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Petrogenetic Significance of the New Petrogenetic Grid (2000) Compared with Synthetic System and Theoretically Computed Grid

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Abstract: The observation of the new biotite isograd (chlorite + chloritoid = andalusite + biotite) in the Mungyong coal field requires the modification of Harte and Hudson's (1979) metapelite grid which eliminates the stability field of staurolite + cordierite assemblages. The newly proposed metapelite grid by Ahn and Nakamura (2000) can define more properly the isograd reaction observed from nature. We discuss first topological interrelations between synthetic system (FASHO-, KFASHO-, KFMASH system) on an isobaric section at 2kbar, where phase relations are well constrained. The following discussion is concentrated on the topological relations between stable reactions. At the last, we discuss the petrogenetic significance of the Ahn's petrogenetic grid compared with theoretically computed grids. Ahn's petrogenetic grid is consistent with synthetic and natural system, and is one of the excellent example of KFMASH approximation in metapelite.

Key words: isograd reaction, petrogenetic grid, synthetic system

INTRODUCTION

Many petrogenetic grids have been proposed for pelitic assemblages. The petrogenetic grid by Harte and Hudson (1979) has been most frequently cited in metamorphic study. The grid has been constructed to explain various mineral assemblages of Dalradian metapelites. Validity of the grid has been tested for morderate pressure metamorphic terranes (Labotka, 1981; Droop, 1981) and in improved forms, for high pressure terranes (Koons and Thompson, 1985; Vuichard and Ballevre, 1988). However, its lower pressure parts have some inconsistency with them. The absence of muscovite + cordierite + staurolite assemblages in natural occurrences is not in accord with large stability field of the assemblage in the grid as pointed out by Spear and Cheney (1989).

The discovery of the univariant reaction muscovite + chloritoid + chlorite = andalusite + biotite + quartz + H_2O leads to a great improvement of Harte and Hudson's grid at low pressures. As shown in Fig. 1, Ahn and Nakamura proposed a new KFMASH invariant point at a lower pressure, where muscovite, biotite, chlorite, chloritoid, andalusite, staurolite and quartz coexist. The new reaction curve muscovite + chloritoid + chlorite = andalusite + biotite + quartz + H_2O starts from the invariant point to lower pressures and temperatures. This improvement does not disturb the effectiveness of the original grid at higher pressures.

The new invariant point restricts the location of the reaction curve muscovite + chlorite + staurolite = andalusite + biotite + quartz + H_2O at relatively higher pressures. Consequently the curve does not intersect the reaction curve muscovite + chlorite + quartz = andalusite + biotite + cordierite + H_2O and thus the muscovite + staurolite + cordirite assemblage has no stability field. The terminal reaction of chlorite in the presence of muscovite was earlier written as muscovite + chlorite + andalusite + quartz = cordierite + biotite + H_2O by Albee (1965, 1972) and incorporated to Harte and Hudson grid. It was, however, later revised to the present form according to the improved knowledge of Mg-Fe partitioning between

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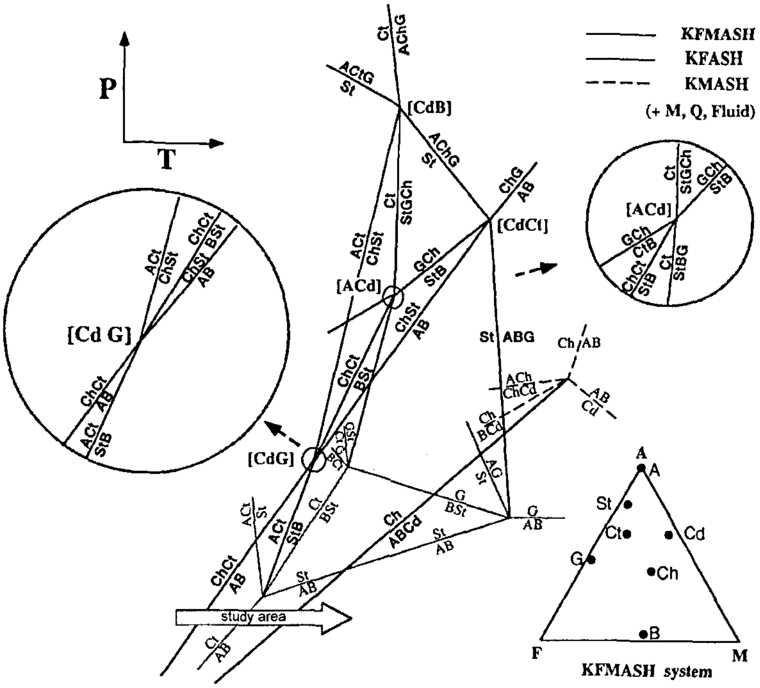

