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THE METAMORPHISM OF GRANULITES AND DEVOLATILIZATION OF THE LITHOSPHERE

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ABSTRACT

Fluids in the lithosphere are treated as mixtures of H_2O, CO_2, CH_4, CO, H_2, O_2. The following three conditions have been utilised to determine the partial pressures of these constituents: (1) a fugacity of H_2 as indicated by biotite - feldspar - magnetite - fluid assemblages with mineral compositions representative of granulites, (2) oxygen fugacity as specified by the quartz - fayalite - magnetite - fluid reference assemblage, and (3) graphite saturation. Fluid pressure equal to lithostatic pressure has not been assumed in the calculation in order to derive the relationship between fluid pressure and lithostatic pressure on the basis of mineral compositions. For oxidation levels along the quartz - fayalite - magnetite - fluid reference assemblage, there are significant segments above 500°C along pressure - temperature - time paths where calculated fluid pressure exceeds lithostatic pressure, and devolatilization is predicted for graphite-saturated rocks containing typical biotite solid-solutions. At lower oxygen fugacities, the condition for devolatilization requires higher temperature for a given depth; at higher oxygen fugacities expected in some granulite-facies rocks (since orthopyroxene is more stable under these conditions than fayalite), the region of devolatilization increases by expanding to lower temperatures for a given depth. Devolatilization of the lower crust is predicted by these calculations, with the hydrogen reservoir (held in hydrous silicate minerals) and the carbon reservoir (excess graphite) being depleted in the process. The commonly observed CO_2-rich fluid inclusions in granulites are consistent with the type of residual fluids expected from the process described above.

Keywords: granulite, graphite, oxygen, hydrogen, fluid, devolatilization, outgassing, lower crust, P–T–t path.

SOMMAIRE

On peut considérer la phase fluide qui circule dans la lithosphère comme mélange de H_2O, CO_2, CH_4, CO, H_2 et O_2. Les trois contraintes suivantes permettent le calcul de la pression partielle de chacune de ces composantes: (1) une fugacité de H_2 telle qu'indiquée par les assemblages biotite + feldspath + magnétite + fluide dont les compositions de phases solides sont représentatives de granulites, (2) une fugacité d'oxygène telle que spécifiée par l'assemblage de référence quartz + fayalite + magnétite + fluide, et (3) saturation en graphite. La pression de la phase fluide n'est pas considérée fixée (à la valeur de la pression lithostatique) pour ce calcul, afin de pouvoir dériver la relation entre pression de la phase fluide et la pression lithostatique impliquée par la composition des minéraux. Pour des niveaux d'oxydation régis par l'assemblage de référence quartz + fayalite + magnétite + fluide, la pression calculée de la phase fluide surpasserait la pression lithostatique sur des intervalles importants le long de trajectoires pression - température - temps, à des températures supérieures à 500°C. Nous prévoyons ainsi une dévolatilisation pour des roches saturées en graphite et contenant une composition de biotite typique. A fugacité d'oxygène inférieure, la condition requise pour la dévolatilisation demande une température plus élevée à une profondeur donnée. A fugacité d'oxygène supérieure dans le facies granulite, comme c'est le cas pour certaines roches à orthopyroxène, qui est stabilisé dans de tels milieux plutôt que la fayalite, le domaine de dévolatilisation augmente par expansion vers les températures plus basses pour une profondeur donnée. Une dévolatilisation de la croûte inférieure serait la conséquence logique de ces calculs, aux dépens des réservoirs d'hydrogène, piégée dans les silicates hydratés, et de carbone, manifesté par la présence de graphite. La présence d'inclusions fluides riches en CO_2, qui sont répandues dans les granulites, concorde avec la nature des fluides résiduels attendus de ce phénomène.

(Traduit par la Rédaction)

Mots-clés: granulite, graphite, oxygène, hydrogène, fluide, dévolatilisation, dégazage, croûte inférieure, trajectoire pression - température - temps.

INTRODUCTION

The importance of fluids in the petrology of the lower crust has been a matter of continuing discussion since the relationships among granulites, melts, and hydrous fluids were considered by Fyfe (1973). Fyfe explained the development of anhydrous mineral assemblages in the lower crust by dissolution of water into a melt phase. The subsequent ascent of these melts could eventually result in a lower activity of water in the zone of melt generation and cause the breakdown of hydrous minerals at lower temperatures than required in a pure aqueous fluid.

Others have related anhydrous mineral assemblages in the lower crust to infiltration of carbon dioxide from depth (Touret 1971, Schuiling & Kreulen 1979, Newton *et al.* 1980, Glassley 1982). In some proposals, the release of carbon dioxide into the lower crust is related to crystallizing melts (Newton *et al.* 1980, Frost & Frost 1987, Bohlen & Mezger 1989).

The present paper considers the possibility that devolatilization of the lower crust is caused by mineral assemblages that require calculated equilibrium pressures of fluid in the chemical system C–O–H to exceed lithostatic pressure as metamorphic grade increases. It should be emphasized that calculated pressures of fluid can exceed lithostatic pressure; actual pressures of fluid in the rock are not expected to exceed lithostatic pressure. The implication of discrepancies between calculated pressures based on mineral compositions and real pressures that are limited by the lithostat is the subject of this paper.

