

# Experimental determination of the fluid-absent melting relations in the pelitic system

## Consequences for crustal differentiation

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**Abstract.** In order to provide additional constraints on models for partial melting of common metasediments, we have studied experimentally the melting of a natural metapelite under fluid-absent conditions. The starting composition contains quartz, plagioclase, biotite, muscovite, garnet, staurolite, and kyanite. Experiments were done in a half-inch piston-cylinder apparatus at 7, 10, and 12 kbar and at temperatures ranging from 750° to 1250° C. The following reactions account for the mineralogical changes observed at 10 kbar between 750° and 1250° C:  $Bi + Als + Pl + Q = L + Gt + (Kf)$ ,  $Ky = Sill$ ,  $Gt + Als = Sp + Q$ ,  $Gt = L + Sp + Q$ , and  $Sp + Q = L + Als$ .

The compositions of the phases (at  $T > 875^\circ\text{C}$ ) were determined using an energy-dispersive system on a scanning electron microscope. The relative proportions of melt and crystals were calculated by mass balance and by processing images from the SEM. These constraints, together with other available experimental data, are used to propose a series of  $P-T$ ,  $T-XH_2O$ , and liquidus diagrams which represent a model for the fluid-present and fluid-absent melting of metapelites in the range 2–20 kbar and 600°–1250° C.

We demonstrate that, even under fluid-absent conditions, a large proportion ( $\approx 40\%$ ) of S-type granitic liquid is produced within a narrow temperature range (850°–875° C), as a result of the reaction  $Bi + Als + Pl + Q = L + Gt (+/- Kf)$ . Such liquids, or at least some proportion of them, are likely to segregate from the source, leaving behind a residue composed of quartz, garnet, sillimanite, plagioclase, representing a characteristic assemblage of aluminous granulites.

The production of a large amount of melt at around 850° C also has the important effect of buffering the temperature of metamorphism. In a restitic, recycled, lower crust undergoing further metamorphism, temperature may reach values close to 1000° C due to the absence of this buffering effect. Partial melting is the main process leading to intracontinental differentiation. We discuss the crustal cross-section exposed in the North Pyrenean Zone in the context of our experiments and modelling.

### 1 Introduction

Several models, based on experimental data and the geometrical analysis of phase relationships, have recently been

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proposed for the anatexis of pelitic rocks (Abbott and Clarke 1979; Clemens and Wall 1981; Thompson 1982; Grant 1985). Most of these studies emphasize the effects of water on the melting processes and the generation and evolution of water-undersaturated granitic melts (Clemens 1984). However, we are still ignorant of (i) the actual compositions of the melts formed at various conditions, (ii) their change in composition with increasing degree of melting, and (iii) the proportion of melt formed as a function of temperature. In order to provide some constraints, the experimental melting of a metapelite has been undertaken between 7–12 kbar and 750–1250° C. Clemens (1984) showed that the majority of granitic magmas were initially water-undersaturated, indicating either that a fluid phase with a  $a_{H_2O} \ll 1$  was present during melting or that the melting reactions were fluid-absent. In the absence of free water, melting depends upon water from hydrates like muscovite or biotite. Such amounts of water are usually not sufficient to saturate a melt formed by the breakdown of the hydrates and the water released during this process is dissolved in the melt without formation of a vapor phase (Burnham 1967). This is what has been called “fluid-absent melting” (Burnham 1967; Clemens 1984), “dehydration melting” (Thompson 1982), or “vapor-absent melting” (Grant 1985) (see also Robertson and Wyllie 1971). The experimental work reported here has been performed under fluid-absent conditions because it is believed that such conditions prevail in the lower part of the crust. The purpose of these experiments was to determine

- (i) the reactions involved in the partial melting of the lower crust,
- (ii) the compositions of the liquids at various temperatures,
- (iii) the mineralogical composition of the residuum,
- (iv) the proportion of melt as a function of temperature in order to determine the temperature necessary to generate enough granitic liquid to form a mobile magma.

We then use these constraints in constructing a  $T-XH_2O$  diagram and a model for both the water-saturated and the fluid-absent melting of pelites between 2 and 20 kbar. Finally, we explore the consequences of this model for the metamorphic structure of the crust and for intracontinental differentiation.

### 2 Experimental and analytical techniques

Most of the experiments were performed in a 0.5 inch (1.27 cm) diameter non-end-loaded piston-cylinder apparatus (Patera and

**Table 1.** Bulk composition of the rock starting material (average of atomic absorption analysis and EDS microprobe analyses of a glass; water content determined by thermogravimetric analysis), and representative microprobe analyses of the constituent minerals

	Gt27	St33	Bi20	Mu21	Pl40	Chl	Bulk comp.	av. clay <sup>a</sup>
SiO <sub>2</sub>	37.52	27.30	35.72	46.41	59.88	24.55	64.35	64.84
Al <sub>2</sub> O <sub>3</sub>	20.76	51.00	20.50	36.47	25.55	23.01	18.13	17.86
FeO	31.58	14.35	18.29	0.95	0	23.38	6.26	6.35
MgO	3.83	1.93	10.65	0.88	0	15.94	2.44	2.66
CaO	5.82	0.12	0	0	6.42	0.01	1.52	1.85
Na <sub>2</sub> O	0	0	0.43	1.25	8.35	0.59	1.66	1.93
K <sub>2</sub> O	0	0	8.38	9.13	0	0.32	2.56	3.64
TiO <sub>2</sub>	0.23	0.64	1.78	0.8	0	0.12	0.82	0.86
MnO	0.29	0	0	0	0	1.08	0.09	
H <sub>2</sub> O <sup>b</sup>	0	4.65	4.25	4.11	0	11.00	2.15	
Total (anh.)	100.03	95.35	95.75	95.89	100.19	89.00	97.85	100
<i>X</i> Mg	0.179	0.194	0.509	0.624		0.548		
Si	5.976	3.907	5.336	6.091	2.663	5.093		
Al	3.896	8.600	3.609	5.641	1.339	5.626		
Fe	4.206	1.717	2.284	0.104	0	4.056		
Mg	0.910	0.413	2.371	0.172	0	4.927		
Ca	0.993	0.018	0	0	0.306	0.002		
Na	0	0	0.123	0.317	0.720	0.239		
K	0	0	1.596	1.529	0	0.085		
Ti	0.027	0.069	0.199	0.078	0	0.018		
Mn	0.039	0	0	0	0	0.190		
nb. ox.	24	23	22	22	8	28		

<sup>a</sup> Normalized to 100% anhydrous (Shaw, 1956).

<sup>b</sup> By difference to 100%

Holloway 1978). The solid media assemblies were all salt below 950° C and salt + pyrex glass at higher temperatures, with a 6 mm ID graphite tube furnace and powdered pyrex surrounding the capsule. Temperatures were controlled and read by W-Re<sub>26</sub>/W-Re<sub>5</sub> thermocouples and are believed to be precise to within  $\pm 5^\circ$  C. No correction was made for the effect of pressure on the EMF output of the thermocouples. Temperature gradient measurements were made (Esperança and Holloway 1986; Jakobsson and Holloway 1986) and a gradient of 14° C found from the normal thermocouple position to the center of the capsule. Thus an overall gradient of 28° C is estimated for the length of the capsule. Therefore, reported temperatures are believed to be accurate to within  $\pm 20^\circ$  C. Precision from run to run is estimated to be better than  $\pm 5^\circ$  C. Reported pressures were not corrected for the effects of friction because Esperança and Holloway (1986) found recorded pressures to be within 0.5 kbar of the published position for the Fa + Q = Fs reaction (Bohlen et al. 1980). Sealed capsules (5 mm in diameter and 7 mm in length) were of gold below 1000° C and Pd<sub>40</sub>-Ag<sub>60</sub> at higher temperatures. They were filled with 100 to 200 milligrams of powdered rock starting material (< 5 microns) which had been dried overnight at 150° C and stored in a vacuum dessicator over magnesium perchlorate. Experiments were done by heating directly to run temperature using the hot piston-out technique. None of the reactions were reversed.

All quenched run products were identified by optical petrographic techniques and X-ray powder diffraction. Polished thin sections were made and examined by scanning electron microscopy. The SEM photographs were made in electron backscatter mode. Elemental analyses were done using an energy-dispersive analyser on the SEM. Natural minerals and a glass were used as standards. Results were normalized to 100%.

### 3 Starting material and subsolidus equilibria

A pelitic rock from the Cariño gneisses was used as the starting material for this experimental study. This rock is from the Cabo

Ortegal complex (Galicia, NW Spain) which consists of three major rock types: (1) ultramafic rocks (peridotites and pyroxenites), (2) mafic rocks, and (3) rocks of sedimentary origin. All these underwent high-grade metamorphism ranging from high-pressure amphibolite and granulite facies to the eclogite facies (Vogel 1967; Engels 1972; Arps et al. 1977). In the "amphibolite-facies zone" the pelitic rocks (Cariño gneisses) which are non-migmatitic, are composed of quartz, plagioclase (An<sub>30</sub>), kyanite, muscovite, biotite, garnet,  $\pm$  staurolite,  $\pm$  secondary chlorite. In the "granulite facies zone", the pelitic rocks (Chimparra gneisses) display the same paragenesis, except for the absence of staurolite, suggesting that these gneisses crossed the staurolite-out isograd. It is noteworthy that in a few places, incipient anatexis can be observed (Arps et al. 1977). In the "eclogite-facies zone", the associated felsic rocks are strongly migmatitic in character. Quartz, muscovite, and plagioclase formed mobilized pegmatitic fractions while garnet, kyanite, and biotite remained behind as "infusible residues" (den Tex et al. 1972). Note that, except for the presence or absence of staurolite and the migmatitic character, there is no difference in the pelitic parageneses between the different zones. The subdivision into different facies is based on typomorphic parageneses in the mafic rocks only (den Tex et al. 1972). Mafic and ultramafic rocks form up to 75% of the surface area of the catazonal Cabo Ortegal Complex and the close association with pelitic rocks has been interpreted as a volcano-detrital sequence of pelagic sediments with submarine basic lavas or tuffs (den Tex et al. 1972).