Fig. 1. The new petrogentic grid by Ahn and Nakamura (2000) of metapelites. Abbreviation : St, staurolite; G, garnet; A, aluminosilicate (andalusite, sillimanite or kyanite); M, muscovite; Ch, chlorite; Ct, chloritoid; B, biotite; A, andalusite; Cd, cordierite; Kf, K-feldspar. Chemographic relations between phases are shown on the inset triangle (Thompson AFM diagram).

cordierite, chlorite and biotite (Guidotti *et al.*, 1975; Burnell and Rutherford, 1984; Labotka, 1981). The KFMASH univariant curve originates from the KMASH invariant point, determined by Seifert (1970), where Mg-cordierite, Mg-chlorite, phlogopite, aluminosilicate and quartz coexist.

Several KFMASH univariant curve are generated from KFASH invariant points as shown in the original Harte and Hudson's grid. The new univariant reaction curve muscovite + chloritoid + andalusite = biotite + staurolite + quartz + H_2O is also generated from the KFASH invariant point where muscovite, aluminosilicate, annite, Fe-chloritoid and Fe-staurolite coexist as shown in the Fig. 1. It is not clear whether or not the reaction curve muscovite + chlorite + chloritoid = andalusite + biotite + quartz + H_2O terminates at another KFMASH invariant point in which cordierite is a candidate to join.

The pelitic assemblages from the Mungyong coal field represent one of the best examples of KFMASH approximation. The observed reactions of Mungyong metapelites may be regarded as good experimental data provided by nature. Therefore, it may be most appropriate to compare them first with those in synthetic systems and to see if two types of data can be consistently linked with each other.

COMPARISON WITH EXPERIMENTAL DATA

Relevant experiments are generally made on several subsystems of the KFMASH system. Therefore, we discuss first topological interrelations between them on an isobaric section at 2kbar, where phase relations are well constrained. Figures 2, 3 and 4 is a $-\ln f_{O_2}$ versus $-1/T$ diagram. In this plot, oxidation-reduction reactions can be represented by straight lines, except in low f_{O_2} regions below the QFM buffer, where straight line approximation is no more valid if dehydration is coupled, because X_{H_2} in the fluid phase increases, resulting in the considerable deviation of X_{H_2O} from unity.

The following discussion is concentrated on the topological relations between stable reactions. Consistency is not rigorously pursued to metastable extensions.

Magnetite and hematite are not discriminated for simplicity. Oxygen fugacity values in highly oxidizing regions are least quantitative.

FASHO SYSTEM

Reaction curves in the FASHO system are shown in Fig. 2. Magnetite- and hercynite-free reaction curves are tentatively drawn parallel to the f_{O_2} axis. As exemplified by the chloritoid breakdown reaction (Grieve and Fawcett, 1974), hercynite-bearing assemblages lie on the oxidizing side of reaction curves when magnetite is not involved, because hercynite is more enriched in Fe^{3+} than coexisting silicates.

Accoding to Turnock (1960) and James *et al.* (1976), cordierite breaks down to magnetite + mullite + quartz and cordierite + hercynite reacts to form magnetite + mullite by oxidation. Mullite + quartz is most likely metastable at temperatures concerned and is regarded as Al_2SiO_5 (andalusite). The high temperature extention of the cordierite breakdown reaction is cordierite = spinel solid solution + mullite + quartz, which probably persists to the solidus temperature. At 1 atm it terminates at an isobaric invariant point involving liqud at about 1180 and 10^{-10} atm f_{O_2} (Muan, 1957). The latter reaction (cordierite + hercynite = magnetite + mullite) evaporates at 860°C on the hercynite-magnetite solvus crest (Turnock and Eugster, 1962).

Richardson (1968) investigated, on the QFM buffer, two following reactions limiting the stability of staurolite + quartz; sillimanite + chloritoid = staurolite + quartz + H_2O and staurolite + quartz = sillimanite + cordierite + H_2O. Staurolite + quartz is stable only within a narrow temperature range between 500°C and 575°C. Sillimanite is metastable in this temperature range and instead andalusite is stable.