PRESSURE–TEMPERATURE–TIME PATHS

Calculations described below suggest that during the tectonic evolution of the lower crust, the pressure – temperature – time paths followed by comparatively oxidized (typically supracrustal) rocks cross into a region in which calculated pressure of the fluid phase exceeds lithostatic pressure. At this point, the sum of the calculated partial pressures, p_i, of gaseous species, i, exceeds the lithostatic pressure of the overlying rock,

$$\Sigma\ p_i \geq P_{lithostatic}. \qquad (1)$$

Since rocks of the lower crust do not have sufficient strength to contain a fluid overpressure, the fluid must escape as it is produced by mineral reaction until one of the fluid components in the rock mass is exhausted. This process is comparable to that of a typical prograde metamorphic sequence, where the vapor pressure in equilibrium with an assemblage containing hydrous silicates exceeds the lithostatic pressure at an isograd. In the present calculation, however, homogeneous equilibria within the fluid phase in addition to mineral–fluid equilibria combine to cause the fluid pressure to exceed lithostatic pressure and lead to devolatilization.

Eckert (1989) has explained the widespread development of granulites in the lower crust as a likely result of tectonic processes such as crustal thickening rather than magma production or crystallization. The calculations described in this paper demonstrate that reasonable pressure – temperature – time paths could result in the production of anhydrous mineral assemblages during the tectonic evolution of the lower crust, provided there is sufficient carbon present in the rock–fluid system. The carbon could be present in the rock as graphite, or it could be introduced by a process such as infiltration of carbon dioxide. The widespread and pervasive presence of CO_2-rich fluid inclusions in granulites demonstrates that a carbon source certainly exists.

The question of clockwise or counterclockwise time paths for granulites in pressure–temperature coordinates is not examined. The stability field for sillimanite is shown below to fall within the calculated region of devolatilization, and granulites contain sillimanite as the most common aluminosilicate mineral; any type of pressure – temperature – time path through the sillimanite field enters the region of devolatilization described in this paper.

The problem of whether or not a pervasive fluid phase exists continuously in granulites along the time path is not considered in this discussion. A transient process of fluid production is described, with the calculated composition of the fluid phase at the end of the process being mainly carbon dioxide. No assumption is made about the presence of a fluid phase before the onset of the process nor about the persistence of a fluid following the process.

THERMODYNAMIC CONSTRAINTS ON FLUID SPECIES

Many authors have made significant contributions in recent years to the discussion of fluids in the lower crust; these include Rye *et al.* (1976), Ohmoto & Kerrick (1977), Touret (1981), Walther & Orville (1982), Etheridge *et al.* (1983), Valley *et al.* (1983), Lamb & Valley (1984, 1985), Lamb *et al.* (1987), Crawford & Hollister (1986), Yardley (1986), Kreulen (1988), and Jansen *et al.* (1989). All of this research is consistent with the modeling of fluids in the crust by calculations based on the three-component system C–O–H, with the principal species being CO_2, CH_4, H_2O, CO, H_2, and O_2. The partial pressures of these six species then constitute six unknowns that must be determined in order to define the relationship between fluid pressure and lithostatic pressure.

Homogeneous equilibria among gaseous species provide three independent thermodynamic equations (equations 2–4 below) that constrain fluid compositions as functions of temperature and pressure. The geological assumption that the fluids are saturated with graphite provides a fourth equation (such as equation 5 below). Equilibrium constants for equations 2 to 5 have been taken from

Ohmoto & Kerrick (1977) as follows (T in K, P in atmospheres):

$$CO + {}^{1}/{}_{2}O_2 = CO_2$$
$$\log K = \frac{14751}{T} - 4.535 \qquad (2)$$

$$H_2 + {}^{1}/{}_{2}O_2 = H_2O$$
$$\log K = \frac{12510}{T} - 0.979 \log T + 0.483 \qquad (3)$$

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$
$$\log K = \frac{41997}{T} + 0.719 \log T - 2.404 \qquad (4)$$

$$C + O_2 = CO_2$$
$$\log K = \frac{20586}{T} + 0.0421 + 0.028\frac{(P-1)}{T} \qquad (5)$$

Two additional relationships must be found to solve for the partial pressures of the six fluid species listed above. Additional chemical equilibria among these fluid species are not algebraically independent, so that it is necessary to find further constraints based on geological information to calculate the partial pressure of each of the six fluid constituents.

GEOLOGICAL CONSTRAINTS ON FLUID COMPOSITION

The use of geological constraints to obtain equilibrium compositions of the fluid in the chemical system C–O–H was demonstrated by French (1966) and subsequently used, for example, by Eugster & Skippen (1967), Ohmoto & Kerrick (1977), Glassley (1982), Valley *et al.* (1983), and Ferry & Baumgartner (1987).

Geological constraints that can be used to calculate fluid compositions include: 1) a hydrogen reservoir contained in hydrous and anhydrous silicates that is modeled below by the assemblage biotite - feldspar - magnetite (see, for example, Eugster & Wones 1962, Eugster & Skippen 1967, Glassley 1982, Ferry & Baumgartner 1987), 2) an oxygen reservoir contained in oxide–silicate assemblages that can be modeled by the solid-phase oxygen buffers (Eugster 1957), and 3) a carbon reservoir that has been modeled by the mineral graphite (for example, Miyashiro 1964, Glassley 1982, Lamb & Valley 1984, Hansen *et al.* 1987). In subsequent calculations, the activity of carbon has been set at unit value, which corresponds to saturation with graphite.

