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Micas in carbonate-saturated pelites: The transformation from biotite to phengite, melting and melt geochemistry

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Abstract

In this study, a series of high-pressure piston-cylinder and multi-anvil experiments have been conducted on three synthetic carbonate-saturated pelite bulk compositions in the model systems $K_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O-CO_2$ (KCaMAS-HC) and $K_2O-Na_2O-CaO-FeO-Fe_2O_3$ $-MgO-Al_2O_3-SiO_2-H_2O-CO_2$ (KNCaFMAS-HC) to investigate the subsolidus and melting phase petrology for subducted carbonaceous pelites. The results can be used to draw conclusions about reaction grids, devolatilization and melting in carbonate-bearing metasediments during prograde subduction, which is important for the origin of arc magnatism and the recycling of water and CO₂.

Melting experiments on a Fe-rich carbonate-saturated pelite in KNCaFMAS-HC (chapter 5) were performed at 850-1300 °C and 2.5-5.0 GPa to define the conditions to which carbonates remain residual to sediment melting. For this purpose, phase relations, melting conditions and melt compositions were determined. In this fertile bulk composition, 30 wt% potassic granite (2.5 GPa) to phonolite (5.0 GPa) melts are generated at the fluid-absent solidus. The solidus is located at 900 °C, 2.4 GPa and 1070 °C, 5.0 GPa. Phengite+quartz/coesite control initial silicate melting and melt productivity through the reaction phengite+coesite+clinopyroxene+calcite = silicate melt+ kyanite+garnet, leaving most of the Mg-calcite in the residue. Mg-calcite disappears only through the formation of Ca-carbonatite at 1100 °C, 3.5 to 5.0 GPa. The experiments demonstrate a possible source for Ca-carbonatites in combination with alkaline granitic to phonolitic melts at temperatures unlikely to be achieved during ongoing subduction, but which can easily be attained when burying rates slow down or subducted crust becomes incorporated into the mantle. Consequently, it appears likely that carbonates will not be quantitatively recycled in a typical subarc region, extending and confirming earlier results from subsolidus studies (Connolly 2005), that >70-80% of the subducted carbonate will bypass the volcanic arc region and get buried to larger depths.

Subsolidus and melting experiments were performed at 2.0-3.7 GPa and 750-1300 °C in KCaMAS-HC (chapter 4) to define K-mica stability fields and to establish fluid-present melting conditions. The biotite to phengite (Si-rich white mica) transformation occur with pressure from 2.4 to 2.6 GPa between 750 and 850 °C, and the amphibole to clinopyroxene reaction to 875 °C at 2.0 GPa to 740 °C at 2.5 GPa. These reactions conserve K2O, but not conserve H2O, as H2O is produced from decomposition of zoisite and amphibole. Dolomite constitutes the carbonate throughout the studied P-T grid, and is stable to temperatures higher than the solidus above 2.3 GPa. Phengite controls fluid-saturated melting at > 2.6 GPa, whereas biotite dominates at < 2.4GPa (and at ≤ 2.0 GPa also amphibole). The solidus is located at 850-950 °C, at which 7-24 wt% metaluminous K-rich granitic melts are produced. Initial melting occurs through the reactions phengite+zoisite+coesite = silicate melt+clinopyroxene+kyanite (> 2.5 GPa) and biotite+zoisite+ quartz (±amphibole) = silicate melt+clinopyroxene+kyanite (< 2.5 GPa). Lliquidus surface is dominated by peritectic melting first by zoisite and with increasing temperature clinopyroxene. The experiments suggest that in most subduction zones, CO₂ and H₂O will be carried to depths in excess of 120-150 km through carbonates and K-micas, as melting occurs at temperatures unlikely for most subduction zones. However, the release of H₂O through pressurized decomposition of amphibole and zoisite provides a H2O source for arc magma formation. Further, melting at higher temperatures (due to slower burying rates or by crustal incorporation into the mantle), will provide a substantial volatile source for the formation of arc magmas.

The experiments on a carbonate-saturated Mg-rich pelite (i.e. a carbonated whiteschist) in KCaMAS-HC (chapter 6), performed at 850-1100 °C and 2.5-6.0 GPa, indicate that biotite is stable from 2 and up to 6 GPa (at 950 °C). Biotite coexists with either dolomite, aragonite (high-P) or magnesium calcite (high-T). The stability of biotite depends strongly on bulk composition, in the KCaMAS-HC system especially on the Ca/(Ca+Mg)-ratio The results suggest that biotite is more stable in bulk compositions with a low Ca/(Ca+Mg) ratio compared to compositions with a high Ca/(Ca+Mg) ratio.

Zusammenfassung

In dieser Arbeit wurden Stempel-Zylinder- und Vielstempelexperimente an drei synthetischen, karbonatgesättigten pelitischen Zusammensetzungen in den Modellsystemen $K_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O-CO_2$ (KCaMAS-HC) and $K_2O-Na_2O-CaO-FeO-Fe_2O_3-MgO-Al_2O_3-SiO_2-H_2O-CO_2$ (KNCaFMAS-HC) durchgeführt, um Subsolidus- und Schmelzphasenbeziehungen von subduzierten pelitischen Gesteinen zu untersuchen. Die Ergebnisse werden verwendet, um Rückschlüsse auf Reaktionsbeziehungen, Devolatilisierung und Schmelzbeginn von karbonathaltigen Metasedimenten zu ziehen, was bedeutend für die Entstehung von Arc-Magmatismus und für den Kreislauf von Wasser und CO₂ ist.

Experimente an einer eisenreichen, karbonatgesättigten, pelitischen Zusammenset-zung im System KNCaFMAS-HC wurden bei 850-1300 °C und 2.5-5.0 GPa durchgeführt, um die Bedingungen zu definieren, bei denen die Karbonate residual im schmelzenden Gestein verbleiben. Für diesen Zweck wurden Phasen- und Schmelzbeziehungen und Schmelzzusammensetzungen bestimmt. Bei dieser Gesamtzusammensetzung werden unter Fluid-abwesenden Bedingungen 30 Gew% kaliumreiche granitische bis zu 50 Gew% phonolitische Schmelzen produziert. Der Solidus liegt bei 2.4 GPa bei 900°C und bei 5.0 GPa bei 1070°C. Phengit und Quarz/Coesit kontrollieren das initiale Schmelzen und die Schmelzproduktivität durch die Reaktion Phengit+ Coesit+Klinopyroxen+Kalzit = Schmelze+Kyanit+Granat, wobei der Grossteil des Mg-Kalzit im Residuum verbleibt. Mg-Kalzit wird nur durch die Bildung von Ca-Karbonatit bei 1100 °C und 3.5 bis 5.0 GPa aufgelöst. Die Experimente zeigen eine mögliche Quelle für Ca-Karbonatite im Zusammenhang mit alkalinen granitischen und phonolotischen Schmelzen bei Temperaturen auf, die wahrscheinlich nicht während normaler Subduktion erreicht werden, aber die leicht erzielt werden können, wenn sich Subduktionsraten verlangsamen oder subduzierte Kruste mit in den Mantel verlagert wird. Daher ist es wahrscheinlich, dass Karbonate nicht quantitativ in typischen Sub-Arc Regionen recycled werden, sondern dass >70-80% der subduzierten Karbonate die vulkanische Arc region umgehen und zu grösseren Tiefen transportiert werden.

Subsolidus und Schmelzexperimente im System KCaMAS-HC wurden bei 2.0-3.7 GPa und 750-1300 °C durchgeführt, um die Stabilität von K-Glimmer und Fluid-anwesenden Schmelzreaktionen zu untersuchen. Die Biotit zu Phengit (Si-reicher heller Glimmer) Phasentransformation findet von 2.4-2.6 GPa bei 750 und 850 °C statt, und die Amphibol zu Klinopyroxen Reaktion bei 875°C und 2.0 GPa und 740 °C bei 2.5 GPa. Diese Reaktion präserviert K2O, aber H2O wird während der Zersetzung von Zoisit und Amphibol freigesetzt. Das Karbonat ist über den gesamten P-T Bereich an Dolomit gebunden, welcher bei Drücken oberhalb von 2.3 GPa auch bei Temperaturen über dem Solidus stabil ist. Phengit kontrolliert fluidgesättigtes Schmelzen bei Drücken über 2.6 GPa, während Biotit bei Drücken <2.4 GPa dominiert (und ebenfalls Amphibol bei < 2.0 GPa). Am Solidus, der bei Temperaturen von 850-950°C bestimmt wurde, werden 7-24 wt% metaaluminöse, K-reiche granitische Schmelzen produziert. Initiales Schmelzen ensteht durch die Reaktionen Phengit+Zoisit+Quarz = Schmelze+Klinopyroxen+Kyanit (>2.5 GPa) und Biotit+Zoisit+Quarz(±Amphibol) = Schmelze+Klinopyroxen+Kyanit (<2.5 GPa). Die Liquidusoberfläche wird durch peritektisches Schmelzen von Zoisit und bei höheren Temperaturen von Klinopyroxen kontrolliert. Die Experimente zeigen, dass in den meisten Subduktionszonen CO2 und H2O durch Karbonate und K-Glimmer zu Tiefen grösser als 120-150 km transportiert wird, da Aufschmelzen dieser Zusammensetzungen bei Temperaturen auftritt, die für die meisten Subduk-tionszonen unwahrscheinlich sind. Die Freigabe von Wasser durch druckinduzierte Zersetzung von Amphibol und Zoisit, stellt jedoch eine Quelle für die Enstehung von Arc-Magma dar. Weiterhin können durch das Schmelzen bei höheren Temperaturen durch Verlangsamung von Subduktionsraten, oder den Einbau in den Mantel signifikante Mengen an Volatilen zur Generation von Arc-Magmas zur Verfügung gestellt werden.

Experimente an karbonatgesättigten Mg-reichen Peliten im KCaMAS-HC, die bei 850-1100°C und 2.5-6.0 GPa durchgeführt wurden, weisen darauf hin, dass Biotit von 2 bis zu 6 GPa (bei 950°C) stabil ist. Biotit koexistiert entweder mit Dolomit, Aragonit (bei hohem Druck) oder Mg-Kalzit (bei hohen Temperaturen). Das Stabilitätsfeld von Biotit hängt stark von der Gesamtzusammensetzung und im System KCaMAS-HC speziell vom Ca/(Ca+Mg) Verhältnis ab. Die Resultate zeigen, dass Biotit stabiler bei Gesamtzusammensetzungen mit niedrigem Ca/(Ca+Mg) Verhältnis im Vergleich zu Zusammensetzungen mit hohem Ca/(Ca+Mg) Verhältnis ist.