The chloritoid breakdown reaction forming hercynite + cordierite + staurolite + H_2O is well constrained. Grieve and Fawcett (1974) have placed it at 560°C and 590°C on the NNO buffer and on the QFM

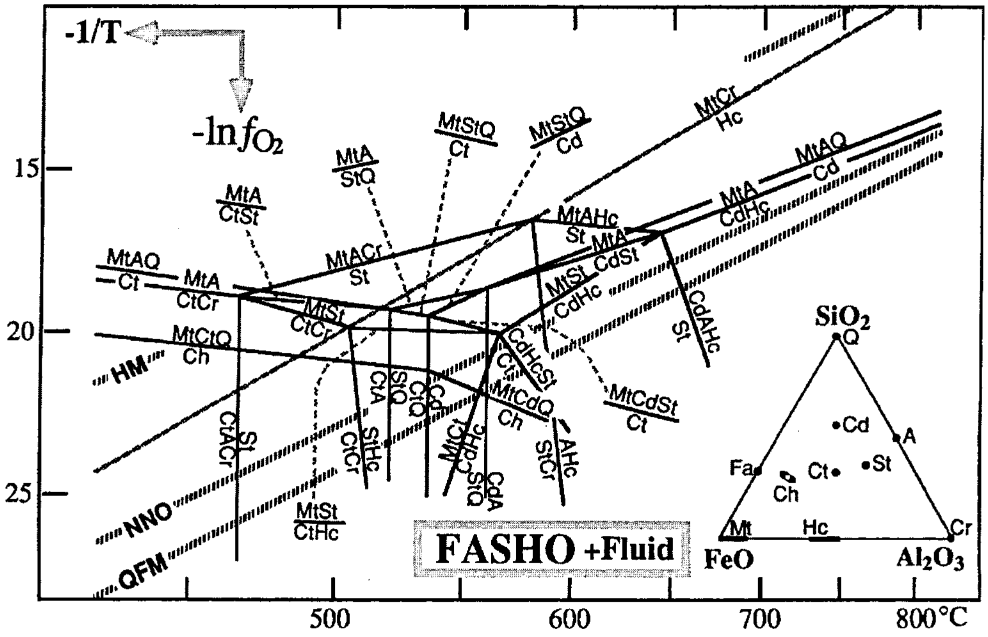

Fig. 2. Temperature-oxygen fugacity diagram at about 2 kbar for reactions in FASHO systems (see text). Abbreviations : Cr, corundum; Mt, magnetite; Fa, fayalite; Hc, hercynite; others are the same as in Fig. 1.

buffer, respectively. They regarded the reaction degenerated, assuming that the compositions of cordierite, chloritoid and hercynite are co-linear on the AFS plane. However, staurolite is appended here to the breakdown product to keep consistency with the significant shift of hercynite composision toward magnetite.

Chlorite breaks down to cordierite + magnetite + quartz + H_2O at 540°C on the NNO buffer according to Fig. 10 of James *et al.* (1976). Magnetite contains appreciable amount of hercynite component.

The location of the reaction hercynite = magnetite + corundum determined by Turnock and Egster (1962) is at variance with the hercynite stability in the data by Grieve and Fawcett (1974) and hence shifted in Fig. 2 to a more oxidizing region.

Other reactions shown in Fig. 2, mostly quartz-free ones, are not experimentally constrained. As a whole, however, topological relations for quartz-bearing reactions shown in Fig. 2 can be regarded as well constrained. Ambiguity remains only for quartz-free reactions. Reactions involving other phases such as garnet, orthoamphibole and clinoamphibole are not relevant to the present problem and not considered here.

KFASHO SYSTEM

Eugster and Wones (1962) investigated the system K-feldspar-FSHO, a subsystem of the KFASHO system, and placed an isobaric invariant point at 705°C, where biotite, K-feldspar, magnetite, fayalite and quartz coexist. This inivariant point generates a KFASHO univariant reaction fayalite + biotite = magnetite + K-feldspar + quartz + H_2O (Fig. 3). Topology of the generation is such as shown in the Fig. 3, because biotite takes more "excess" Al than coexisting magnetite, which, in turn, takes more "excess" Al than fayalite and K-feldspar. The principle of the topological consideration is given in Thompson (1976).

