CO_2 solvus is predicted to occur at higher temperature ($T = 310^\circ\text{C}$ and $X_{\text{H}_2\text{O}} = 0.75$ at $P = 1$ kbar) than experimental determinations ($T \approx 277^\circ\text{C}$ and $X_{\text{H}_2\text{O}} \approx 0.66$; Todheide & Franck, 1963). This discrepancy suggests that H_2O fugacities and concentrations in Table 1 and Fig. 1(b) are probably slightly overestimated.

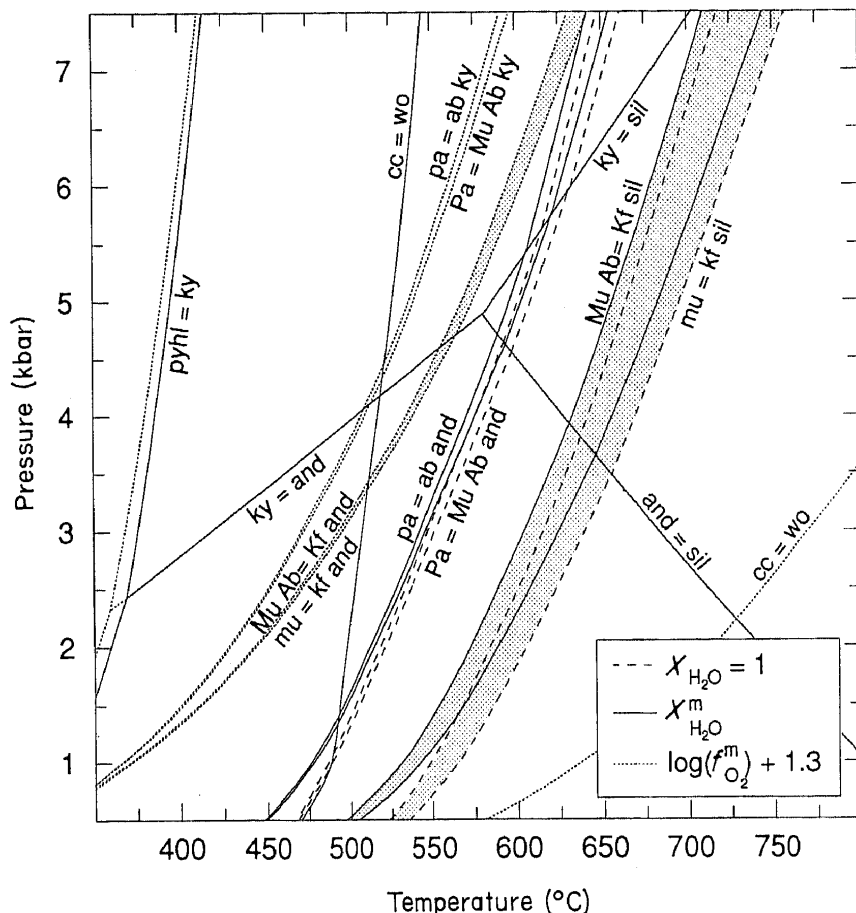
Buffering of GCOH fluid during dehydration

Following Ohmoto & Kerrick (1977), it is often stated that the maximum H_2O content of GCOH fluid corresponds to the condition at which $X_{\text{CH}_4} = X_{\text{CO}_2}$. This constraint is strictly valid provided CH_4 , CO_2 and H_2O are the only significant C–O–H species, an excellent approximation for GCOH fluids at metamorphic conditions. However, a more general constraint can be deduced by noting that the maximum H_2O activity of miscible GCOH fluids must correspond to the composition of the fluid at which the H/O ratio of the fluid is equal to that of water. This follows because it is not possible to produce a GCOH fluid with higher H_2O activity than that produced by the reaction of graphite and pure H_2O fluid, but such a fluid must have the water H/O ratio. For the C–O–H species considered here, this implies $2 X_{\text{CH}_4} + X_{\text{H}_2} = 2 X_{\text{CO}_2} + X_{\text{CO}}$, which, when H_2 and CO become negligible, reduces to $X_{\text{CH}_4} = X_{\text{CO}_2}$. In a simple dehydration reaction, the only

source of hydrogen and oxygen for the fluid phase is the hydrate (the term hydrate is used here to refer to hydroxyl-bearing phases as well as true hydrates). Consequently, fluids produced solely by dehydration in the presence of graphite must maintain the water H/O ratio, which implies the conditions $X_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}}^m$ and $f_{\text{O}_2} = f_{\text{O}_2}^m$. There is no thermodynamic constraint on the maximum H_2O content of non-ideal GCOH fluids, but for metamorphic conditions the calculated H/O ratios of maximum H_2O activity and H_2O content fluids differ by $<0.1\%$ and can be considered identical for practical purposes.

Because GCOH fluid produced by simple dehydration is constrained to have a constant H/O ratio, the fluid has only one compositional degree of freedom, and this degree of freedom is removed by the graphite saturation constraint. Thus, the presence of graphite and the consequent generation of GCOH fluid cannot affect the thermodynamic variance of pure dehydration equilibria, although it will lower equilibrium dehydration temperatures. This effect is shown in Fig. 2 for phase equilibria in the quartz + fluid-saturated system K_2O – Na_2O – Al_2O_3 – SiO_2 –C–O–H. Comparison of dehydration equilibria in pure H_2O fluids with those for the simple dehydration model ($X_{\text{H}_2\text{O}} = X_{\text{H}_2\text{O}}^m$) demonstrates that the reduction in dehydration temperature caused by GCOH fluid speciation is negligible except at extremely low pressure or high temperature.

