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PHASE EQUILIBRIA AND P-T-X (Fe-Mg) RELATIONS INVOLVING Gt-St-Cd-Als-Bi-Mu-Qz-Kfs-H_2O IN MEDIUM-HIGH GRADE METAPELITES (KFASH, KMASH AND KFMASH SYSTEMS)

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ABSTRACT

In different areas of the Hercynian in the Iberian Peninsula some reactions are repeatedly observed in pelites, these reactions are:

Staurolite + muscovite + quartz = Biotite + Al_2SiO_5 + H_2O

Garnet + muscovite = Al_2SiO_5 + biotite + quartz

Biotite + Al_2SiO_5 + quartz = Cordierite + K feldspar + H_2O

In order to examinate the P-T stability fields of these, and other similar reactions, all the univariant equilibria in multisystems with Gt-Cd-St-Bi-Mu-Als-Qz-H_2O, Gt-St-Bi-Mu-Fk-Als-Qz-H_2O and Cd-St-Bi-Mu-Fk-Als-Qz-H_2O in K_2O-FeO-Al_2O_3-SiO_2-H_2O (KFASH) system have been calculated, and their corresponding P-T grids have been constructed. The expansion of these reactions into divariant surfaces through the P-T-X (Fe-Mg) space was made by studying the assemblage Gt-Cd-St-Bi-Mu-Fk-Als-Qz-H_2O in K_2O-FeO-MgO-Al_2O_3-SiO_2-H_2O (KFMASH) with a Fe/Fe+Mg relationship Gt>St>Bi>Cd such as observed in most of natural pelites.

A resultant grid was obtained by combining those obtained in the above systems. This grid has been P-T located for $P_{H2O}=P_t$, near QFM buffer, and excess muscovite and quartz conditions Reaction slopes in this grid were calculated within different P-T surroundings from thermodynamic data as well as by considering the existing experimental data.

In addition to the stability fields of reactions the P-T-$X_{Fe\text{-}Mg}$ theoric relations for three univariant and thirteen divariant reactions have been obtained. The grid confirms the imposibility of staurolite-K feldspar and Garnet-Cordierite-Muscovite coexistence, as well as the extension of the stability fields for Garnet-Staurolite, Cordierite-Staurolite and Garnet-Cordierite assemblages in muscovite-poor metapelites.

Key words: *phase equilibria, stability fields, petrogenetic grid.*

RESUMEN

En rocas metapelíticas de diversas áreas en el Hercínico de la Península Ibérica se observan a menudo las siguientes reacciones:

Estaurolita + moscovita + cuarzo = biotita + Al_2SiO_5 + H_2O

Granate + moscovita = Al_2SiO_5 + biotita ± cuarzo

Biotita + Al_2SiO_5 + cuarzo = cordierita + feldespato potásico + H_2O

Se han estudiado en el sistema con K_2O-FeO-Al_2O_3-SiO_2-H_2O (KFASH) tres asociaciones con Bi-Mu-St-Als-Qz-H_2O además de Cd-Gt-Fk, eliminando en cada una de ellas una de las tres últimas fases. La expansión de las reacciones que se obtienen con estas asociaciones, en superficies divariantes a través del espacio P-T-X(Fe-Mg), se realizó estudiando la asociación Gt-St-Cd-Bi-Mu-Fk-Als-Qz-H_2O en el sistema KFMASH con una relación Fe/Fe+Mg según Gt St Bi Cd, tal como se observa en la mayoría de roca pelíticas.

A partir de las anteriores redes se ha obtenido otra para condiciones de $P_{H20}=P_t$ baja fugacidad de oxígeno (tampón QFM), y exceso de moscovita y cuarzo. Las pendientes de las reacciones en esta última red se calcularon para diferentes condiciones P-T. Se han obtenido las relaciones teóricas P-T-X(Fe-Mg) para tres reacciones univariantes y trece divariantes. La red confirma la imposibilidad de la coexistencia entre estaurolita y feldespato potásico y entre granate, cordierita y moscovita. Se constata, además, la extensión de los campos de estabilidad de Gt-St, Cd-St y Gt-Cd en metapelitas pobres en moscovita.

Palabras clave: *equilibrios de fases, campos de estabilidad, red petrogenética.*

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Introduction

Studies on mineral equilibria in pelitic rocks and their stability fields location in P-T or P-T-X diagrams for both low-medium grade (f.i. Brown, 1975; Day, 1976; Thompson, 1976 a,b) and high-grade conditions were abundant in the last two decades. In the present study relations involving garnet (Gt), staurolite (St), cordierite (Cd), aluminium silicate (Als), biotite (Bi), muscovite (Mu), quartz (Qz), K-feldspar (Fk) and H_2O are dealt with.

Reactions between these phases like the destruction of staurolite in the presence of muscovite and quartz according to: Staurolite + muscovite + quartz → Biotite + + $Al_2SiO_5 + H_2O$; the resorption of garnet through: Garnet + muscovite → Sillimanite + biotite + quartz; or the occurrence of cordierite with K feldspar from: Biotite- + sillimanite + quartz → Cordierite + K feldspar + H_2O have been observed in metapelites in a number of locations across the Hercynian belt in the Iberian peninsula like in thermal domes and their peripheries (Durán, 1985; Martínez & Rôlet, 1988; Martínez *et al.,* 1988).

Some reactions between the phases considered in this paper have been theoretically or experimentally studied by different authors, therefore the following paragraphs are mainly addressed to the study of their P-T stability fields. These fields have been constructed in KFASH, KMASH and KFMASH systems with $P_{H2O} = P_t$ and excess quartz. The presence of melt as an extra phase is not considered in this study, although in natural systems, at high temperature and near $P_{H2O} = P_t$ conditions, melt occurrence is very likely.

The different grids that will be shown are meant for several zones in the Hercynian of the Iberian Peninsula, although obviously they can be applicated to similar parageneses elsewhere.

For the sake of simplicity reactions are shown numbered, although they are also labeled as in Zen (1966).

Phase composition and thermodynamic parameters

Due to phase composition influence on thermodynamic parameters and thus on topology, their compositions has been taken as close as possible to those appearing in natural metapelites in Iberia.

In order to calculate the water percent in cordierite the model of Newton & Wood (1979) was taken, its molar volume was calculated after Helgeson *et al.,* (1978) method; starting from Holdaway & Lee's (1977) cordierite. Its Al^{IV} was taken following Hochella *et al.* (1977) recommendations. Thermodynamic data for water were obtained from Helgeson & Kirkham (1974). The composition of staurolite was chosen following the considerations of Pigage & Greenwood (1982, p. 984). It should be noted that the results obtained using the biotite of Table 1 are similars to those obtained using the composition of Holdaway (1980). Finally, the entropy calculated by the formula (73) of Helgeson *et al.,* (1978), for Holdaway's (1980) muscovite, has given values similars (+0.6 cal) to those in Table 1, therefore this latter was taken in order to simplify the estequiometry of reactions.

Reaction slopes for some end-member phases were calculated using data by Helgeson *et al.,* (1978), Berman *et al.,* (1987) and Berman (1988). The better topological agreement between these slopes and those obtained by the method of Albee (1965) was obtained when Helgeson *et al.'s* data, shown in Table 1, were used.

GT-ST-CD-BI-MU-ALS-QZ-H_2O assemblages in the KFASH system

Multisystem estequiometry appears totally determined by a set of R independent reaction set, where R=N−C, being C the number of system components and N the number of species (phase components of Thompson, 1982) in equilibrium; further discussion can be found in Brinkley (1946).