The Cariño gneisses were selected as starting materials for the melting studies at high pressure because they display a high pressure paragenesis, at equilibrium, diagnostic of temperatures just below the onset of partial melting. Furthermore, they show coexistence of muscovite and biotite which are two minerals important for the understanding of fluid-absent partial melting of pelitic rocks. The chemical composition of the rock which has been used is given in Table 1 together with the compositions of the major minerals. The modal proportions were determined by point counting ( $\approx 4000$  points). The water content of the sample was determined by thermo-gravimetric analysis as 2.15 wt% total, of which

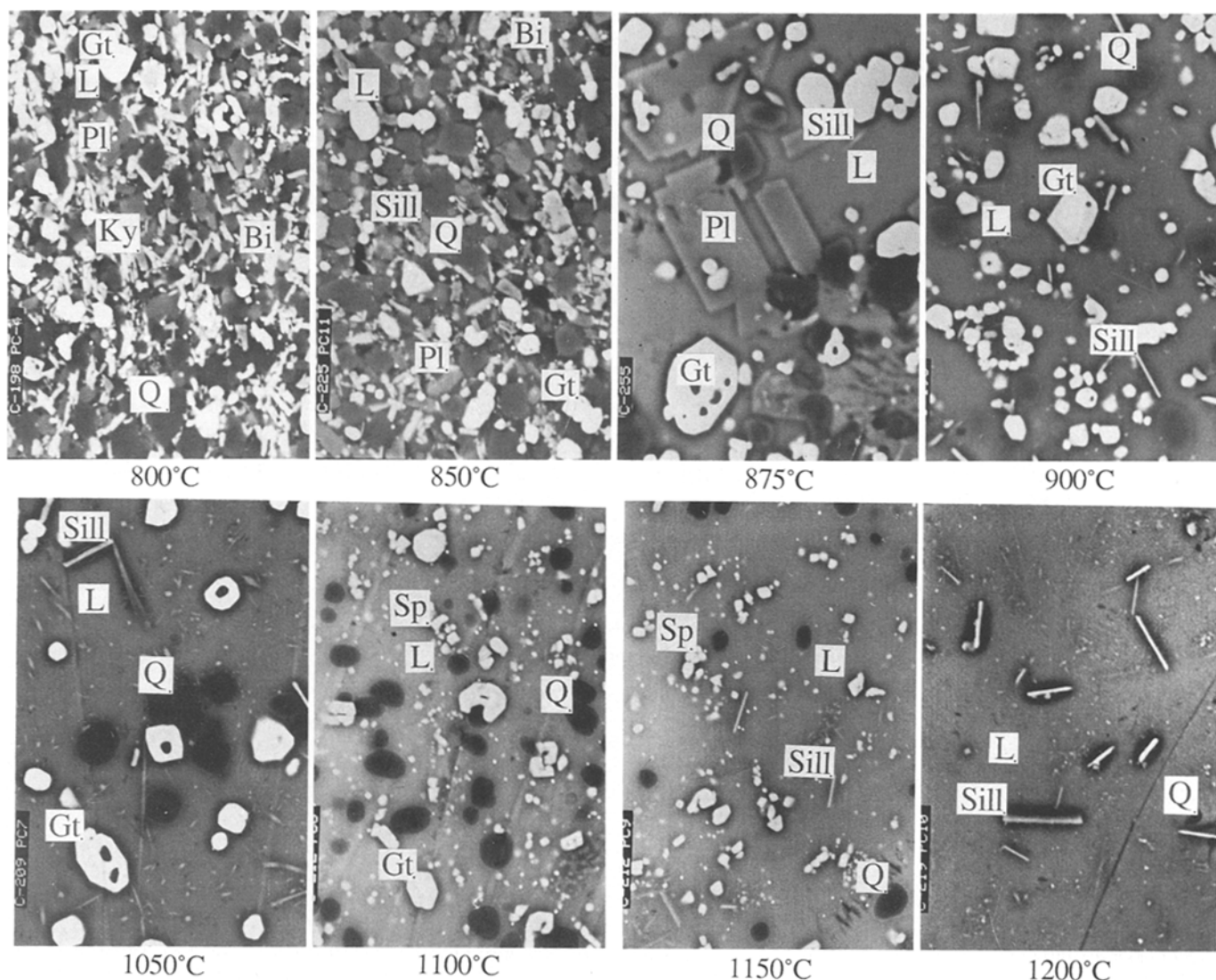


Fig. 1. SEM backscatter photographs of some runs at 10 kbar. One centimeter = 15  $\mu$

0.29% was found to be adsorbed water. The chemical composition of this rock is very close to the average of clays as determined by Shaw (1956) except for  $K_2O$  which is significantly lower (cf. Table 1).

The physical conditions of metamorphism for the Cariño gneisses can be estimated from geothermobarometers based on mineral solid-solutions. The garnet-biotite geothermometer (Thompson 1976; Holdaway and Lee 1977; Ferry and Spear 1978) yields temperatures ranging from 640° to 680° C at 10 kbar. The  $P-T$  diagram for the assemblage garnet, biotite, kyanite, quartz, muscovite, vapor in the system KFMASH constructed by Spear and Selverstone (1983), provides an estimate of 640° C and 6 kbar, plotting outside the kyanite field. Perchuk et al. (1981) proposed a grid to determine the  $P$  and  $T$  of crystallization of Bi, Gt, Sill, Mu, and Q assemblages. In the case of the Cariño gneisses this gives 610° C and 6.5 kbar. The plagioclase-biotite-garnet-muscovite geobarometer (Ghent and Stout 1981) yields a pressure of 8.5 kbar for a temperature of 660° C while a pressure of 10.5 kbar is determined by using the garnet-plagioclase-kyanite-quartz geobarometer (Newton and Haselton 1981). Considering that this last geobarometer is one of the most reliable in rocks of this type (Newton 1983), and that this rock crystallized in the field of kyanite, a pressure of 9.5+/-1 kbar and a temperature of 660+/-20° C are inferred for the conditions of crystallization of the Cariño gneisses. These are close to the conditions determined by den Tex et al. (1972) on the basis of experimental equilibria.

## 4 Results

### 4.1 Description of the run products

The results of the experiments are shown in the SEM images of Fig. 1, and in Table 2. It is known that in the range 4–10 kbar, partial melting of the muscovite, quartz, alkali-feldspar assemblage occurs at temperatures below 700° C (Thompson and Algor 1977). Our lowest temperature experiment was 750° C and muscovite was not observed in any of our run products. We also did not observe staurolite and it is assumed that staurolite disappeared in the subsolidus area. At 10 kbar, and from 750° to 860° C, the phase assemblage is composed of quartz, plagioclase, biotite, garnet, aluminum-silicate (kyanite and/or sillimanite), and glass. On the SEM images, it can be seen that the liquid forms a film around the crystals and is concentrated at triple junctions. The proportion of liquid is small, certainly less than 10%. The size of the crystals is about 5  $\mu$ . Between 832° and 850° C, kyanite reacted to produce distinct sillimanite needles. At higher temperatures (between 850° and 862° C) the proportion of liquid increases dramatically; this important change corresponds to the disappearance of biotite. The resulting assemblage is composed of quartz, pla-

**Table 2.** Experimental results

Run number	T° C	P kbar	Duration	Assemblage	Remarks
PC21	750°	10	7 days	L Gt Ky Q Pl Bi	disappearance of muscovite and staurolite below 750° C
PC04	800°	10	7 days	as above	progressive increase of garnet and decrease of biotite and kyanite
PC05	832°	10	6 days	as above	
PC11	850°	10	7 days	L Gt Ky – Sill Q Pl Bi	appearance of sillimanite needles
PC18	862°	10	6 days	L Gt Sill Q Pl	disappearance of biotite and large increase in the proportion of melt
PC17	875°	10	5.5 days	L Gt Sill Q Pl	
PC20	887°	10	5 days	L Gt Sill Q Pl	
PC03	900°	10	4 days	L Gt Sill Q (Pl)	large increase in sillimanite, very small amount of plagioclase
PC02	950°	10	24 hrs	L Gt Sill Q	disappearance of plagioclase
PC06	1000°	10	24 hrs	as above	progressive decrease of garnet
PC07	1050°	10	24 hrs	as above	
PC08	1100°	10	2 hrs	L Gt Sp Q	crystallization of spinel, increase of quartz, decrease of garnet, disappearance of sillimanite
PC09	1150°	10	30 min	L Sp Sill Q	disappearance of garnet. Sillimanite reappears
PC10	1200°	10	20 min	L Sill (Q)	disappearance of spinel and large decrease of quartz
PC01	1250°	10	30 min	L	liquidus
PC16	950°	12	15 hrs	L Gt Ky (Sill) Q	rare needles of sillimanite
PC15	975°	12	14 hrs	as above	
PC27	850°	7	7 days	L Gt Bi Sill Q Pl	
PC24	875°	7	7 days	L Gt Sill Q Pl	disappearance of biotite

(in all the runs below the liquidus, kyanite persisted metastably in the field of sillimanite)

gioclase, aluminum–silicate, garnet, and glass. At 875° C the sample was accidentally quenched after 18 h (a brief high temperature excursion occurred) and then rerun at 875° C for 5 days. This procedure produced large euhedral crystals of garnet (10  $\mu$ ), quartz (5  $\mu$ ), and plagioclase (20 microns), and the nucleation of numerous small garnets. At 900° C, the proportion of plagioclase is very small and probably close to the Pl-out curve. In some of these runs, it is likely that garnet did not equilibrate completely with the melt. The cores of these crystals are relicts from the starting garnets separated from the newly-formed rims by regions of small glass inclusions. The differences in the chemical compositions of the cores and rims will be discussed later. Between 900° and 1050° C, there is a large interval in temperature over which no mineralogical changes occur; quartz, garnet, aluminum–silicate, and glass coexist. Metastable kyanite persists together with stable sillimanite. An important boundary is crossed above 1050° C with the appearance of spinel and disappearance of sillimanite; the assemblage is then composed of quartz, garnet, spinel, and glass. In the 1050–1100° C interval, the amount of garnet decreases while the modal proportion of quartz increases strongly. At 1150° C there is no more garnet, spinel is abundant, and the phase assemblage is composed of quartz, spinel, sillimanite, and glass.

Interestingly, aluminium–silicate (sillimanite or mulite?) re-appears. At 1200° C spinel is absent and the glass coexists with sillimanite and quartz. The liquidus is reached between 1200° and 1250° C.

#### 4.2 Composition of the phases

**Spinel.** Spinel was analysed in two runs at 1100° and 1150° C (Table 3); they belong to the spinel–hercynite series. Their  $X_{Mg}$  ( $Mg/Mg + Fe$ ) increases with temperature (0.51 at 1100° C and 0.61 at 1150° C), it is greater than

$X_{Mg}$  in the glass (0.38) but not significantly different from  $X_{Mg}$  in the garnet (0.48 at 1100° C).

**Garnet.** In most cases garnet did not reach equilibrium with the glass, as shown by the presence of relict cores and newly-formed rims. The compositions of the cores are usually close to the composition of the starting garnet (= 6% CaO and  $X_{Mg} = 0.18$ ) while the compositions of the rims are always poorer in calcium, and far more magnesian.  $X_{Mg}$  in the garnet increases from 0.40 at 875° C to 0.48 at 1100° C. In a previous paper (Vielzeuf 1983), and on the basis of coexisting spinel, glass, and garnet in a xenolith, it has been argued that, at very high temperature,  $X_{Mg} Sp > X_{Mg} Gt > X_{Mg} Gl$ . This apparently contradicts the data given by Clemens and Wall (1981) who observed that  $X_{Mg} Gl > X_{Mg} Gt$ , and Grant (1985) who concluded that the situation described by Vielzeuf (1983) did not represent an “approach to equilibrium”. It must be stressed that the present study gives an answer to this apparent contradiction. Above 950° C  $X_{Mg} Gt$  is greater than  $X_{Mg} Gl$ , on the contrary at 950° C and at lower temperatures  $X_{Mg} Gt$  is less than  $X_{Mg} Gl$ . This is in agreement with other experimental studies (Green 1977; Ellis 1986). According to the present experiments, the reversal of the Fe–Mg partitioning between garnet and glass would occur between 950° and 1050° C at 10 kbar.

