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OXYGEN, CARBON DIOXIDE, AND SULFUR FUGACITIES DURING DIAGENESIS AND LOW-GRADE METAMORPHISM OF LATE PRECAMBRIAN SUBGRAYWACKES FROM NORTHERN UTAH

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ABSTRACT

Two or more minerals in the group magnetite, hematite, pyrite, siderite, and graphite of apparent diagenetic or low-grade metamorphic origin coexist in late Precambrian subgraywackes in northern Utah. If equilibrium was approached between these minerals and the pore fluid during diagenesis (25±25°C) and again during metamorphism (400±100°C), thermodynamic calculations indicate the following increases in oxygen, carbon dioxide, and sulfur fugacities during low-grade metamorphism (expressed in orders of magnitude): f_{O_2}, 35–70; f_{CO_2}, 0–9; f_{S_2}, 20–45. Progressive disappearance of siderite and appearance of hematite as a function of metamorphic grade suggest that oxidation accompanied metamorphism.

INTRODUCTION

Two or more minerals in the group magnetite, hematite, pyrite, siderite, and graphite which appear to be of diagenetic or metamorphic origin coexist in late Precambrian subgraywackes (and conglomeratic subgraywackes) in northern Utah (Condie, 1967). Their occurrence suggests a method of estimating oxygen, carbon dioxide, and sulfur fugacities that accompanied diagenesis and later, low-grade (greenschist facies) metamorphism of these rocks. Unmetamorphosed samples were collected from the upper part of the late Precambrian section in the Big Cottonwood Canyon area southeast of Salt Lake City. Metamorphosed samples were collected lower in this section and from stratigraphically and lithologically equivalent sections in the Great Salt Lake area.

MINERALOGICAL ASPECTS

The subgraywackes and conglomeratic subgraywacke matrices are composed of rounded quartz and minor sodic plagioclase and microcline grains in a fine matrix of predominantly chlorite, mica, and quartz (Condie, 1967). Of the accessory minerals that occur in the matrix, magnetite, euhedral hematite, pyrite, siderite, and carbonaceous matter (including graphite) are of importance to this study. The ranges (dashed vertical lines) and mean values (small circles) of the concentrations (modes) of these minerals and ilmenite in 20 samples from each of the unmetamorphosed (UM) and metamorphosed (M) terranes are shown in Figure 1. Lines connecting the mean values suggest changes that may have accompanied progressive low-grade metamorphism.

Because of the difficulty in distinguishing magnetite from ilmenite in the rock matrices, these two minerals are combined into one mode; studies under reflected light, however, indicate that ilmenite is the more abundant of the two minerals. Although some of the ilmenite and magnetite may be of clastic origin, the fact that they commonly surround and embay clastic quartz and feldspar grains suggests a diagenetic or metamorphic origin. The carbonaceous matter occurs as very fine, disseminated particles in the rock matrices and in rock fragments contained in the subgraywackes. Because graphite could not easily be distinguished from carbonaceous matter, it is included with the carbonaceous matter mode given in Figure 1.

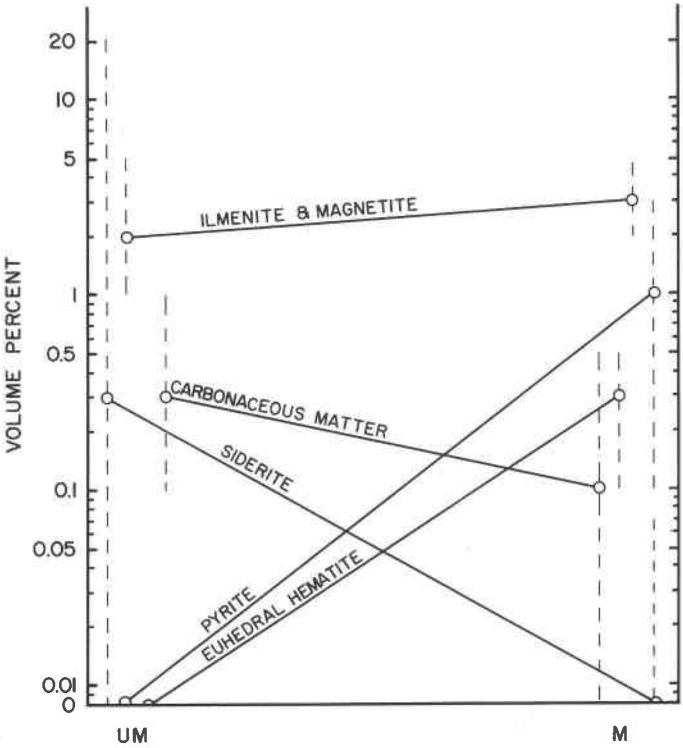

FIG. 1. Accessory mineral variation between unmetamorphosed (UM) and metamorphosed (M) late Precambrian terranes in northern Utah.