A set of three independent reactions was chosen for the system here dealt with; this was made through algebraic calculation by means of a basis change. Calculations were performed through a computer program (Sebastián, in preparation). The three independent reactions set was chosen such as to maximum facilitate the subsequent calculation of the complete univariant reaction set for the KFASH system. This latter set was obtained by linear combination of the three independent reactions and was then tested by means of a modified version of the Vielzeuf & Boivin's (1981) program for univariant reactions calculation.

Table 2 shows the complete univariant reactions set, volume and entropy increment for each reaction as well as slopes. Entropies have been calculated following Third Law and Albee's (1965) method. In this latter case, mixing entropy has not been considered. Nor have been considered the variations of entropy due to Al^{VI}-Al^{V} and Al^{V}-Al^{IV} coordination changes (see Hess, 1969).

From data of table 2, the different invariant points for the multisystem have been constructed by the method of Schreinemaker (1915-1925), taking also into account the thermodynamic restrictions due to slopes. For reaction design a modified version of Vielzeuf *et al.* (1982) program was used. Results are shown in fig. 1. Their slopes are calculated from the entropies obtained by the method of Albee (1965).

The construction of a petrogenetic grid for this KFASH system has been made taking into account the propositions of Day (1972). Its design was carried

Table 1.—**Phase compositions, molar volumes and entropies from Helgeson *et al.* (1978) unless otherwise specified**

Phase	Formula						Molar Vol	Al^{IV}	Entropie
	SiO_2	Al_2O_3	FeO	MgO	K_2O	H_2O	cm^3/mol		cal/mol°K
H_2O	0	0	0	0	0	1	26.13(a)*	0	34.20(a)*
Qα	1	0	0	0	0	0	22.69	0	9.88
Qβ	1	0	0	0	0	0	23.06	0	10.22
And	1	1	0	0	0	0	51.53	1	22.20
Sill	1	1	0	0	0	0	49.90	1	23.13
Ky	1	1	0	0	0	0	44.09	1	20.00
Fk	3	0.5	0	0	0.5	0	108.87	1	51.13
Mu	3	1.5	0	0	0.5	1	140.71	1	68.80
FeBi(1)	2.69	0.87	2.17	0	0.5	1	155.18(1)	1.31	92.40(1)
MgBi(1)	2.69	0.87	0	2.17	0.5	1	146.84(1)	1.31	71.40(1)
FeSt(2)	2.75	4.5	2	0	0	1	223.38(b)	0.25	119.10(c)
MgSt(2)	3.75	4.5	0	2	0	1	221.61(d)	0.25	105.32(d)
FeGt	3	1	3	0	0	0	115.28	0	75.6
MgGt	3	1	0	3	0	0	113.27(f)	0	62.32(f)
FeCd(3)	5	2	2	0	0	0.5*	241.07(g)*	4	130.28(e)*
MgCd(3)	5	2	0	2	0	0.5*	237.22(g)*	4	111.43(e)*

(1) Perchuk *et al.* (1981)
(2) Griffen & Ribbe (1973)
(3) H_2O from Newton & Wood (1979) model
* Different values for different P-T conditions

(a) Helgeson *et al.* (1974) 3Kb 600°C
(b) Ganguly & Newton (1968)
(c) Pigage & Greenwood (1982)
(d) Loomis (1986)
(e) Calculated from ecuation (73) Helgeson *et al.* (1978)
(f) Robie *et al.* (1978)
(g) See text

Abbreviations:

(Qα)	Alpha-quartz	(And)	Andalusite	(Fk)	K-feldspar	(Mu)	Muscovite
(Qβ)	Beta-quartz	(Sill)	Sillimanite	(Als)	Al_2SiO_5	(Gt)	Garnet
(Qz)	Quartz	(Ky)	Kyanite	(St)	Staurolite	(Cd)	Cordierite
(Bi)	Biotite						

Table 2.—**Univariant reactions and slopes for Gt-Cd-St-Bi-Mu-And-Qz-H_2O assemblages in KFASH system**

		Reaction	ΔV cm^3	ΔS1	ΔS2	Slope1	Slope2
				dJ/mol°K		bar deg.$^{-1}$	
(1)	(Bi,Mu,St)	$1.8Gt+2.6And+H_2O+3.3Qz=2Cd$	89.3	—56.7	1398.4	— 0.6	15.7
(2)	(Bi,Mu,Gt)	$2St+7.5Qz=2Cd+5And+H_2O$	149	1840	3910.8	12.3	26.2
(3)	(Bi,Mu,Cd)	$1.5St+3.1Qz=Gt+5.7And+1.5H_2O$	44.8	1422.5	1884	31.7	42.1
(4)	(Bi,Mu,And)	$2.4Gt+2.3St+15.7Qz+H_2O=6.60d$	361.6	1981.4	7467.1	5.5	20.7
(5)	(St,Gt)	$1.8Bi+5.2And+5.4Qz+H_2O=1.8Mu+2Cd$	40.6	—363.3	621.2	— 8.9	15.3
(6)	(St,Cd)	$1.4Mu+Gt=1.4Bi+1.9And+1.6Qz$	36.5	230	583.2	6.3	16
(7)	(St,And)	$2Mu+2.6Gt+1.1Qz+H_2O=2Bi+2Cd$	141.2	271.1	2230.2	1.9	15.8
(8)	(Gt,Cd)	$Mu+1.1St+1.1Qz=Bi+5.6And+1.1H_2O$	58.8	1195.3	1784.6	20.3	30.6
(9)	(Gt,And)	$57.1Bi+64St+407.7Qz=57.1Mu+126Cd+H_2O$	6027.6	47618.6	40348.10^9	7.9	24
(10)	(And,Cd)	$2.8Mu+2.7Gt+H_2O=2.8Bi+5.3Q+St$	44.9	—477.2	—6	—10.6	—1.4

ΔS1 = Calculated following Albee's (1965) method using a dehidratation entropy of 590 dJ/mol (Fyfe Turner and Verhoogen 1958) and a Al^{VI}-Al^{IV} value of 100 dJ/mol (Hess 1969)
ΔS2 = Data according to Third Law entropies
Slopes 1 and 2 calculated from ΔS1 and ΔS2