The observation that the variance of a simple dehydration process is unaffected by the presence of graphite contradicts the common assertion that isobarically invariant dehydration equilibria in non-graphitic rocks



become univariant in graphitic rocks, such that $X_{\text{H}_2\text{O}}$ is 'driven' or 'buffered' from low values to $X_{\text{H}_2\text{O}}^m$ with increasing temperature (e.g. Ohmoto & Kerrick, 1977; Frost, 1979; Pattison, 1989; Seignin & Ghent, 1989). Such models are untenable unless a fluid with $\text{H}/\text{O} \neq 2$ is supposed to have been present prior to metamorphism, or if such a fluid were introduced during metamorphism. In these scenarios, $X_{\text{H}_2\text{O}}$ would increase during prograde dehydration from the value of the initial or introduced fluid and would asymptotically approach $X_{\text{H}_2\text{O}}^m$. If the initial fluid is more oxidizing than an $\text{H}/\text{O} = 2$ GCOH fluid (e.g. a fluid produced by decarbonation), the fluid would become more reducing during dehydration; similarly, a reducing fluid (e.g. a fluid derived from organic matter) would become more oxidizing.

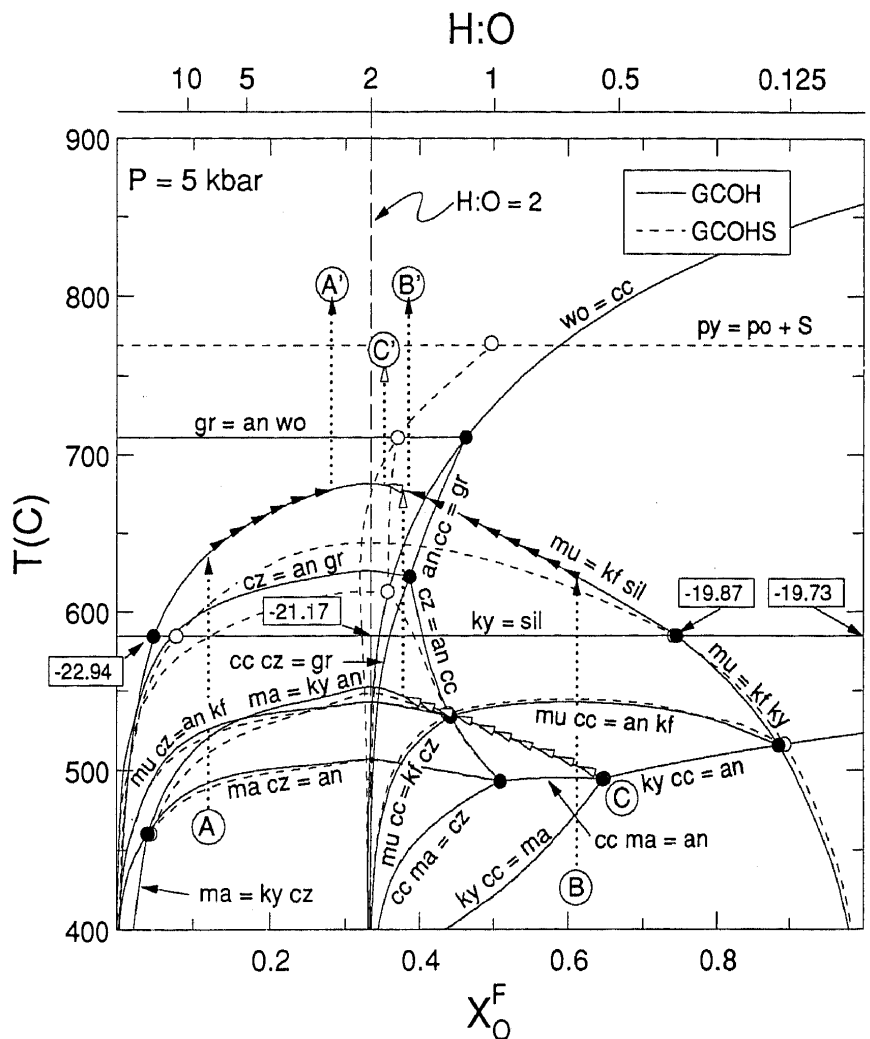
The buffering of GCOH fluids during metamorphism can be illustrated by projecting phase fields onto a coordinate frame defined by temperature and the atomic fraction of oxygen relative to oxygen + hydrogen (X_{O}^{F}) in the fluid phase. The $X_{\text{O}}^{\text{F}} = 0.333$ composition corresponds to $X_{\text{H}_2\text{O}}^m$; at lower X_{O}^{F} , GCOH fluid is primarily a CH_4 - H_2O mixture and approaches pure CH_4 at $X_{\text{O}}^{\text{F}} = 0$; at $X_{\text{O}}^{\text{F}} > 0.333$, GCOH fluid is primarily a CO_2 - H_2O mixture and approaches pure CO_2 at $X_{\text{O}}^{\text{F}} = 1$. Consequently, the maximum temperature of a simple dehydration equilibrium (e.g. $\text{mu} = \text{kf} + \text{sil}$ in Fig. 3) occurs at $X_{\text{O}}^{\text{F}} = 0.333$, and the maximum temperature of a simple decarbonation (or deoxygenation) equilibrium (e.g. $\text{cc} = \text{wo}$ in Fig. 3) occurs at $X_{\text{O}}^{\text{F}} = 1$. The evolution of a GCOH fluid derived

