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A Note on the Significance of the Assemblage Calcite-Quartz-Plagioclase-Paragonite-Graphite

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Abstract. The biotite zone assemblage: calcite-quartz-plagioclase (An_{25})-phengite-paragonite-chlorite-graphite, is developed at the contact between a carbonate and a pelite from British Columbia. Thermochemical data for the equilibrium paragonite + calcite + 2 quartz = albite + anorthite + CO_2 + H_2O yields:

$$\log f_{H_2O} + \log f_{CO_2} = 5.76 + 0.117 \times 10^{-3} (P - 1)$$

for a temperature of 700° K and a plagioclase composition of An_{25} . By combining this equation with equations describing equilibria between graphite and gas species in the system C-H-O, the following partial pressures: $P_{H_2O} = 2572b$, $P_{CO_2} = 3162b$, $P_{H_2} = 2.5b$, $P_{CH_4} = 52.5b$, $P_{CO} = 11.0b$ are obtained for $f_{O_2} = 10^{-26}$. If total pressure equals fluid pressure, then the total pressure during metamorphism was approximately 6 kb. The total fluid pressure calculated is extremely sensitive to the value of f_{O_2} chosen.

Among the micas, paragonite is not uncommon in metamorphosed pelitic rocks; however, it has rarely been reported as a member of a carbonate-bearing assemblage. In this note we report the occurrence of a calcite-quartz-plagioclase-phengite-paragonite-chlorite-graphite assemblage in the biotite zone rocks of the Horsethief Creek Formation, Esplanade Range, Selkirk Mountains, British Columbia (51°35'N, 117°35'W). Pelitic rocks of this Proterozoic unit locally contain chloritoid and paragonite whereas biotite is generally more abundant in the metasediments. Thin interbeds of metacarbonate, up to 10 feet thick, contain calcite-mica-quartz (\pm dolomite) assemblages. At contacts between pelitic and carbonate beds more diverse assemblages are developed, including the assemblage calcite-quartz-plagioclase-phengite-paragonite-chlorite-graphite.

In recent years hydroxyl-bearing silicate and silicate-carbonate assemblages have been studied to obtain estimates of fluid pressures during metamorphism (e.g. Wones and Eugster, 1965; Greenwood, 1967). In this note thermochemical and experimental data are used in an attempt to assess the significance of the assemblage calcite-quartz-plagioclase-paragonite-graphite as a fluid pressure indicator during metamorphism.

Partial analyses with the electron microprobe indicate about 3.3 mole percent $MgCO_3$ solid solution in calcite from this assemblage. This value, in light of recent experimental data (Goldsmith and Newton, 1969) and an estimated load pressure of 3-6 kilobars indicates a minimum temperature of approximately 700° K (427°C). This temperature is consistent with results obtained from the partition of Mg between calcite and dolomite in adjacent rocks.

Assemblage e-Graphite

Calgary, Alberta, Canada

z-plagioclase (An₂₅)-phengite-paragonite-
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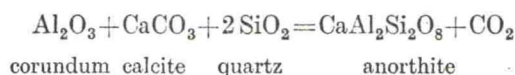
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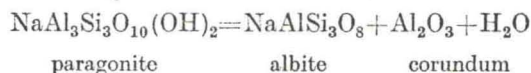
Plagioclase is present as untwinned grains generally less than 100 μ across and partial microprobe analyses give a composition range of An₂₄-An₃₀ (average value near An₂₅). Phengite and paragonite have been identified by both X-ray diffraction methods and by partial electron microprobe analyses. Graphite is present throughout low-grade metamorphic rocks of the Esplanade Range and, where abundant, it has been identified by X-ray diffraction patterns and reflected light studies of insoluble residues.

Assuming that the assemblage calcite-quartz-plagioclase-paragonite-graphite equilibrated at a temperature of near 700°K (427°C) and that fluid pressure was equal to total pressure, then thermochemical and experimental data can be used to estimate the partial pressures of the species of the fluid phase in equilibrium with the mineral assemblage.