Biotite of various compositions has been used to model the hydrogen reservoir, on the basis of the equilibrium studied experimentally by Wones & Eugster (1965),

$$KFe_3AlSi_3O_{10}(OH)_2 = Fe_3O_4 + KAlSi_3O_8 + H_2 \qquad (6)$$

with the equilibrium constant for equation 6 given by

$$\begin{aligned}\ln K_6 = {} & \frac{-7676.67219}{T} + 10.30428 + \frac{0.00825}{T}(P_{bars} - P_r) \\ & - 12.10273 \left[\ln\left(\frac{T}{T_r}\right) - 1 + \frac{T_r}{T} \right] \\ & + 340.85882 \left[2\frac{T_r^{\frac{1}{2}}}{T} + 2T_r^{-\frac{1}{2}} - 4T^{-\frac{1}{2}} \right] \\ & - 661375.2509 \left[\frac{1}{2T_r^2} + \frac{1}{2T^2} - \frac{1}{TT_r} \right] \\ & - 45911417.88 \left[\frac{1}{6T^3} + \frac{1}{3T_r^3} - \frac{1}{2TT_r^2} \right] \\ & + 0.00393 \left[\frac{T_r^2}{2T} + \frac{T}{2} - T_r \right]\end{aligned}$$

where the reference pressure, P_r, is one bar, and the reference temperature, T_r, is 298.15 K.

Thermodynamic data and heat capacity terms from Berman (1988) have been used with an integrated free energy equation comparable to equation 8.15 from Skippen & Carmichael (1979) to express the equilibrium constant as a function of temperature in equation 6 (Fig. 1). Hydrogen fugacities have been calculated for a mineral assemblage containing pure annite and feldspar as well as for an assemblage with a mole fraction of iron in biotite of 0.45 (activity = X^3) and a mole fraction of the potassium component in the feldspar of 0.906 (activity = X). These curves represent a range of values expected in high-grade metamorphic rocks.

An independent determination of hydrogen fugacity in high-grade rocks can be obtained from equation 3 using oxygen and water fugacities reported by Lamb & Valley (1984) for a charnockite from the Adirondacks. The calculated fugacity of hydrogen falls within the range defined by equation 6 and is plotted on Figure 1.

A second mineralogical constraint based on the oxygen reservoir has been adopted in order to calculate fluid compositions; oxygen fugacities in natural assemblages can be determined by analysis of oxide pairs or oxide–silicate assemblages, as described by Lamb & Valley (1984), Anderson & Lindsley (1985), and Lamb *et al.* (1987). Assemblages such as quartz – fayalite – magnetite – fluid (QFM) are used to represent the characteristics of this oxygen reservoir in subsequent calculations.

The choice of the QFM as a reference assemblage to model the oxygen reservoir in the calculation does not imply that quartz, fayalite, magnetite and fluid are actually thought to be present throughout the time path of granulites. Rather, the assemblage

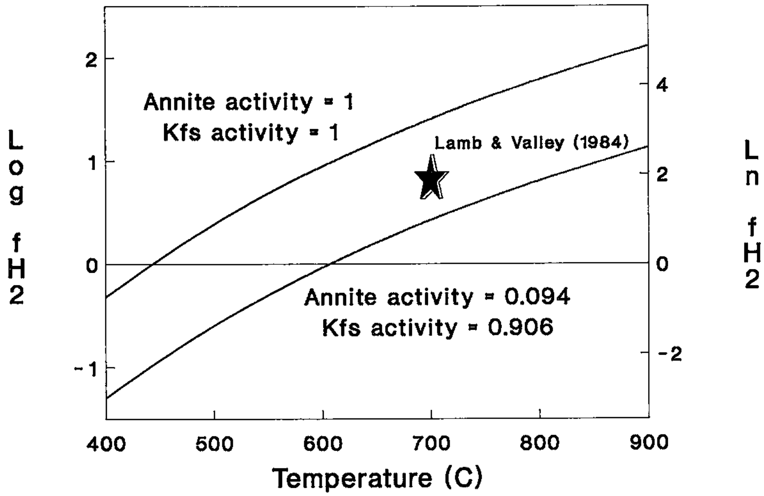

FIG. 1. Equilibrium among biotite - K-feldspar - magnetite - fluid as calculated from the data-base of Berman (1988). The upper curve is calculated for an annite activity of 1.0, and the lower curve is for annite and feldspar solid-solutions. An independently determined fugacity of hydrogen (logarithm of hydrogen fugacity = 0.84) for a granulite from the Adirondack Mountains is based on oxygen and water fugacities reported by Lamb & Valley (1984) and equation 3 from the text. The result is shown by the star symbol for comparison with curves calculated using equation 6.

serves as a convenient reference in oxygen fugacity - temperature - pressure coordinates. Actual rocks will have higher or lower oxygen fugacities as can be determined, for example, by oxide phase barometry (Anderson & Lindsley 1985). It is advantageous to select a mineral assemblage such as QFM to define oxygen fugacity rather than use a constant number so that oxygen fugacity shifts with total pressure and temperature in a realistic manner to provide better insight into petrological processes. Fayalite is selected because of uncertainties in the thermodynamic data for other ferrous silicates. The use of alternative reference-assemblages (such as wüstite - magnetite) for oxygen fugacity in subsequent calculations illustrates the effect of varying oxygen fugacity.

Equations 2–5 have been solved at specified values of oxygen and hydrogen fugacity; the resulting compositions are illustrated on Figure 2. Fugacity coefficients from Holloway (1977), as modified by Flowers (1979), have been used in the calculation. Similar calculations have been carried out by French (1966), Eugster & Skippen (1967), Lamb *et al.* (1987) and Ferry & Baumgartner (1987). The calculated pattern of changing fluid composition, from water-dominant under amphibolite-facies conditions to carbon-dioxide-dominant at higher grade, has been observed in the field by many investigators, including Touret (1970), Frey *et al.* (1980), and Konnerup-Madsen (1977).