Fig. 2. P - T phase diagram projection demonstrating the effects of C-O-H fluid speciation on pyrophyllite (pyhl), paragonite (Pa) and muscovite (Mu) dehydration in the quartz + fluid-saturated system K_2O - Na_2O - Al_2O_3 - SiO_2 -C-O-H. The univariant curve along which calcite (cc) becomes metastable with respect to wollastonite (wo) and quartz is also shown for GCOH fluids. Lower case abbreviations indicate stoichiometric (end-member) mineral compositions. Equilibria at $X_{\text{H}_2\text{O}} = 1$, $X_{\text{H}_2\text{O}}^m$ and $1.3 \log_{10}$ units above $f_{\text{O}_2}^m$ are represented by dashed, solid and dotted curves, respectively. Because of non-stoichiometry in alkali feldspar (Kf), Pa, Mu and albite (Ab), mica dehydration occurs over divariant regions; that of Mu (shaded) is spanned by the equilibria $\text{Mu} + \text{Ab} = \text{Kf} + \text{aluminosilicate (as)}$ (andalusite, and; kyanite, ky; sillimanite, sil) and $\text{mu} = \text{kf} + \text{aluminosilicate}$; and that of Pa by the equilibria $\text{Pa} = \text{Mu} + \text{Ab} + \text{as}$ and $\text{pa} = \text{ab} + \text{as}$. At high P - T mica phase fields become metastable with respect to granitic melts. Conditions for pyrophyllite dehydration at $X_{\text{H}_2\text{O}} = 1$ and $X_{\text{H}_2\text{O}}^m$ are indistinguishable. The $\text{cc} = \text{wo}$ curves define the maximum temperatures at which carbonate may be in equilibrium with the corresponding GCOH fluid in quartz-saturated systems (see also Fig. 3). Equilibria calculated with end-member data from Holland & Powell (1990); Pa, Mu, Ab and Kf mixing properties from Chatterjee & Froese (1975) and Thompson & Waldbaum (1969); and the method of Connolly (1990).

from organic matter in contact with a muscovite + quartz rock would follow a path similar to A-A' in Fig. 3, whereas a GCOH fluid derived from decarbonation (or deoxygenation) would evolve along B-B'. In either case, the amount of dehydration which takes place as a function of temperature will depend on the amount of the externally derived fluid that interacts with the dehydrating rock. Because most metamorphic rocks are unable to sustain high porosities (Connolly & Thompson, 1989), the amount of dehydration that occurs at temperatures below the maximum dehydration temperature (i.e. at $X_{\text{H}_2\text{O}}^m$) will be insignificant unless the rocks are titrated by a fluid far from $X_{\text{H}_2\text{O}}^m$ (cf. Greenwood, 1975).

The variance of dehydration processes would also be increased if fluid pressure were independent of, and presumably less than, lithostatic pressure, i.e. mechanical disequilibrium. In this case, as well as that of the introduction of a fluid with $\text{H}/\text{O} \neq 2$, the variance of the dehydration process would be increased regardless of whether graphite was present. The most plausible scenario in which fluid pressure (P_f) would be independent of lithostatic pressure requires that metamorphic rocks are capable of maintaining underpressured pores. In such rocks the variance of the dehydration process is increased, but at any given fluid pressure the fluid will have its maximum H_2O content. If dP_f/dT is less than the slope of the $X_{\text{H}_2\text{O}}^m$ isopleths for GCOH fluid (Fig. 1), the fluid composition would become progressively less H_2O -rich during dehydration. Such buffering is not likely to have

Fig. 3. Isobaric ($P = 5$ kbar) T - X_{O}^{F} phase diagram projection for the graphite + fluid + quartz-saturated system K_2O - CaO - Al_2O_3 - SiO_2 - C - O - H - S . X_{O}^{F} represents the total atomic oxygen content of the fluid relative to hydrogen + oxygen, corresponding H/O ratios are indicated along the upper axis. Solid curves represent equilibria in sulphur-free systems (GCOH fluids) and dashed curves represent equilibria for GCOHS fluids in equilibrium with py + po. At low temperature, univariant curves for GCOH and GCOHS fluids are indistinguishable. Paths A-A', B-B' and C-C' (arrows) describe the evolution of GCOH fluids in scenarios discussed in the text. $\log_{10}(f_{\text{O}_2})$ values for GCOH fluid are indicated on the ky = sil phase boundary. Equilibria calculated with data from Holland & Powell (1990) and the method of Connolly (1990). Notation: anorthite, an; clinozoisite, cz; grossularite, gr; margarite, ma (other notation as in Fig. 2).



modally significant consequences because fluid pressure would increase rapidly during dehydration.