**Plagioclase.** This mineral has been analysed only in one experiment at 875° C; it is slightly more albitic than the starting plagioclase ( $Ab_{73}$  compared to  $Ab_{70}$ ). The coexistence of garnet, plagioclase, quartz, aluminum–silicate allows the use of the Gt–Pl–Als–Q geobarometer (Newton and Haselton 1981). This barometer gave a pressure of 16 kbar at 875° C with sillimanite and 15 kbar with kyanite (instead of 10 kbar). This discrepancy is probably due to (1) difficulties in analysing small crystals (<10 microns)

in the experimental charges, and (2) disequilibrium between plagioclase and liquid (Johannes 1978); hence the compositions of the minerals listed in Tables 3 a, b, c should be judged accordingly.

**Glass.** Careful attention has been paid to analysing the glasses: they were analysed at different times, with different sets of standards including a glass made of the starting material CO821. The results for runs between 875° and 1200° C are listed in Table 4. All of them plot in the adamelite field. From low to high temperatures, SiO<sub>2</sub> decreases regularly up to 1100° C, and then increases slightly or remains constant up to 1250° C in connection with the crystallization of spinel. Al<sub>2</sub>O<sub>3</sub> and MgO increase regularly throughout the studied temperature interval, while FeO shows an abrupt increasing step between 1000 and 1050° C, perhaps in connection with the reversal of the Fe–Mg partitioning between glass and garnet. CaO concentration is low at 875° C where a significant amount of plagioclase is observed, a pronounced increase can be noted between 875° and 900° C, then the calcium content of the liquid remains remarkably constant until the liquidus is reached. Na<sub>2</sub>O and K<sub>2</sub>O decrease regularly from low to high temperatures. The evolution of the XMg in the liquid is interesting: at first it decreases up to 950° C then remains constant up to 1100° C (if we except the value for the run performed at 1000° C), and finally increases until the liquidus is reached. This can be ascribed to the crystallization/dissolution of garnet, and the crystallization of spinel together with the partitioning of Fe–Mg between these phases and the glass. In his review of this paper, Grant plotted the analyses of the glasses on an isocon diagram (Grant 1986a) and noted that Ti, Mg, and Fe change coherently from 875° to 900° to 1000° C, but that the FeO value for 950° C should be more like 1.9 than 2.9. As a consequence, the XMg value of 0.53 at 1000° C may be less suspect than the value of 0.43 obtained for the glass at 950° C.

The variation of the composition of the liquids as a function of temperature is also shown in the AKF diagram (Fig. 2). This diagram clearly shows that the major change in the analytical data on the glasses between 1000° and 1050° C is largely due to major dissolution of garnet in the liquid.

#### 4.3 Proportion of melt

It is possible to calculate the modal proportions of the phases in the run products using a mass balance approach based on a least squares method. Some of the calculated values have been checked by image-processing of SEM photographs (Table 5). No suitable means has been found to calculate the modal proportions below 875° C and, as a result, the estimates at low temperatures in Fig. 3 are approximate. Only one estimate of the proportion of melt (at 1050° C) is inconsistent with the others (Table 5). The interpolated line between these points results from the assumption that a reaction promotes a sudden increase of the proportion of melt while the dissolution of phases (eg. garnet, sillimanite in the 900°–1050° C interval) produces a smooth, incremental increase in melt proportion. In Fig. 3, three main stages of melting can be distinguished:

(1) the first one (speculative) occurs below 800° C and corresponds to the melting of muscovite; the proportion of melt is small and did not exceed 10–15%;

(2) the range 850–900° C is marked by a dramatic increase in the proportion of melt changing from about 10% to 50–60%. This step corresponds to the melting of biotite and is followed by a “plateau” along which garnet and sillimanite are progressively dissolved by the liquid;

(3) the third (and last) stage is represented by the melting of garnet and spinel at very high temperatures (above 1100° C).

Concerning the other phases, the following points can be made (Table 5). Up to 1050° C, the proportion of sillimanite is constant; this mineral disappears at 1100° C and crystallizes again at 1150° C. Quartz increases markedly at 1100° C in connection with the first crystallization of spinel, the decrease of garnet, and disappearance of sillimanite. In the starting material, garnet represents 2% of the mode; at 875° it represents 24%. Thus, a large amount of garnet is produced in the range 600–875° C. This proportion decreases regularly up to 1000° C and abruptly above this temperature.

### 5 Modelling the partial melting of metapelites and metagraywackes

The partial melting processes can be modelled using the same principles which are commonly used in the subsolidus region. However, complications arise from the fact that a melt may be regarded as an “ultimate solid-solution” changing rapidly in composition as a function of *P*, *T*, *a*H<sub>2</sub>O. These changes are likely to produce some modifications in the chemographic relationships. The articles published by Thompson (1982) and Grant (1985) represent important contributions to the understanding of phase equilibria in partial melting of pelitic rocks. In this paper we will emphasize some less developed aspects in these previous studies. Our purpose is to construct internally consistent *P–T*, *T–XH<sub>2</sub>O*, and liquidus diagrams representing three complementary ways of viewing the partial melting processes. This model is based on available experiments and natural observations; but it should be kept in mind that such models are hypothetical because they are also based on some assumptions. Even so, they are good support for reasoning, represent efficient ways of emphasizing the critical aspects of the partial melting processes and have predictive power. There is no doubt that some of the depicted phase relations will have to be changed as more information and constraints become available.

#### 5.1 Subsolidus equilibria

One of the first crucial points is to determine the subsolidus phase relationships in the high-grade region which will be overlapped by melting. The phase relationships among aluminum–silicate (Als), muscovite (mu), K-feldspar (Kf), biotite (Bi), garnet (Gt), and cordierite (Cd) (+ quartz (Q) and vapour (V)) in the system Al<sub>2</sub>O<sub>3</sub> (A)–K<sub>2</sub>O (K)–FeO (F) or MgO (M) (+ SiO<sub>2</sub> (S) and H<sub>2</sub>O (H)) (*case 1*) have been studied by Thompson (1976, 1982), Vielzeuf and Boivin (1984), and Vielzeuf (1984). In the following model, phengitic substitution in the muscovite (Mu<sub>ss</sub>) is taken into consideration leading to the replacement of the degenerate reaction (Mu + Q = Kf + Als + V by one of the following: Mu<sub>ss</sub> + Q = Cd + Kf + Als + V, Mu<sub>ss</sub> + Q = Bi + Kf + Als + V, and Mu<sub>ss</sub> + Q = Gt + Kf + Als + V, depending upon the pres-

**Table 3.** EDS microprobe analyses of garnet, plagioclase, and spinel in different runs at 10 kbar. Structural formulae on the basis of 24, 8, and 32 oxygens respectively. Analyses are normalized to 100%. a – garnets

Gt Start. mat.	1100° C				1050° C				950° C				900° C				875° C			
	Gt19°	Gt20°	Gt21°	Gt22°	Gt26	Gt27	Gt28	Gt83°	Gt84°	Gt85°	Gt86°	Gt90°	Gt92	Gt93°	Gt94°	Gt98°	Gt38°	Gt39°	Gt40°	
SiO <sub>2</sub>	39.1	42.0	36.9	37.0	39.1	40.6	39.7	38.4	42.5	38.1	40.3	40.1	42.0	38.8	42.2	38.5	42.3	37.7		
Al <sub>2</sub> O <sub>3</sub>	21.6	22.7	20.6	21.6	22.0	22.1	21.7	19.6	21.3	19.4	20.8	19.9	21.5	20.3	20.8	21.1	21.6	20.8		
FeO	31.58	28.0	32.3	27.1	25.1	23.8	24.4	31.6	24.5	32.3	28.4	29.5	23.9	29.9	24.6	30.1	24.1	30.8		
MgO	3.83	7.1	5.3	10.9	12.3	11.8	12.5	5.0	9.0	4.1	5.9	4.8	9.4	4.6	9.5	4.4	9.2	4.2		
CaO	5.82	4.2	1.6	2.2	1.1	1.1	1.0	4.5	2.4	6.0	4.6	5.6	3.1	5.6	2.6	5.5	2.9	4.8		
TiO <sub>2</sub>	0.23	0.3	0.3	0.3	0.4	0.2	0.4	0.8	0.2											
MnO <sub>2</sub>	0.29	0.3	0.8	0.8	0.4	0.4	0.4	0.8	0.2											
Total	100.03																			
24 ox.																				
Si	5.976	6.06	5.90	5.74	5.95	6.10	6.00	6.11	6.40	6.09	6.25	6.28	6.32	6.13	6.37	6.06	6.35	6.06		
Al	3.896	3.94	3.88	3.95	3.93	3.92	3.87	3.67	3.78	3.65	3.80	3.68	3.82	3.77	3.71	3.93	3.83	3.93		
Fe	4.206	3.63	4.31	3.52	3.19	2.99	3.09	4.20	3.09	4.32	3.68	3.86	3.01	3.95	3.11	3.97	3.03	4.13		
Mg	0.910	1.64	1.26	2.52	2.79	2.65	2.81	1.18	2.03	0.97	1.37	1.12	2.12	1.09	2.14	1.03	2.05	1.01		
Ca	0.993	0.70	0.68	0.36	0.17	0.18	0.16	0.77	0.39	1.03	0.76	0.95	0.50	0.94	0.43	0.93	0.46	0.83		
Ti	0.027	0.04	0.04	0.04	0.05	0.02	0.04	0.10	0.03											
Mn	0.039	0.04	0.12	0.10	0.05	0.05	0.05	0.10	0.03											
X <sub>Mg</sub>	0.18	0.31	0.23	0.42	0.47	0.47	0.48	0.22	0.40	0.18	0.27	0.23	0.41	0.22	0.41	0.21	0.40	0.20		
Alm.	0.684	0.608	0.677	0.540	0.514	0.510	0.505	0.671	0.558	0.683	0.634	0.651	0.535	0.650	0.545	0.664	0.546	0.692		
Pyr.	0.148	0.275	0.197	0.388	0.450	0.451	0.460	0.189	0.367	0.154	0.235	0.189	0.376	0.179	0.375	0.173	0.370	0.169		
Gro.	0.161	0.117	0.107	0.056	0.028	0.031	0.026	0.124	0.070	0.163	0.131	0.159	0.089	0.154	0.075	0.155	0.083	0.139		
Spe.	0.006	0.008	0.019	0.016	0.008	0.008	0.008	0.017	0.005	0.017	0.005	0.017	0.005	0.017	0.005	0.008	0.005	0.008		

°: core; °: rim

c - Spinel

	1150° C					1100° C		
	Sp10	Sp11	Sp12	Sp13	Sp17	Sp18		
Al <sub>2</sub> O <sub>3</sub>	67.5	67.3	67.4	67.0	63.8	65.3		
FeO	17.1	17.0	17.2	17.7	22.9	21.6		
MgO	15.4	15.8	15.4	15.2	13.3	13.1		
Al	16.26	16.20	16.25	16.20	15.85	16.09		
Fe	2.92	2.90	2.94	3.04	4.03	3.77		
Mg	4.69	4.80	4.69	4.65	4.19	4.09		
XMg	0.62	0.62	0.61	0.60	0.51	0.52		

Structural formulae on the basis of 32 ox. Normalized to 100%

b - plagioclases

	875° C		
	Pl Start. mat.	Pl42	Pl44
SiO <sub>2</sub>	59.9	64.4	64.4
Al <sub>2</sub> O <sub>3</sub>	25.5	23.2	23.3
CaO	6.4	4.0	4.0
Na <sub>2</sub> O	8.3	7.5	7.5
K <sub>2</sub> O	0	0.8	0.7
Si	2.66	2.83	2.83
Al	1.34	1.20	1.21
Ca	0.31	0.19	0.19
Na	0.72	0.64	0.64
K	0	0.05	0.04
Ab	0.701	0.735	0.736
An	0.298	0.213	0.217
Or	0	0.053	0.047

Structural formulae on the basis of 8 ox. Normalized to 100%

sure (see Thompson 1982 for a careful discussion of this problem).