MECHANICAL EQUILIBRIUM

A geological constraint used in many calculations is an assumption of mechanical equilibrium among a fluid phase and mineral phases at lithostatic pressure. Equilibrium requires that no pressure gradient exists among phases, so that equation 1 is an equality between the sum of the partial pressures of the fluid species and lithostatic pressure.

Mechanical equilibrium in the presence of a fluid phase should not be assumed at high metamorphic grade without regard to the mineral compositions that it implicitly requires. Mineral compositions can be checked to insure that they are compatible with the presence of a fluid phase at a particular temperature and pressure. A procedure for checking mineral compatibility involves the simultaneous solution of equations 1 to 6, with mineral activities in equation 6 based on measured mineral compositions; compatibility of the resulting fugacity of oxygen with the observed oxide mineral assemblage in the rock is necessary in the presence of a fluid. Alternatively, an oxygen fugacity based on mineral compositions can be specified in addition to equations 1 to 5, and a hydrogen fugacity

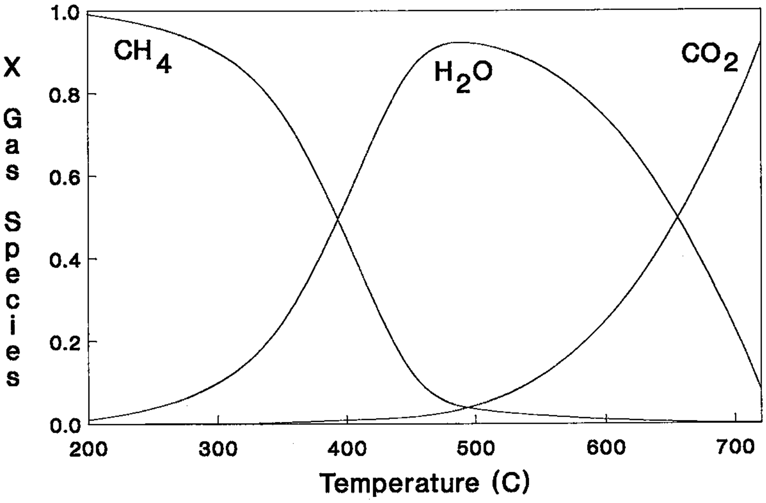

FIG. 2. Proportion of gaseous species *versus* temperature in the system C–O–H for graphite-saturated fluids in equilibrium with the quartz – fayalite – magnetite – fluid reference assemblage minus 1 log unit (QFM–1), inferred from the data-base of Berman (1988). Hydrogen fugacity is specified independently by the assemblage biotite (annite activity 0.1) – magnetite – K-feldspar (activity 0.9) – fluid. Temperature and pressure are assumed to be given by a 30°C/km gradient for calculation of fugacity coefficients and definition of the free energy of solid phases although, rigorously, fluid pressure cannot be arbitrarily specified with three independent mineralogical constraints. Fugacity coefficients are from Holloway (1977), as modified by Flowers (1979). According to data presented later on Fig. 5, it is possible for rocks at QFM–1 to maintain a C–O–H fluid at mechanical equilibrium within the sillimanite field whereas the higher oxygen fugacity of QFM would result in mechanically unstable fluids at less than the 700°C maximum temperature shown on Fig. 2.

calculated. The composition of the biotite in the rock can then be compared with a predicted composition of biotite through equation 6.

The presence of a fluid phase at a particular time in the metamorphic history of a rock cannot always be assumed on the basis of geological observation, as pointed out by Thompson (1983) and Lamb & Valley (1984). A fluid phase at mechanical equilibrium has not, therefore, been assumed as a precondition of the calculations in the present work.

MINERAL ASSEMBLAGES AND THE PRESENCE OF A FLUID PHASE

The relationship between lithostatic pressure and the sum of calculated partial pressures of the fluid for various mineral assemblages and a pressure – temperature relationship of 30°C/km is shown on Figure 3. Under comparatively reducing conditions, such as indicated by the assemblage wüstite – magnetite – fluid, the calculated total fluid pressure of species in C–O–H for the specified mineralogical constraints does not exceed lithostatic pressure until 1100°C. For oxygen pressures along the quartz – fayalite – magnetite – fluid reference assemblage, the calculated sum of the partial pressures of fluid species exceeds lithostatic pressure at temperatures in excess of approximately 540°C. Although biotite and feldspar compositions from a typical granulite (mole fraction of annite = 0.454, activity of annite component 0.094; mole fraction of potassium feldspar = activity = 0.906) have been used to define hydrogen fugacity in this calculation, the temperature for the onset of calculated excess fluid pressure is only decreased to 519°C with the hydrogen fugacity from equation 6 calculated on the basis of pure annite (activity of annite component = 1.0) and pure potassium feldspar.