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List of mineral abbreviations used in this study

amp/amph	amphibole
bt	biotite
carb	carbonate
сс	calcite
coe	coesite
cor	corundum
срх	clinopyroxene
C-melt	carbonatite melt
czoi	clinozoisite
dol	dolomite
F	fluid
FM-cc	Fe-Mg calcite
gros	grossular garnet
gt	garnet
M/melt	silicate melt
Mg-cc	Mg-calcite
mus	muscovite
kfsp	K-feldspar
ky	kyanite
omp	omphacite
opx	orthopyroxene
phe	phengite white mica
phl	phlogopite
plag	plagioclase feldspar
ру	pyrope garnet
qtz/q	quartz
tlc	talc
zoi	zoisite

Chapter 1

General Introduction

1. General introduction

1.1 Rationale of the project

Natural marls are sedimentary rocks composed of a pelite and a carbonate component (typically calcite or dolomite), e.g. carbonate-bearing clays, often with volcanic ash, greywacke and siliceous component in addition (Plank & Langmuir 1998). Such compositions are common shelf and platform sediments (Bucher & Frey 2002). They are also present in most metamorphic high pressure terrains, such as in the European Alps (Droop et al. 1990), but due to their chemical complexity, carbonaceous pelites are rarely used for depicting pressure-temperature-oxidation (P-T- f_{O_2}) conditions and fluid composition (X_{co_2}). Most studies on high pressure metamorphic terraines focus on carbonate-free lithologies like metabasalts or metapelites, but with a few exceptions (e.g. Ogasawara et al. 2000) carbonate-bearing mica-rich lithologies (i.e. metamorphosed Al-rich marls) are merely mentioned and briefly described with no significant exploration of the phase relations. Thus, reaction grids at elevated pressures and temperatures are poorly constrained for marls, and in particular melting conditions and melt compositions are unknown. It is the purpose of this project to investigate these lithologies.

Potassium minerals (like K-micas) are among the phases that usually disappear first during melting in pelites, greywackes and marls, thus the stability of micas are important in establishing melting temperatures and melt compositions. Low-pressure, high-grade marls contain biotite as a mica, and high-pressure marls phengite (i.e. Si-rich muscovite). The conditions and nature of the biotite to phengite transformation is poorly constrained in any lithology, but has major implications for the melting behaviour and on the geochemistry of recycling into the Earth's mantle (and thus the global cycle) as micas host many key trace elements and isotopes such as LILE (K, Rb, Ba, Sr), B, ¹⁰Be and ²⁰⁷Pb (Dominak et al. 1993, Plank & Langmuir 1998, Ishikawa & Nakamura 1994).

1.2. Aims of this study

The chemical complexity of carbonaccous pelites can be turned to an advantage as the richness in metamorphic reactions resulting from this complexity, and the common complete buffering of mineral compositions over a wide P-T range, allows deduction of information from marls that cannot be readily deduced from other lithologies. Thus, the targets of this research project are to investigate experimentally the phase petrology of carbonate-saturated pelites (i.e. Al-rich marls) of medium to high metamorphic grade at high pressures, i.e. in the vicinity of the solidus, with special focus on:

- the subsolidus reactions controlling composition and stability of carbonates and pelite minerals under high pressure conditions, emphasizing on the transformation from biotite to phengite with increasing pressure,
- (2) the reactions responsible for initial partial melting (solidus), melt conditions, and melt compositions in carbonate-saturated pelites, and
- (3) a thermodynamic model for high pressure subsolidus marls, including improved thermodynamic data for the biotite and phengite solid solution series.

This research project therefore lays an experimental fundament for further investigation of carbonate-saturated pelites, including carbonatites originating from metasedimentary rocks, and can be used in a more general sense for the investigation of high-pressure metasediments.

1.3 Research strategy

In order to successfully investigate such complex rock types, the thermodynamic composition space was reduced by maximizing component saturation at sub- and near-solidus conditions, i.e. to have the highest possible number of saturated phases. Thus, the solid bulk compositions used in the equilibrium experiments were saturated in CO_2 , producing carbonates, and with $SiO_2 > Al_2O_3$ (except MA, chapter 6), resulting in the stability of a SiO_2 -polymorph and kyanite. In this way, the phase compositions produced under subsolidus conditions were fully buffered, and are expected to change systematically with temperature and pressure.

A major problem in the application of experimentally established phase equilibria to natural rocks is the composition of the fluid that is generally difficult to constrain in natural rocks. Experimentally, focusing on equilibria that are independent from fluid composition (but may occur in the presence of a fluid) can overcome this problem. The transformation from biotite to phengite fulfils this condition if all other phases involved are anhydrous as both phases have the same K:H ratio. Similarly, the most important compositional vector in both micas, the aluminoceladonite substitution (see chapter 2), can be buffered by equilibria involving three or four phases among garnet, diopside, anorthite, kyanite and quartz or two of these silicates with calcite and dolomite. The experiments thus constrain mica composition as a function of buffer assemblage, which is also a function of bulk composition. The breakdown reactions of micas also depend on fluid composition. However, in the above mentioned assemblages, fluid composition is buffered by solid phase equilibria and is not an independent parameter, if the fluid is not an additional phase.

1.4. Published material

Parts of this thesis have been prepared for publication and are either in review or in preparation. These parts are included in this thesis unaltered, with the exception that the layout, table and figure numbers have been brought in line with the rest of the thesis:

3

- Thomsen TB and Schmidt MW (in review) The biotite to phengite transformation and micadominated melting in carbonate-saturated pelites at high pressures: Implications for water and CO₂ in subduction zones. (chapter 4 with additional results from chapter 6). Journal of Petrology.
- Thomsen TB and Schmidt MW (submitted) Melting of carbonaceous pelites at 2.5-5.0 GPa, silicate-carbonatite liquid immiscibility, and potassium-carbon metasomatism of the mantle (chapter 5). Earth and Planetary Science Letters.
- Thomsen TB, Caddick M, Connolly JAD and Schmidt MW (in prep) A thermodynamic solution model for K-micas in carbonate-saturated pelites (in KCaMAS-HC) at high pressures.

Furthermore, abstracts from international conferences and meetings are:

- Thomsen TB and Schmidt MW (2004) Melting and immiscible liquids in carbonate saturated pelites at high pressures. Goldschmidt 2004. Geochimica and Cosmochimica Acta, vol. 68, issue 11, A602. (chapter 5)
- Thomsen TB and Schmidt MW (2004) The biotite to phengite transition and mica-dominated melting in carbonate-saturated model systems. EMPG-X (poster). Lithos 73, p. S110. (chapter 4+6)
- Thomsen TB and Schmidt MW (2004) Micas in marls: the biotite to phengite transition and mica-dominated melting in carbonate-saturated model rocks. ISPET3 sem. (chapter 4)
- Thomsen TB and Schmidt MW (2006) Subsolidus relations and mica-dominated melting of carboneceous pelites at 2 to 5 GPa: an experimental study. 4th Swiss Geoscience Meeting. (chapter 4+5)

Chapter 2

Micas: crystal chemistry and petrological aspects

2. Micas: crystal chemistry and petrological aspects

Micas are among the most abundant rock-forming minerals in the Earth's crust (~4.5 vol%), widespread in most metamorphic rocks (abundance ~11%) at almost all metamorphic pressures and temperatures (Preface in Rev. in Min. & Geochem. 46). The literature dedicated to micas is enormous, but as all micas produced in this study are K-micas (with negligible Na-amount) within or between the phengite and biotite solid solution series (Rieder et al., 1999), this chapter emphasizes primarily on K-micas, providing a basis for further argumentation. For more detailed and general information about micas, the Reviews in Mineralogy & Geochemistry no. 13 (1987) and 46 (2002) as well as Guidotti & Sassi (1998) are recommended.

2.1 Mica crystal chemistry

2.1.1 General formula and classification

The official nomenclature for micas elaborated by the International Mineralogical Association (IMA), Commission on New Minerals and Mineral Names (CNMMN) Mica Subcommittee, is compiled in Rieder et al. (1998, 1999) and Rieder (2001), and is further discussed in Tischendorf et al. (2004). The general formula of micas, based on the chemical composition, can be written as:

 $I[M_{2+x} \square_{1-x}][T_4 O_{10}]A_2$, where $x \in [0,1]$, and

I =interlayer cations, mainly K, Na or Ca, but also Ba, Cs, Rb, Sr, NH₄, H₃O

M =octahedral cations, mainly Mg, Fe²⁺, Fe³⁺, Al, but also Li, Ti, Mn, Cr, V, Ni, Cu, Zn

- \Box = octahedral vacancy
- T = tetrahedral cations, mainly Si, Al and Fe³⁺ but also Ti, Be, B
- A = anions, mainly (OH), but also Cl, F, O (oxy-micas) and S

Depending on the interlayer cation (*I*), the micas are divided into *true micas* (if \geq 50% *I*-cations are univalent, e.g. K' or Na'), *brittle micas* (if \geq 50% *I*-cations are divalent, e.g. Ca²⁺) or *interlay-er-cation-deficient micas* (if the formula shows < 0.85 and \geq 0.6 positive interlayer charges) (Fig. 2.1). Regardless of the mica group, micas are termed *dioctahedral* if they contain < 2.5 octahedral cations pfu, and *trioctahedral* if they have \geq 2.5 octahedral cations pfu. Phengite is a series name for true dioctahedral K-micas in the solid solution between muscovite K[A1₂□][AlSi₃O₁₀](OH)₂, aluminium-celadonite K[Al(Mg,Fe²⁺)□][Si₄O₁₀](OH)₂, and celadonite K[Fe³⁺(Fe²⁺,Mg)□][Si₄O₁₀] (OH)₂, and generally have a molar Si > 3.2 pfu. Biotites are true trioctahedral Fe-Mg micas in the solid solutions between phlogopite K[Mg₃][AlSi₃O₁₀](OH)₂, eastonite K[Mg₂Al][Al₂Si₂O₁₀](OH)₂, annite K[Fe²⁺,][AlSi₃O₁₀](OH), and siderophyllite K[(Fe²⁺,Al][Al₂Si₂O₁₀](OH)₂.