At higher temperatures, the phase relationships among Als, Kf, Bi, Opx, Gt, Cd (Q, V) in the KFMASH system (*case 2*) were modelled by Vielzeuf (1980a) and Vielzeuf and Boivin (1984). In a more recent study (Vielzeuf 1984), aluminous biotite (Bi<sub>ss</sub>) was used instead of a biotite in the annite-phlogopite series (see Holdaway 1980) changing the degenerate reaction  $Bi + Q = Opx + Kf + V$  into one of the following reactions:  $Bi_{ss} + Q = Cd + Opx + Kf + V$ ,  $Bi_{ss} + Q = Opx + Als + Kf + V$ , or  $Bi_{ss} + Q = Opx + Kf + Gt + V$ , depending upon the pressure and the Mg/Fe ratio in the system.

A third multisystem of great interest at very high temperatures is the one involving the phases Als, Cd, Opx, Sp, Gt (+Q) in the FMAS system (*case 3*). These relations were studied by Vielzeuf (1983) and discussed by Grant (1985) and Hensen (1986). The modifications proposed by Hensen (1986) concern the slope of the reaction  $Sp + Q = Opx + Als$  located in the high temperature portion of the diagram which is metastable with respect to melting reactions in our experiments; this aspect will not be discussed in this paper.

It is interesting to note that, in each of these three systems, the high-temperature region is obliterated by some melting reactions representing successively (and as a first approximation) the muscovite melting stage, the biotite melting stage, and the garnet melting stage. Now the problem is to determine what subsolidus reactions will be interrupted by melting. As a very good approximation this important change occurs close to the (1)  $Kf + Q + V = L$  reaction in the KFMASH system or at lower temperature, and close to the  $Ab + Kf + Q + V = L$  reaction in the KNFMASH system. However, the reactions under consideration are not only dependent on  $P$  and  $T$  but also on  $a_{H_2O}$  in the system. Most importantly, the majority of the reactions present in the subsolidus systems involve Fe-Mg solid solutions. Variations in the XMg of the system may affect the location of the divariant fields by several tens of degrees and/or several kilobars. Also, it has been demonstrated that Fe-Mg substitution can shift reaction boundaries in a grid sufficiently to cause a topological inversion (Vielzeuf 1983; Vielzeuf and Boivin 1984). Later work (Montel et al. 1986; Hensen 1986) has confirmed the utility of this approach for pelitic systems. Such inversion occurs in cases 2 and 3 and, as a result, reaction (1)  $Kf + Q + V = L$  will not necessarily intersect the same reactions in the pure Fe and pure Mg systems. Considerable attention has been given to these aspects by Thompson (1982) and Grant (1985). Thompson emphasized the effects of a change in the relative position of reaction (1) in a given grid and Grant dealt with the effects of reversals of the geometrical relationships on the melting reactions. A method of studying the effects of Fe-Mg solid solutions on the geometrical relations has been proposed in a previous paper (Vielzeuf and Boivin 1984) and these aspects will not be emphasized here. Based on the fact that shales and graywackes have remarkably constant XMg (atomic Mg/Mg+Fe) (between 0.4 and 0.5; Blatt et al. 1972), we will construct a model for a fixed and average value of XMg close to 0.5. For clarity the divariant bands in the diagrams will be represented as lines on Figs. 5 and 7.

The following reactions are important for positioning the grid in  $P-T$  space:

**Table 4.** Composition of the liquids as a function of temperature at 10 kbar

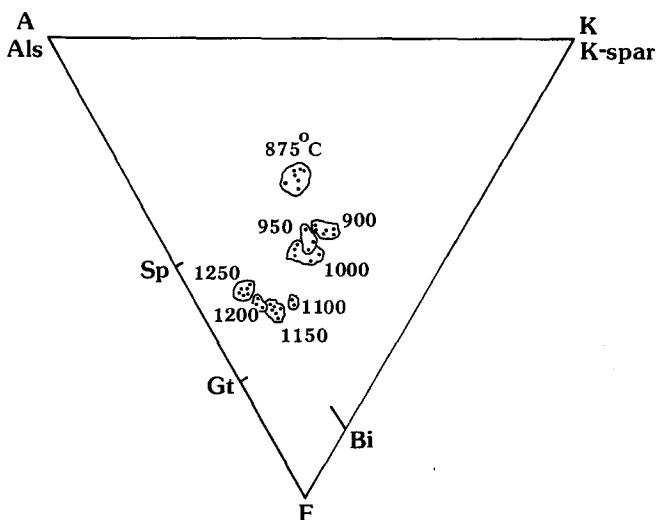
Wt% Oxide	Anhydrous liquid compositions									
	T° C									
	1250	1200	1150	1100	1050	1000	950	900	875	800
SiO <sub>2</sub>	65.8	64.8	65.6	65.5	66.6	69.3	69.3	71.3	73.2	74.7
TiO <sub>2</sub>	0.8	1.0	0.9	1.1	1.0	0.6	0.6	0.6	0.3	0.1
Al <sub>2</sub> O <sub>3</sub>	18.6	18.2	17.5	17.6	17.7	17.2	17.0	16.1	16.1	16.4
FeO	6.4	6.8	6.5	5.5	5.1	2.4	2.9	1.9	1.5	2.2
MgO	2.5	2.5	2.2	2.1	2.0	1.6	1.2	1.3	1.0	1.2
CaO	1.6	1.6	1.7	1.9	1.7	1.7	1.8	1.6	0.4	2.0
Na <sub>2</sub> O	1.7	2.2	2.6	2.7	2.8	3.5	2.8	3.0	3.1	0.2
K <sub>2</sub> O	2.6	3.1	3.1	3.6	3.1	3.7	4.2	4.2	4.4	2.9
XMg	0.41	0.39	0.38	0.41	0.42	0.53	0.43	0.55	0.54	0.50
H <sub>2</sub> O <sup>a</sup>	2.15 <sup>b</sup>	2.33	2.65	2.96	2.83	3.43	3.36	3.50	3.74	9.61 <sup>d</sup>

<sup>a</sup> Calculated from the proportion of melt and water content in the starting material (except for <sup>b</sup> and <sup>d</sup>)

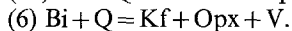
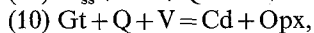
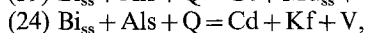
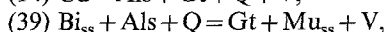
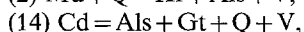
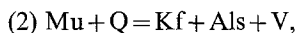
<sup>b</sup> Determined by thermo-gravimetric analysis

<sup>c</sup> Composition of the liquid in equilibrium with Bi, Sill, Q, Gt, and V at 8 Kbar and 800° C

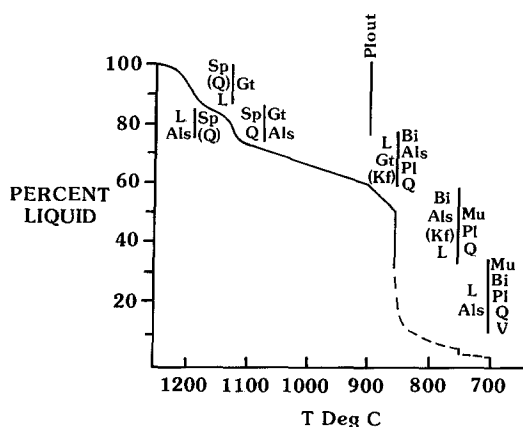
<sup>d</sup> Calculated using Burnham's model (1979)



**Fig. 2.** Composition of liquids as a function of temperature in the AKF diagram (mole %).  $A = \text{Al}_2\text{O}_3 - (\text{K}_2\text{O} + \text{Na}_2\text{O} + \text{CaO})$ ;  $K = \text{K}_2\text{O}$ ;  $F = \text{FeO} + \text{MgO}$



The univariant reaction (2)  $\text{Mu} + \text{Q} = \text{Kf} + \text{Als} + \text{V}$  has been investigated in several experimental studies, and a summary of the results is given by Helgeson et al. (1978). Since Fe or Mg preferentially enter muscovite, the addition of Fe or Mg must increase the stability field of muscovite until saturation, which corresponds to the crystallization of cordierite, biotite or garnet, depending on the pressure (Thompson 1982). Theoretical and experimental data on the melting reactions of the muscovite-quartz assemblage (i.e. at the intersection of reactions (2) and (3)  $\text{Mu} + \text{Kf} + \text{Q} + \text{V} = \text{L}$ ) (Figs. 4 and 5) are given by Lambert et al. (1969), Storre and Karotke (1972), Storre (1972), Thompson and Algor (1977), Thompson (1982).



**Fig. 3.** Weight percent liquid versus  $T$ , estimated by mass balance, and inferred melting reactions

$\text{PH}_2\text{O} - T$  conditions for the iron end-member of reaction (24) have been determined by Holdaway and Lee (1977): 640° C at 2 kbar and 710° C at 2.7 kbar. A  $P - X\text{Fe} - \text{Mg}$  diagram for the Fe-Mg analogue of this reaction has been constructed from these data and natural  $K_d$  values. Hoffer (1976) has performed hydrothermal experiments on this reaction using natural minerals ( $\text{CdFe}_{34}$ ,  $\text{BiFe}_{50}$ ) and his results average about 0.8 kbar lower than Holdaway and Lee's extrapolation. Reaction (24) is terminated at high temperature by the intersection with the melting reaction (28)  $\text{Bi}_{\text{ss}} + \text{Als} + \text{Kf} + \text{Q} + \text{V} = \text{L}$  at  $T = 720^\circ \text{C}$  and  $P = 3.7$  kbar. Reaction (28) was studied at 7 and 10 kbar ( $P_s = \text{PH}_2\text{O}$ ) by Hoffer (1976). The first melt is generated at 703° C at 7 kbar and 685° C at 10 kbar. Beyond the invariant point [Cd, Gt, Opx], reaction (28) becomes metastable and is replaced by (25)  $\text{Mu}_{\text{ss}} + \text{Bi}_{\text{ss}} + \text{Kf} + \text{Q} + \text{V} = \text{L}$  (see Fig. 5).