The preceding discussion discounts the effects of redox reactions. For systems in which f_{O_2} is unbuffered, the tendency of prograde reactions will be to reduce mineral oxides, with a concomitant decrease in the H/O ratio of the fluid. Unless the amount of oxygen liberated by redox processes is comparable to the amount of H_2O , this will not be important. In sulphide-free graphitic metapelites, the reduction of Fe^{3+} in biotite is probably the greatest potential source of oxygen. The complete reduction-dehydration of a very Fe^{3+} -rich biotite containing 0.2 mole Fe_2O_3 per mole H_2O (cf. Guidotti & Dyar, 1991) would generate a fluid with $\text{H/O} = 1.67$, or $X_{\text{O}}^{\text{F}} = 0.375$. This is an extreme example, but the consequences would be to increase f_{O_2} by $<0.2 \log_{10}$ units and to decrease $X_{\text{H}_2\text{O}}$ by <2 mol% relative to an $\text{H/O} = 2$ GCOH fluid. This example also serves to demonstrate that massive infiltration of oxygen would be necessary to maintain external control of f_{O_2} in a graphitic system undergoing dehydration. Were such control to occur, profound reductions in the stability of hydrates would result if f_{O_2} were to deviate significantly from $f_{\text{O}_2}^{\text{m}}$. Figures 2 & 3 show that an increase in f_{O_2} by 1.3 log units relative to $f_{\text{O}_2}^{\text{m}}$ would cause muscovite dehydration (the 'second sillimanite' isograd) to occur entirely outside the sillimanite stability field. The widespread stability of

hydroxyl-silicates in graphitic rocks at medium to high metamorphic grades thus provides indirect evidence that f_{O_2} in such environments usually does not deviate very far from $f_{\text{O}_2}^{\text{m}}$.

The effectiveness of graphite as a buffer of fluid composition during dehydration can be measured by the ratio of the molar volume of GCOH fluid (at $X_{\text{H}_2\text{O}}^{\text{m}}$) to that of graphite (Fig. 1d). At temperatures below 600°C , this ratio is generally substantially greater than 100; thus, at these conditions, $<0.001 \text{ cm}^3$ of graphite would be consumed to generate 0.1 cm^3 of fluid. This amount of fluid is comparable to that which would be produced by the dehydration of 1 cm^3 of pelite containing 4 wt% H_2O (c. $0.11 \text{ g H}_2\text{O}$ per cm^3 rock). As regional geotherms have comparable P - T slopes to the $X_{\text{H}_2\text{O}}^{\text{m}}$ isopleths (Fig. 1b), upward migration of GCOH fluids will cause only minor precipitation or consumption of graphite.

Carbonate stability

Calcite is the only stable carbonate predicted from thermodynamic calculations in silica-saturated systems with an $\text{H/O} = 2$ GCOH fluid (at $T > 400^\circ\text{C}$ and $P < 12$ kbar). Under such conditions, calcite becomes metastable with respect to wollastonite at about 500°C (Fig. 2); this temperature corresponds to the point at

which the isobaric $T-X_{\text{O}}^{\text{F}}$ cc=wo univariant curve crosses the $\text{H/O}=2$ composition (Fig. 3). Because the conditions for the calcite=wollastonite equilibrium are extremely sensitive to fluid composition, a small perturbation in the H/O ratio of a GCOH fluid could cause a large increase in calcite stability. This is also true of the stability fields of other carbonates, the $T-X_{\text{O}}^{\text{F}}$ limits of which near, and are subparallel to, the $\text{H/O}=2$ composition at low temperature. Solid solution together with the Al_2O_3 component in silicate systems restricts the $T-X_{\text{O}}^{\text{F}}$ stability fields of carbonates, such that for Al_2SiO_5 -saturated compositions carbonates will be stable only if the H/O ratio of GCOH fluids is markedly less than two. The suggestion that the H/O ratio of GCOH fluids in metapelites is usually close to two, together with these predicted phase relations are consistent with the observation that when carbonate is present in graphitic pelites (i) it does not occur with aluminosilicate and (ii) it is present only at low grades (Ferry, 1981; Nesbitt & Essene, 1983; Burton & O'Nions, 1991).

Unless carbonates are present in significant quantities in a pelite protolith, the ultimate product of a closed-system devolatilization will be a GCOH fluid near $X_{\text{H}_2\text{O}}^{\text{m}}$. However, even minor amounts of carbonate could have a major effect on the evolution of the fluid from fluid-absent conditions. In the absence of pore fluid, fluid will first be generated by a univariant P - T equilibrium that corresponds either to an invariant point in isobaric $T-X_{\text{O}}^{\text{F}}$ section or to the thermal maxima of a univariant $T-X_{\text{O}}^{\text{F}}$ curve (cf. Thompson, 1983; Connolly & Trommsdorff, 1991). Provided this equilibrium involves carbonate, it will generate GCOH fluid with $\text{H/O}<2$. As an example relevant to Fig. 3, the equilibrium prograde devolatilization of a fluid-free rock containing the assemblage anorthite + margarite + muscovite + kyanite and minor calcite will generate fluid at point (C) until calcite is completely exhausted. Fluid composition will then evolve towards $X_{\text{H}_2\text{O}}^{\text{m}}$ along the margarite = kyanite + anorthite equilibrium until margarite is consumed, and then along muscovite = K-feldspar + sillimanite. The GCOH fluid evolution is more complicated if the Na_2O component and mineral solutions are considered, but the general features are similar. Under some circumstances, buffering from fluid-absent conditions, e.g. by the clinozoisite = anorthite + calcite equilibrium (Fig. 3), could produce prograde carbonate.