Pyrite occurs as discrete well-developed crystals in the metamorphosed subgraywackes, but was not positively identified in the unmetamorphosed samples. It is usually ≤0.1 mm in size but occasional crystals ≥1 cm occur. Small euhedral hematite crystals (0.05–0.3 mm) of prob-

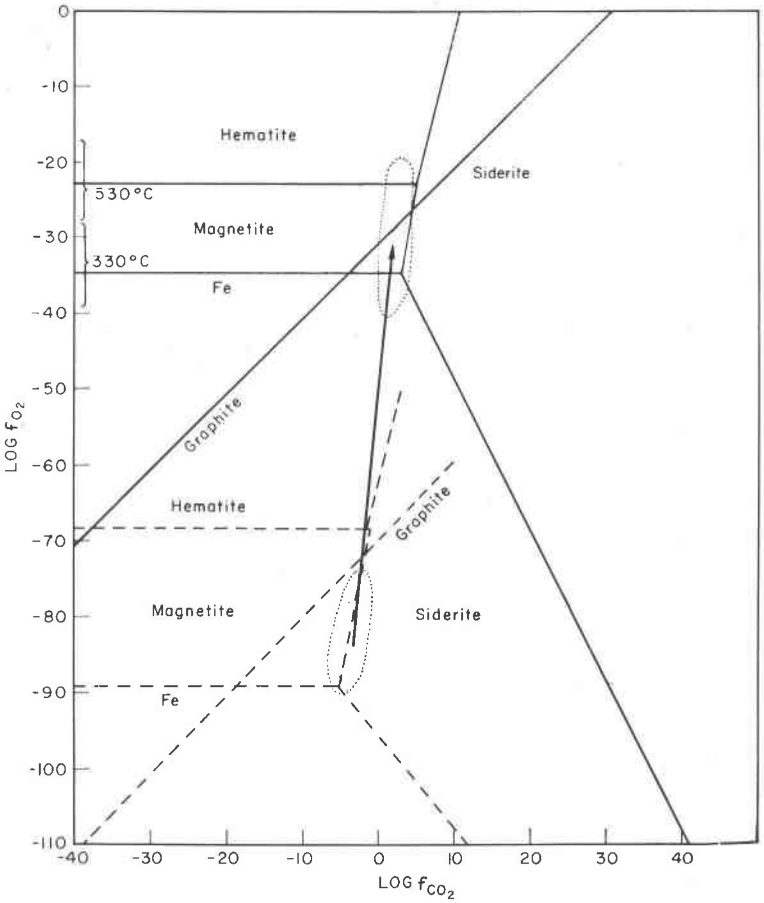

FIG. 2. Stability relations of some iron oxides, native iron, and siderite as functions of f_{CO_2}, f_{O_2} and temperature. Dashed lines at 25°C and solid lines at 400°C. Arrow indicates transition from unmetamorphosed to metamorphosed fields.

able metamorphic origin occur in the matrices of the metamorphosed samples. Such crystals are quite distinct from irregular hematite patches and veinlets of secondary origin which are common in some of the rocks. Euhedral hematite crystals were not found in the unmetamorphosed samples: a few, however, were found in the incipiently metamorphosed samples from the lower portion of the Big Cottonwood Canyon section.

Siderite, which occurs as fine, closely packed euhedral crystals in the more argillaceous parts of the subgraywackes, is almost exclusively confined to the unmetamorphosed samples. A small amount (≤ 0.1 percent) occurs in the incipiently metamorphosed subgraywackes from the lower