2.1.2 The mica module

The mica structure consists of sheets of tetrahedra of composition T_2O_5 arranged in pairs, enclosing (in a sandwich-fashion) a sheet of edge-sharing octahedra, thus forming a layer (termed *T-O-T* or 2:1 layer; Fig. 2) that is separated from adjacent *T-O-T* layers by planes of nonhydrated interlayer cations (*I*), i.e. in the sequence: *I-T-O-T-I*. The apices of the tetrahedra connect to the octahedra of the central layer, thus, a total of four apical oxygens are shared by each octahedron, viz. two from the upper respectively lower tetrahedral sheet. The coordination of the octahedra is completed by the anions *A* (in our experiments OH). The octahedral sheet can be made up in two ways: either dominantly of divalent cations such as Mg^{21} and Fe^{21} , in which case all three octahedral sites (*M1*, *M2*, *M3*) are filled forming trioctahedral mica (e.g. biotite; Fig. 2A), or else dominantly trivalent cations such as Al^{31} or Fe^{31} , in which case one of the three sites (*M1* or *M2*) is left vacant and dioctahedral micas (e.g. phengite; Fig. 2B) form (Ferraris & Ivaldi 2002, Nespolo & Durocic 2002, Brigatti & Guggenhaim 2002, Rieder et al. 1998). Alternatively, the mica structure may be regarded as having a central brucite-like trioctahedral sheet Mg(OH)₂, which in

TRUE	MICAS	BRITTLE	E MICAS	INTERLAYER-DE	EFICIENT MICAS
Di-octahedral	Tri-octahedral	Di-octahedral	Tri-octahedral	Di-octahedral	Tri-octahedral
Muscovite K(Aı₂⊏][AlSi₃O _{to}](OH)₂	Annite K[Fe ^{2⁺} 3][AISI ₅ O₁₀](OH) ₂	Margarite	Clintonite	illite	Wonesite
^V R ²⁺ /(^V R ²⁺ + ^V R ³⁺) < 0.25 ^V A V(^V A + ^V Fe ³⁺) = 0.5-1.0 2 0.85 (K = 0.7-1.0)	Phlogopite K[Mg ₃][AISi ₃ 0. ₁₀](OH) ₂	Chernykhite	Bityite	Glauconite	
Alumino-celadonite	Siderophyllite		Anandite	Brammalite	
K[AI(Mg,Fe ²⁺)□][Si₄O ₁₀](OH) ₂	K[AIFe ^{2*} 2][Al ₂ Si ₂ O ₁₀](OH) ₂				
vR ²⁷ I(^v R ²⁺ + ^v R ³⁺) ≥ 0.25 VAI(^M AI + ^v Fe ³⁺) = 0.5-1.0 VAI(^M AI - ^v IC-3 ⁺) = 0.5	Eastonite K[AlMg ₂][Al ₂ Si ₂ O ₁₀](OH) ₂		Kinoshitalite		
Alumino-ferro-celadonite	Hendricksite				
K[Al(Fe ²⁺ ,Mg)□][Si₄O ₁₀](OH) ₂					
^{v/} AJ{ ^{(v} A + ^v Fe ³⁺) = 0.5-1.0 Mg/(Mg + ^{v/} Fe ³⁺) ≤ 0.5	Montdorite				
Celadonite	Tainiolite				
K[Fe ³⁺ (Mg,Fe ²⁺)□][Si₄O ₁₀](OH) ₂					
^{VI} R ²⁺ /(^{VI} R ²⁺ + ^{VI} R ³⁺) ≥ 0.25 ^{VI} AI{(^{VI} AI + ^{VI} Fe ³⁺) < 0.5-1.0	Polylithionite				
Mg/(Mg + ^{vr} Fe ³⁺) > 0.5					
Ferro-celadonite	Tilithionite				
K[Fe ³⁺ (Fe ²⁺ ,Mg)D][Si₄O ₁₀](OH) ₂ ^{v/} Al/(^{v/} Al + ^{v/} Fe ³⁺) < 0.5	Masutomilite				
Mg/(Mg + ^{Vi} Fe ³⁺⁾ ≤ 0.5					
Roscoelite	Norrishite				
Chromphyllite	Tetra-ferri-annite				
Boromuscovite	Tetra-ferri-phlogopite				
Paragonite	Aspidolite				
Nanpingite	Preiswerkite				
Tobelite	Ephesite				

Fig. 2.1. Nomenclature of micas. Micas produced in this study are all in the composition space constituted by names in bold.









Fig. 2.2. Ideal trioctahedral brucite-like (A) and dioctahedral gibbsitelike (B) sheets. Two ideal tetrahedral sheets (C) share their apical oxygens atoms with an octahedral sheet to form the T-O-T (or 2:1) layer (D). Hydroxyl (OII) groups are represented by the black dots (after Ferraris & Ivaldi, 2002). (E) Perspective view of I-T-O-T-I layers in biotite down [100] and vertical [001] (from Mickey Gunter, University of Idaho).

micas become $Mg_3O_4(OH)_2$, or a gibbsite-like dioctahedral sheet $Al(OH)_3$, which in micas become $Al_2O_4(OH)_2$, that is sandwiched between the two oppositely orientated tetrahedral sheets (Ferraris & Ivaldi 2002, Deer et al., 1992). In true micas, Al substitutes for Si in the tetrahedra, and charge balance is maintained by K⁺, Na⁺ or Ca²⁺ in the interlayer site (*I*). If the tetrahedra are occupied solely by Si and the octahedra have a cation valence of 6, the sandwich is charge-balanced and there is essentially no need for interlayer cations; the resulting minerals are then talc (trioctahedral) and pyrophyllite (dioctahedral), demonstrating the close structural relation of micas to these phyllosilicates.

2.1.3 Normalization of K-micas

Mica formulas were calculated on the basis of 12 oxygens (including 2 (OH) groups) allowing for octahedral (*M*) and interlayer (*I*) cation vacancies. Normalization with 2H⁺ was justified from the microprobe analysis totals of 95-96 wt%, corresponding to a H₂O content of 4-5 wt%, comparable to the calculated H₂O contents of micas with 2 (OH). For the Fe-bearing bulk composition used in this study (AM in Tab.3.1), Fe^{2+}/Fe^{3+} ratio of the produced phengites was not determined (e.g. from Mössbauer spectroscopy), thus assumption of $Fe^{2+}/Fe_{tot} = 1$ calculated all iron as Fe^{2+} . By calculating all iron as FeO compared to Fe_2O_3 , high totals might suggest the amount of ferrous and ferric iron in the micas. However for the produced phengites (FeO_{tot} < 4 wt%), the differences were small and within analytical error, thus did not give information of the valence state of iron. Fe-bearing biotites were not produced in the experiments.

2.2 Exchange mechanisms and deviation from mica solid solution ideality

K-micas show a wide compositional variation (Fig. 2.3) in response to pressure, temperature and bulk rock composition changes. The compositional variation can be expressed through several substitutions working in conjunction. Such complex solid solutions can be described in terms of idealized simple exchange vectors such as $Fc^{2+}Mg_{.1}$, or coupled exchange vectors such as the Al-Tschermak's substitution $Al_2Mg_{.1}Si_{.1}$, through which all chemical variations occurring can be described (Thompson 1982a+b, 1979, Bragg 1937). The base of the vector concept is the fundamental requirement of charge balance for compositional exchanges in the crystal structure.



Fig. 2.3. Principal compositional space for the phengite (A) and biotite (B) solid solution series. The shaded region in (A) represent the phengite series, and in (B) the composition space for most natural biotites. Compositions are interrelated with via the FeMg₋₁ and Tschermak's exchange $Al_2Mg_{-1}Si_{-1}$ (Guidotti & Sassi, 2002).

For ideal di- and trioctahedral potassic micas, the coupled *alumino-celadonite substitution*, i.e. ^{IV}(Si) + ^{VI}(Fc²⁺,Mg²⁺) \leftrightarrow ^{IV}(Al³⁺) + ^{VI}(Al³⁺), is the most important exchange vector (^{IV} and ^{VI} denote tetrahedral respectively octahedral sites). This substitution combines two cation exchanges, viz. the simple *iron-magnesium exchange* ^{VI}(Fe²⁺) \leftrightarrow ^{VI}(Mg²⁺) and the coupled *Altschermak's exchange* ^{VI}(R²⁺) + ^{TV}(Si⁴⁺) \leftrightarrow ^{VI}(Al³⁺) + ^{TV}(Al³⁺), where R²⁺ refers to a divalent cation (in our experiments Fe²⁺ or Mg²⁺) (Fig. 2.4). Other substitutions that may take place (but in less extent) within the phengite and biotite solid solution series, are the *interlayer cation exchanges* K⁺ \leftrightarrow H₃O⁺ and K⁺ \leftrightarrow Na⁺.



Fig. 2.4. Principal variations and exchange vectors for dioctahedral and trioctahedral potassic micas, with octahedral occupancy (M) and the planes of Si, Al and (Mg, Fe²⁺) atoms pfu (based on 11 oxygens). ^{VI} is octahedral and ^{IV} tetrahedral sites. ^{VI} denote octahedral vacancy.

In terms of crystallochemical effects, deviation from the ideal phengite solid solution towards the biotite solid solution series at high pressures may occur through the coupled *di-trioctahedral substitution* $2^{VI}(Al^{3+}) + ^{VI}\square \leftrightarrow 3^{VI}(Fe^{2+}, Mg^{2+})$, resulting in a higher octahedral occupancy for phengites and a lower occupancy for biotites. For dioctahedral micas the *ferri-muscovite exchange* $^{VI}(Fe^{3+}) \leftrightarrow ^{VI}(Al^{3+})$ is important in terms of the Fe³⁺/Fe_{tot} and Mg²⁺/Fe²⁺ ratios, although the endmember (K,Na)(Fe³⁺)₂[AlSi₃O₁₀](OH)₂ is hypothetical. The ferri-muscovite typically accompanies the alumino-celadonite substitution, thus representing solid solution towards celadonite (Guidotti et al. 1994). In addition, the *K-edinite-type substitution* K⁺ + ^{IV}(Al³⁺) $\leftrightarrow \Box + ^{IV}(Si^{4+})$ for biotites towards tale was recently suggested by Hermann (2002) and Wunder & Melzer (2002), and discussed in Comodi et al. (2004) as a significant exchange vector for high pressure biotites.