Fe-Ti oxide stability

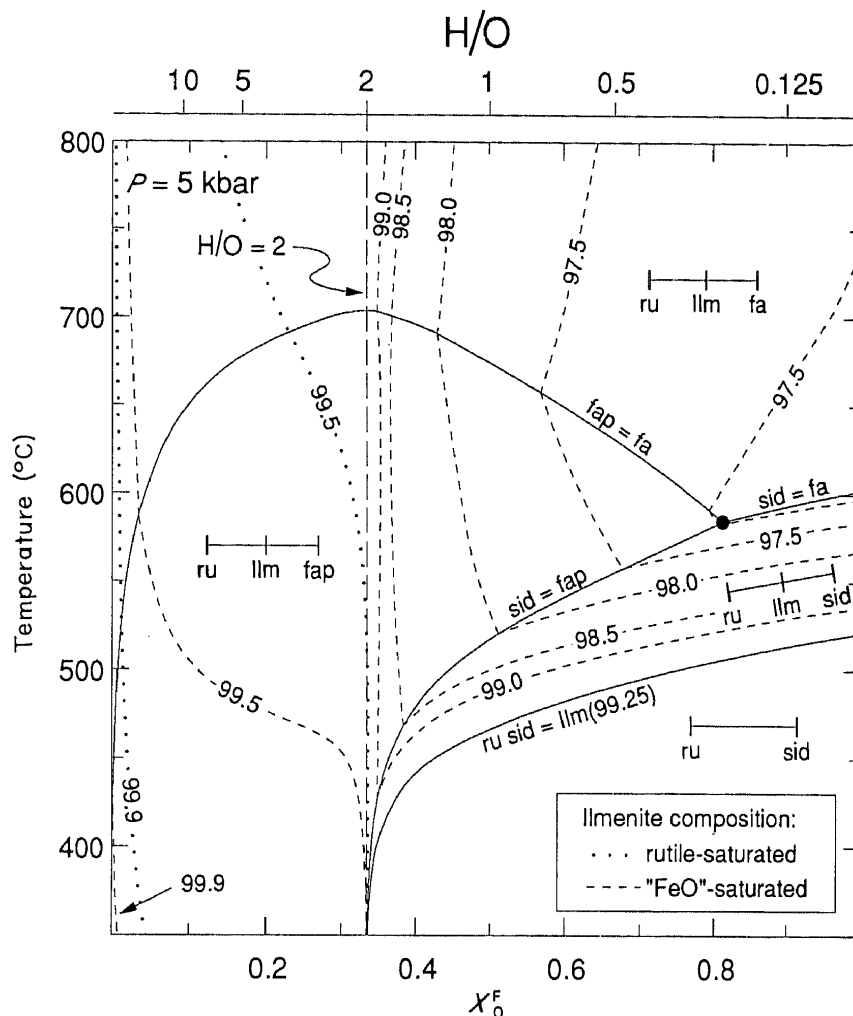
Ilmenite is the only Fe-Ti oxide predicted to be stable at $f_{\text{O}_2}^{\text{m}}$ with silica ($T>400^\circ\text{C}$, $P<10$ kbar), based on calculations with the data of Anderson & Lindsley (1988) and Holland & Powell (1990). At $P<10$ kbar and $f_{\text{O}_2}^{\text{m}}$, the hematite content of rutile-saturated ilmenite is <0.7 mol% and nearly independent of pressure and temperature. For $\text{H/O}=2$ conditions, the maximum hematite content, i.e. iron-silicate saturated, of ilmenite increases from 0.6 mol% at 400°C to 1.2–1.8 mol% at 900°C . The hematite content decreases with increasing Al_2O_3 component. If GCOH

fluid composition is permitted to vary, the hematite content of ilmenite is maximized along the siderite = fayalite phase boundary (Fig. 4), reaching 4.4 mol% at 10 kbar ($T=730^\circ\text{C}$ and $X_{\text{O}}^{\text{F}}=1$). A counterintuitive feature of Fig. 4 is that within the siderite stability field the hematite component of ilmenite is reduced with increasing X_{O}^{F} (and f_{O_2}). At low pressure and temperature ($P<1$ kbar, $T<440^\circ\text{C}$), a small stability field for magnetite, with a composition ranging from pure magnetite to about 7 mol% ulvoespinel component, is predicted to occur at $X_{\text{O}}^{\text{F}}>0.9$. Ilmenite is usually the only Fe-Ti oxide reported in graphitic pelites and it rarely contains more than 1 mol% hematite component (e.g. Pigage & Greenwood, 1982; Holdaway *et al.*, 1988; Sevigny & Ghent, 1989); thus natural Fe-Ti oxide mineralogy is consistent with the existence of an $\text{H/O}=2$ GCOH fluid during metamorphism. An exception is the paragenesis calcite + quartz + ilmenite + magnetite + graphite + muscovite reported by Burton & O'Nions (1991). Although this paragenesis may have formed in an oxygen-rich GCOH fluid, it poses several problems, most notably that the f_{O_2} inferred by Burton & O'Nions is above the limit for graphite stability calculated here and that the estimated pressure for the paragenesis (c. 5 kbar) is well above the maximum pressure estimated for magnetite stability.