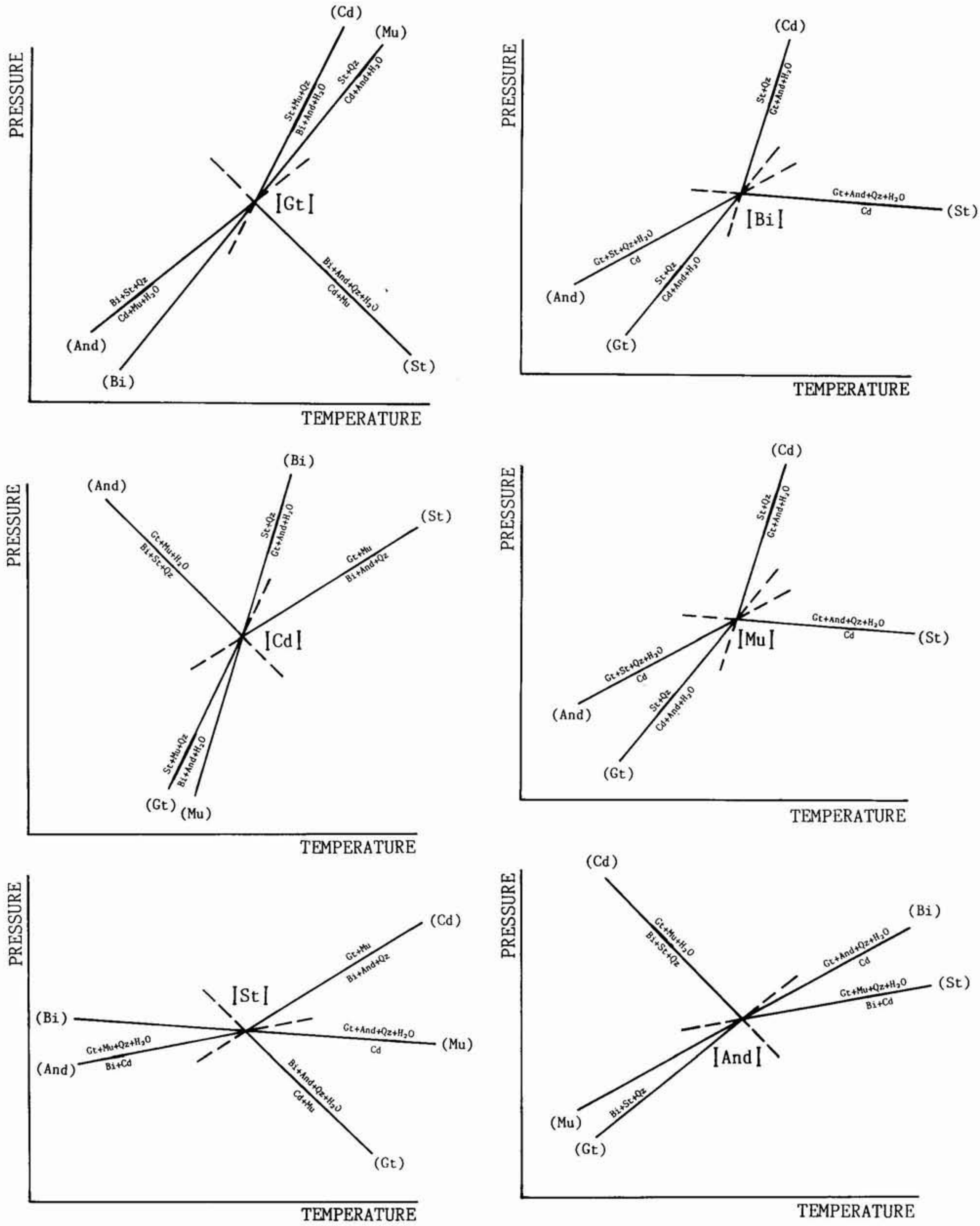


Fig. 1.—P-T arrangement of univariant equilibria and divariant fields arount invariant points in KFASH system. Phases are Gt-Cd-St-Bi-Mu-And (excess Qz and H_2O). Dashed lines are metastable extensions of univariant equilibria. Aproximate slopes 1Kb/100°C.

out by means of the program REAC3C (Vielzeuf *et al.,* 1982). The topology was tested by the method of Mohr & Stout (1980) and Stout (1985).

Although the reaction slopes vary according to the method used to calculate ΔS, the topologic relations obtained keep constant; this fact supports the internal consistence of the thermodynamic data used. The equilibrium slopes for the studied P-T surroundings as well as their stability fields have been cheked with experimental and theoretical data in order to verify its agreement. Some pertinent comments are made further on.

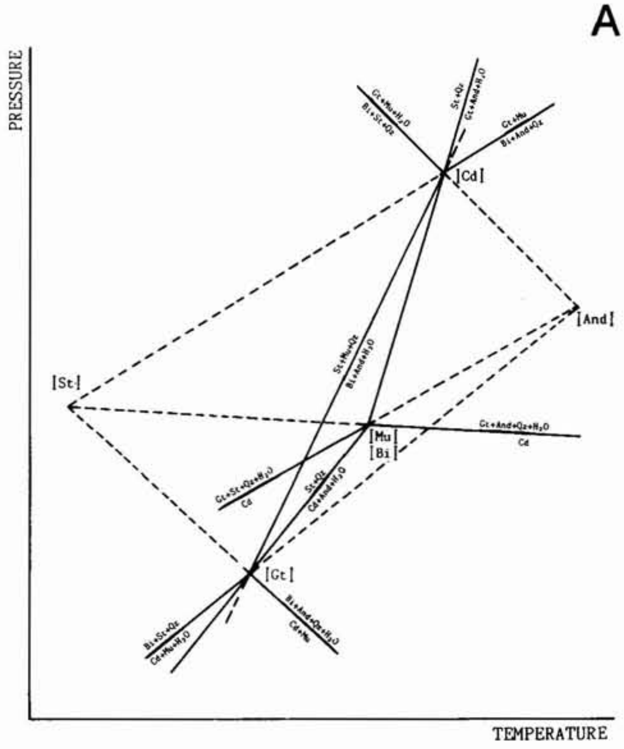
Discussion

The two grids that obey the thermodynamic and geometric restrictions are shown in fig. 2. The selection of fig. 2A as the most likely has been made on both the basis of observations carried out in natural assemblages and on existing experimental data for the different reactions. The following considerations can be made:

a) The same reactions, except (7) and (8), are stable in both figures. Reaction (8) is quite common in low-medium pressure metapelites and has been quoted by Thompson (1957), Green (1963), Guidotti (1968), Novak & Holdaway (1981), etc. References about textural evidences of muscovite and staurolite reaction to give biotite plus Al_2SiO_5 are numerous as well, a resume of which can be found in Kwak (1974). The experimental data of Hoschek (1969) for this reaction (8) are coincident with fig. 2A and these data locates its stability upper boundary at temperatures previous to the reaction $Mus + Qz \rightarrow Sill + Fk + H_2O$ and at pressures lower than reaction (3).

b) Reaction (7), of great importance in fig. 2B, has not been refered in natural assemblages and may only be found as a stable extension in some theoretical studies like those of Thompson (1976b) and Vielzeuf (1979).

c) The invariant point [Mu,Bi] has been located between 680°C, 3.5 Kb (Richardson, 1968) and 620°C, 3.2 Kb (Bickle & Archibald, 1984). The invariant point [St] of fig. 2B is located at higher



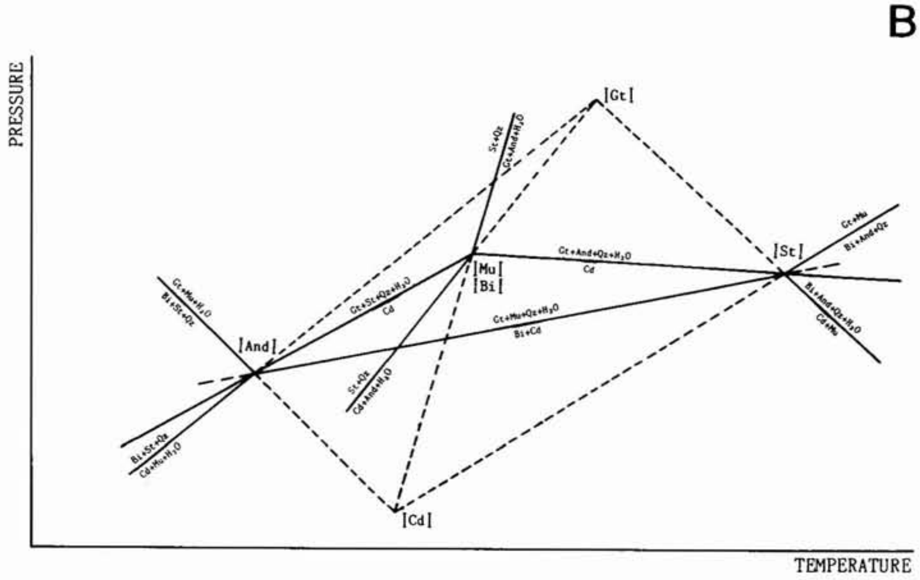


Fig. 2.—Equilibria arrangement involving Gt-Cd-St-Bi-Mu-And (excess Qz and H_2O) in KFASH system. Dashed lines are metastable extensions. A: more likely construction; B: residual grid. In fig. 2A the invariant point [Mu] is stable, and [Bi] is metastable, whereas the reverse holds in fig. 2B.