The points of geological relevance on Figure 3 are the crossover points at which calculated fluid pressure equals lithostatic pressure. Calculated fluid pressures that are less than lithostatic at temperatures below the crossover and calculated fluid pressures that exceed lithostatic at higher temperatures are artifacts of the calculation and

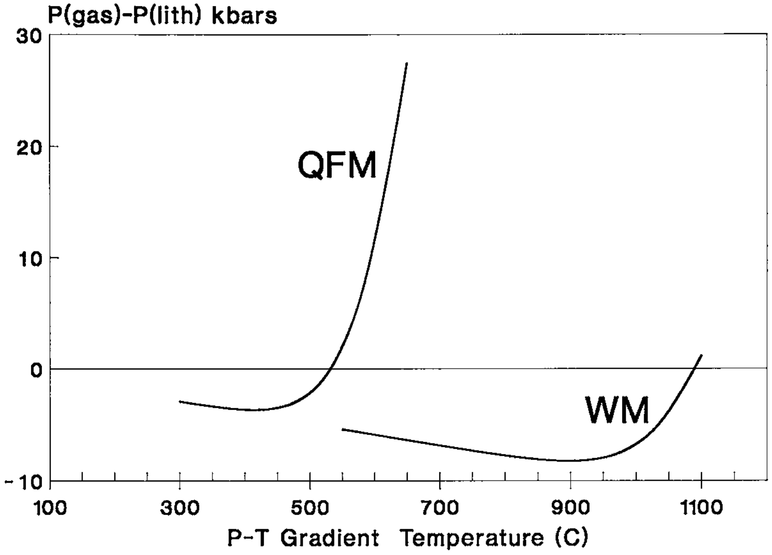

FIG. 3. The calculated sum of partial pressures of the fluid species minus lithostatic pressure for the reference assemblages quartz - fayalite - magnetite - fluid (QFM) (Berman *et al.* 1988), and wüstite - magnetite - fluid (WM) (Eugster & Wones 1962). The calculated fluids are graphite-saturated and equilibrated with biotite (activity 0.1) - K-feldspar (activity 0.9) - magnetite. Temperature and lithostatic pressure are related by a 30°C/km gradient. Fugacity coefficients are from Holloway (1977), as modified by Flowers (1979). The horizontal line corresponds to mechanical equilibrium between the fluid phase and the solid phases at lithostatic pressure. The points at which the calculated curves cross the horizontal line indicate the temperatures (and pressures) at which mechanical equilibria involving a fluid phase are possible for the specified mineralogical constraints. Points above or below the horizontal line do not correspond to mechanical equilibrium in the presence of a fluid phase; such points are artifacts that illustrate the results of a calculation and do not apply to rocks in a state of equilibrium.

imply fluid-absent phase relations in the actual rock. It is unlikely that rocks undergoing ductile deformation could maintain open pore-spaces where actual fluid pressure is less than lithostatic; a fluid phase with calculated total pressure in C–O–H less than lithostatic could be supported by additional components such as sulfur, nitrogen, or salts that make up the difference between C–O–H partial pressures and lithostatic pressure. A fluid phase could also maintain mechanical equilibrium at lower temperature by a progressive change in mineral compositions along the pressure - temperature - time path toward the final compositions used in the calculation.

In stressing that the fluid underpressures and overpressures of Figure 3 are artifacts of a calculation and that they are not meant to apply to an actual rock, it can be pointed out that realistic mineralogical constraints have been used to produce the curves. Oxygen fugacity is set at a representative value by the QFM; graphite is a common mineral phase in rocks of the crust; the mineral compositions from equilibrium 6 are based on electron-microprobe data on actual mineral assemblages from granulite terranes. The fact that such mineralogical constraints are not compatible with the assumption of fluid pressure equal to lithostatic pressure at most temperatures on Figure 3 demonstrates the difficulty with the presumption that a fluid phase is present at lithostatic pressure, without regard to the compositions of minerals.

The relationships on Figure 3 demonstrate that granulites with typical values of hydrogen fugacity and oxygen fugacity are incompatible with the presence of a graphite-saturated fluid phase at temperatures in excess of about 540°C. Under such conditions, it is not possible to maintain mechanical equilibrium between fluids and the mineral phases. An important question, therefore, is whether or not fluids in the lower crust are graphite-saturated.

GRAPHITE IN THE LOWER CRUST

Graphite is a common minor phase in high-grade schists (*e.g.*, Grew 1974, Glassley 1982, Duke & Rumble 1986, Vry *et al.* 1990), but it is not ubiquitous. The equilibrium stability-limit for graphite in the dimension of oxygen fugacity is given by equation 5 applied to the system C–O, with the maximum fugacity of CO_2 fixed by lithostatic pressure (neglecting the contribution of CO and other minor species). Graphite stability is displaced to lower oxygen fugacities in the system C–O–H relative to C–O owing to dilution of CO_2. As is evident from equation 5, the oxygen fugacity cannot exceed values along the graphite stability-line for C–O on Figure 4 for any graphite-saturated system at mechanical equilibrium. Conditions above the line are indicative of fluids undersaturated with respect to graphite. Oxygen fugacity values below the graphite stability-line in C–O correspond to dilution of carbon dioxide in the presence of graphite by other constituents in C–O–H, such as water and methane as well as other components, or to fluid-absent phase relations.

Figure 4 contains a summary of oxygen fugacities measured by oxide barometry and reported by Lamb & Valley (1984) and Lamb *et al.* (1987). These data indicate that many rocks of the lower crust fall within the region of graphite saturation for C–O fluids and for C–O–H fluids at higher oxygen fugacities, such as the quartz – fayalite – magnetite – fluid assemblage. This observation applies whether or not graphite is a widely distributed mineral constituent of high-grade metamorphic rocks. It may be significant that many of the rocks that plot beneath the C–O graphite saturation line on Figure 4 are of plutonic igneous rather than supracrustal origin; oxygen fugacities inherited from deeper sources could have been low enough to avoid graphite saturation of multicomponent C–O–H fluids.