GCOHS FLUIDS

The introduction of sulphur by desulphidation reactions into C-O-H fluid cannot affect its H/O ratio; therefore, for a specified sulphur fugacity, H_2O activity will be a maximum when the H/O ratio is 2:1. Pyrrhotite is the most common sulphide in metapelites, but pyrite (py) + pyrrhotite (po) assemblages are not uncommon, particularly at low metamorphic grades, and the sulphur fugacity necessary to stabilize this assemblage ($f_{\text{S}_2}^{\text{po+py}}$) can be taken as an upper limit for many pelitic environments (Ohmoto & Kerrick, 1977; Poulson & Ohmoto, 1989). At $f_{\text{S}_2}^{\text{po+py}}$, the only significant sulphur species predicted for graphite-saturated fluids is H_2S , in which case the H/O ratio constraint implies $2X_{\text{CH}_4} + X_{\text{H}_2} + X_{\text{H}_2\text{S}} = 2X_{\text{CO}_2} + X_{\text{CO}}$. Figure 5 shows the values of $X_{\text{H}_2\text{O}}$, X_{CH_4} , $X_{\text{H}_2\text{S}}$, X_{CO_2} and f_{O_2} for $\text{H/O}=2$ GCOHS fluid in equilibrium with pyrrhotite and pyrite. The H_2S concentrations reported here are much higher than reported by Ohmoto & Kerrick (1977) owing to an error in their expression for $f_{\text{S}_2}^{\text{po+py}}$ (Poulson & Ohmoto, 1989). However, $X_{\text{H}_2\text{S}}$ estimated here is also notably lower than that reported elsewhere (e.g. Holloway, 1981; Ferry & Baumgartner, 1987; Poulson & Ohmoto, 1989) because of an error in the Redlich-Kwong parameter $b_{\text{H}_2\text{S}}$ used in earlier studies. This discrepancy may not be significant in view of the potentially large errors associated with the use of the Redlich-Kwong equation of state to predict H_2S properties at high pressure. Given that H_2S is capable of forming weak hydrogen bonds, Redlich-Kwong predictions will in all probability slightly overestimate $f_{\text{H}_2\text{S}}$ and underestimate $X_{\text{H}_2\text{S}}$.

Fig. 4. Isobaric ($P = 5$ kbar) $T-X_{\text{O}}^{\text{F}}$ phase diagram projection for the graphite + fluid + quartz-saturated system $\text{FeO}-\text{TiO}_2-\text{SiO}_2-\text{C}-\text{O}-\text{H}$. The molar fraction of the ilmenite component in ilmenite-hematite solution (Ilm) in divariant phase fields is contoured at 0.05-mol% intervals; short-dashed curves indicate TiO_2 -saturated compositions, dashed curves indicate 'FeO'-saturated compositions (i.e. saturation with respect to siderite, sid; fayalite, fa; or 'ferro-anthophyllite', fap). The stability and extent of Ilm solution is reduced by the Al_2O_3 component in silicates. Schematic chemographies along the TiO_2 -FeO join are shown for different divariant fields. Calculated with the method of Connolly (1990) and data from Anderson & Lindsley (1988) and Holland & Powell (1990). At very low X_{O}^{F} , calculated phase relations may be metastable with respect to wuestite or iron.



Comparison of Figs 1(a) and 5(a) reveals that sulphur causes a small increase in f_{O_2} for $\text{H/O} = 2$ GCOHS fluid relative to that in the C-O-H system. Over the range of the calculations the deviation increases to a maximum of about $1.0 \log_{10}$ units at 950°C , but below 600°C the difference is negligible. The H_2S species forms at low temperature at the expense of CH_4 (Fig. 5c); once CH_4 has been exhausted, $X_{\text{H}_2\text{S}}$ increases by the removal of hydrogen from H_2O over an interval of about 200°C . The proportion of H_2S increases rapidly near the thermal limit of muscovite + quartz (Fig. 5a). However, the consequent reduction in $\ln(f_{\text{H}_2\text{O}})$ at these conditions is relatively minor and reduces the thermal stability of muscovite + quartz by only about 25°C (compare Figs 5a, 2 & 3).

Within the muscovite + quartz stability field, the influence of sulphur species on phase equilibria is minor, but at its maximum, in $\text{H/O} = 2$ fluids (Fig. 3). At $\text{H/O} < 2$, CH_4 is a minor species and hence the presence of H_2S must reduce the activity of H_2O relative to a GCOH fluid and depress the temperature of dehydration equilibria. In more hydrogen-rich fluids, the roles of CH_4 and H_2O are reversed, and sulphur causes a slight increase in H_2O activity and dehydration temperatures. Sulphur also increases CO_2 content and hence the stability of carbonates, but these increases are only significant at high temperatures (Fig. 3).

Typically, pyrite does not persist to the thermal limit of muscovite + quartz, and therefore $f_{\text{S}_2}^{\text{py}} + \text{py}$ results in an overestimate of the importance of H_2S . In an exceptional case reported by Tracy & Robinson (1988), pyrrhotite + pyrite assemblages are inferred to have been stable at $T \geq 700^\circ\text{C}$ and $P = 6$ kbar. Since these assemblages occur in rocks with muscovite + quartz or K-feldspar + sillimanite + quartz, the P - T conditions imply a GCOHS fluid composition very near $\text{H/O} = 2$ (Fig. 5d). At these conditions, $X_{\text{H}_2\text{S}}$ of GCOHS $\text{H/O} = 2$ fluid would be about 32 mol%, a value in accord with the estimate of Tracy & Robinson (1988).