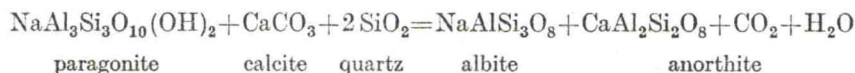
Combining thermochemical data (Robie and Waldbaum, 1968) for the reaction:



with experimental data (Evans, 1965; Chatterjee, 1968) for the reaction:



gives for the combined equilibrium:



the following equation, if the solid phases are present as the pure end-members:

$$\log f_{H_2O} + \log f_{CO_2} = \frac{-8821}{T} + 17.63 + \frac{0.0819}{T} (P-1) \quad (1)$$

T is temperature in degrees Kelvin, P is the pressure on the solids in bars, f_{H_2O} and f_{CO_2} are the fugacities of H_2O and CO_2 in the fluid phase, and the logarithms are to the base 10.

This equation is for the pure end members as products and reactants, neglecting the effect of solid solutions. If mole fractions of $NaAlSi_3O_8$ and $CaAl_2Si_2O_8$ (average value An₂₅) are substituted for activities of the plagioclase components, Eq. (1) at a temperature of 700°K becomes:

$$\log f_{H_2O} + \log f_{CO_2} = 5.76 + 0.117 \cdot 10^{-3} (P-1) \quad (2)$$

Equations describing the equilibria between graphite and the most abundant gas species in the system C-H-O (French, 1966) for a temperature of 700°K are:

$$\log f_{H_2O} - \log f_{H_2} - \log f_{O_2}^2 = 15.58 = \log K_1, \quad (3)$$

$$\log f_{CH_4} - \log f_{H_2}^2 = 0.94 = \log K_2, \quad (4)$$

$$\log f_{CO_2} - \log f_{O_2} = 29.50 = \log K_3, \quad (5)$$

$$\log f_{CO} - \log f_{O_2}^2 = 12.95 = \log K_4 \quad (6)$$

(data from Robie and Waldbaum, 1968).

Assuming that total pressure is equal to fluid pressure, then the total pressure is also the sum of the partial pressures of the gas species, i. e.:

$$P = P_{\text{H}_2\text{O}} + P_{\text{CO}_2} + P_{\text{CH}_4} + P_{\text{CO}} + P_{\text{H}_2} + P_{\text{O}_2}$$

$$= \frac{f_{\text{H}_2\text{O}}}{\gamma_{\text{H}_2\text{O}}} + \frac{f_{\text{CO}_2}}{\gamma_{\text{CO}_2}} + \frac{f_{\text{CH}_4}}{\gamma_{\text{CH}_4}} + \frac{f_{\text{H}_2}}{\gamma_{\text{H}_2}} + \frac{f_{\text{O}_2}}{\gamma_{\text{O}_2}} \quad (7)$$

where γ_i is the appropriate fugacity coefficient for species i at 700°K and a total pressure P . For the purposes of this note fugacity coefficients of all species except H_2O are taken as unity whereas the fugacity coefficients of H_2O are interpolated from values tabulated by Burnham, Holloway and Davis (1969). By making the appropriate substitutions the following two equations can be obtained from Eqs. (2-7).

$$\log f_{\text{H}_2\text{O}} = -23.74 + 0.117 \times 10^{-3} (P - 1) - \log f_{\text{O}_2} \quad (8)$$

$$f_{\text{H}_2\text{O}} + B/A f_{\text{H}_2\text{O}}^2 + \frac{C \cdot P}{A} = 0$$

where

$$A = K_2 K_1^{-2} f_{\text{O}_2}^{-1}, \quad B = \gamma_{\text{H}_2\text{O}}^{-1} + K_1 f_{\text{O}_2}^{-1/2}, \quad C = K_3 f_{\text{O}_2} + K_4 f_{\text{O}_2}^{1/2} + f_{\text{O}_2} \quad (9)$$

Knowledge of f_{O_2} allows Eqs. (8) and (9) to be solved graphically for the two remaining variables by plotting $f_{\text{H}_2\text{O}}$ versus P .

Coexisting magnetite-graphite and ilmenite-graphite in adjacent pelitic rocks are compatible with an oxygen fugacity in the range 10^{-35} to 10^{-26} . In the absence of definitive oxide assemblages from the pelitic-carbonate assemblage we have used this latter value in the calculations (Table and Fig. 1).