A new KFASHO isobaric invariant point is formed at the intersection of this KFASHO univariant curve and the FASHO univariant curve cordierite + fayalite = magnetite + quartz. The latter reaction (Cd +

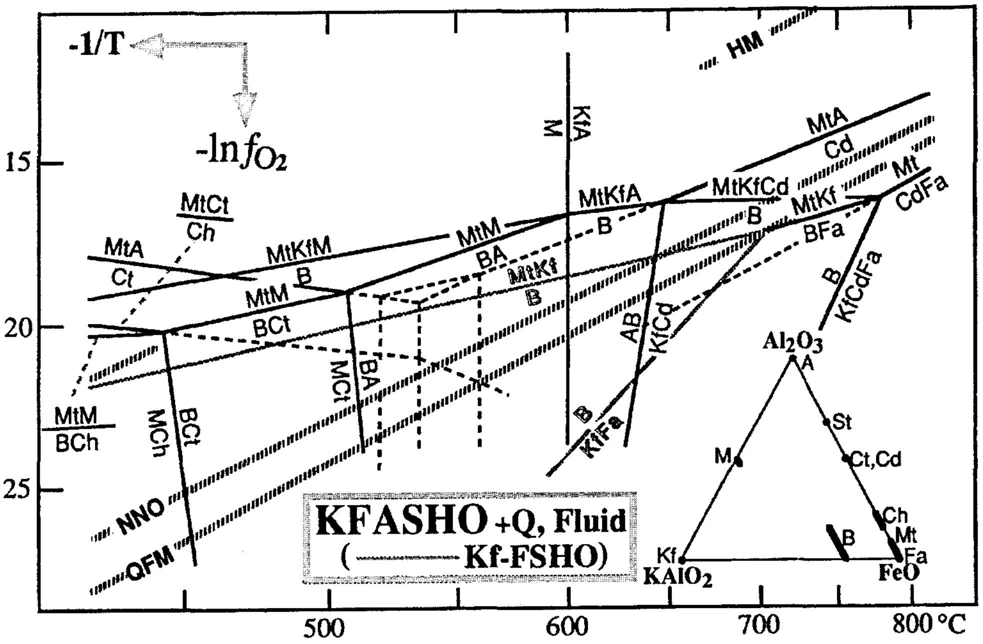

Fig. 3. Temperature-oxygen fugacity diagram at about 2 kbar for reactions in KFASHO systems (see text). Abbreviations are the same as in Figs. 1 and 2.

Fa = Mt + Q) is placed not far below the QFM buffer curve at low temperatures. At higher temperatures this reaction is probably extended to the solidus temperature, where spinel solid solution replaces magnetite. At 1 atm, it terminates at 1050°C solidus at f_{O_2} within wustite stability field (Muan, 1957).

From this KFASHO isobaric invariant point, two KFASHO isobaric univariant reactions limiting the stability of biotite + quartz emanate. Other two KFASHO isobaric invariant points exist on the high-f_{O_2} stability limits of biotite in the presence of quartz (Fig. 3). Experimentally constrained reactions relevant to these are aluminosilicate + biotite + quartz = cordierite + K-feldspar + H_2O (Holdaway and Lee, 1977) and muscovite + quartz = aluminosilicate + K-feldspar + H_2O (Chatterjee and Johannes, 1974).

KFMASHO SYSTEM

Figure 4 shows FMASHO and KFMASHO isobaric univariant reaction curves which are generated from quartz-bearing FASHO and KFASHO isobaric invariant points. Orientation of generated univariant curves relative to invariant points of "minus-one component" systems depends on Mg-Fe partitioning between minerals (Thompson, 1976). Fe-enrichment is in the order of Mt > St > Ct > Bt > Ch > Cd. Magnetite-absent KFMASHO reactions, tentatively drawn parallel to the f_{O_2} axis in Fig. 4, represent ordinary KFMASH reactions, for which reducing conditions and resultant absence of magnetite are implicitly assumed. Fig. 4 clearly demonstrates that the univariant reaction muscovite + chlorite + chloritoid = andalusite + biotite + quartz + H_2O, as well as the reaction muscovite + chlorite + quartz = biotite + andalusite + cordierite + H_2O, is quite compatible with known experimental data.

Two KFMASHO univariant reactions in the oxidzing region, ie. muscovite + chlorite = magnetite + cordierite + biotite and magnetite + muscovite + cordierite = aluminosilicate + biotite, are reported by Spear (1981) in the aureole and xenoliths from Liberty Hill, S. Carolina, although the chemographic relation between chlorite and cordierite differs from ours, leading to the misplaced magnetite position in the former equation.