Ilmenite + pyrite = pyrrhotite + rutile

Based on calculations with the data of Barton & Skinner (1979) and Holland & Powell (1990), the assemblage pyrrhotite + rutile is always stable relative to ilmenite + pyrite in $\text{H/O} = 2$ fluids at $T > 247^\circ\text{C}$. The thermal stability of ilmenite + pyrite increases to a maximum of 322°C in hydrogen-free GCOS fluids. The increase in f_{O_2} of GCOHS fluid relative to GCOH fluid does not cause a significant increase in magnetite stability. These results are in agreement with the absence of magnetite and the occurrence of rutile rather than ilmenite in most metapelites containing pyrrhotite + pyrite (e.g. Ferry,

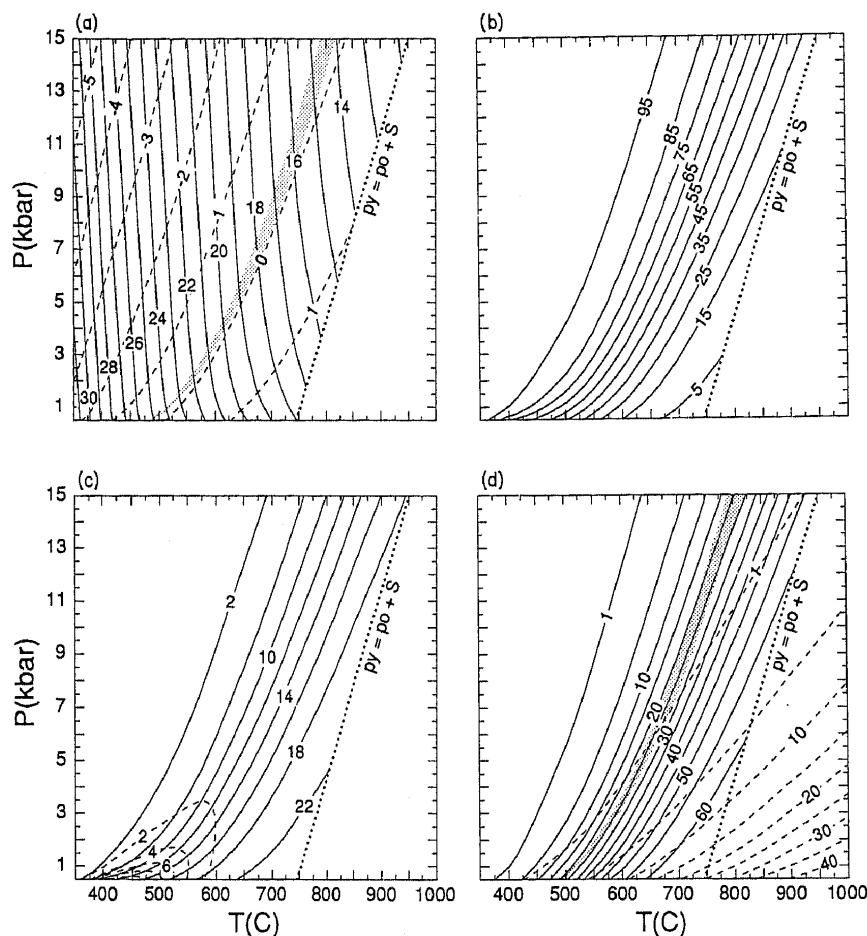


Fig. 5. Properties of GCOHS $H/O = 2$ fluids in equilibrium with $py + po$ at temperatures below the (approximate) pyrite melting reaction $py = po + S_1$ (Barton & Skinner, 1981): (a) $-\log_{10}(f_{O_2})$ (solid curves) and \log of the atomic S/H ratio (dashed curves) contoured at unit intervals; (b) X_{H_2O} contoured at 5-mol% intervals; (c) X_{CO_2} (solid curves) and X_{CH_4} (dashed curves) contoured at 4- and 2- mol% intervals, respectively; (d) X_{H_2S} (solid curves) contoured at 5-mol% intervals and X_{H_2S} of GCOHS fluid in equilibrium with po ($Fe_{0.95}S$, without py) contoured at 5-mol% intervals (dashed curves). In (a) and (d) shaded regions correspond to the limit of muscovite + quartz stability in GCOHS $H/O = 2$ fluid with $py + po$ in the $K_2O-Na_2O-Al_2O_3-SiO_2$ system (see Fig. 2).

1981; Tracy & Robinson, 1988). However, the assemblages pyrrhotite + pyrite + ilmenite and pyrrhotite + ilmenite + magnetite do occur in low-grade graphitic rocks that probably equilibrated at temperatures above the limit suggested here (Nesbitt & Essene, 1983).

Desulphidation at $H/O = 2$ in graphitic rocks

GCOHS fluid produced entirely by dehydration and desulphidation has no compositional degrees of freedom if it is in equilibrium with an assemblage that buffers f_{S_2} , such as pyrrhotite + pyrite. Thus, in systems where such models are appropriate, dehydration and desulphidation processes must be coupled so as to maintain the equilibrium S/H ratio of GCOHS $H/O = 2$ fluid. If the S/H ratio of the fluid is low, then desulphidation can only occur if H_2O is introduced in relatively large quantities by infiltration or dehydration. For the pyrrhotite + pyrite assemblage, at temperatures more than $100^\circ C$ below the thermal stability limit of muscovite + quartz, the atomic S/H ratio of GCOHS fluid is so low that pyrite decomposition by the reaction $pyrite = pyrrhotite + S$ (sulphur forms H_2S in the fluid) would require massive infiltration by a sulphur-free H_2O -rich fluid (cf. Ferry, 1981). Large quantities of fluid are not required if pyrite decomposes by sulphur-conserving reactions in which ferrous iron from ilmenite or silicates is consumed to form pyrrhotite. Iron depletion of