The total fluid pressure (sum of the partial pressures) obtained with this procedure is extremely sensitive to the value of f_{O_2} chosen. This is illustrated in Fig. 1 where calculated total pressure (= fluid pressure) is plotted against f_{O_2} . As shown, a variation in f_{O_2} of $10^{0.2}$ from the chosen value of 10^{-26} results in a variation of calculated total fluid pressure of approximately 1,000 bars. If, for example, the value selected for f_{O_2} were $10^{-25.5}$ instead of 10^{-26} the calculated fluid pressure would be greater than 10,000 bars instead of 6,000 bars. A value of more than 10,000 bars is much greater than the load pressure of 3-6 kb consistent with the occurrence of kyanite and almandine in higher grade rocks.

Table. Fugacities, partial pressures and total fluid pressure of gas species in equilibrium with the calcite-quartz-plagioclase-paragonite-graphite assemblage at 700°K and $f_{\text{O}_2} = 10^{-26}$

Species	Fugacity	Fugacity coefficient	Partial pressure
H_2O	925	0.336	2,752
CO_2	3,162	1	3,162
H_2	2.5	1	2.5
CH_4	52.5	1	52.5
CO	11.0	1	11.0

$P = 5,980$ bars

fluid pressure, then the total pressure
the gas species, i. e.:

$$P_{\text{CO}_2} + P_{\text{H}_2} + P_{\text{O}_2} \\ \frac{f_{\text{H}_2}}{\gamma_{\text{H}_2}} + \frac{f_{\text{O}_2}}{\gamma_{\text{O}_2}} \quad (7)$$

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$$10^{-3}(P-1) - \log f_{\text{O}_2}, \quad (8)$$

$$+ \frac{C-P}{A} = 0$$

$$C = K_3 f_{\text{O}_2} + K_4 f_{\text{O}_2}^{-1} + f_{\text{O}_2}. \quad (9)$$

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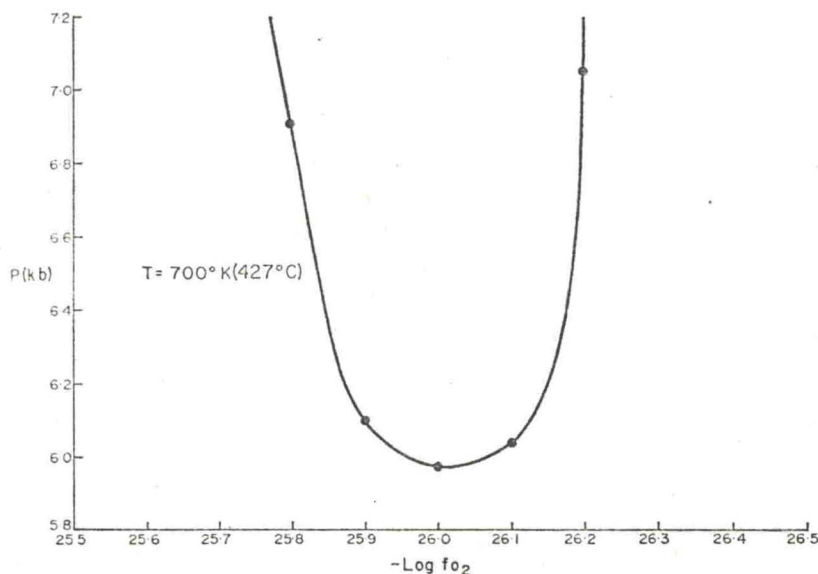


Fig. 1. Plot of calculated total pressure (=fluid pressure) versus oxygen fugacity at 700°K . Dots represent graphical solutions of Eqs. (8) and (9); see text. The minimum is not precisely determined

From the above calculations, the estimated H:O ratio in the fluid phase is 0.6:1. Thus the presence of graphite need not indicate a high H:O ratio in the fluid (Miyashiro, 1964), if CO_2 pressure is high. Conversely, a low H:O ratio in a fluid which has equilibrated with graphite need not indicate a high f_{O_2} .

Even if the above calculations are only approximate, the usefulness of calcite-quartz-plagioclase-paragonite-graphite assemblages in the estimation of fluid pressures is readily apparent. This assemblage and the analogous K-rich assemblage, muscovite-calcite-quartz-anorthite-orthoclase (Hewitt and Orville, 1966), merit further experimental investigation.

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