temperature and similar pressure with respect to the point [Mu,Bi]. This P-T situation of the point [St] is in disagreement with the situation of reaction (5) given by Holdaway & Lee (1977) and Thompson (1982). Likewise is in disagreement with the same point's location of Vielzeuf & Boivin (1984, fig. 9) and Thompson (1982, fig. 5B).

The situation of [St] in fig. 2A, however, is compatible with the previous authors' constraints.

Testing

Grid topology varies when the relative slopes of at least two reactions reverse at an invariant point (Vielzeuf & Boivin, 1984). This may happen because the change in phase composition and/or in their thermodynamic parameters. In the present grid dehydration entropy and molar volume, the two parameters that most influence the topology of dehydration reactions, have been tested. The results indicate that the grid maintain its topology below a dehydration entropy of 650 dJ/mol and 55 cm^3/mol of water. This noticeable range of values indicates the validity of the grid for a large P-T field. Likewise the substitution of β-quartz for α-quartz and sillimanite for andalusite has also been tested.

The slopes of 'dry' reactions are very sensitive to compositional changes. However the present grid topology is maintained when the composition of biotite in table 1 is replaced either by that of Holdaway & Lee (1977) or Holdaway (1980). Finally the topology was also maintained for hydration values of cordierite between 0 and 1 mol of water.

Applications

Among the more outstanding characteristics of the grid appears: 1) Its delimitation of garnet and cordierite stability fields for a given Fe/Mg relationship (see also Hudson & Harte, 1985 for assemblages with orthoamphibol).

2) The location of reaction (3) in the high-temperature side of (8) as suggested by Hoschek (1969, p. 217).

3) The upper stability boundary location for staurolite in the presence of quartz.

Moreover it should be noted that, in metapelites with excess muscovite, the reactions (2) and (3) are metastable between the invariant points [Gt] and [Cd]; reaction (3) only occurs at relatively high pressures, and (2) occurs at low pressures. The equilibria (2) and (3) for most of the metamorphic trajectories will only take place, during a prograde episode, if the estequiometric staurolite quantity in the rock surpasses that of muscovite in reaction (8). This fact partially explains the limited references made for these reactions (2) and (3) in natural assemblages within the pressure interval between the invariant points [Gt]-[Cd] and their corresponding univariant developments in systems with one more component. This has lead different authors to think that those reactions never take place in the mentioned P-T conditions.

Likewise for rocks with excess muscovite, reactions (1) and (4) will be metastable in the surroundings of point [Mu,Bi].

GT-CD-ST-BI-MU-ALS-QZ-H_2O assemblages in the KFMASH system

It is well known that in nature many of the phases here considered are at least Fe-Mg solid solutions. Therefore univariant reactions in KFASH would become divariant in a more realistic system KFMASH. In such a system P-T-X relations for table 2 reactions have been studied. The following Fe/Fe+Mg ratios hold in this paper: $X_{Fe}^{Gt}=0.9$, $X_{Fe}^{St}=0.85$, $X_{Fe}^{Bi}=0.7$, $X_{Fe}^{Cd}=0.5$, which are similar to those existing in metapelites from several areas in the Hercynian Iberia. The same order of ratios has been found by different authors (Hounslow & Moore, 1967; Hensen, 1971; Harte & Hudson, 1979; Holdaway *et al.*, 1982) in similar rocks elsewhere.

Table 3 shows the univariant reactions as well as ΔV, ΔS and reaction slopes. These slopes have been obtained by the method of Albee (1965) due to its better agreement with those obtained experimentally.

The resultant grid, containing seven univariant points with a maximum of six univariant reactions emanating from each one, is displayed around reaction (20). In this grid [Bi], [Sill], [Gt], [Cd], [Mu] and [St], [Fk] are respectively stable and metastable points. This grid, mainly at points [Bi] and [Cd], presents topological changes for not very large variations in the thermodynamic parameters.

P-T-X diagram

This diagram has been constructed reducing one degree of freedom the system KFMASH and expanding a new grid corresponding to system KFASH starting from the projection point [Fk] in KFMASH system. Fig. 3 shows a P-T projection of the P-T-X diagram that results from carrying out the above mentioned operations. In fig. 3 the expansion into divariant fields of the KFASH univariant reactions of fig. 2A are shown, and so are the divariant fields intersection (univariant lines of fig. 3). The construction is an homology that following Vielzeuf & Boivin (1984) is named homotectic.

Table 3.—**Univariant theoric relations in KFMASH system**

	Reaction	ΔV cm^3	ΔS dJ/ºK.mol	Slope bar/deg.
(11)	$8St+18.3Qz=29.3Sill+Cd+4.7Gt+7.5H_2O$	226.6	7558.3	33.4
(12)	$3.7Bi+7.7Sill+7.5Qz+H_2O=1.3Gt+2Cd+3.7Mu$	10.3	—671.3	—65.1
(13)	$1.3St+2.2Mu+Cd=2.2Bi+9.4Sill+1.3Qz+1.8H_2O$	31.9	1658.4	51.9
(14)	$4.3St+Mu+7.9Qz=2.2Gt+18Sill+Bi+4.3H_2O$	119.8	4272.6	35.7
(15)	$2.2St+3.8Bi+12.8Qz=2.7Gt+2.4Cd+3.8Mu+H_2O$	72.3	1358.1	18.8
(16)	$2.8Bi+3Sill+8.4Qz=Gt+1.5Cd+2.8Fk+2H_2O$	63.6	1402.3	22.1
(17)	$6.8Bi+22.8Sill+10.9Qz=4.2St+3.1Cd+6.8Fk+H_2O$	37.1	—536.8	—14.5
(18)	$4.3St+Fk+6.9Qz=2.2Gt+16.9Sill+Bi+3.3H_2O$	99.6	3582.6	36.0
(19)	$St+3.4Bi+12.6Qz=1.8Gt+2Cd+3.4Fk+3.4H_2O$	106.9	2678.6	25.1
(20)	$Mu+Qz=Sill+Fk+H_2O$	20.3	690	34.1
(21)	$4.7Gt+Cd+29.3Mu+11Qz=8St+29.3Fk+21.8H_2O$	367.6	12681	34.5
(22)	$2.7Bi+3Mu+11.3Qz=Gt+1.5Cd+5.7Fk+5H_2O$	123.6	3448.5	27.9
(23)	$2.2Bi+7.2Mu+10.7Qz=1.3St+9.4Fk+Cd+7.6H_2O$	158.2	4821.6	30.5
(24)	$2.2Gt+Bi+17Mu+10.1Qz=4.3St+18Fk+13.6H_2O$	243.7	8114.0	33.3