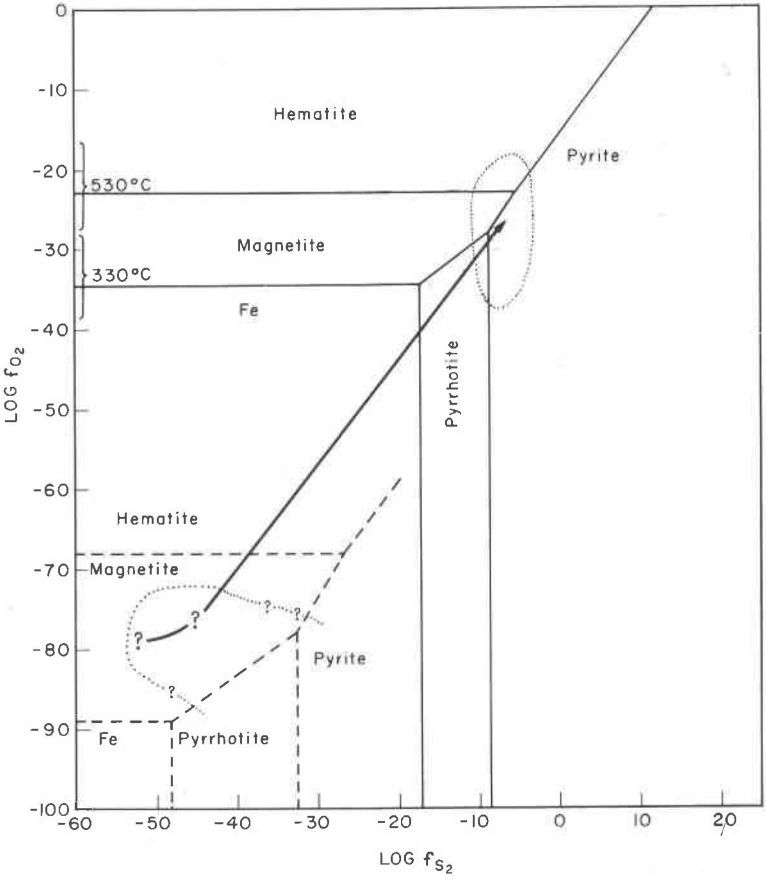

FIG. 3. Stability relations of some iron oxides and sulfides and native iron as functions of f_{O_2}, f_{S_2}, and temperature. Dashed lines at 25°C and solid lines at 400°C. Arrow as in Fig. 2.

part of the Big Cottonwood Canyon section. Because of the large range in concentration of siderite in the unmetamorphosed samples, it is difficult to estimate a mean value; the value shown in Figure 1 should be considered a minimum value.

The fact that magnetite, hematite, pyrite, and siderite occur as well-formed crystals and commonly penetrate and embay grains of clastic origin, suggests that they grew during diagenesis (magnetite and siderite) or low-grade metamorphism (magnetite, hematite, and pyrite).

FUGACITY DIAGRAMS

In order to estimate f_{O_2}, f_{CO_2}, and f_{S_2} values, diagenetic and low-grade metamorphic temperatures must first be estimated. Coexisting muscovite and paragonite from the metamorphosed late Precambrian subgraywackes in northern Utah (Condie, 1967) indicate an equilibrium temperature of approximately 400°C; the fugacity diagrams for low-grade metamorphism were constructed at this temperature. The fugacity calculations and general conclusions of this study will not be greatly affected if the metamorphic temperature was anywhere in the range 300–500°C. A diagenetic temperature of 25°C has been assumed; however, any temperature in the range 0–50°C will not greatly affect the results of the study.

TABLE 1. DATA USED IN CONSTRUCTING THE FUGACITY DIAGRAMS IN FIGURES 2 AND 3

Reaction	$\Delta G^{400°C}$ cal/mole	Fugacity equation
$Fe_3O_4+3CO_2 \rightarrow 3FeCO_3+1/2\ O_2$	81,124	$\log f_{CO_2}=8.8+1/6 \log f_{O_2}$
$Fe+CO_2+1/2\ O_2 \rightarrow FeCO_3$	−43,858	$\log f_{CO_2}=-14.2-1/2 \log f_{O_2}$
$Fe_2O_3+2CO_2 \rightarrow 2FeCO_3+1/2\ O_2$	65,871	$\log f_{CO_2}=10.7+1/4 \log f_{O_2}$
$3Fe+2O_2 \rightarrow Fe_3O_4$	−212,696	$\log f_{O_2}=-34.5$
$2Fe_3O_4+1/2\ O_2 \rightarrow 3Fe_2O_3$	−35,365	$\log f_{O_2}=22.9$
$C+O_2 \rightarrow CO_2$	−94,490	$\log f_{CO_2}=30.7+\log f_{O_2}$
$Fe_2O_3+2S_2 \rightarrow 2FeS_2+3/2\ O_2$	75,055	$\log f_{S_2}=11.9+3/4 \log f_{O_2}$
$Fe_3O_4+3S_2 \rightarrow 3FeS_2+2O_2$	91,890	$\log f_{S_2}=9.9+2/3 \log f_{O_2}$
$Fe_3O_4+3/2\ S_2 \rightarrow 3FeS+2O_2$	131,574	$\log f_{S_2}=28.5+4/3 \log f_{O_2}$
$FeS+1/2\ S_2 \rightarrow FeS_2$	−13,295	$\log f_{S_2}=-8.6$
$2Fe+S_2 \rightarrow 2FeS$	−54,014	$\log f_{S_2}=-17.5$

The reactions used in constructing the fugacity diagrams at 400°C (Figs. 2 and 3) are given in Table 1 with corresponding free energy values and fugacity equations. The free energies were calculated from the high temperature heat capacity and entropy data of Kelley (1960). Entropies at 25°C are from Kelley (1950) and enthalpies from Rossini, *et al* (1952). The 25°C portions of the diagrams (shown as dashed lines) are after Garrels and Christ (1965, p. 153). Also shown on the f_{O_2} axes of the diagrams with brackets is the location of the magnetite stability field at 330°C and 530°C. It is clear that a temperature difference of about

400 ± 100°C does not greatly affect this part of the diagrams. The other phase boundaries, although not indicated on the diagrams, are affected even less at the same temperatures.