2.3 Pressure and temperature effects for K-micas at high pressure conditions

The effect of pressure increase on the substitutions in the tetrahedral and octahedral sites for K-micas is extensive and has been known at least since Ernst (1963). With increasing pressure, the inverse tschermak's substitution $^{IV}(A1^{3+}) + ^{VI}(A1^{3+}) \rightarrow ^{IV}(Si) + ^{VI}(Fe^{2+},Mg^{2+})$ joined with $^{VI}(Fe^{2+}) \rightarrow ^{VI}(Mg^{2+})$ exchange are the principal compositional variations within the phengite and biotite solid solutions, producing Si+Mg-enriched K-micas. For phengites, these substitutions is usually accompanied by variable amounts of ferri-muscovite exchange $^{VI}(Al^{3+}) \rightarrow ^{VI}(Fe^{3+})$, typically resulting in higher ferric iron at higher pressures (Comodi and Zannazzi 1995, Guidotti et al. 2000). For biotites, the extent of the $Al^{34} \rightarrow Fe^{34}$ substitution mechanism is virtually unknown. An increase in pressure (and decrease in temperature) favours the K-edinite-type substitution $K' + {}^{\text{IV}}(Al^{3'}) \rightarrow \Box + {}^{\text{IV}}(Si^{4'})$ in biotites, resulting in a larger talc component Mg₃[Si₄O₁₀](OH)₂. Essentially, this is due to a decrease in size of the tetrahedral sheet, coupled in the aluminoceladonite substitution by an increase of the octahedral sheet dimensions (Comodi et al. 2004). This decrease in potassium with increasing pressure is in contrast with the general K increase compared to Na with increasing pressure, which mainly is a response to the effects of pressure on the octahedral and tetrahedral substitutions on the degree of (non-)ideality for the Na-K exchange (Guidotti and Sassi 2002).

The effect of temperature increase on K-micas is less constrained than pressure effects, but is in general controlled by the same two substitutions, $Fc^{2+}Mg_{.1}$ and tschermak's exchange. For the most, this results in lower Si (and Mg) and higher Al (and Fe) content in K-micas with an increase in temperature, but cannot be generalized, as it depends on available buffer mechanisms for the bulk composition. In comparison to white micas, biotites typically show more compositional variation within and from the biotite solid solution plane (Fig. 2.4), including Fe²⁺, Mg, tschermak's exchange, Fe³⁺, vacancies and OH. For biotites, increasing Fe²⁺ \rightarrow Fe³⁺ oxidation is thought to be common in some bulk rock compositions, but a quantitative systematic has not yet been established (discussed further in Eugster & Woones, 1962). As shown by Guidotti et al. (1994), at high pressures, the extensive substitutions in the octahedral and tetrahedral sites may have a very large, still uncalibrated, effect on the Na-K ratio of K-micas.

2.3 P-T stability of K-micas in metasediments at high pressure and temperature

The pressure-temperature stability of K-micas is very dependant of the bulk rock composition in which they occur. Nevertheless, in different metasediments K-micas often have similar P-T stability fields. Generally, low-pressure, high-grade pelites, marls (i.e. carbonatebearing pelites) and impure carbonates have biotite as the dominant potassic mica (c.g. Ferry 1976, 83a,b; Frank 1983; Frey 1978; Thompson 1975, Spear 1995; Bucher & Frey 2002), whereas high-pressure pelites, marls, carbonates and greywackes contain phengite (e.g. Ogasawara et al. 2000, Dominak & Holloway 2000; Dachs 1986, Spear 1995, Bucher & Frey 2002; Schmidt et al. 2004, Auzanneau et al. 2006). Low to medium pressure pelites, greywackes and Al-rich marls have phengitic muscovite at low grade, whereas muscovite+biotite (bt-in at ~400 °C) dominates at higher grades, coexisting until muscovite typically disappears first at medium to high grades (Bucher & Frey, 2002).

The conditions and nature of the biotite to phengite transformation with pressure are poorly defined. Phengite and phlogopite coexists in marls and impure carbonates in the Eclogite Zone, Tauern in the Eastern Alps (Dachs, 1986, 1990) suggesting a broad K-mica transformation reaction zone of ~0.6 to 2.0 GPa at T_{max} ~550-600 °C. Natural mafic, pelitic, and carbonate-bearing eclogites (e.g. *Corsica*: Caron and Pequinot 1986; *Adula nappe, Alps*: Heinrich 1986, Meyre et al. 1999, Droop et al. 1990; *San Franciscan*: Sorenson 1986, Domanik et al. 1993; *Dabie Shan*: Zhang et al. 1997; *Kazakhstan*: Ogasawara et al. 2000) and experiments above 2.4 GPa on such lithologics (Schmidt et al. 2004; Hermann, 2002; Hermann & Green, 2001; Schmidt & Poli, 1998 and references therein; Massonne & Spzurka, 1997; Dominak & Holloway, 1996; Massonne, 1992; Massonne & Schreyer, 1987, 1989) contain phengite as the principal potassic phase. For pelites, greywackes and mafic compositions (e.g. basalts), biotite and amphibole dominate the volumetric major fluid-absent melting reaction at < 2.5-3 GPa (Vielzeuf & Holloway 1988; Winther & Newton 1991; Patiño Douce & Beard 1995; Schmidt et al., 2004; Auzanneau et al., 2006), whereas at > 3 GPa phengite is the only significant hydrous potassic phase within the subducted slab to \sim 9 GPa (Schmidt et al., 2004; Poli & Schmidt, 2002; Ono 1998).

Chapter 3

Experimental and Analytical methods

3. Experimental and Analytical methods

3.1 Experimental apparatus

Experiments were carried out from 2.0 to 6.0 GPa and 750 to 1300 °C, employing endloaded piston cylinders for experiments below 5 GPa, and multi-anvil devices for experiments at 5 and 6 GPa. Most experiments were performed at ETH-Zürich, with a few experiments in addition carried out at CNRS, Clermont-Ferrand (France) and ANU in Canberra (Australia).

3.1.1 Boyd and England type endloaded piston cylinder

The Boyd and England type endloaded, solid media piston cylinder (Fig. 3.1A; Boyd & England, 1960) consists of a piston pressing into a hollow cylinder, compressing the solid materials in the furnace assembly (Holloway & Wood, 1988). At ETH-Zürich, a 14 mm (3/4") piston bore was used, and at ANU a $\frac{1}{2}$ inch bore. The assemblies were first pressurized to ~ 0.4 GPa at room temperature, then pressure and temperature were increased simultaneously to the desired values. The temperature was increased with 50 °C/minute, and then controlled by a Eurotherm controller within ±2 °C using a B-type thermocouple ($Pt_{94}Rh_6-Pt_{70}Rh_{30}$), not corrected for the pressure effect on thermocouple electromotive force (emf). Hydraulic pressure was maintained automatically by a screw worm jack with a relative precision better than ±0.3 bar oil pressure, equivalent to ±2.5 MPa sample pressure. A friction correction of 3 % applied to the nominal pressure was obtained by calibration against the fayalite+quartz = ferrosilite reaction at 1.41 GPa – 1000 °C (Bohlen et al, 1980) and against the quartz to coesite transformation at 3.07 GPa at 1000 °C – 3.2 GPa at 1200 °C (Bose & Ganguly, 1995). Quenching was achieved by turning off power supply to the furnace, resulting in a temperature drop to less than 200 °C within 10 seconds.

Assemblies (Fig. 3.1B) consisted of a pressed NaCl sleeve, surrounding a pyrex (borosilicate) glass cylinder (for most experiments) and a straight, cylindrical graphite heater. Two spacers of either NaCl or MgO were placed inside the furnaces and a corundum insulator disc between thermocouple and capsule was used in all but one experiment (MgO disc). Two graphite discs at one end and at ETH-Zürich a brass ring at the other end of the graphite furnace ensured good electrical contact between the tube furnace, the end plug containing the thermocouple ceramics and the piston. Capsules of Au_{100} or $Au_{80}Pd_{20}$ were applied at < 1100 °C and $Au_{50}Pd_{50}$ capsules at \geq 1100 °C. All capsules were arc-welded at one end, cleaned with ethanol and fired at > 400 °C to remove impurities, then filled with starting material, previously dried at 110 °C, closed and welded shut. H₂O loss during welding was prevented by wrapping a Kimwipe tissue soaked



Fig. 3.1. (A) The Boyd and England type endloaded piston cylinder used at ETH-Zürich (figure from P. Ulmer). (B) The pyrex glass-graphite-MgO assembly used in most piston cylinder experiments. In 7 experiments with the MA bulk composition, the MgO rods were replaced with NaCl cylinders, and in one experiment with the AM bulk composition, the corundum disc was replaced with a MgO disc.

(A) Boyd & England Type Piston cylinder

(B) Pyrex-Graphite-MgO asembly

in deionised H₂O around the capsule. One capsule of 3 mm O.D. or two capsules placed side by side of 2.0 or 2.3 mm O.D. and 2.0 to 3.8 mm length were run vertically and centred at the hot spot to within ± 0.5 mm, the thermocouple tip thus recording the coldest temperature in the capsule. Thermal gradients along the length of the capsules at 2.0 GPa and 1300 °C were measured to be ± 10 °C/2 mm.

3.1.2 Walker-type multi-anvil apparatus

The Walker-type (Walker et. al, 1990) multi-anvil device at ETH-Zürich (Fig. 3.2A) consists of a 600 tons O-frame press with a cylindrical pressure module holding 25 mm second-stage tungsten-carbide (WC) anvils. Pressure on the sample assembly is generated through the hydraulic ram exerting an axial force, which is distributed in six directions onto the faces of a cubic arrangement of eight corner truncated WC cubes, which provides a void for an octahedral MgO pressure cell, holding the sample assembly. At ETH-Zürich, 25 mm WC-cubes were employed, whereas 32 mm WC-cubes were applied at CNRS. At ETH-Zürich, 19 mm octahedra were cast from a two-component MgO-based ceramic. The octahedra comprised integral gaskets between



Fig. 3.2 (A) The Walker-type multi-anvil module available at ETH-Zürich (figure from P. Ulmer). (B) The stepped graphite-MgO-boron nitirde (BN) pressure assembly used at ETH-Zürich. Here shown for a two capsule experiment with a central thermocouple. At CNRS, a ZrO₂ sleeve, a stepped LaCrO₃ furnace with a graphite disc and ring between the graphite furnace and WC cubes was used.