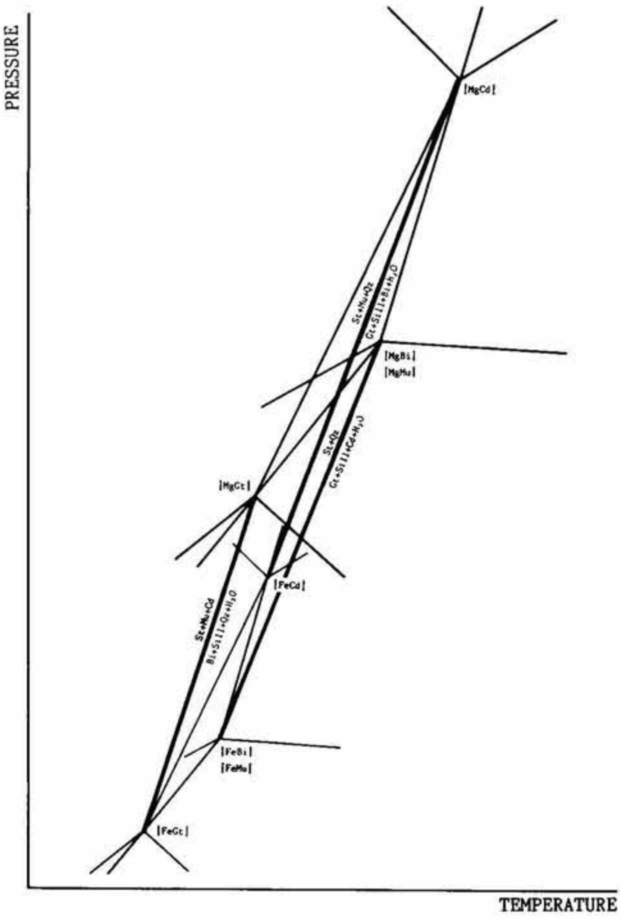


Fig. 3.—Schematic diagram of P-T-$X_{Fe\text{-}Mg}$ relationships between Gt-Cd-St-Bi-Mu-Als projected on the P-T plane. Systems KFASH-KMASH-KFMASH. Univariant reaction slopes taken from Table 3. Light line: Fe pole; regular line: Mg pole; Heavy line: KFMASH univariant reactions.

Applications

The information obtained from fig. 3 coincides and completes previous authors' proposals and results which are commented as follows:

(a) This Fig. agrees with what was expected by Richardson (1968) about the extension of the staurolite stability field at high temperatures for magnesian compositions. Richardson hypothesis of a more magnesian staurolite in assemblages with andalusite than with kyanite has been corroborated in natural parageneses by Kepezhinkas & Khlestov (1977).

(b) The narrow divariant field of reaction (8) coincides with Hoschek's (1969) stating.

With respect to the end members it must be considered that divariant reactions dont take place along the complete Mg-Fe range. Thus the majority of pure-Mg reactions in fig. 3 should be considered metastable, because in natural assemblages they are replaced by other equilibria more stable in which new phases occur. In particular at low temperature chlorite mainly appears or in occasions chloritoid, whereas at high temperatures talc and pyroxenes are stable. For instance the terminal reaction (1) does not reach the magnesian pure member, both in assemblages with hydrous (Martignole & Sisi, 1981; Lonker, 1981) or anhydrous cordierite. Chlorite and talc are stables at respectively low and high temperature (Schreyer, 1968; Seifert & Scheryer, 1970; Newton, 1972) in hydrous systems, whereas enstatite and hyperstene respectively occur at low- and high-temperature in anhydrous systems (Hensen & Green, 1971; 1972).

With respect to assemblages with staurolite, its desapearence towards the magnesian pole can be observed in the T-X diagrams of Loomis (1986) or in the grids by Harte & Hudson (1979) and Holdaway & Lee (1977).

Table 4.—**P-T-$X_{(Fe\text{-}Mg)}$ relationships for divariant and univariant equilibria**

Reaction	T_{Fe}-T_{Mg} P=Ct.	P_{Fe}-P_{Mg} T=Ct.	Reaction	T_{Fe}-T_{Mg} P=Ct.	P_{Fe}-P_{Mg} T=Ct.	Reaction	T_{Fe}-T_{Mg} P=Ct.	P_{Fe}-P_{Mg} T=Ct.
(1)	<*	<	(6)	>	<	(11)	<	<
(2)	>	<	(7)	Metastable		(12)	Metastable	
(3)	<	>*	(8)	>	<*	(13)	<	<
(4)	>	<	(9)	>	<	(14)	<	<
(5)	<*	<	(10)	<	<	(15)	Metastable	

* See text.

Table 4 shows P-T-$X_{Fe\text{-}Mg}$ relations deduced from fig. 3 for the different univariant and divariant reactions. The following observations should be made:

(a) T_{Fe}-T_{Mg} relation for reaction (1) at constant pressure has been controversial. Hutcheon *et al.* (1974) and Martignole & Sisi (1981), using respectively anhydrous and hydrous cordierite, have found positive slopes for both the Fe and Mg end members. Positive slopes only for the magnesian member have been found by Currie (1971, 1974) and Newton & Wood (1979). Finally negative slopes for both end members have been found based either on experiments (Hensen & Green, 1971, 1972, 1973; Holdaway & Lee, 1977) or on K_D values (Thompson, 1976b; Lonker, 1981).

(b) P_{Fe}-P_{Mg} relation for reaction (3) at constant temperature must be inverted at high pressures in the kyanite field when reaction slope becomes negative (see fig. 6).

(c) T_{Fe}-T_{Mg} relation at constant pressure should reverse in reaction (5) for magnesium-rich members, if experimental data of Massone (1988) are considered. This author obtains a positive slope for the magnesian end member of the reaction.

Discussion

The P-T-X construction has also been used as a restriction to investigate the most suitable grid in fig. 2. The residual grid is only compatible for a P-T-X construction with a projection point stable at a higher pressure than that of the grid. An homotetic construction in such a grid gives, in general, reverse P-T-X relations to those obtained in table 4 and, therefore, in disagreement with the results obtained by most of authors. The other posibility, an antithetic construction with the grid of fig. 2A as magnesian pole, would also imply serious disagreements in some equilibria with what is observed in natural assemblages. An example of such disagreements would be the beginning of reaction (8) stability field at a pressure higher than that of reaction (3), with a minimum of 3.5 to 4 Kb.

In consequence it is assumed that the construction of fig. 2A is the most suitable one for natural pelites within a wide range of bulk compositions.

Relation of different assemblages with reaction MU + QZ = SILL + Fk + H_2O

Two more assemblages have been studied following the preceding method with the purpose of connecting fig. 2 with the muscovite plus quartz destruction, as well as with other grids that hold for higher metamorphic conditions in pelites, f.i Grant (1973, 1985), Holdaway & Lee (1977), Thompson (1982) and Vielzeuf & Boivin (1984).

The two assemblages studied occur in the KFASH system for $P_{H2O} = P_t$ and excess quartz conditions. Equivalent reactions involving the same phases keep their previous notation for simplicity.

Gt-St-Mu-Bi-Fk-Sill-Qz-H_2O assemblages

The theoretical estequiometric relations for these assemblages are shown in table 5. Their slopes are calculated for an surrounding around point [Cd] in fig. 2A. The equilibria topologic relations appear in fig. 4A and the residual grid in fig. 4B.