DISCUSSION

If magnetite, siderite, and the coexisting pore fluid approached equilibrium during diagenesis, the corresponding f_{O_2} and f_{CO_2} values lie along the siderite-magnetite phase boundary in Figure 2. The presence of graphite in these rocks restricts the f_{O_2}-f_{CO_2} values to the lower three-fourths of the phase boundary line if the graphite also approached equilibrium in the system. Considering that chemical equilibrium is probably not attained in low-temperature mineral assemblages, a possible range of f_{O_2} (10^{-90} to 10^{-75} atm) and f_{CO_2} (10^{-5} to 10^{-5} atm) values is shown by the dotted line on the 25°C portion of Figure 2. The corresponding region on the f_{O_2}-f_{S_2} diagram (Fig. 3) is less easy to depict because neither pyrite nor pyrrhotite was positively identified in the unmetamorphosed samples. However, using the range of f_{O_2} values from Figure 2, a possible region is indicated with a dotted line on the 25°C portion of this diagram ($f_{S_2} \leq 10^{-30}$ atm). From this data it is apparent that f_{CO_2} has a rather limited range of diagenetic values (varying by only several orders of magnitude) as compared to those of f_{O_2} and f_{S_2} which may vary by 10 to 20 orders of magnitude.

At 400°C the fugacity diagrams change considerably; notable is the increase in area of the metallic iron stability field and corresponding decreases in the hematite, siderite, and pyrite fields. Thermodynamic calculations indicate that hematite and graphite cannot exist in equilibrium at any reasonable metamorphic temperature, yet both phases occur together with magnetite in the subgraywackes. If these phases are of metamorphic origin as suggested by textural data, equilibrium was apparently not attained during metamorphism. Equilibrium may have been approached in this system, however, because only a few orders of magnitude difference in f_{O_2} occur between the hematite and graphite stability field at 400°C. The fact that graphite was not observed to occur within several millimeters, or more often within several centimeters distance of euhedral hematite crystals may indicate that gradients of several orders of magnitude in f_{O_2} existed over these distances. A probable range of f_{O_2} (10^{-40} to 10^{-20} atm) and f_{CO_2} (10^{-1} to 10^{4} atm) under such circumstances is shown by the dotted line on the 400°C portion of the diagram.

It is not likely that hematite, pyrite, and magnetite in the metamorphosed subgraywackes were in equilibrium during metamorphism because all three can coexist in equilibrium only at an invariant point on the fugacity diagram (Fig. 3). Usually only two out of three of these minerals were observed to coexist in the rock matrices at distances less than several centimeters. Pyrite is especially sparsely distributed in the rocks. If local equilibrium was approached between two out of three of these phases at various times during metamorphism, a region of probable f_{O_2} (10^{-40} to 10^{-20} atm) and f_{S_2} (10^{-10} to 10^{-5} atm) values can be outlined; such a region is shown by a dotted line on the 400°C portion of Figure 3. The presence of pyrite rather than pyrrhotite in these rocks places a lower limit on f_{S_2} of approximately 10^{-9} atm at 400°C.

Arrows have been drawn connecting the fields of diagenesis and low-grade metamorphism in Figures 2 and 3 indicating generalized paths of f_{O_2}, f_{CO_2}, and f_{S_2} during progressive metamorphism. It is interesting to note that while an increase of less than ten orders of magnitude in f_{CO_2} occurs between unmetamorphosed and metamorphosed terranes, f_{O_2} increases 35 to 70 orders of magnitude and f_{S_2} increases 20 to 45 orders of magnitude. Although f_{O_2} appears to have increased greatly during progressive metamorphism, corresponding slight increases in f_{CO_2} appear to have prevented the complete destruction of graphite and carbonaceous matter. The f_{CO_2}, on the other hand, did not reach values high enough to stabilize siderite during metamorphism.

If hematite grew and siderite decomposed during metamorphism as indicated by field and petrographic data and as suggested in Figure 1, oxidation appears to have accompanied progressive low-grade metamorphism of the late Precambrian subgraywackes in northern Utah. It is interesting to note that this trend is opposite to that reported by Engel and Engel (1962) and by Schwarcz (1966) for progressive high-grade metamorphism in which case reduction appears to have accompanied metamorphism.

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