Also shown on Figure 4 is the oxygen fugacity obtained from the data base of Berman (1988) for coexisting quartz – fayalite – magnetite – fluid. Graphite is not expected as a stable phase at oxygen fugacities along or above the QFM in granulites, as shown by the relationship of the QFM and the C–O graphite saturation line on Figure 4.

Orthopyroxene is a more stable phase than fayalite in granulites; the common occurrence of pyroxene in association with quartz and magnetite indicates that any pervasive fluids that may have equilibrated with pure magnetite-bearing assemblages in granulites could not have been graphite-saturated. Graphite is not, therefore, expected to be a widespread constituent of

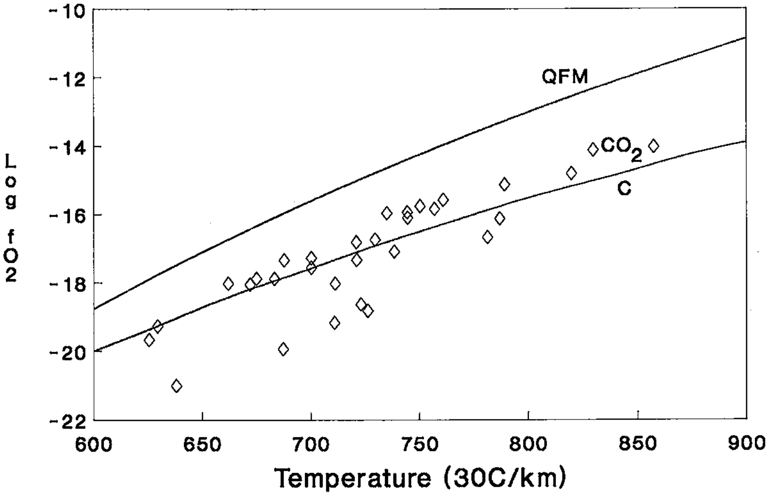

FIG. 4. Graphite stability *versus* temperature along a 30°C/km pressure – temperature gradient. Graphite-saturated fluids in equilibrium with carbon dioxide cannot exist above the field labeled CO_2/C, along a 30°C/km pressure – temperature gradient. Fugacity coefficients from Holloway (1977), as modified by Flowers (1979). The quartz – fayalite – magnetite – fluid reference assemblage (QFM) calculated from the data-base of Berman (1988) is also indicated. Measured oxygen fugacities based on oxide barometry (Lamb & Valley 1984, Lamb *et al.* 1987) of mainly igneous rocks from granulite terranes are indicated for comparison.

granulites at the conclusion of prograde metamorphism unless the activity of Fe_3O_4 is decreased by additional components such as Ti in the oxide phases.

It is possible that graphite is a more important constituent during the early stages of granulite formation. Glassley (1982) and Lamb & Valley (1984) have considered fluid evolution and graphite genesis in rocks of the lower crust. The addition of carbon dioxide to an aqueous fluid at constant (or decreasing) oxygen fugacity forces the fluid to evolve toward the graphite saturation-surface. Lamb & Valley (1984) have concluded that the production of 10 volume % orthopyroxene from amphibole due to the addition of carbon dioxide would result in the precipitation of 1.5% graphite. The infrequency of such high contents of graphite in granulites does not support widespread CO_2 infiltration as a significant mechanism in the genesis of granulites, in spite of evidence from field relationships (Janardhan *et al.* 1982), isotopic evidence (Kreulen 1988) and fluid-inclusion studies (Touret 1981) in support of the addition of CO_2 to the lower crust.

An apparent contradiction exists between the tendency toward graphite saturation that is indicated by CO_2-dominant fluids commonly reported from granulites (Touret 1970) and the incompatibility of graphite with pyroxene - magnetite - quartz rocks under conditions of the granulite facies. Fluid evolution during granulite metamorphism may explain this contradiction, as considered below.

FLUID INSTABILITY

The previous discussion suggests the possibility that pressure - temperature - time paths for granulites could pass through a region in which mechanical stability could not be maintained with a graphite-saturated C–O–H fluid phase present. Connolly & Thompson (1989) have determined pressure - temperature - time paths for rocks undergoing instantaneous crustal thickening from 35 to 70 km either in a uniform manner or by the superposition of one thermally equilibrated slice on top of another. Eckert (1989) has also discussed such paths. The curves for the superposition model (neglecting the minor thermal affects of prograde and retrograde mineral-reactions) are reproduced on Figure 5. The time points obtained by Connolly & Thompson (1989) along the calculated curves are omitted from the figure; approximately 110 million years are required to reach the temperature maximum along the curves originating in the lower crust.

Also shown on Figure 5 are the stability fields for the aluminosilicate minerals, as determined by Holdaway (1971) and Richardson *et al.* (1969). These have been located on the assumption of an average rock-density of 3.0 g/cm^3. The pressure - temperature - time paths calculated by Connolly & Thompson (1989) do not pass through the sillimanite field for the assumed average rock-density. The suggested maximum temperature for any depth along the calculated pressure - temperature - time paths can be treated as a minimum value for granulites, since sillimanite is the most common aluminosilicate mineral observed in these rocks. The calculated pressure - temperature - time curves of Connolly & Thompson suggest the accumulation of heat by means other than crustal thickening to account for the widespread presence of sillimanite in granulite-facies rocks.