The reaction (14)  $\text{Cd} = \text{Als} + \text{Gt} + \text{Q} + \text{V}$  and its Fe-Mg divariant field have been studied by numerous authors; a summary of these results will be found in Lonker (1981). From an extensive review of the literature, Newton (1983) considers that cordierite is usually not stable at pressures greater than 6 kbar in most common metapelites. A similar conclusion has been independently reached from the geo-



**Table 5.** Modal proportion of minerals and glass calculated by mass balance (Wt%). Results of the image processing are indicated in the brackets. The modal proportion of the starting material was determined by combining point-counting and mass balance calculations

Wt%	1250	1200	1150	1100	1050	1000	950	900	875	850
L	100	92	81	72	75	63	64	62	57	
Sill	—	3	1	—	5	6	6	6	5	
Q	—	5	12	18	10	13	11	11	9	
Sp	—	—	6 (4)	9 (11) <sup>a</sup>	—	—	—	—	—	
Gt	—	—	—	1	10 (8)	18 (12)	19 (20)	21 (15)	24 (21)	(9)
Pl	—	—	—	—	—	—	—	—	5	

Starting material: Ky 7, Q 39, Gt 2, Pl 19, Mu 9, Bi 21, St 1, Chl 1, Op 0.2

<sup>a</sup> Spinel and garnet cannot be separated by image processing.

barometric study of the granulites found in some Hercynian massifs where the disappearance of cordierite can be observed as a function of depth (Vielzeuf 1984).

The mineral pair cordierite—orthopyroxene, whose stability field is bounded by the reaction (10)  $Gt + Q + V = Cd + Opx$ , has long been considered as typical of the pyroxene hornfels facies (Turner and Verhoogen 1960). According to de Waard (1965) its breakdown marks the boundary between pyroxene contact metamorphism and pyroxene granulite facies. However this association is also present in high grade metamorphic rocks which crystallized or recrystallized in low pressure regional metamorphism or plutono—metamorphism (Bard 1969; Vielzeuf 1980a; Harris and Holland 1984). We believe that in most cases, for a average Fe—Mg ratio in the rock, a pressure of crystallization less than 3 kbar can be expected for rocks with cordierite—orthopyroxene assemblages.

From the experimental data on reactions 2, 14, and 24, it can be calculated that the position of the iron end-member of reaction (39)  $Bi_{ss} + Als + Q = Gt + Mu_{ss} + V$  is almost independent of temperature and is located between 6.5 and 7 kbar (Vielzeuf 1984). On the other hand, calculations using the standard thermodynamic properties of these minerals indicate much lower pressures for this reaction (<1 kbar according to Spear and Selverstone (1983); 2 kbar at 600° C and a much steeper slope according to Perchuk et al. (1981)). However, the errors associated with the thermodynamic properties of these Fe minerals are so large that there is no certainty in the results. The situation is complicated by the fact that  $\Delta H$ ,  $\Delta S$ , and  $\Delta V$  of this reaction are very small and a small error in any one of these will have a drastic effect on the calculations. Finally it must be stressed that the multivariant field of reaction (39) has to be very wide because the association of biotite, aluminum—silicate, quartz, garnet, muscovite is observed at pressures as low as 4 kbar in the stability field of andalusite (Novak and Holdaway 1981) and as high as 28 kbar in the stability field of kyanite and pyrope + quartz (Chopin 1984).

According to Eugster and Wones (1962) and Rutherford (1969), the iron end-member of reaction (6)  $Bi + Q = Kf + Opx + V$  would be at about 720° C at 2 kbar. On the other hand, if we consider that the Fe—Mg solid-solutions in biotite and orthopyroxene are close to ideal, the  $P$ — $T$  locations of the Mg and Fe end-members should not be very different since the Mg—Fe distribution coefficient between biotite and orthopyroxene is only slightly greater than 1 (1.2 according to Clemens (1984); 1.1 using the data from the granulites in the Pyrenees (Vielzeuf 1984)) with

$X_{MgBi} > X_{MgOpx}$  (see also Grant 1981 p. 1135). This prediction of a narrow divariant field conflicts with the reversal reported by Wones and Dodge (1966) at about 840° C and 0.5 kbar. Helgeson et al. (1978) suggested that these very high temperatures for the Mg end-member could be a result of Al/Si disorder in the phlogopite formed in Wones and Dodge's experiments. The univariant equilibrium curve generated from retrieved thermodynamic data by Helgeson et al. (1978) is located 150° C—200° C below the curve generated from Wones and Dodge's reversal. On the other hand, Clemens et al. (1987) have shown that both natural and synthetic biotites are nearly completely Al—Si disordered at  $T > 600$ ° C but suggest that the synthetic Fe-rich micas may show significant degrees of tetrahedral order. This might explain the experimental observations. The curve calculated by Clemens et al. (1987) for the Mg end-member of reaction (6)  $Bi + Q = Opx + Kf + V$  has been used in Fig. 5.

The addition of excess alumina to the system will increase the stability field of biotite until saturation and crystallization of one of the following phases occurs: cordierite, garnet, or sillimanite (see Fig. 5). Reaction (6) terminates in melting a few degrees below the  $Kf + Q + V = L$  reaction at the invariant point  $I_2$  (Luth 1967; Wendlandt 1981; Bohlen et al. 1983).

## 5.2 Construction of the model

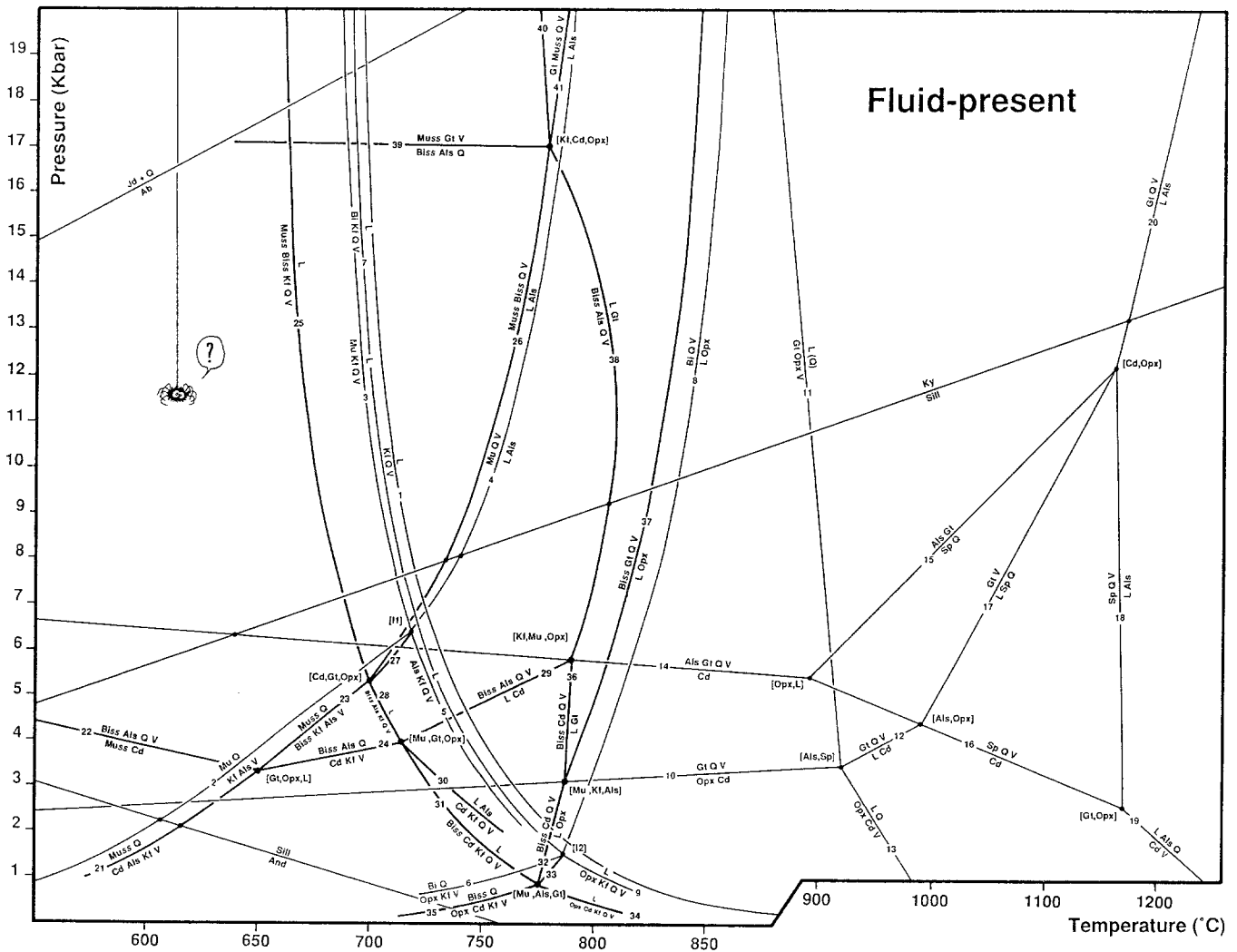
### 5.2.1 Melting at $PH_2O = P_{total}$

In predicting phase relationships, it is useful to start from simple systems and then to study the influence of additional components rather than attempt to immediately derive the phase relations in the full system. This is because the reactions in the simplest system represent limiting conditions for the complex systems.

For the study of the Q- and V-saturated melting of metapelites and metagraywackes, the simplest limiting reaction is (1)  $Kf + Q + V = L$  in the KASH system (where  $KAlSi_3O_8$  is the only independent component). This reaction has been located in the  $P$ — $T$  space by Tuttle and Bowen (1958), Luth et al. (1964), Shaw (1963), and Lambert et al. (1969). Its displacement as a function of  $a_{H_2O}$  has been experimentally investigated and calculated by Clemens (1981) and Bohlen et al. (1983).