Cd-St-Mu-Bi-Fk-Sill-Qz-H_2O assemblages

Theoretical phase relations and slopes appear in table 6, and topology is shown in fig. 5. Thermodynamic data for this grid have been chosen for a P-T surrounding with respectt to [Gt] in fig. 2A. The following precisions must be made about the grid:

(a) The metastable [Mu] invariant point is located outside of the fig. field.

(b) The point [Cd] should be metastable in assemblages with garnet since it is located within the garnet stability field.

(c) The expansion of point [St] towards a Mg-rich pole should be in part metastable due to the beginning of melting at $P_{H2O} = P_t$ conditions (see Schreyer & Seifert, 1969, p. 382), becoming stable for water deficient conditions.

Table 5.—**Univariant reactions and slopes for Gt-St-Bi-Mu-Fk-Sill-Qz-H_2O assemblages in KFASH system**

		Reaction	Slopes bar deg.$^{-1}$
(3)	(Mu,Bi,Fk)	$1.5St+3.1Qz=Gt+5.7Sill+1.5H_2O$	44.9
(25)	(Mu,St)	$2Gt+2.8Fk+2.8H_2O=2.8Bi+Sill+6Qz$	—101.2
(26)	(Mu,Gt)	$12.8St+11.8Fk+1.6Qz=11.8Bi+53.1Sill+H_2O$	18.0
(27)	(Mu,Sill)	$8.6Gt+10.8Fk+11.8H_2O=10.8Bi+St+25.2Qz$	—189.3
(20)	(Bi,St,Gt)	$Mu+Qz=Sill+Fk+H_2O$	36.3
(28)	(Bi,Sill)	$Gt+5.7Mu+2.6Qz=1.5St+5.7Fk+4.2H_2O$	32.8
(6)	(St,Fk)	$Gt+1.4Mu=1.4Bi+1.9Sill+1.6Qz$	6.9
(29)	(St,Sill)	$2.8Bi+Mu+7Qz=2Gt+3.8Fk+3.8H_2O$	498.6
(8)	(Gt,Fk)	$1.1St+Mu+1.1Qz=1Bi+5.5Sill+1.1H_2O$	25.4
(30)	(Gt,Sill)	$Bi+4.5Mu+4.4Qz=1.1St+5.5Fk+4.4H_2O$	45.2
(10)	(Fk,Sill)	$2.7Gt+2.8Mu+H_2O=St+2.8Bi+5.3Qz$	— 10.1

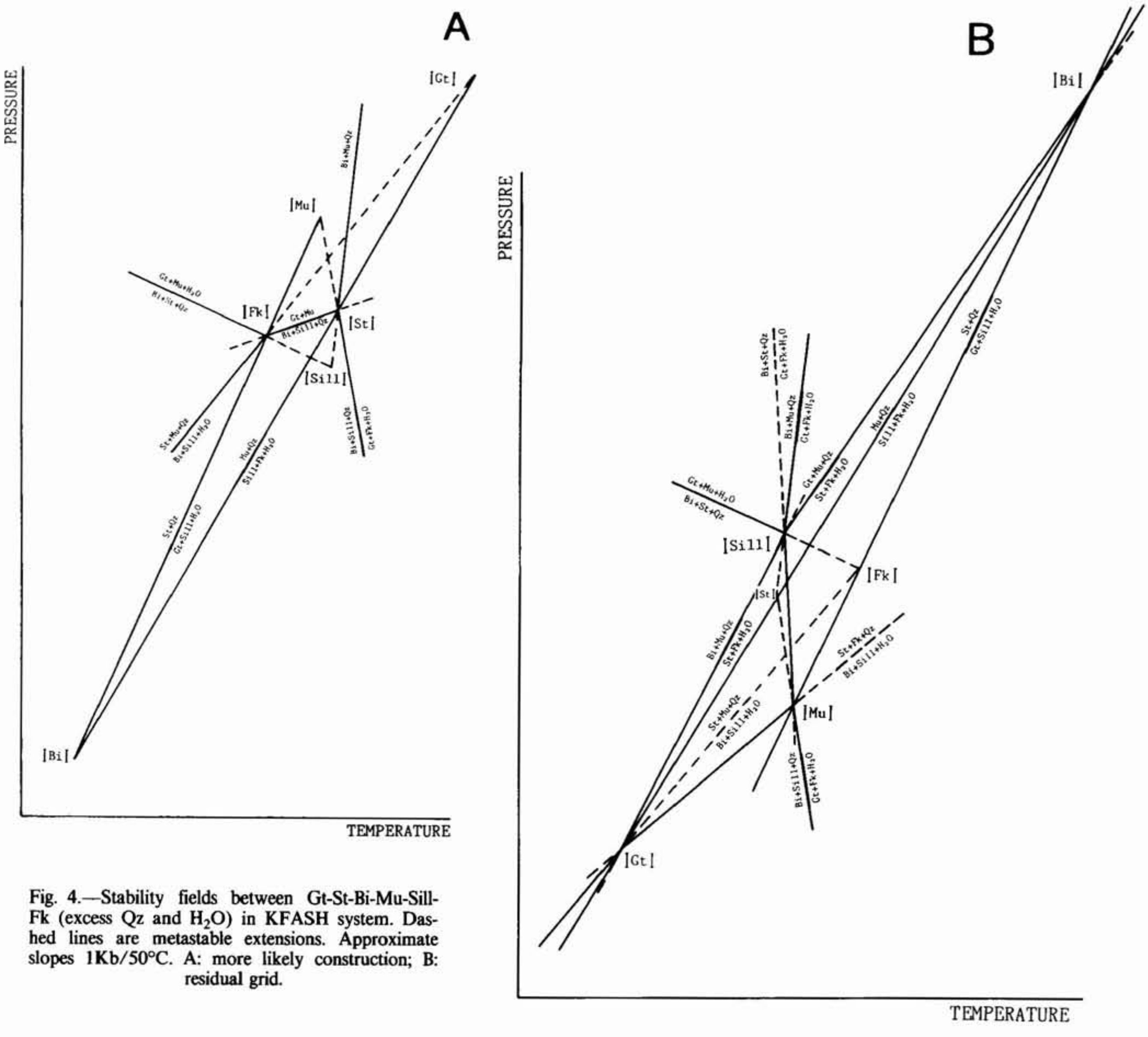


Fig. 4.—Stability fields between Gt-St-Bi-Mu-Sill-Fk (excess Qz and H_2O) in KFASH system. Dashed lines are metastable extensions. Approximate slopes 1Kb/50°C. A: more likely construction; B: residual grid.