It is possible to superimpose the boundaries indicating mechanical equilibrium for graphite-saturated C–O–H fluids as derived above onto pressure - temperature - time paths such as those calculated by Connolly & Thompson (1989). Figure 5 shows the relationship between the two types of curves; the figure shows the equilibrium boundary for the quartz - fayalite - magnetite (QFM) reference assemblage, as well as the QFM minus one logarithmic unit with hydrogen fugacity fixed by the assemblage biotite (annite mole fraction = 0.454, activity = 0.094) - K-feldspar (mole fraction = activity = 0.906) - magnetite - fluid. With the three geological constraints (hydrogen fugacity determined, oxygen fugacity determined, graphite saturation), there is only one temperature for any particular lithostatic pressure (depth) in the crust at which the calculated pressures of fluid from equations 2 through 5 will sum to the lithostatic pressure determined by rock density; it is the locus of such points that is given by the curves labeled QFM and QFM–1 on Figure 5. Mechanical equilibrium in the presence of a fluid is not possible for temperatures greater than indicated by these curves at a given depth and for the specified mineral compositions; this situation was shown previously for one pressure–temperature gradient on Figure 3, where fluid pressure exceeded lithostatic pressure at 540°C and a depth of 18 km. Other points along the QFM curve are calculated in a manner similar to that in Figure 3, but with different pressure - temperature relationships.

According to the calculations summarized on Figure 5, the pressure - temperature - time paths for granulites with oxygen fugacities at or higher than the QFM pass through a region where calculated pressures of fluid are in excess of lithostatic pressure. Since the oxygen fugacities in granulites are typically higher than QFM and since the actual pressure - temperature - time paths must

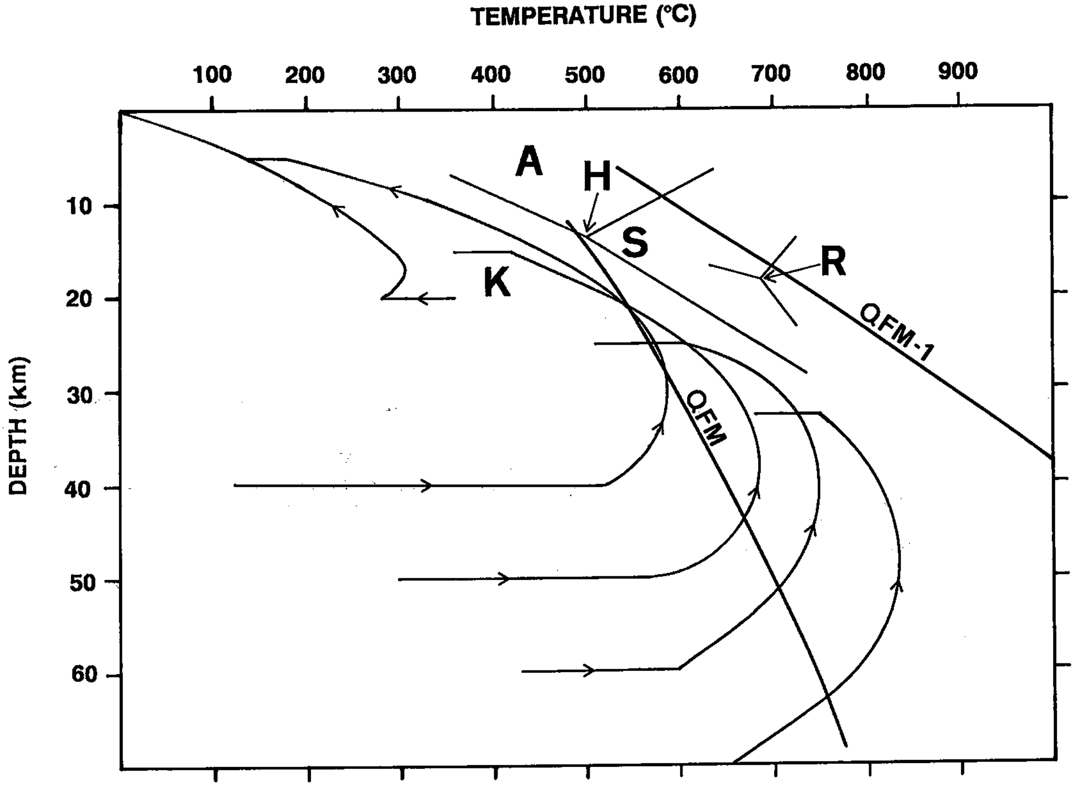

FIG. 5. Pressure – temperature – time curves calculated by Connolly & Thompson (1989) for an instantaneous superposition of one 35-km slice of crust on another. The stability fields of the aluminosilicate minerals, andalusite (A), kyanite (K), and sillimanite (S), are taken from Holdaway (1971) (H) and Richardson *et al.* (1969) (R), on the assumption of a mean rock-density of 3.0 g/cm^3. Mechanical stability curves for graphite-saturated fluids in C–O–H with the fugacity of hydrogen fixed by biotite (annite activity = 0.1) – K-feldspar – magnetite – fluid and oxygen fugacity fixed by the quartz – fayalite – magnetite assemblage (QFM), or the same assemblage with one logarithmic unit arbitrarily subtracted (QFM–1) to illustrate the effect of decreasing oxygen fugacity. The position of the QFM was calculated using the data-base of Berman (1988). Fugacity coefficients from Holloway (1977), as modified by Flowers (1979).

pass through the stability field of sillimanite according to mineral assemblages typically observed in the field, it is likely that devolatilization occurs within the region of mechanical instability of fluids as shown on Figure 5 for typical pressure – temperature – time paths of granulite.