The addition of  $Al_2O_3$  in excess of normative feldspar will necessarily increase the stability of the liquid and reaction (1) will move towards lower temperature until the system is saturated in muscovite or aluminum—silicate, de-





**Fig. 5.** Pressure-temperature diagram for the fluid-present (pure  $H_2O$ ) and quartz saturated partial melting of metapelites and metagraywackes ( $X_{Mg}$  close to 0.5). Reaction 1 refers to the pseudo-unary system  $KAlSi_3O_8$  with the phases Kf, Q, V, L. Reactions 2–5 around the invariant point  $[I_1]$  refer to the pseudo-binary system  $KAlSi_3O_8 - Al_2SiO_5$ , with the phases Kf, Mu, Als, L, Q, V. Reactions 6–9 around  $[I_2]$  refer to the pseudo-binary system  $KAlSi_3O_8 - (Fe, Mg) SiO_3$ , with the phases Kf, Bi, Als, L, Q, V. Reactions 10–20 around the invariant points  $[Als, Sp]$ ,  $[Opx, L]$ ,  $[Als, Opx]$ ,  $[Gt, Opx]$ , and  $[Cd, Opx]$  refer to the pseudo-binary system  $(Fe, Mg) SiO_3 - Al_2SiO_5$ , with the phases Gt, Als, Sp, Cd, Opx, L, Q, V. Note the refractory character of this subsystem. Reactions 21 to 41 (*heavy lines*) around the invariant points  $[Gt, Opx, L]$ ,  $[Cd, Gt, Opx]$ ,  $[Mu, Gt, Opx]$ ,  $[Mu, Als, Gt]$ ,  $[Mu, Kf, Als]$ ,  $[Mu, Kf, Opx]$ , and  $[Kf, Cd, Opx]$  refer to the pseudo-ternary system  $Al_2SiO_5 - KAlSi_3O_8 - (Fe, Mg) SiO_3$  with the phases Als,  $Mu_{ss}$ , Kf,  $Bi_{ss}$ , Opx, Gt, Cd, L, Q, and V. Note that the temperature scale changes above  $900^\circ C$ . The following reactions are shown by number only: (27)  $Mu_{ss} + Q = L + Als + Kf$ ; (33)  $Bi_{ss} + Q + V = L + Opx + Kf$ ; (40)  $Bi_{ss} + Mu_{ss} + Q + V = L + Gt$

ity field of the liquid until saturation in these two extra components is reached. In this multisystem the phases involved are aluminum-silicate, muscovite (ss), K-feldspar, biotite (ss), orthopyroxene, garnet, cordierite, spinel, and liquid (+ quartz and vapor). In this compositional triangle, assumptions have to be made about the chemographic position of the liquid. In this respect one of the questions is to which side of the extension of the join biotite (ss) - orthopyroxene the liquid composition lies. Considering (i) that in the absence of sillimanite (which is often the case when orthopyroxene is present) biotites are not aluminum-rich and (ii) that orthopyroxenes can be significantly aluminous, we consider that the composition of the liquid is located on the sillimanite side of the extended join  $Opx - Bi_{ss}$ . Grant (1985) chose the other case. When the liquid is located on the sillimanite side of the join  $Bi_{ss} - Opx$ , as in

Fig. 5, the reaction (8)  $Bi + Q + V = L + Opx$  is located at higher  $T$  than the reaction (37)  $Bi_{ss} + Gt + Q + V = L + Opx$  (excess  $Al_2O_3$  in the system decreases the stability field of  $Bi + Q + V$ ). When the liquid is located on the Kf side of the join  $Bi_{ss} - Opx$ , the reaction (8) is located at lower  $T$  than the  $Bi_{ss} + Q + V = Gt + Opx + L$  (excess  $Al_2O_3$  in the system increases the stability field of  $Bi + Q + V$ ). This problem is related to the relative activities of  $Al_2O_3$  in biotite and liquid. Selecting the first possibility, we keep the symmetry with the relations involving muscovite around  $I_1$  and  $[Cd, Gt, Opx]$ . The liquid composition R15-B reported by Hoffer and Grant (1980) supports this choice though the alternative chemography cannot be completely ruled out. On the basis of his experiments, Seifert (1976) concluded that the quartz, K-feldspar, cordierite, vapor assemblage melts congruently. According to Grant (1985) the simplest

interpretation is that a thermal barrier exists generating the relations shown in his Fig. 3.6 indicating that an aluminous minimum melt can be produced at low pressure. For the sake of simplicity, this aspect has been neglected in our model (Fig. 5). The breakdown of sillimanite, biotite (ss), and quartz in the presence of albite, to melt + cordierite was determined experimentally at conditions of  $PH_2O = P$  total by Hoffer (1978). This reaction is the analogue of reaction (29)  $Bi_{ss} + Als + Q + V = L + Cd$  with the addition of Na to the system. Hoffer found that the reaction curve has a steep negative slope (nearly vertical) at temperatures of about 650° C. In our  $P-T$  diagram we drew a positive slope for this reaction because of the location of the reactions (24)  $Bi_{ss} + Als + Q = Cd + Kf + V$  and (38)  $Bi_{ss} + Als + Q + V = L + Gt$ . This is the same relationship as shown in Grant (1985) Fig. 3.10 for the system KFMASH. Some hydrothermal experiments were performed on reaction (38) at 4, 6, and 8 kbar in an internally heated pressure vessel (Vielzeuf 1980b), starting with a mixture of natural minerals: biotite ( $XMg$  0.50), sillimanite, K-feldspar, garnet ( $XMg$  0.35), and quartz. The QFM buffer was used to control the oxygen fugacity. These experiments show that the  $Bi_{ss}$ -Sill assemblage is still stable at 8 kbar-800° C. The composition of the liquid in equilibrium with  $Bi_{ss}$ , Sill, Q, Gt, and V at 8 kbar and 800° C is given in Table 4. Thus, reaction (38) must be located at temperatures as high as 800° C, with a nearly vertical slope if we compare it to its subsolidus equivalent  $Bi_{ss} + Sill + Q = Gt + Kf + V$  (Phillips 1980; Vielzeuf 1984). It seems possible that Hoffer mapped the solidus in the system  $Ab + Q$  with excess alumina and addition of FeO and MgO, rather than the reaction  $Bi_{ss} + Ab + Sill + Q + V = L + Cd$  itself. Concerning the reaction  $Bi + Ab + Q + Cd + V = L + Opx$ , it seems unlikely that cordierite and orthopyroxene of average compositions will coexist at pressures as high as 7 kbar as is implied by Hoffer and Grant (1980). Finally, due to the uncertainty on the curvature of reaction (38)  $Bi_{ss} + Als + Q + V = L + Gt$  and the fact that this reaction and the reaction (26)  $Mu_{ss} + Bi_{ss} + Q + V = L + Als$  have very steep slopes, the uncertainty in the pressure location of the invariant point [Kf, Cd, Opx] is very important.

The  $P-T$  diagram of Fig. 5 has been constructed on the basis of these data and assumptions; it represents an hypothetical model for the water saturated melting of pelites and graywackes between 2 and 20 kbar and 600°-1250° C. Our model differs from those proposed by Thompson (1982) and Grant (1985) in the following points:

- the choice in some chemographic relationships differ, namely: the relations between biotite-orthopyroxene-liquid are different from those used by Grant (1985); cordierite is assumed to be hydrous (see Thompson 1982, Fig. 4); reaction 39  $Mu_{ss} + Gt + V = Bi_{ss} + Als + Q$  is considered to be vapor present (see Thompson 1982, Fig. 4; Grant 1985, Figs. 3.10 and 3.11);

- reactions 10  $Opx + Cd = Gt + Q + V$  and 35  $Bi_{ss} + Q = Opx + Cd + Kf + V$  do not intersect in the subsolidus domain (see Thompson 1982, Fig. 4);

- this model is made for a single, average Fe-Mg ratio ( $XMg \approx 0.50$ ), and is thus less general but perhaps more applicable to common natural rocks;

- the mutual relationships between simple (AKSH, AFMSH) and more complex (KFMASH) systems are shown allowing the construction of consistent  $P-T$ , liquidus AKF, and  $T-XH_2O$  diagrams;

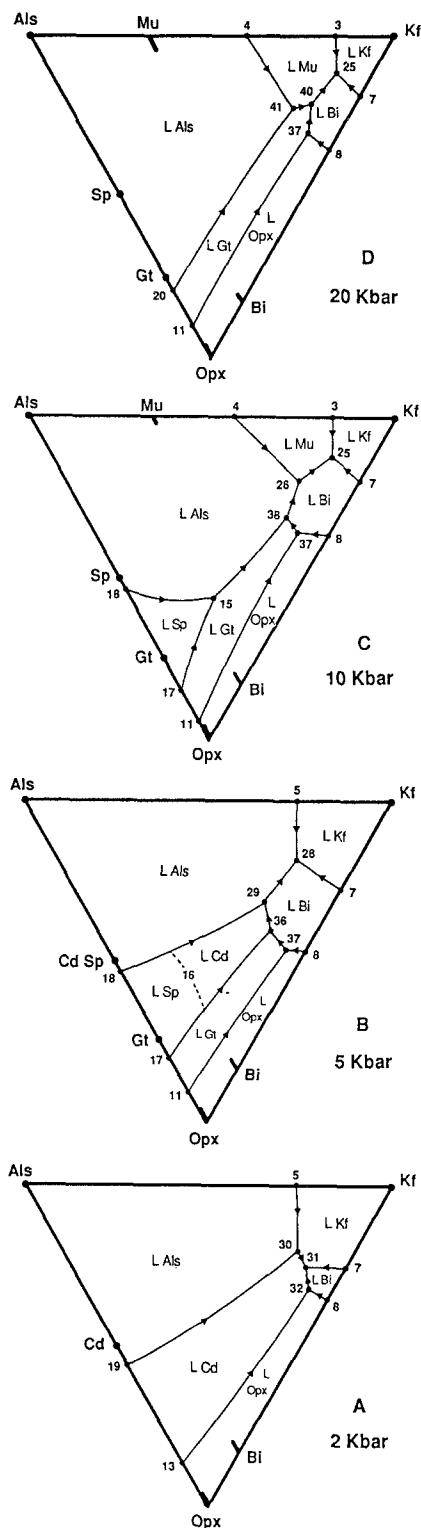


Fig. 6. Isobaric liquidus diagrams at  $PH_2O = 2, 5, 10,$  and  $20$  kbar derived from Fig. 5

- the diagram covers the complete temperature range (600°-1250° C) relevant to melting in pelites and graywackes.

As shown by Eggler (1973), the simultaneous use of  $P-T$  and liquidus diagrams is a powerful tool to depict partial melting processes (see also Grant 1985). Four



Under fluid-absent conditions, in the domain of melting, the activity of water in the system can be buffered by the presence of an assemblage involving a crystalline hydrate and its breakdown products. Under such conditions, the only reactions that can occur are fluid-absent providing that the melt is able to dissolve more water than is present in the crystalline hydrates.

The melting reaction obtained in a fluid-absent situation and the line defined by the migration of the invariant point (in a mixed-fluid system) will coincide if the diluting species in the fluid-phase is insoluble in all the other phases, and in the melt in particular.

When fluid-absent reactions intersect, they are likely to generate additional invariant points of "higher order" (Vielzeuf 1983); in this respect, the effects on the geometrical phase-relations of changing the composition of the fluid-phase are comparable to what has already been described for Fe–Mg substitutions (Vielzeuf 1983; Vielzeuf and Boivin 1984). The shift in the positions of the reactions due to a change in composition of the fluid-phase can be sufficient to reverse the grid by crossing an invariant point of higher order.

The various fluid-present reactions shown in Fig. 5 (for pure water) may have a different status in the fluid-absent situation. Those involving a crystalline hydrate are replaced by fluid-absent reactions involving additional phases. It is interesting to note that, due to chemographic relations, some phases present on the low-temperature side of a fluid-present curve may be on the high-temperature side of the corresponding fluid-absent reaction (e.g.  $Bi_{ss}$  in reactions 26 and 48; and  $Gt$  in reactions 37 and 57). On the contrary, reactions involving only melt as a potential hydrous phase (e.g. reactions 11, 12, 13, 17–20) will still exist under fluid-absent conditions but will be displaced towards higher temperatures as a function of reduced activity of water. Note that there is a significant uncertainty on the  $T$  location of these reactions in Fig. 7. Reactions involving no hydrous phases (e.g. (15)  $Als + Gt = Sp + Q$ ) are insensitive to the presence or absence of a fluid-phase. In this model, cordierite is considered as a hydrous mineral but can be anhydrous also, at high temperatures. The model presented in Fig. 7 is derived from the fluid-present model and the few available experiments in the fluid-absent domain.