silicates is a common feature of sulphidic schists and provides a strong argument for the latter mechanism of pyrite decomposition (e.g. Guidotti *et al.*, 1975; Mohr & Newton, 1983; Nesbitt & Essene, 1983; Tracy & Robinson, 1988). This mechanism becomes less effective with increasing temperature and increasing S/H ratio of coexistent GCOHS fluid because significant quantities of sulphur will be required to maintain the fluid phase equilibrium. At such conditions, pyrite decomposition will become driven by dehydration; if the S/H ratio of GCOHS fluid is unity then the release of 1 mole of H_2O from a hydrate effectively requires that 2 moles of pyrite are reduced by the reaction $pyrite = pyrrhotite + S$. Coincidentally, the limit of muscovite + quartz stability occurs when the S/H ratio is near unity; thus, in muscovite-bearing metapelites, the abundance of pyrite should decrease abruptly at the second-sillimanite isograd. Given the relatively minor variation in pyrrhotite stoichiometry and sulphur content of GCOHS fluid, it is unlikely that iron depletion of silicates continues without an external sulphur source once pyrite has been consumed.

In the absence of pyrite, the f_{S_2} of pyrrhotite-bearing pelites is unconstrained, but it is possible to estimate GCOHS speciation for a specified pyrrhotite composition (Toulmin & Barton, 1964). Figure 5(a) shows that for a relatively sulphur-poor pyrrhotite composition ($Fe_{0.95}S$), the X_{H_2S} of GCOHS $H/O = 2$ fluid is negligible for most

conditions of interest. Thus, in pyrite-free rocks, the progressive dilution of GCOHS fluid by dehydration need not destabilize pyrrhotite.

CONCLUSIONS

One of the important conclusions of Ohmoto & Kerrick's (1977) work was that dehydration reactions would tend to drive the composition of GCOH fluids toward $X_{\text{H}_2\text{O}}^m$. This conclusion is a weak form of that which can be drawn if it is recognized that the GCOH fluid produced by dehydration must maintain the water H/O ratio and is therefore generated with the $X_{\text{H}_2\text{O}}^m$ composition. Because the dominant fluid source in the metamorphic transformation from low- to high-grade pelites is dehydration, the composition of GCOH fluids during pelite metamorphism typically will be close to $X_{\text{H}_2\text{O}}^m$. For such rocks, the functions for $f_{\text{O}_2}^m$ and $f_{\text{H}_2\text{O}}^m$ given in Table 1 provide a simple means of estimating metamorphic f_{O_2} and $f_{\text{H}_2\text{O}}$. Although secondary, the effects of prograde redox and decarbonation reactions in pelites will be to decrease the H/O ratio of the metamorphic fluid. At low to medium metamorphic grades, desulphidation will have a negligible effect on C-O-H-S fluid speciation and f_{O_2} . Hydrocarbons or the serpentinization of ultramafics (Thayer, 1966) are potential sources of reduced, H/O > 2, fluids, but neither will be important on a large scale or at medium to high metamorphic grades. Thus, $f_{\text{O}_2}^m$ (Fig. 1a) and $X_{\text{CH}_4}^m$ (Fig. 1c) may be regarded as lower and upper limiting values, respectively, for GCOH(S) fluids in metapelites. An increase in f_{O_2} on the order of one \log_{10} unit above $f_{\text{O}_2}^m$ would cause profound reductions in the stabilities of hydrates and extensive stability fields for carbonate. The stability of hydrates at medium to high metamorphic grades and the scarcity of carbonates in graphitic pelites thus supports the conclusion that metamorphic f_{O_2} is usually close to $f_{\text{O}_2}^m$. In lithologies where decarbonation has introduced oxygen into the fluid phase, the maximum metamorphic f_{O_2} for GCOH(S) fluids cannot have been more than about 1.4 \log_{10} units above $f_{\text{O}_2}^m$ because higher f_{O_2} values are inconsistent with graphite saturation.

The intention of this study was not to present a panacea for the problem of fluid composition in graphitic pelites, but rather to emphasize a simple mass-balance constraint that has been undervalued. In some pelites, graphite appears to form by the reduction of CO_2 fluids from adjacent carbonates; these and graphitic rocks that contain magnetite or abundant carbonate are obvious examples where an H/O = 2 model for the fluid is inappropriate. The T - X_{O}^F phase diagram representation (Figs 3 & 4) suggested here provides a simple means for understanding the phase relations of such systems. In comparison with representations that employ f_{O_2} as an independent variable, this approach has the advantage that X_{O}^F is a physically meaningful variable that reflects both mass-balance constraints and fluid composition. In real metamorphic systems there are a number of other factors which limit the validity of the C-O-H-S models used here, including the possibilities that (i) no fluid phase was

present (Edwards & Essene, 1988; Skippen & Marshall, 1991), (ii) electrolytes or other fluid components were present, (iii) the activity of graphite was less than unity (Grew, 1974) or (iv) the fluid was not in equilibrium with the graphitic phase (Barnes, 1987). In principle, it should be possible to use phase equilibria to estimate H_2O activity, but in most cases the uncertainties associated with thermobarometry and mineral equilibria are so large as to make the results ambiguous. For this reason, the authors share the view of Holdaway *et al.* (1988) that often it is better to assume reasonable fluid compositions for purposes of testing the consistency of P - T estimates, rather than to estimate fluid composition from an assumed or estimated P - T condition.

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