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the WC-cubes, which had 12 mm anvil truncations. The sample assembly fits into a central cylindrical hole drilled in the octahedron. The assembly (Fig. 3.2B) used at ETH-Zürich was composed of a stepped graphite furnace to minimize thermal gradients. Two internal MgO cylinders holding the capsules and filled with boron nitride powder insulated the capsule from the furnace. Molybdenum end discs between the furnace and the WC cubes ensured a stable electrical contact and avoided electrical erosion of the WC. At CNRS, the pressure cell consisted of a 25 mm prefabricated octahedra used in combination with pyrophyllite gaskets and 17 mm anvil truncations. The assembly was composed of a ZrO₂ sleeve for thermal insulation, a stepped LaCrO, furnace with inner MgO spacers and a graphite disc and ring between the graphite furnace and WC cubes for electrical contacts. Two or three Au₁₀₀ capsules of 2.0 or 1.6 mm O.D. (CNRS) or two $Au_{50}Pd_{50}$ capsules of 2.0 or 2.3 mm O.D. and ~ 2.0 mm length (ETH) were used in each experimental run. The capsules were placed on each side of the central thermocouple (Fig. 3.2B). Capsule welding and preparation were carried out as for the piston cylinder experiments. The temperature was controlled automatically by Eurotherm controllers, using either a B-type $(Pt_{94}Rh_{6}/Pt_{70}Rh_{30})$ (ETH), or S-type $(Pt_{100}/Pt_{90}Rh_{10})$ thermocouple (CNRS) with no correction for the effect of pressure on the thermocouple emf. Temperature gradients within the lengths of the capsules (~2 mm) were estimated to be ±20 °C (at 1000-1050 °C). In both laboratories, pressure was calibrated against the quartz-cocsite (Bose & Ganguly 1995, see section 3.1.1) and cocsite to stishovite transformation at 9.2 GPa - 1200 °C (Yagi and Akimoto 1976, Zhang et al. 1996), the fayalite to γ-spinel reaction at 5.25 GPa - 1000 °C (Yagi et al. 1987) and the garnet-perovskite reaction at 6.1 GPa and 1200 °C (Susaki et al. 1985). Pressure was controlled automatically with a precision of ± 0.2 GPa. Quenching was done by turning off power to the furnace, resulting in quench rates of 400-600 °C/sec.

3.2 Bulk starting materials

Three bulk starting compositions were used in this study (Table 3.1), two model compositions in the K₂O–CaO–MgO–Al₂O₃–SiO₂–H₂O–CO₂ (KCaMAS-HC) system and a pseudonatural composition in K₂O–Na₂O–CaO–FeO–MgO–Al₂O₃–SiO₂–H₂O–CO₂ (KNCaFMAS-HC). For the two Fc- and Na-free compositions (MA and MC), the basis of the initial starting material was a synthetic glass composed of the oxides SiO₂, Al₂O₃, MgO and CaO (made from dissociation of CO₂ from CaCO₃) and mixed with natural alkali feldspar (orthoclase). The glass was ground to < 5 µm in an automatic mill employing agate mortars with ethanol, and then melted at 1100-1200 °C during 30-45 minutes (for MA composition) or 1300 °C during 45 minutes (for MC composition) in a new Pt-crucible. The milling, grinding and melting was repeated three times to ensure homogeneity of the glass, which was controlled by microprobe analysis using a defocused beam. The glass was then pulverized, weighted and mixed with Al(OH)₃ and CaCO₃ to

Table 3.1. Bulk starting compositions (in wt%)						
	MC	AM	MA	Ant543 ^a	Frey (78) ^b	
\$iO ₂	51.44	47.60	40.76	46.57	44.50	
Al ₂ O ₃	21.79	22.80	24.3	17.99	18.30	
FeO _{tot}	0	9.20	0	7.38	4.80	
MgO	7.36	2.00	15.22	1.61	2.80	
CaO	11.79	6.80	8.44	5.45	9.70	
Na ₂ O	0	2.40	0	1.91	1.40	
K ₂ O	1.94	3.60	3.91	2.83	3.40	
H ₂ O	3.6	1.10	0.74	11.97	2.80	
CO ₂	2.09	4.80	6.62	3.83	10.70	
SUM	100.0	100.3	100.0	99.5	98.40	
Al/(Na+K+2*Ca) ^{molar}	0.48	0.70	0.70	0.69	0.44	
Al/(Na+K) ^{molar}	10.38	2.91	5.74	2.90	3.06	
Na/K ^{molar}	-	1.01	-	1.03	0.63	
X _{Mg} ^c	1.00	0.28	1.00	0.28	0.51	
Xco2 ^d	0.19	0.64	0.79	0.12	0.61	

Table 3.1. Bulk starting compositions (in wt%)

^a Fe-calcareous claystone from Antilles (p. 339 in Plank & Langmuir, 1998).

^b Calc-schist from Alps (Frey, 1978).

 $^{c} X_{Mg} = Mg^{2+}/(Fe_{tot}+Mg^{2+})$

^d molar CO₂/(CO₂+H₂O)

introduce the desired proportions of H_2O and CO_2 . No free water or CO_2 was added to have a precise control of the amounts of volatiles and to prevent volatile-loss during welding of the capsules. To enhance reaction rates, the MC composition had approximately 2 wt% H_2O in excess compared to the amount of H_2O bound in the hydrous phases expected to form under subsolidus conditions (e.g. biotite, muscovite, zoisite and amphibole). The KNCaFMAS-HC bulk composition is based on Fe-calcareous clay from the Antilles (Ant543 in Tab. 1, p. 339 in Plank & Langmuir, 1998). The starting material was made of SiO_2 , Al_2O_3 , Fe_2SiO_4 (fayalite), CaMg-SiO_6 (diopside), NaAlSi₃O₈ (albite) and a synthetic $KAl_{1,33}Mg_{0.5}Si_{3.5}O_{10}$ glass, which was milled and grinded, then mixed with the $Al(OH)_3$ and $CaCO_3$ to introduce the desired H_2O and CO_2 proportions.

3.3 Factors controlling oxygen fugacity (f_{O_2}) in the Fe-bearing (AM) experiments

3.3.1. Factors controlling the experimental oxygen fugacity

In natural systems, f_{O_2} is often regarded as an independent parameter, in contrast to (closed-system) equilibrium experiments, where f_{O_2} is dependent on the water dissociation constant of the reaction $H_2O = H_2 + \frac{1}{2}O_2$, linking the f_{O_2} of an experimental charge to the hydrogen fugacity f_{H_2} . In the absence of an O_2 or H_2 buffering technique, the assembly surrounding the noble-metal capsules exerts an important control on f_{H_2} (thus f_{O_2}), strongly influencing phase stabilities, in particular the oxidation state in Fe-phases and of carbonates. However, estimates from various studies for comparable experimental setups differ significantly, demonstrating the strong dependence of pressure and temperature on f_{O_2} . For graphite-NaCl assemblies, estimates for f_{O_2} range from 0.5 log units above the Ni-NiO (NNO) buffer (Caroll & Wyllie, 1989, 90; Wolf & Wyllie, 1994) to QFM or 2 log units below the quartz-magnetite-fayalite (QFM) buffer (Patino Douce & Johnston, 1991; Patino Douce & Beard, 1994, 1995). The effects of different assemblies and Fe-pre-conditioning of capsules on the f_{O_2} and redox state in piston cylinder experiments

was discussed e.g. by Kägi et al. (2005) and Truckenbodt et al (1997). The latter study concluded that boron nitride assemblies are nearly impermeable to H₂ (at 1.0 GPa and 900 °C), preventing hydrogen loss from the material in the noble-metal capsule to the surrounding assembly. Thus, the f_{O_2} is dominated by the "intrinsic" f_{O_2} of the starting material rather than by the assembly. In the study of Kägi et al. (2005) the best results in terms of Fe- and H₂O-conservation and f_{O_2} control were obtained using Fe-preconditioned gold-palladium inner capsules in combination with MgO assemblies, compared to Fe-unconditioned noble metal capsules and boron nitride assemblies. The (optimum) setup strongly reduced the Fe-loss to the capsule walls, conserved H₂O and kept a constant f_{O_2} close to QFM+1 in the sample material during the experiments. They concluded that the "intrinsic" f_{O_2} is strongly dependant on the assembly applied (MgO assemblics resulting in more oxidizing conditions than boron nitride assemblies) and capsule Fepreconditioning (Fe-loss of ~10% (relative) in non-preconditioned capsules compared to <3% in Fe-preconditioned capsules).

3.3.2. The experimental f_{O_2} of the Fe-bearing bulk composition (AM)

The oxygen fugacity (f_{O_2}) in the AM experiments was not measured directly or controlled through a buffering technique. However, the experiments did not produce graphite, indicating a f_{O_2} above the graphite-CO-CO₂ (CCO) buffer, which at 2.5-5.0 GPa and 750-1300 °C most probably represent f_{O_2} conditions near or above NNO or QFM buffers. Maximum Fe²⁺ to Fe³⁺ oxidation from the complete loss of bulk hydrogen (in H₂O) by diffusion of H₂ through the capsule walls is for the AM starting material calculated to 95 % relative, corresponding to a Fe₂O₃/ (Fe₂O₃+ FeO)=0.91 and production of 9.6 wt% Fe₂O₃. Thus, it is possible to oxidize almost all bulk FeO to Fe₂O₃ simply by loosing the 1.1 wt% bulk H₂O, strongly affecting the f_{O_2} in the sample material. Use of boron nitride powder (in combination with MgO liners and MgO octahedra) in the multi-anvil experiments compared to MgO only in the piston-cylinder experiments might also result in relative more reducing f_{O_2} . At temperatures of > 1100 °C, iron diffusion (of ~2 wt% FcO_{tot} from the experimental charge to the capsule material) indicates alloying of metallic Fe⁰ and the AuPd-capsules, resulting in more oxidizing conditions than at lower temperatures.