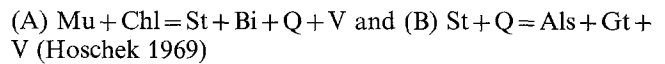
Data for the reaction (42)  $Mu + Q = L + Kf + Als$  were obtained by Storre (1972) between 7 and 20 kbar. Reaction (48)  $Mu_{ss} + Q = Bi_{ss} + Als + Kf + L$  is the analogue of reaction (42) in the system with FeO and MgO. From the present experiments and those presented by Le Breton and Thompson (in prep.), it is shown that reaction (52)  $Bi_{ss} + Als + Q = L + Gt + Kf$  is located at about 860° C and has a nearly vertical slope. Reactions (52) and (48) intersect and generate an invariant point. If we consider that reaction (49) has a very small slope, not very different from that of reaction (39)  $Bi_{ss} + Als + Q = Mu_{ss} + Gt + V$  (Thompson (1982) and Grant (1985) consider that reaction (39) is fluid-absent and degenerate), then we have, with this invariant point, an indirect indication of the location of reaction (39) with respect to pressure.

The melting of phlogopite–quartz under fluid-absent conditions has been determined from 5 to 20 kbar by Bohlen et al. (1983). At 10 kbar, the temperature of melting is close to 900° C. Peterson and Newton (1987) found a much lower temperature of about 815° C implying a gap of only 25° C between the fluid-present and the fluid-absent

reactions. This latter result is incompatible with the location of the reaction  $Bi_{ss} + Als + Q = L + Gt + Kf$  at about 860° C. This apparent discrepancy may be due to the effects of other components (e.g. excess Al, Fe, Ti) in the system. The modifications of the phase-relations involving quartz, K-feldspar, phlogopite, enstatite, liquid, and vapor proposed by Grant (1986b) and in particular the existence of a thermal divide, are not taken into consideration in our Figs. 5 and 7 because they are based on the experimental results of Wendlandt (1981) which are difficult to interpret.

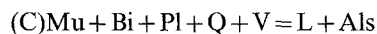
## 6 Interpretation of the experiments at 10 kbar

The experiments at 10 kbar can be interpreted in the light of the above model. Since no experiments were done below 750° C, the interpretation of the breakdown of chlorite, staurolite, and muscovite is hypothetical. The following reactions could be responsible for the disappearance of chlorite and staurolite respectively:



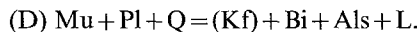
However it is unlikely that equilibrium was reached during the rapid increase in temperature in our experiments.

In the absence of K-feldspar in the starting material (excess aluminum–silicate on the high pressure-low temperature side of the  $Mu + Q = Kf + Als + V$  reaction) the eutectic melting reaction  $Mu + Bi + Kf + Pl + Q + V = L$  did not occur. A small amount of free water was available in the starting material (adsorbed water plus that released by the breakdown of chlorite, staurolite, and part of the muscovite). Thus, we believe that the following reaction:



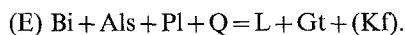
took place until disappearance of the vapor phase, and that the first drop of liquid was saturated in water. A mass balance approach indicates that the amount of liquid which can be produced by reaction (C) is close to 4 Wt%. This reaction is able to consume all the free water and thus it represents the transition between a fluid-present and a fluid-absent situation.

The disappearance of muscovite is probably a result of the fluid-absent reaction:

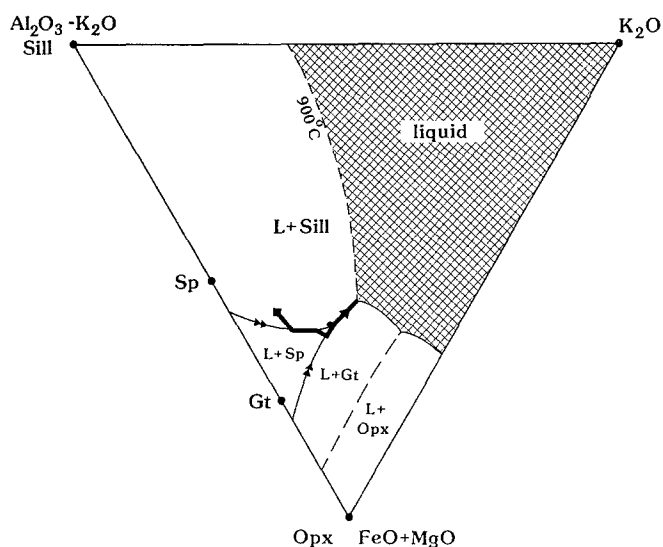


Mass balance calculations show that reaction (D) produces only a tiny amount of liquid ( $\approx 1\%$ ) and also some K-feldspar which could possibly enter as a solid-solution in the plagioclase or dissolve in the liquid already present. From these results, we conclude that under fluid-absent conditions the muscovite melting stage of metapelites generates only a small amount of nearly water-saturated liquid. However, the proportion of melt is strongly dependent on the proportion of muscovite in the starting material.

The next step corresponds to the "biotite melting stage" marked by the reaction



The mass balance approach indicates that, contrary to what is suggested by previous models (including ours), K-feldspar is not required as a product of such reactions as (E). The appearance of K-feldspar depends upon the amount of biotite present in the starting rock (Thompson, pers. com.). These calculations indicate also that a large amount



**Fig. 8.** Phase relations at high temperature and 10 kbar in the pseudo-ternary AKF diagram. The heavy line shows the path followed by the liquid. A schematic liquid field is shown for  $T=900^\circ\text{C}$ . Compare with Fig. 2

( $\approx 45\text{--}50\%$ ) of water-undersaturated melt can be generated by this reaction. This amount depends on the modal proportion of biotite in the starting material. In order to confirm this important result, calculations were done based on modelling of fluid-absent melting in the simplified system  $\text{Q} - \text{Or} - \text{Ab} - \text{H}_2\text{O}$  (Clemens and Vielzeuf 1987). The amounts of melt predicted in this model are consistent with those produced in these experiments.

Above  $875^\circ\text{C}$ , the evolution of the modal proportions and of the liquid composition can be interpreted in terms of selective dissolution of plagioclase and garnet in the liquid and crystallization of a small amount of sillimanite and quartz. The intervention of the reaction  $\text{Pl} + \text{Q} = \text{L}$  is ruled out because, in our runs, the modal proportion of quartz increased instead of decreasing.

From this point, the experimental data can be interpreted in the light of the path shown on the ternary liquidus diagram in Fig. 8. With increasing temperature, and particularly above  $1000^\circ\text{C}$ , the liquid dissolves a large proportion of the garnet (and a small amount of aluminum-silicate) until the boundary of the  $\text{Gt} - \text{Als}$  assemblage is reached (between  $1050^\circ$  and  $1100^\circ\text{C}$ ). This limit corresponds to the peritectoid reaction  $\text{Gt} + \text{Als} = \text{Sp} + \text{Q}$ . This observation is in agreement with the experimental data reported by Bohlen et al. (1986) on the Fe end-member of that reaction. Interestingly, the Fe-Mg divariant field of this reaction is probably narrow since the Fe-Mg partitioning between spinel and garnet is small (Vielzeuf 1983). The peritectoid reaction  $\text{Gt} + \text{Als} = \text{Sp} + \text{Q}$  stops when all the sillimanite is consumed. Thereafter the liquid evolves along the  $\text{Gt} - \text{Sp}$  cotectic which corresponds to the peritectic reaction  $\text{Gt} = \text{L} + \text{Sp} + (\text{Q})$  until all the garnet is consumed. Then the liquid leaves this peritectic and dissolves spinel (and quartz) until a second peritectic reaction is reached:  $\text{Sp} + (\text{Q}) = \text{L} + \text{Als}$ . It is interesting to note that the aluminum-silicate (sillimanite or mullite) disappears when Sp and Q crystallize and re-appears when the Sp-Q assemblage breaks down. Above  $1200^\circ\text{C}$  all the spinel disappears and the liquid dissolves the aluminum-silicate until the liquidus is reached at about  $1250^\circ\text{C}$ .

For a granitic liquid composition at a given pressure, the temperature at which the liquid coexists with quartz and plagioclase of a certain composition places close constraints on the  $\text{H}_2\text{O}$  content of the melt (Nekvasil and Burnham 1987). For instance, the  $875^\circ\text{C}$  run products include quartz and  $\text{An}_{30}$  plagioclase. For a granitic melt with the  $875^\circ\text{C}$  composition to coexist with those phases at 10 kbar and  $875^\circ\text{C}$  requires a melt water content of about 4 Wt.%  $\text{H}_2\text{O}$  (based on the Burnham-Nekvasil [1986] model). This is in very close agreement with the 3.7 Wt.% calculated by mass balance (Table 3). These  $\text{H}_2\text{O}$  contents are equivalent to  $\text{H}_2\text{O}$  activities of about 0.3, illustrating the highly  $\text{H}_2\text{O}$ -undersaturated condition existing just above the biotite-out temperature.

The important question is, how wide is the  $T$  interval over which biotite melts? The actual width will depend in part on the melting loop caused by Mg-Fe partitioning between the phases, and in part on the reaction geometry with respect to  $\text{H}_2\text{O}$ . The initial  $\text{H}_2\text{O}$  content of the rock is lower (2.15%) than the  $\text{H}_2\text{O}$  content of the melt (minimum of 3.7%). This would place the bulk composition to the left (away from the  $\text{H}_2\text{O}$  end-member) of any peritectic or eutectic involving biotite in diagrams such as shown by Egger and Holloway (1977, Fig. 2). Such a position would result in no melting interval for the simple system case considered by Egger and Holloway (1977). In the system studied here, we conclude that the melting interval will be due solely to the solid solutions, and that it will be small, probably less than  $20^\circ\text{C}$ .