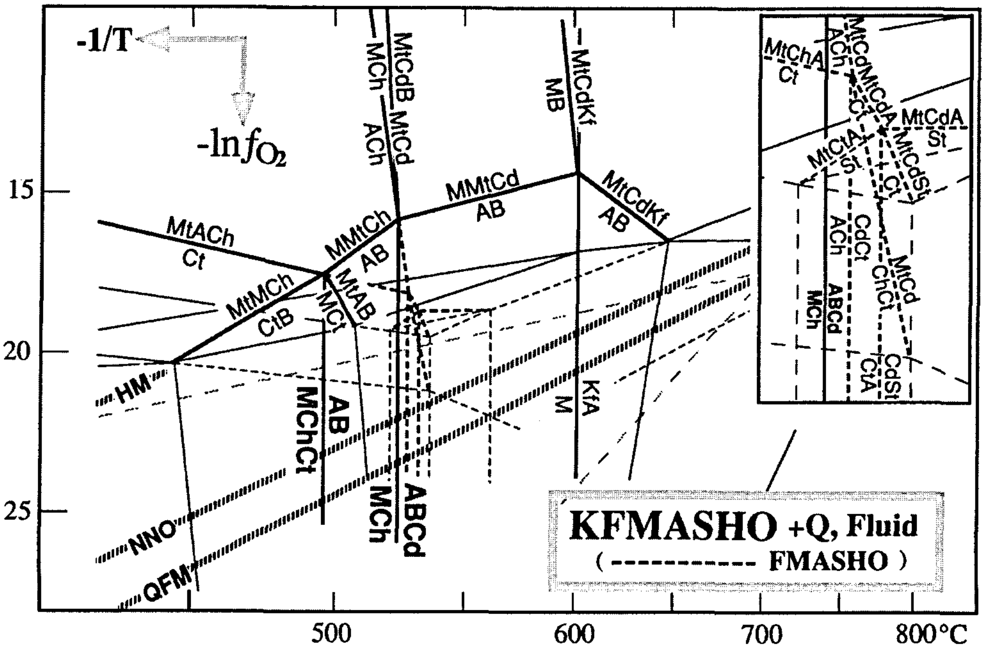

Fig. 4. Temperature-oxygen fugacity diagram at about 2 kbar for reactions in KFMASHO systems (see text). Abbreviations are the same as in Figs. 1 and 2.

Temperatures of the three univariant reactions in the most oxidizing region approach to those of Fe-free reactions, because, in the extremely oxidizing conditions, all iron is in ferric state and is accommodated in hematite (designated as magnetite in Fig. 4). These temperatures are not inconsistent with data by Seifert (1970, 1976) and Seifert and Schreyer (1970).

DISCUSSION AND CONCLUSION

The petrogenetic grid proposed by Spear and Cheney (1989) includes the univariant reaction muscovite + chlirite + chloritoid = aluminosilicate + biotite + quartz + H_2O only at pressures about 15 kbar, but not at low pressures. Wang and Spear (1991), however, improved low pressure part of the grid by introducing the reaction muscovite + chlorite + chloritoid = biotite + staurolite + quartz + H_2O at low pressures. The identical reaction is now placed in two separated part, at low and high pressures. As long as low pressure part is concerned, further improvement may possibly create the invariant point [Cd, G] and the reaction muscovite + chlorite + chloritoid = aluminosilicate + biotite + quartz + H_2O, generated thereform, as shown in Fig. 1.

The biotite + aluminosilicate assemblage has limited stability field at low pressures in the grid by Powell and Holland (1990). They attempted to expand the stability by incorporating Fe^{3+} into biotite. This attempt apprears to be successful and the same topology as Fig. 1 is obtained for the invariant point [Cd, G] (Fig. 7 of their paper). It should be noted, however, that this made only at the sacrifice of the cordierite stability field. In the Mungyong contact aureole, on the other hand, two univariant curves are successively transected as temperature increases; the higher temperature reaction involves cordierite. The Powell and Holland grid is, therefore, not consistent with the natural occurrence. In oxidizing conditions, garnet is likely to disappear while cordierite is still persistent (James *et al.*, 1976). The reverse is the case with the Powell and Holland grid. The limited stability of biotite + aluminosilicate in their grid may result from excessively large stability field of garnet+cordierite. We suspect if garnet stability is overestimated at low pressures in their grid.

A number of experimentally established reactions among Fe-free rock forming phases are surprisingly well reproduced by the computation using thermodynamic data base (Berman, 1988; Chernosky *et al.*, 1989). However, this does not seem to be case with Fe-bearing phases. Inconsistency between reactions based on natural or experimental occurrences and those based on thermodynamic data appears to arise mostly from that in the FASH system, for which we await further experimental investigation.

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