3.4 Approach to equilibrium

Attainment of complete equilibrium for synthesis experiments can be difficult to demonstrate in experimental petrology. Experiments with the MC and AM bulk compositions in this study generally produced idiomorphic crystal shapes and chemically homogeneous phases (i.e. no compositionally zonation) throughout each capsule (Fig. 3.3A). The only exception is garnet showing growth zonation, which in a few experiments of the MC composition occur as inhomogeneous zonation in Ca-Mg content, and in four experiments with the AM composition as zonation with Fe-rich cores and Mg-rich rims or inhomogeneous Fe-Mg zonation (Fig. 3.3B). The homogeneous chemical composition of the garnet rims and all other phases within the samples together with regular trends throughout the entire experimental grid of the calculated phase proportions and phase compositions (including garnet) suggests a close approach to equilibrium. At subsolidus conditions and just above the solidus, textural equilibrium between the phases was also indicated by 120° triple point junctions. Small amounts of non-reacted starting material was encountered (as inclusions) in several of the phases in the experiments, indicating fast nucleation of the inclusion-bearing phases (garnet, kyanite, corundum, quartz, zoisite).

For 6 of the 11 experiments with the MA bulk composition, the carbonate generally reacted with biotite or silicate melt to produce Ca-Mg silicates such as garnet, clinopyroxene or zoisite (Fig. 3.3C), indicating that complete chemical equilibrium was not attained. Further, throughout the experimental P-T grid, phase compositions show no systematic change with P or T, thus also indicating general disequilibrium conditions. In all the MA experiments, needle-like and up to several µm large crystals resulted from quench crystallization, either as overgrowths on



Fig. 3.3. BSE-images of run products. (A) complete equilibrium crystallization (MC bulk composition at 3.0 GPa and 850 °C). (B) Fe-Mg-zonation in garnet (AM bulk at 5.0 GPa and 1100 °C). (C) Disequilibrium crystallization resulting in reaction-zones of garnet (or cpx or zoisite) between biotite and carbonate (MA bulk at 3.5 GPa and 1150 °C), and (D) Crystallization of quench products (muscovite, calcite and zoisite) overprinting the equilibrium phase assemblage (bt, gt, silicate melt, cor and carb) (MA bulk at 3.0 GPa and 1150 °C).

"stable" crystals or at the interface between settled crystals and melt (Fig. 3.3D). However, the MA experiments produced compositional fairly homogeneous biotites (lower octahedral occupancy than ideal biotite solid solution) as well-crystallized grains of $> 10 \,\mu\text{m}$ in size, suggesting that biotite is a stable phase in the entire investigated P-T grid.

3.5 Polishing methods

After quench and recovery, the capsules were mounted longitudinally in epoxy resin, then ground and polished to approximately the centre of the capsule, impregnated and then finepolished. Most experiments were polished by an automatic method using acid silica colloid
$(Syton) + H_2O$ or a by hand using diamond or aluminium paste. For the KNCaFMAS-HC experiments potentially producing carbonatite melt, dry-polishing using a aluminium sheet and boron nitride powder was applied before impregnation to avoid alkali-loss. Analyses showed only slightly higher alkali-contents of the dry-polished experiments compared to experiments polished with the wet-silica colloid method.

3.6 Analytical techniques

3.6.1 Electron Microprobe analyses (EMPA)

Experimental charges were analysed by a JEOL JXA8200 Superprobe mounted with five wavelength dispersive spectrometers (WDS) and one energy dispersive spectrometer (EDS) or a Cameca SX50 electron microprobe with five WDS spectrometers. Before analysing, all samples were coated with a ~20-30 nm thick layer of carbon. Operation conditions were 15 kV acceleration voltages, beam currents of 20 nA for silicate minerals and 5-10 nA for carbonates and quenched silicate and carbonate glasses. Natural and synthetic silicates, carbonates and oxides were used as standards. For the carbonates and quenched carbonate glasses, Ca and C were standardized on calcite, Mg on magnesite and Fe on siderite, and the carbon content was measured with a precision of 1.5 to 3 wt% C using a LDE2 type crystal. Acquisition time was 10-20 seconds for all elements except carbon (40 s), measuring sodium (10 s), potassium (10 s) and carbon first to avoid most elemental loss. A fully focused beam was applied to most water-free crystalline phases providing totals close to 100 wt%. Because micas, carbonates, coesite and glasses exhibited electron beam damage at a diameter less than 5 μ m, a defocused beam (2-50 μ m) was used whenever possible for these phases. The resulting data was automatically corrected for dead time of the detector, background and matrix effects (ZAF correction procedure; Pouchou & Pichoir, 1984). Textural phase relations were analysed from secondary and back-scattered electron images.

3.6.2 Scanning Electron Microscope (SEM)

Textural phase relations were also analysed from secondary and back-scattered electron images obtained from the JEOL JSM6300 high field emission SEM and the Camsean CS44LB SEM both mounted with an EDS. Operation conditions for the Camsean CS44LB SEM was ~1.8 mA beam current, 15 kV acceleration voltage and working distances between 11 and 35 mm. The JEOL JSM6300 high field emission SEM was used for the KNCaFMAS-HC experiments for textural relations between silicate and carbonatite melts, and operated with 5 kV acceleration voltage, 6 μA beam current and a working distance of 39 mm.

3.6.3 Micro-Raman spectroscopy

To distinguish between quartz or coesite, clinozoisite or zoisite and calcite or aragonite polymorphs, Raman spectra was obtained using a Dilor Labram 2 multi-channel laser system, equipped with a confocal optical microscope, a Peltier cooled CCD detector and an external Ar⁺ laser (coherent Innova 90C series), operating at of λ =488 nm, a ~0.5 W emission power and currents of 25-30 A. Spectral resolution was ~5 cm⁻¹, and spectra were recorded with Labspec software. To enhance the signal-to-background ratio and improve counting statistics, at least 5 spectra were acquired at counting times of 60 to 120 seconds. All measurements were carried out with a 100x magnification objective, resulting in a sample spot size of ~9 µm. Before analyzing, the peak position of the beam was calibrated on a quartz standard with peak at ~520 cm⁻¹. For the determination, acquired spectra were compared to spectra of phases of known composition (own data base).

3.7 Mass balance calculations

Mass balance calculations were performed for experiments indicating chemical and textural equilibrium. A modified version of the FORTRAN software MSROCK and MSCARLO

(Contributors: A. Colombi, S. Poli, E. Reusser and modified by M.W. Schmidt 1997-2005) were used to calculate modal amounts (in wt%, cat%, and oxy%) from mineral (in apfu or wt%) and bulk compositions (in wt%). MSROCK (performing regression) was used for simple mass balance, calculating a best fit of the modal phase proportions. MSCARLO was employed for error calculation propagation using a Monte-Carlo technique. This method repeats mass balance calculations, each time varying the input data randomly within their limits of precision (e.g. Anderson, 1980), resulting in mass balance phase abundances with a mean error value. For MSCARLO, the standard deviation (1σ) of individual oxide concentrations obtained from the microprobe analyses of each phase were used to calculate the error of the phase proportions that best fitted with the proportions calculated by the MSROCK regression procedure. The number of repeats for each experimental charge was between 10.000 and 20.000. In many of the calculations, some oxides were excluded from the calculations (described in detail in chapters 4, 5 and 6).

Chapter 4

The biotite to phengite transformation and mica-dominated melting in carbonate-saturated pelites at high pressures: Implications for water and CO₂ in subduction zones

The biotite to phengite transformation and micadominated melting in carbonate-saturated pelites at high pressures: implications for water and CO₂ in subduction zones

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Abstract

Subsolidus and melting experiments were performed at 2.0-3.7 GPa and 750-1300 °C in KCaMAS-HC to define K-mica stability fields and to establish fluid-present melting conditions. The biotite to phengite transformation occur with pressure from 2.4 to 2.6 GPa between 750 and 850 °C, and the amphibolc to clinopyroxene reaction to 875 °C at 2.0 GPa to 740 °C at 2.5 GPa. These reactions preserve K₂O, but are not H₂O conservative, as H₂O is produced from decomposition of zoisite and amphibole. Phengite controls fluid-saturated melting at > 2.6 GPa, whereas biotite dominates at < 2.4 GPa (and at 2 GPa also amphibole). The solidus is located at 850-950 °C. at which 7-24 wt% metaluminous K-rich granitic melts are produced. Initial melting occurs through the reactions phengite+zoisite+coesite = silicate melt+clinopyroxene+kyanite (at>2.5 GPa) and biotite+zoisite+quartz (\pm amphibole) = silicate melt+clinopyroxene+kyanite (at <2.5 GPa). The liquidus surface is dominated by peritectic melting first by zoisite and with increasing temperature clinopyroxene. The experiments suggest that in most subduction zones, CO, and H₂O will be carried to depths in excess of 120-150 km through carbonates and K-micas, as melting occurs at temperatures unlikely for most subduction zones. However, the release of H₂O through pressurized decomposition of amphibole and zoisite provides a H₂O source for arc magma formation. Further, melting at higher temperatures (due to slower burying rates or by crustal incorporation into the mantle), will provide a substantial volatile source for the formation of arc magmas.

4.1. Introduction

Subsolidus reactions and melting in the crust are generally controlled by the availability of fluids, mainly composed of H_2O and CO_2 , or, in absence of a free fluid phase, by the stability of hydroxylated and carbonated minerals. The latter control the recycling of volatile components into the mantle (Thompson, 1988; Ono et al., 1998; Schmidt & Poli, 1998; Vielzeuf & Schmidt, 2001). Natural marls are oceanic shelf or platform type sediments (Bucher & Frey, 2002) composed of a carbonate and a pelitic component with possible volcano-sedimentary (volcanic ashes) and siliccous components in addition (Plank & Langmuir, 1998). Marls or calc-silicates are present in minor volumes in most metamorphic high pressure terrains, nevertheless are widely distributed in the European Alps (Enami, Liou & Mattinson, 2004; Droop et al., 1990). In subduction zones, they have the potential to carry water and carbon into the upper mantle, and through devolatilization or melting to influence arc magmatism.