Table 6.—**Univariant reactions and slopes for Cd-St-Mu-Bi-Fk-And-Qz-H_2O assemblages in KFASH system**

		Reaction	Slope bar/deg
(2)	(Mu,Bi,Fk)	$1.7St+6.2Qz=1.7Cd+4.2And+H_2O$	12.9
(26)	(Mu,Cd)	$12.8St+11.8Fk+1.6Qz=11.8Bi+53.1And+H_2O$	14.1
(31)	(Mu,St)	$1.8Bi+3.2And+7Qz=1.9Cd+1.8Fk+H_2O$	11.9
(32)	(Mu,And)	$1.4Bi+1St+9.2Qz=2.5Cd+1.4Fk+1.4H_2O$	12.4
(20)	(Bi,Cd,St)	$1Mu+1Qz=1And+1Fk+1H_2O$	28.6
(33)	(Bi,And)	$1St+2.5Fk+1.2Qz+1.9H_2O=1Cd+2.5Mu$	—47.4
(8)	(Cd,Fk)	$1.1St+1Mu+1.1Qz=1Bi+5.5And+1.1H_2O$	20.0
(30)	(Cd,And)	$1Bi+4.5Mu+4.4Qz=1.1St+5.5Fk+4.4H_2O$	35.6
(5)	(St,Fk)	$2.3Bi+6.5And+6.8Qz+H_2O=2.5Cd+2.3Mu$	— 5.9
(34)	(St,And)	$1Bi+1.8Mu+5.7Qz=1.1Cd+2.8Fk+2.4H_2O$	19.9
(9)	(Fk,And)	$4.2Bi+4.7St+30Qz=9.3Cd+4.2Mu+1H_2O$	8.9

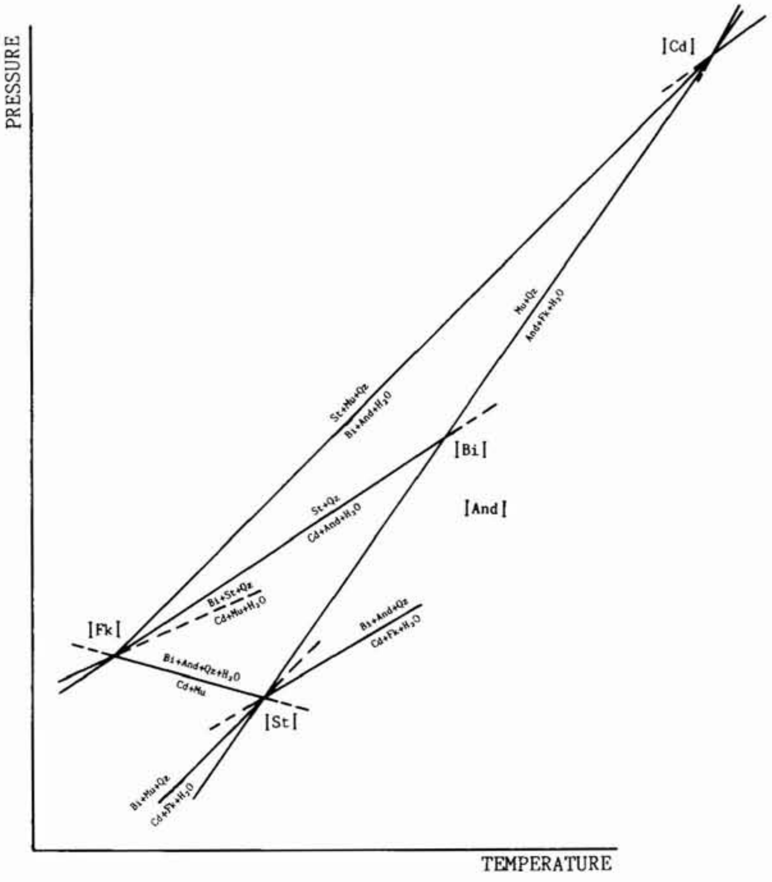


Fig. 5.—P-T arrangement of reactions between Cd-St-Bi-Mu-And-Fk (excess Qz and H_2O) in KFASH system. Dashed lines are metastable extensions. Approximate slopes 1Kb/50°C.

Semiquantitative P-T location of the equilibria

A P-T-X grid for low fO_2 and excess water ($P_{H2O}=P_t$) quartz and muscovite has been constructed starting from the preceding grids of this study. Several slope values for different P-T surroundings along every reaction has been calculated in order to obtain a more accurate reaction display. Moreover several

Table 7.—**Reaction slopes for different surroundings**

Surrounding Kb °C	Reaction	Slope bar/deg.
2 550	2	12.5
	5	-6.4
	8	19.6
	9	8.6
	13	31.0
2 600	5	-4.3
	20	24.9
	31	11.6
	34	18.2
3 600	4	5.9
	8	20.3
	13	33.7
3 625	1	-0.3
	2	12.6
	3	31.0
	4	6.1
	11	26.3
	20	28.9
3 725	1	1.3
	25	929.1
	31	11.3
4 625	8	21.0
	13	36.1
4 675 (Qα)	3	41.4
	11	32.9
	20	33.2
(Qβ)	3	42.8
	11	33.9
	20	33.8
5 675	3	44.9
	8	25.4
5 700 (Qα)	6	6.9
	11	34.4
	20	35.5
(Qβ)	6	6.8
	11	35.5
	20	36.2
6 675	3	47.8
	10	-9.8
	14	39.4
6 725 (Qα)	6	6.9
	11	35.5
	20	37.3
	25	-92.1
	29	904.4
(Qβ)	6	6.8
	11	36.7
	20	38.1
	21	-80.9
	29	10371
7 700 (Sill)	3	49.4
	14	40.5
	29	-715.1
(Ky)	3	-307.7
	14	3363
	29	-715.1
6 650 (Sill)	10	-9.7
(Ky)	10	-9.7

experimental reactions have been considered so as to quantitatively fix the grid with respect to P and T.

Reaction slope for different P-T surroundings has been calculated with two objectives: (1) To obtain data for those equilibria in which experimental data are scarce or lacking. (2) To compare results in reactions for which there exist experimental data, in order to test their topological consistence with the equilibria of paragraph (1).

Mica tschermakitic content has been maintained constant and water content of cordierite has been considered under different P-T conditions in order to calculate slopes by the method of Albee (1965). Quartz polimorphs has been taken from Keith & Tuttle (1952). The results are shown in table 7.

Experimental data have been considered for the investigated equilibria under similar conditions to those presented in this study. No topological inconsistencies have been observed. The studies chosen in order to P-T locate the reactions are shown in table 8.

Table 8.—**Listing of authors for some reactions shown in fig. 6**

Reaction	Pole	Author
(1)	Fe	Bickle & Archibald (1984)
(3)	Fe	Rao & Johannes (1979); Dutrow & Holdaway (1983, 1986)
(5)	Mg	Massonne (1988)
(10)	Fe	Rao & Johannes (1979)
(16)		Holdaway & Lee (1977); Lee & Holdaway (1977)
(20)		Chatterjee *et al.* (1974); Helgeson *et al.* (1978)
(31)	Fe	Holdaway & Lee (1977)

The resultant grid may be observed in fig. 6 and reactions in table 9. The equilibria are written with positive volume increase.