The choice of a clockwise or counterclockwise time-path through pressure – temperature space to represent granulites is a matter of discussion in the current literature (for example, Bohlen 1987). The determination of the applicable time-path for granulites is not essential for the present discussion. The relationship of the QFM curve on Figure 5 to the stability field of sillimanite indicates that rocks that achieve sillimanite-grade metamorphism under the mineralogical constraints considered in this paper will cross into a region of mechanical instability for fluids regardless of the characteristics of the time path.

DEVOLATILIZATION IN THE ZONE OF MECHANICAL INSTABILITY

Consider a biotite schist or other rock type that passes through the mechanical equilibrium boundary for fluid (Fig. 4 or 5). Devolatilization resulting from calculated graphite-saturated fluid pressure in excess of lithostatic pressure will continue with the addition of heat until one of the fluid reservoirs is exhausted. It is evident that the hydrogen reservoir is depleted by devolatilization during granulite-facies metamorphism. Where there is sufficient carbon available to the granulite precursor, it is expected that all the hydrogen will be lost. In other cases, where insufficient carbon exists, hydrous phases will remain, to account for the common presence of hydrous minerals in granulite terranes.

The condition of mechanical equilibrium in a graphite-saturated C–O–H fluid on Figure 4 is only slightly below the same boundary in the system C–O. This is to be expected, since calculations such as shown on Figure 2 indicate that C–O–H fluids constrained by fayalite - quartz - magnetite approach pure carbon dioxide under granulite-facies conditions. The depletion of the hydrogen reservoir indicated by the development of mineral assemblages typical of granulites must, therefore, be accompanied by the exhaustion of the carbon reservoir contained in graphite, since graphite-saturated C–O fluids enter the region of mechanical instability only slightly later along the pressure - temperature - time path than graphite-saturated C–O–H fluids with oxygen fugacities greater than QFM. Thus, not only hydrous minerals but also residual graphite will disappear to allow equilibrium to be maintained between the mineral assemblage and remaining fluids. It is not surprising, therefore, that graphite is not an abundant mineral in granulites, since any graphite present is oxidized within the region of mechanical instability of fluid along the pressure - temperature - time path.

The widespread occurrence of oxide phases in silicate rocks from the lower crust and upper mantle indicates that the oxygen reservoir is not depleted by deeper processes. There is no shortage of oxygen to burn off any graphite within the region of mechanical instability. The residual fluid phase would be dominantly carbon dioxide at oxygen fugacities above the QFM reference assemblage. It is not known how long such fluids would persist along the pressure - temperature - time path following the transient process of devolatilization.

Concluding Statement

Two widely supported mechanisms have been discussed in the literature to account for the devolatilization of rocks in the lower crust. The role of melts in the petrology of granulites was discussed originally by Fyfe (1973) and, more recently, for example, by Bohlen (1987) and Bohlen & Mezger (1989). The removal of the melts and dissolved water to higher levels would deplete the lower crust in water and could lead to lower activities of water, as well as the instability of hydrous phases and the undersaturation of melts with respect to water. However, the proportion of melt (for example charnockite and granite) to unmelted residuum, as represented by granulite, is smaller than expected to account for devolatilization. In some granulite terranes, such as in southern India (Janardhan *et al.* 1982, Condie *et al.* 1982), the Kapuskasing structure (Percival & McGrath 1986) or the Grenville Province (Davidson 1986), an additional mechanism to account for granulite formation could help to explain the large volumes of granulite not obviously associated with melts.

Newton *et al.* (1980) have advocated the influx of carbon dioxide from the mantle as originally proposed by Touret (1970) and supported more recently by Glassley (1983). It has, however, been argued that oxygen and deuterium isotopes do not support the large fluid/rock ratios implied by this process (for example, Jansen *et al.* 1989). The fluid sampled by the channel sites of cordierite (Vry *et al.* 1990), the widespread development of wollastonite in calc-silicate lithologies, and the low oxygen fugacities that restrict the value of carbon dioxide fugacity (Lamb *et al.* 1987), as well as evidence for channelized rather than pervasive flow of fluid (Valley *et al.* 1983), have all been cited as evidence against a major influx of carbon dioxide into the deep crust.

The possibility that pressure - temperature - time paths for rocks of the deeper crust might pass through a region of granulites without the pervasive influence of melts or extensive volatile infiltration has been advocated by Eckert (1989); such rocks have been referred to as tectonic granulites. A demonstration of the local transition of gneiss into charnockite by internal processes has been given by Raith *et al.* (1988). Rocks with a low fluid/rock ratio could have undergone devolatilization by outgassing in the zone of mechanical instability for fluid. A sudden expulsion of fluid from lower levels of the crust could promote deformation along deep zones of ductile deformation (Rice 1990) and enhance the migration of dissolved species from lower to higher crustal levels (Cox 1990).

The origin of the carbon needed to bring about large-scale devolatilization of the crust is not well understood. If the carbon reservoir of the crust is large enough to account for devolatilization of the granulite precursor, then it should be possible to detect a carbon decrease from amphibolite- to granulite-grade rocks. It is also possible that infiltration of carbon dioxide from the mantle is important in supplying the necessary carbon.

Future work is needed to demonstrate higher oxygen fugacities in granulites than the quartz - fayalite - magnetite - fluid reference assemblage and to establish fluid/rock ratios in cases of granulite metamorphism. Such data will test the possibility that graphite-saturated fluids are not mechanically stable along significant portions of the pressure - temperature - time paths of granulites.

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