Low-pressure, high-grade marls and pelites contain biotite as the dominant potassic mica (e.g. Ferry 1976, 83a,b; Frank 1983; Frey 1978; Thompson 1975, Spear 1995; Bucher & Frey 2002), whereas high-pressure marls, pelites, and greywackes have phengite, i.e. Si-rich muscovite (e.g. Ogasawara et al. 2000, Dominak & Holloway 2000; Dachs 1986, Spear 1995, Bucher & Frey 2002; Schmidt at al. 2004), but the conditions and nature of the biotite to phengite transition with pressure are poorly defined. Coexistence of phengite and phlogopite in marls and impure carbonates are reported by Dachs (1986, 1990) in the Eastern Alps (Eclogite Zone, Tauern) suggesting a broad mica transition zone between ~ 0.6 and 2.0 GPa at $T_{max} \sim 550-600$ °C. Natural mafic, pelitic, and carbonate bearing eclogites (e.g. Corsica: Caron and Pequinot 1986; Adula nappe, Alps: Heinrich 1986, Meyre et al. 1999, Droop et al. 1990; San Franciscan: Sorenson 1986, Domanik et al. 1993; Dabie Shan: Zhang et al. 1995; Kazakhstan: Ogasawara et al. 2000) and experiments above 2.4 GPa on such lithologies (Schmidt et al. 2004; Hermann, 2002; Hermann & Green, 2001; Schmidt & Poli, 1998 and references therein; Massonne & Spzurka, 1997; Dominak

& Holloway, 1996; Massonne, 1992; Massonne & Schreyer, 1987, 89) have phengite as the principal potassic phase. For pelites, greywackes and basalts, biotite and amphibole dominate the volumetric major fluid-absent melting reaction at pressures below 2.5-3 GPa (Vielzeuf & Holloway 1988; Winther & Newton 1991; Patiño Douce & Beard 1995; Schmidt et al., 2004; Auzanneau et al., 2006), whereas at pressures higher than 3 GPa (and to ~8-10 GPa) phengite is the only hydrous potassic phase (Schmidt et al., 2004; Poli & Schmidt, 2002; Ono 1998). The biotite to phengite transformation thus has major implications for the melting behaviour, also because the potassium minerals are among the phases that disappear first during melting. Hence, the aims of this work were to study the phase petrology of carbonate-saturated pelites focusing on (1) the reactions controlling the composition and stability of the potassic micas i.e. the biotite to phengite transformation at subsolidus conditions, and (2) the melting reactions, conditions and melt compositions at pressures in the vicinity of the transition.

4.2. Experimental methods

Experiments were performed in the model system $K_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O-CO_2$ (KCaMAS-HC), constituting the simplest chemical system able to produce the mineralogy of carbonate saturated pelites. The major differences of this simplified system with respect to the natural system are the lack of iron and sodium. The absence of Na₂O suppresses crystallization of jadeitic or omphacitic clinopyroxene and of sodic amphiboles, whereas FeO is distributed among the magnesian phases, thus not producing additional phases. Nevertheless, the lack of FeO greatly shifts the stability field of garnet to higher pressures and temperatures.

4.2.1 Experimental apparatus

Experiments were conducted in an end-loaded 14 mm bore piston cylinder apparatus. Assemblies were all composed of an outer NaCl sleeve, a pyrex glass sleeve, a straight graphite heater, a corundum disc between thermocouple and capsule and cylinders of crushable MgO inside the furnaces. A friction correction of 3 % applied to the nominal pressure was obtained by calibration against the fayalite+quartz = ferrosilite reaction at 1000 °C and 1.41 GPa (Bohlen et al, 1980) and against the quartz-coesite transition reaction at 3.07 GPa and 1000 °C (Bose & Ganguly, 1995). Hydraulic pressure was maintained by an automatically controlled screw worm jack with a relative precision better than 0.3 bar oil pressure, equivalent to 2.5 MPa sample pressure. Temperature was controlled by a Eurotherm controller within ± 2 °C using a B-type thermocouple (Pt₉₄Rh₆-Pt₇₀Rh₃₀), not corrected for the pressure effect on thermocouple emf. The capsules were centred at the hot spot to within ± 0.5 mm, the thermocouple tip thus recording the coldest temperature in the capsule. Thermal gradients within the capsules at 2.0 GPa and e.g. 1300 °C were measured to ± 10 °C. Below 1000 °C pure gold capsules were used and at ≥ 1000 °C Au_{so}Pd_{so} capsules. All capsules were welded at one end, fired and then filled with starting material, previously dried at 110 °C, and then welded shut. One capsule of 3 mm O.D. or two capsules (placed side by side) of 2.3 mm O.D. and 3.8 mm length were used. Experiments were quenched by turning off power to the furnace, resulting in a temperature drop to < 200 °C within 10 seconds. Capsules were mounted longitudinally in epoxy, ground and polished to the centre of the capsule.

4.2.2 Starting material

The bulk composition (Tab. 4.1) corresponds to a mica-rich marl producing ~ 20 wt% mica and ~ 4.5 wt% carbonate if all potassium and CO₂ is stored in micas and carbonates, respectively. The base of the starting material is a synthetic glass made of oxides (SiO₂, Al₂O₃, MgO, CaO) mixed with natural alkali feldspar. The glass was ground to $< 5 \,\mu$ m in an automatic mill employing agate mortars with ethanol and then fired at 1300 °C during 45 minutes using a new Pt-crucible. The milling, grinding and firing was repeated three times to ensure homogeneity of the glass (controlled by microprobe, using a defocused beam). The glass was then pulverized,

Table 4.1. Bulk starting composition (in wt%) and two mark

	Bulk MC	Ant543ª	Frey(78) ^b	GLOSS
\$iO ₂	51.44	46.57	44.5	58.57
Al ₂ O ₃	21.79	17.99	18.3	11.91
FeO _{tot}	0	7.38	4.8	5.21
MgO	7.36	1.61	2.8	2.48
CaO	11.79	5.45	9.7	5.95
Na ₂ O	0	1.91	1.4	2.43
K ₂ O	1.94	2.83	3.4	2.04
H ₂ O	3.60	11.97	2.8	7.29
CO2	2.09	3.83	10,7	3.01
SUM	100.0	99.5	98.4	98.9
Al/(K+2*Ca) ^{molar}	0.48	0.79	0.47	0.50
AI/K ^{molar}	10.38	5.87	4.97	5.39
X_{co2}^{d}	0.19	0.12	0.61	0.14

Fe-calcareous claystone (Plank and Langmuir 1998)

^b Calc-schist from Alps (Frey, 1978),

^c Global Subducting Sediment (GLOSS, Plank and Langmuir 1998). ^d molar CO₂/(CO₂+H₂O)



Fig. 4.1. Composition space and subsolidus chemography of carbonate-saturated pelites in KCaMAS-HC with MC starting bulk composition and theoretical phase assemblages (thin lines) near the biotite to phengite transformation. Mineral solid solutions are indicated by thick solid bars and grey fields represent the range of experimental produced melt compositions.

weighted and mixed with the Al(OH), and CaCO₄ to introduce the desired proportions of H₂O and CO₂. Free water or CO₂ was not added to allow precise control of the amounts of volatiles and to prevent volatile-loss during welding. To enhance reaction rates, the composition had approximately 2 wt% water in excess relative to the amount of H₂O bound in the expected hydrous phases under subsolidus conditions (biotite, muscovite, zoisite and amphibole). Furthermore, most sub- and nearsolidus runs were saturated in dolomite, buffering the CO_2 content in the fluid. The bulk composition was chosen to maximize component saturation at sub- or near-solidus conditions (with SiO₂ > Al₂O₃ resulting in a SiO₂polymorph and kyanite), i.e. to achieve the highest possible number of saturated phases, reducing the thermodynamic composition space (Fig. 4.1). Phase compositions produced under subslidus conditions were fully buffered, thus are expected to change systematically with temperature and pressure.

4.3. Techniques

4.3.1 Analytical techniques

Experimental charges were analysed by a JEOL JXA8200 or a Cameca SX50 electron microprobe using silicates, carbonates and oxide standards, 15 kV acceleration voltages, a beam current of 20 nA for silicate minerals and 10 nA for carbonates and quenched glasses. Acquisition times were 10-20 seconds for all elements, measuring potassium first (10 s) to avoid most alkali loss. A fully focused beam was applied to most water-free crystalline phases providing totals close to 100 wt%. Because micas, carbonates, coesite and glasses exhibited electron beam damage at a diameter less than 5 μ m, a defocused beam (2-50 μ m) was used whenever possible for these phases. No attempt has been made to correct for potassium loss of phases analysed with < 5 μ m beam for analyses resulting in equal potassium contents as analyses obtained with a \geq 5 μ m beam size. Textural phase relations were analysed from secondary and back-scattered electron images obtained from the microprobes as well as a Camscan CS44LB scanning electron microscope equipped with an EDS. Polymorphs of phases were determined by micro-Raman spectroscopy using an argon laser with λ =488 nm.

4.3.2 Attainment of equilibrium and mass balance calculations

All runs in this study are synthesis experiments. Generally, all samples show textural equilibrium between the phases (e.g. 120° triple point junctions and well-developed crystal shapes). Apart from garnet, which in a few samples exhibit zonation in Ca-Mg content, the phases used in mass balance calculations were compositionally homogeneous (for garnet, rim compositions were used). Except at 2.0 and 2.5 GPa, both 850 °C, the number of phases in the experiments does not exceed those permitted by the phase rule, indicating no metastable phases present. Regular trends throughout the entire experimental grid of the calculated phase proportions and phase compositions also indicate that equilibrium conditions were reached in

most experiments. Two experiments at 2.0 and 2.5 GPa at 750 °C remained extremely fine grained, resulting in suboptimal analytical conditions, and for the experiment at 2.5 GPa and 900 °C, the melt composition could not be determined due to fine intermixing of kyanite with melt. Hence, for the five experiments mentioned above, phase proportions are estimated from BSE and element distribution maps. Calculated phase proportions were obtained by a non-weighted least square fit mass balancing the bulk starting composition against averaged mineral phases. Standard deviations of the resulting phase proportions were determined by Monte Carlo error propagation from the uncertainties in the phase compositions which were dominated by phase homogeneities. At subsolidus conditions, 6 phases and excess fluid were produced in the 7 component system, thus it was necessary to include a fluid in the mass balance calculations. However, as the experimental fluid composition was not determined, we selected a X_{co_s} of 0.14, as calculated at 750-850 °C along a high-temperature geotherm (Kerrick and Connolly, 2001) for an average marine sediment bulk composition (GLOSS in Plank and Langmuir, 1998) comparable to our system (Tab. 4.1). For experiments above the solidus producing less than 6 phases (incl. glass and fluid) mass balance calculations were carried out without H2O and CO2 (as the solubility of H₂O and CO₂ in the melts and hence fluid composition is unknown). Calculated deficiencies in K₂O are attributed to the analytical procedure of small glass pools (electron beam damage).