$T - \text{XH}_2\text{O}$  diagram - In all crustal geological systems undergoing partial fusion, water is an important limiting factor in determining the amount of melt formed at a given temperature. Figure 9 displays a  $T$ -composition section for a pseudo-binary join  $\text{A} - \text{H}_2\text{O}$  (Yoder and Kushiro 1969; Egger 1973; Egger and Holloway 1977; Whitney 1975) where A is a composition in the  $\text{Al}_2\text{O}_3 - \text{K}_2\text{O}/\text{K}_2\text{O}/\text{FeO} + \text{MgO}$  triangle. Quartz is in excess and it has been considered that biotite is in excess with respect to muscovite in the reaction  $\text{Mu} + \text{Bi} + \text{Q} + \text{V} + (\text{Pl}) = \text{L} + \text{Als}$ , sillimanite in excess with respect to biotite in the reaction  $\text{Bi} + \text{Als} + (\text{Pl}) + \text{Q} = \text{L} + \text{Gt} + \text{Kf}$ , and garnet in excess with respect to sillimanite in the reaction  $\text{Gt} + \text{Als} = \text{Sp} + \text{Q}$ . Temperature coordinates are given for a system in which plagioclase coexists with the other phases below  $900^\circ\text{C}$ . This diagram was constructed by recording the phases coexisting along the  $\text{A} - \text{XH}_2\text{O}$  join at various temperatures. It illustrates the mutual relationships between excess fluid-present and fluid-absent reactions. The dashed line schematically shows the path of the liquid for the bulk composition studied. This evolution should be compared to what is shown in the  $P - T$  and liquidus diagrams. It can be seen that below  $860^\circ\text{C}$  the water content of the liquid is buffered by the presence of hydrous minerals. This ceases to be the case at higher temperatures.  $P - T$ ,  $T - \text{XH}_2\text{O}$ , and liquidus diagrams represent three complementary useful ways to understand the different aspects of the melting processes.

## 7 Discussion

### 7.1 Magma production

The experimental observations lead to the following considerations: melts below  $860^\circ\text{C}$  and corresponding to the mus-

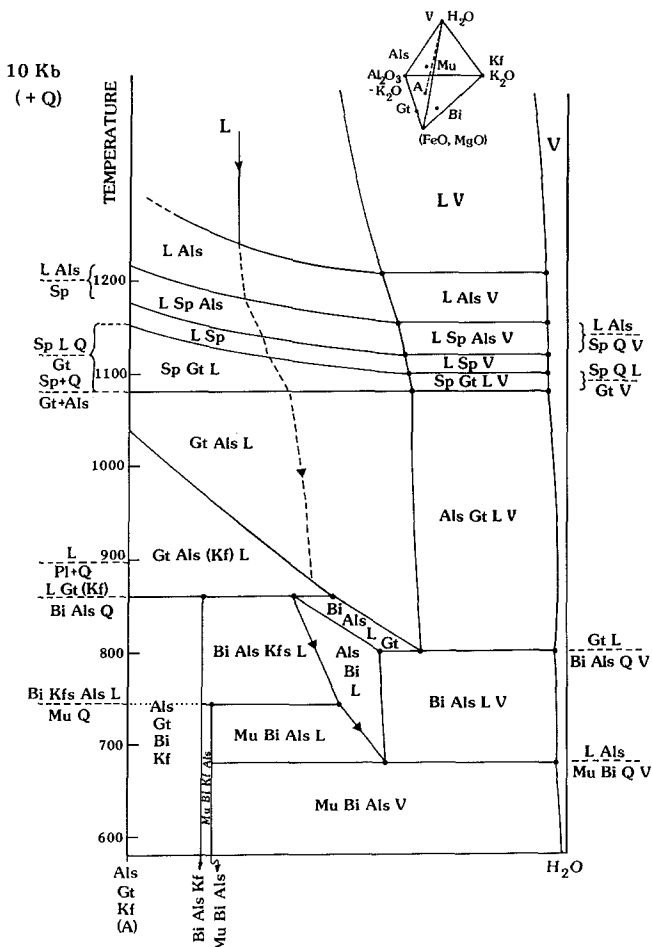


Fig. 9.  $T-X$  section for the pseudo-binary join  $A-H_2O$  at 10 kbar, where  $A$  is a composition in the  $Al_2O_3-K_2O/K_2O/FeO+MgO$  triangle. Quartz is in excess and temperature coordinates are given for a system in which plagioclase coexists with the other phases below  $900^\circ C$ .

covite melting stage are water-rich and are generated in small amount ( $<10\%$ ) in most common metapelites. As suggested by Burnham (1967) and Clemens (1984), at 5 kbar, these nearly  $H_2O$ -saturated melts will probably form veins, pockets and small plutons unable to move from their site of generation. The migmatitic zones developed in metapelites close to the muscovite-out isograd probably have such an origin. At 10 kbar, such liquids are less likely to be  $H_2O$ -saturated since the solubility of  $H_2O$  in melt increases with  $P$  (Goranson 1931; Burnham 1979). As a result they might rise some distance, but still not very far.

One of the most important results of this study is the fact that, at 7 and 10 kbar, the breakdown of the biotite + sillimanite + plagioclase + quartz assemblage produces a large amount of liquid within a narrow range of temperature ( $850^\circ-875^\circ C$ ). This conclusion can be extended to lower pressures since (i) the proportion of melt produced from a given starting material and under fluid-absent conditions increases as pressure decreases (Clemens and Vielzeuf 1987), and (ii) the reaction  $Bi_{ss} + Als + Pl + Q = L + Gt + (Kf)$  is nearly vertical in  $P-T$  space. Such liquids are strongly water-undersaturated; they have water contents of about 4% while a water-saturated liquid of that composition would have a water content of about 12% at 10 kbar.

Such liquid fractions (45–50%) are above the critical melt fraction determined by van der Molen and Paterson (1979) and thus will form a mobile, buoyant magma as soon as biotite disappears. The residual minerals are quartz, garnet, sillimanite, and plagioclase (or K-feldspar). Some of these minerals may be carried up with the magma as a restite fraction (e.g. White and Chappel 1983) or remain in the source region with some residual liquid, where they would form characteristic aluminous granulites. In the lower crust, temperatures as high as  $860^\circ C$  seem reasonable, in particular during the major thermal events which occur during the late stages of evolution of orogenic belts (Albarède 1976; Couturié and Kornprobst 1977; England and Richardson 1977; England and Thompson 1986; see also Pin and Vielzeuf, 1983 for the Hercynian belt, and Frey et al., 1974 for the Alps).

The production of a large amount of melt around  $850^\circ C$ , even under such limiting conditions as the fluid-absent situation, has the important consequence of buffering the temperature of metamorphism in the area of melting. The temperature of metamorphism will not exceed  $850^\circ C$  until the process of partial melting is completed. Melting of 50% of the crust must require a large amount of energy which will rarely, if ever, be available. As a result, temperatures of metamorphism in excess of  $850^\circ C$  will rarely be exceeded in a metapelitic crust undergoing a first thermal event. On the contrary, in the case of a recycled crust in which partial melt had already been extracted in a previous cycle, the temperature of metamorphism would no longer be buffered and temperatures close to  $1000^\circ C$  could be reached if there were sufficient heat supply. In this case, and depending on the composition of the pelitic rocks (restites whose composition is a function of the pressure during the first partial melting event), mineral assemblages such as spinel + quartz, sapphirine + quartz, orthopyroxene + sillimanite, and osumilite may appear. If this is true, these assemblages should be more common in the regional metamorphic terranes belonging to old, recycled cratons. A review of the literature indicates that this is the case. Such assemblages have been described in the old basement of Antarctica (Ellis 1980; Grew 1982a); Eastern Siberia (Karsakov et al. 1975); India (Grew 1982b); Hoggar, Algeria (Ouzegane 1981), Namaqualand, South Africa (Waters 1986); Rogaland, Norway (Maijer et al. 1977) and Central Labrador, Canada (Morse and Talley 1971).

The buffering effect of metamorphism by partial melting processes appears general, and the absence of such a thermal buffer is a reasonable explanation for the occurrence of these unusual, high-temperature parageneses.

In a paper dealing with osumilite – sapphirine – quartz granulites from Enderby Land, Ellis (1980) proposed that crustal rocks in other granulitic terranes may have experienced such extreme conditions of metamorphism also. Ellis further proposed that uplift at high temperature could have eradicated petrographic evidence for this early  $P-T$  history. He concluded that the  $P-T$  path of cooling and uplift may be more important than the extreme conditions of metamorphism in explaining why such high-temperature granulites are not exposed elsewhere in the world. As an example, Ellis considered the Bohemian massif belonging to the Hercynian belt of median Europe, and suggested that such extreme  $P-T$  mineral assemblages from an earlier part of the rock history were obliterated by a later thermal event. Even if metamorphic conditions changed from high-



*P* to low-*P* and high-*T* (Jakeš 1969; Marchand 1974; Lasnier 1977; see also Pin and Vielzeuf 1973 for a summary), early granulitic assemblages belonging to the high-pressure granulite facies are widespread and well preserved in the Hercynian belt. Pelitic granulites here are composed of kyanite + garnet + rutile + K-feldspar + plagioclase + quartz +/- biotite and geobarometry yields pressure estimates up to 21 kbar (Vielzeuf 1984), higher than those recorded by Ellis in Enderby Land. Furthermore, there is no evidence of very-high-temperature metamorphism in the Hercynian belt. Thus, we do not believe that the conditions of formation of the high-temperature granulites are common to all mountain belts. Rather we consider that the presence of a recycled crust is required.

### 7.2 An application to the Hercynian in the Pyrenees

An example of the process of continental differentiation (which is not meant to be generalized) is provided by the North Pyrenean Zone. During Alpine times (40–100 Ma), this zone underwent major tectonic processes (crustal thinning related to transcurent movements and followed by a succession of compressive stages) which allowed the outcropping of various parts of the lithosphere from the upper mantle (Lherzolites) to the upper crustal levels (Vielzeuf and Kornprobst 1984). Thus, it is possible to reconstitute a cross-section of the crust as it was left after the Hercynian orogeny (300–400 Ma) (Vielzeuf 1984). It is believed that an important thermal anomaly, occurring around 310 Ma in response to the extension following collisional processes (Pin and Vielzeuf 1983), is responsible for a complete (re-)structuring of the crust. The following processes could be involved:

- Following compressive stages, the onset of crustal extension may allow upwelling of the asthenosphere accompanied by the intrusion of mafic magmas (now observed as layered complexes) into the lower crust. These processes induced fluid-absent melting of the lower crust. Forty to sixty percent of crustal melts were generated at temperatures buffered around 850° C (the biotite melting stage). These H<sub>2</sub>O-undersaturated melts, or at least some proportion of them, were able to segregate, leaving behind a residue composed of garnet, sillimanite, plagioclase, quartz, rutile and residual liquid. On the basis of mass balance, some granulitic paragneisses found in the North Pyrenean Zone are interpreted as metapelites from which up to 40% of granitic melt was extracted (Vielzeuf 1980b). Following Leterrier (1972) and Debon (1975) it is believed that, in some cases, crustally and mantle derived liquids are able to interact and contaminate each other to generate I-type granites.

- Closer to the surface, the fluid-present melting of metapelites at about 2–3 kbar and 650° C (the muscovite melting stage) generated a thick layer of migmatites unable to migrate because of their nearly H<sub>2</sub>O-saturated character.

- The upper levels of the crust underwent metamorphism within a high temperature gradient and they are now characterized, in the field, by a rapid succession of isograds parallel to that for anatexis.

- The stratified mafic complexes from the lower crust in this region yield an age of 315 Ma (Postaire 1982; Respaut and Lancelot 1983) while the last granites were emplaced 280 Ma ago (Michard-Vitrac et al. 1980). As a result, it is believed that the process of crustal differentiation in the

Pyrenees was promoted by partial melting, and lasted 20 to 40 Ma.

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