Except for reaction 5, only the Fe pole in the

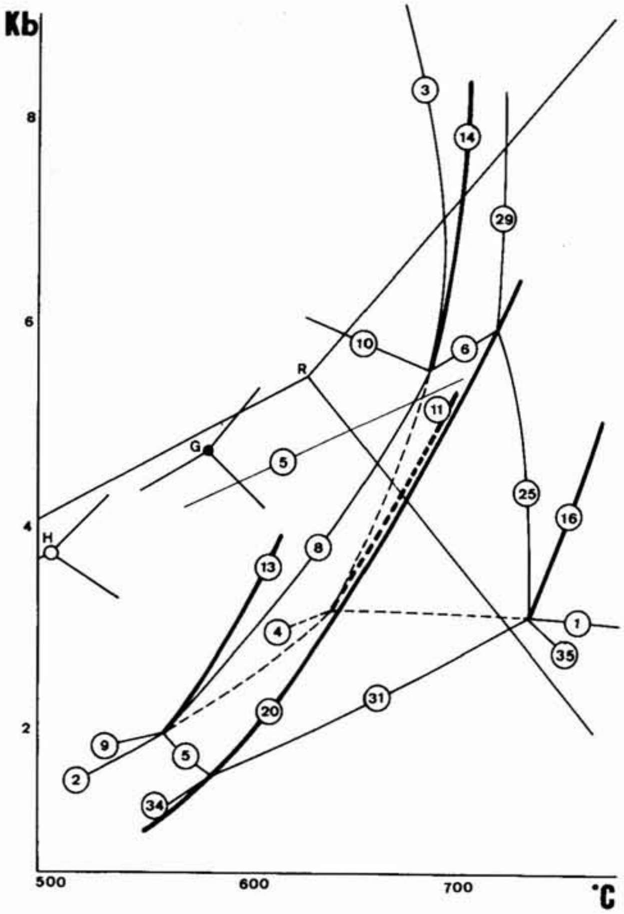


Fig. 6.—Semi-quantitative P-T proyection of studied reactions for low-f_{O2} (QFM buffer). $P_{H2O} = P_t$ in metapelites with excess quartz, muscovite and water.
(R), (H), (G), stand for Al-silicate polimorphs stability after Richardson *et al.* (1969), Holdaway (1971), and Greenwood (1976). Light line: Mg pole; regular lines: Mg pole; Heavy lines: KFMASH univariant reactions. Dashed lines represent metastable segments in metapelites with excess muscovite. Labeled univariant reactions are shown in Table 9.

Table 9.—**Reactions of fig. 6 written according to positive volume**

(1)	Gt + Als + Qz → Cd
(2)	St + Qz → Cd + Als + H_2O
(3)	St + Qz → Gt + Als + H_2O
(4)	Gt + St + Qz + H_2O → Cd
(5)	Bi + Als + Qz + H_2O → Mu + Cd
(6)	Gt + Mu → Bi + Als + Qz
(8)	St + Mu + Qz → Bi + Als + H_2O
(9)	Bi + St + Qz → Mu + Cd + H_2O
(10)	Gt + Mu + H_2O → St + Bi + Qz
(11)	St + Qz → Gt + Cd + Als + H_2O
(13)	St + Mu + Cd → Bi + Als + Qz + H_2O
(14)	St + Mu + Qz → Gt + Als + Bi + H_2O
(16)	Bi + Als + Qz → Gt + Cd + Fk + H_2O
(20)	Mu + Qz → Als + Fk + H_2O
(25)	Gt + Fk + H_2O → Bi + Als + Qz
(29)	Bi + Mu + Qz → Gt + Fk + H_2O
(31)	Bi + Als + Qz → Cd + Fk + H_2O
(34)	Bi + Mu + Qz → Cd + Fk + H_2O
(35)	Gt + Fk + H_2O → Bi + Cd + Qz

divariant reactions and their corresponding univariant intersections have been represented, since the majority of Mg-pure reactions are metastables.

At water saturated conditions melting occur around 730°C at 5 Kb or even lower temperatures if sodic muscovite or Na-rich feldspar are present (Thompson, 1976b). However this presence of melt has not been considered because in the P-T conditions of fig. 6 many natural pelites are not water saturated and, therefore, most of the equilibria and invariant points become stable.

It must be mentioned that Massone's (1988) experimental data for the lower temperature boundary of the reaction (5) magnesian pole show a disagreement of 2.3 Kb and 80°C with those obtained by Seifert (1970) and Bird & Faccet (1973). Fig. 6 considers the data by Massone (1988).

The invariant point where reaction (13) intersects with Chl + Mu = Als + Cd + Bi + H_2O, has been located at 4.0 Kb following Hess (1969). The temperature of this point has been deduced from data taken from table 7.

This temperature results intermediate between Hess' (op.cit.) and that obtained if, at 4.0 Kb, reaction (13) intersect with Chl + Mu = Als + Cd + Bi + H_2O (using for this latter the experimental data of Burnell & Rutherford, 1984).

The low temperature boundaries of reactions (2) and (4) shown in fig. 6 correspond to invariant points in assemblages with chloritoid (Richardson, 1968). The same holds for reaction (9) in assemblages with chlorite (Holdaway & Lee, 1977). The higher pressure boundaries shown in fig. 6 for reactions (13) and (14) correspond again to invariant points for assemblages with chlorite.

Applications

Fig. 6 supplies further information in addition to that obtained in the preceding grids:

(a) The increase of both the stability field of reaction (1) and the stabilization of reaction (4) in muscovite-poor metapelites, originates an increase of the garnet-cordierite stability field towards lower-temperature conditions. However this does not invalidate the impossibility, indicated by Hess (1969) and Kamineni (1971), of garnet —cordierite coexistence in muscovite stability field, except with Mn— or Ca-rich garnets (Osberg, 1971; Okrusch, 1971).

(b) The non-coexistence of staurolite-K feldspar in nature as pointed out by Hess (1969, p. 169). In this regard it should be mentioned that a location of the invariant point, that results of the intersection of (1) and (3) at higher temperature than reaction (20), does not invalidate this fact. This would still hold in pelites with excess muscovite, since that invariant point is metastable. In the case of muscovite-poor pelites that follow a prograde trajectory at not very high pressure, muscovite will be consumed either in reaction (8), (6) or (5). If these reactions came to completion reaction (20) will not take place, and K feldspar occurrence will be delayed, probably until the higher temperature equilibria (25) or (31).

(c) Some precisions should be made about reaction (6) since is has been recorded in natural assemblages with andalusite (Guitard, 1969; Martínez *et al.,* 1988), which seemingly is in disagreement with fig. 6. In staurolite-free rocks this problem no longer exists because in this case the intersection between reactions (6) and (8) disappears, and reaction (6) stability field is enlarged towards lower temperature until likely boundaries imposed by chlorite or chloritoid.

In pelites with staurolite this fact can be explained by a combination of different factors, namely:

(c1) $P_{H2O} < P_t$ conditions may stabilize an invariant point $[H_2O]$ at low temperature, causing the extension of the stability field of degenerate reaction (6), because this reaction goes through its intersection with (8) to lower P-T conditions.

(c2) At $P_{H2O} < P_t$ conditions dehydration reactions are displaced to lower temperatures. In this way Novak & Holdaway (1981, p. 85), for naturall compositions and $X_{H2O} = 0.8$, locates the intersection between (3) and (8) around 3.3 Kb and 590°C.

(c3) $Fe^{3+}-$ Al substitutions in Al_2SiO_5 polimorphs stabilize andalusite at higher P-T conditions.

(c4) A $X_{Fe}^{St} > X_{Fe}^{Gt}$ relation, which is possible in Ca- and Mn-rich pelites (see also Ganguly, 1972; and Rice, 1985), shifts the intersection between (6) and (8) to lower P-T conditions for Mg-rich relations.

New P-T-$X_{Fe\text{-}Mg}$ relations that have been deduced from fig. 6 are: $T_{Fe} < T_{Mg}$ at constant P and $P_{Fe} < P_{Mg}$ at constant T for reaction (25); $T_{Fe} < T_{Mg}$ at constant P and $P_{Fe} > P_{Mg}$ at constant T for reaction (29); $T_{Fe} > T_{Mg}$ at constant P and $P_{Fe} < P_{Mg}$ at constant T for reactions (31) and (34).

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