4.4. Experimental results

Experimental run conditions, resulting phases and calculated phase proportions are listed in Tab. 4.2. A total of 33 experiments were performed at 2.0 to 3.7 GPa and 750-1300 °C defining phase stabilities, devolatilization and melting reactions in P-T space (Fig. 4.2). All experiments above the solidus have rounded vesicles in the glass (e.g. Fig. 4.3G+H), demonstrating that fluid was present. Throughout the investigated P-T grid, dolomite constitutes the carbonate mineral, stable to higher temperatures at higher pressures (~ 950 °C at 3.5 GPa compared to ~ 850

Table 4.2 A. Experiment	al run c	onditic	ons and ca	lculated of	lase propol	rtions (wt%)	e.										B. Compo	sition of dolor
Run no. P	ŀ	Time	biotite	phengite	transitional	Xdo	zoisite	garnet	diass	amphibole	dolomite	calcite	kvanite	conndum	011arth /	fluid ^e	dolomite	u yarriet Zoisite
(GPa)	() (0)	hours)			mica			,	5						coesite	(excess)	X _{Ma} [†]	(njd) bw
MC05° 2.0	750	88	18	ł	ı	ſ	42			10	3	1	7	1	18	2	0.480	0.087 (42)
MC-04° 2.0	850	140	თ	I	I	22	52	1	10	8	ı	ı	15	ı	11	e	1	0.084 (72)
MC-08 2.0	950	112	ı	1	I	48.9(1.7)	I	1	26.9(1.9)	ı	I	1	24.2(1.0)	ı	I	present	1	, , 1
MC-15 2.0	1050	52	ı	ı	I	50.6 (2.3)	I	0.3 -	29.8(1.9)	ı	1	1	19.3(1.2)	ı	I	present	1	I
MC-11 2.3	750	143	20.3	1	ı	1	40.3	I	ı	10.2	3.1	I	6.6	ı	17.4	2.2	0.483	0.082 (24)
MC-20 2.3	800	166	21.7	1	ı	9.9	35.5	1	ı	1	2.9	ł	9.7	1	17.6	2.6	0.466	0.118 (12)
MC-12 2.3	850	112	16.2(1.9)	ı	ı	25.5(1.3)	24.8(2.3)	ı	1	ı	ı	ı	14.8(1.0)	ı	15.4(1.1)	3.3	1	0.125 (43)
MC-13 2.3	906	121	,	ı	1	47.8(1.8)	1	1	25.2(2.0)	ı	1	ı	26.9(0.7)	ı	,	present	·	
MC-22 2.4	750	150	22.7	ı			42.5	1	I	4.8	3.2	ı	6.6	ı	18.1	2.2	0.472	0.135 (40)
MC-17 2.4	800	107	18.8	1		13.3	32.6	i	ı	1	2.8	1	11.6	ı	18.0	2.9	0.488	0.096 (14)
MC-21 2.4	850	116	1	18.8	ı	33.5	12.2	ı	1	ı	2.6	,	17.1	ı	12.5	3.4	0.474	. 1
MC-06° 2.5	750	121	5	თ	v	4	32	1	,	18	ო	ı	17	,	10	present	0.477	0.137 (63)
MC-24 2.5	800	141	ı	18.8	,	32.9	11.7	,	1	ı	2.5	I	18.3	ı	12.4	3.4	0.474	0.066 (14)
MC-03° 2.5	850	104	ı	12	ř	38	თ	,	7	ı	5	ı	20	ı	ക	3.0	0.475	0.068
MC-38° 2.5	006	285	ı	1	,	48	2	1	15	ı	1	ı	25	,	0	present	1	I
MC-07 2.5	950	107	ı	1	I	50.9 (1.4)	ł	,	24.6(2.0)	1	,	ı	24.5(1.6)	ı	ı	present	1	ı
MC-09 2.5	1050	69	ı	1	1	46.2 (2.0)	ι	0.1	32.4(1.3)	ı	1	ı	21.3(1.3)	ı	ı	present	1	ı
MC-26 2.5	1100	88	ı	ı	ı	45.0(1.7)	ı	4.3(2.1)	33.3(1.1)	I	I	ı	17.4 (1.0)	ſ	1	present	1	i
MC-27 2.5	1200	74	1	ι	ı	10.6 (1.4)	ı	16.3(1.7)	71.4 (1.5)	I	ı	ı	,	1.7(0.3)	I	present	1	ı
MC-31 2.5	1250	85	1	1	I	ı	ı	23.2(0.8)	76.8(0.8)	ı	ı	ı	1	⊽	1	present	1	I
MC-35 2.5	1300	87	1	ł	I	t	ı	1	00.0(1.3)	I	1	I	1	1	ı	present	1	ı
MC-16 2.7	800	184	ı	18.2	ı	33.7	11.5	1	ı	ı	2.5	ı	18.5	1	12.3	3.4	0.479	0.081 (41)
MC-25 2.7	850	116	I	18.4	1	35.7	10.9	1	ı	I	2.5	ı	17.6	I	11.6	3.4	0.475	0.081 (8)
MC-01 3.0	850	129	i	18.1	ı	36.0	10.3		I	1	2.5	ı	18.3	I	11.3	3.5	0.489	0.071 (16)
MC-36 3.0	006	121	ı	17.4	I	38.0	8.0	,	ı	1	2.4	ı	19.2	1	11.4	3.6	0.459	0:050
MC-18 3.0	950	172	ı	•	ı	43.0	ı	ī	19.8	1	1.2	v	27.7	1	6.0	present	0.469	I
MC-02 3.5	850	117	t	17.5	I	36.7	8.9	1	ı	,	2.4	ſ	20.4	ı	10.7	3.5	0.467	0.073 (32)
MC-23 3.5	950	68	,	ł	ı	49.9	1.6	1	23.8	1	ı	ı	24.5	I	0.3	present	I	0.013 (23)
MC-28 3.5	1150	68	ι	ı	I	35.2(1.7)	ī	11.2(1.9)	35.8(0.6)	1	ı	r	17.9(0.7)	1	ı	present	1	I
MC-29 3.5	1200	8		I	ı	10.0(2.3)	1	29.2(1.9)	51.1(1.1)	,	ı	1	9.7 (0.6)	I	ı	present	1	ŧ
MC-30 3.5	1250	96	ı	1	ł	ı	1	31.8(1.0)	62.3 (0.8	1	ı	I	5.9 (0.4)	ı	ı	present	I	1
MC-34 3.5	1300	2	,	ı	ı	I	ı	21.5(1.2)	72.2 (1.1	1	ı	1	6.3(0.5)	I	ı	present	1	ł
MC-37 3.7	1100	146	ı	I	ı	49.1 (2.6)	1	1.7(1.0)	26.6 (1.3	1	ı	1	22.7 (1.2)	I	ı	present	I	ı
MC-33 5.0	1050	28	ı	18.9	I	ı	,	38.6	1	I	ī	8.1	11.9	ı	22.5	present	0.444	ı
MC-32° 5.0	1200	99	ı	'	'	-	-	39	15	ı	2		20	I	22	present	1	1
^a Numbers in p. ⁵ Comolete com	aranthe: mositior	ses are	one stand:	ard deviation	n in wt%. Fo	or experimen ments	its with 6 pH	ases and e	xcess fluid,	standard de	eviations ca	nnot be ca	culated.					

0.253 0.241 0.241 0.282

I Т 0.335 0.381 0.353 0.353

0.469 0.464

I

0.220

1 T I = I = I

1

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gamet

B. Composition of dolomite,

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Compete compositions are available in the exertance in the exertance supportance of a physic controlled (only MC03 and MC04) by recalculation and fitting of the analysed phase compositions and estimated proportions to the bulk oxide con Estimated weight proportions from microprobe BSE and elemental mapping images, controlled (only MC03 and MC04) by recalculation and fitting of the analysed phase compositions and estimated proportions to the bulk oxide con For experiments with glass and less than 6 phases, mass balance calculation is performed leaving out H₂O and CO₂. Thus, phase proportions are calculated on a fluid-free basis and sum to f00 wf%.

' XMg = Mg/(Ca+Mg). MgCO₃ endmember content in the calcite-dolomite-magnesite system. ^a XMg = Mg/(Ca+Mg)



Fig. 4.2. Pressure-temperature diagram of the experimental result below 4.0 GPa with stability fields of phase assemblages in KCaMAS-HC. Thick solid lines represent the experimental solidus and liquidus and points individual experiments. Quartz/coesite transition from Bohlen & Boetcher (1982).



Fig. 4.3. BSE-images of run products (P in GPa and T in °C). (A) Phengite stability field, (B) Initial melting at 3.5 GPa (no dolomite), (C) Biotite+clinopyroxene stability field, (D) The first melt at 2.5 GPA coexists with phengite and transitional mica (not shown), (E) Biotite+amphibole stability field, (F) Coexisting biotite+amphibole+melt+clinopyroxene at 2.0 GPa and 850 °C. Rounded holes after fluid in melt+ clino-pyroxene+kyanite stability field (G) and the melt+garnet+clinopyroxene+kyanite stability field (H).

°C at 2.3 GPa). The SiO₂-polymorph (quartz/cocsite) is stable to 850 °C at 2.0 GPa and 1050 °C at 3.5 GPa. Between 2.0 and 2.5 GPa partial melting confines the solidus to ~ 850 °C, whereas at 3.0-3.5 GPa melting occurs at 900-940 °C. Zoisite is stable to a few 10's °C above the solidus, i.e. to ~ 900 °C at 2.5 GPa and to 970 °C at 3.5 GPa, in this pressure range, zoisite is the last hydroxylated phase to disappear through melting. Clinopyroxene is present in almost all experiments of this study, except in the lower pressure and temperature region (≤ 875 °C at 2.0 GPa to ≤ 750 °C at 2.5 GPa), where amphibole replaces clinopyroxene; amphibole being restricted to this part of the P-T grid. Garnet emerges between 950-1050 °C and is stable to the liquidus at 1300 °C (2.5 GPa). Kyanite is almost omnipresent within the P-T diagram except at the highest temperatures at 2.5 GPa, where it is replaced by corundum (at ≥ 1200 °C).

The experiments result in three distinct regions: a phengite and a biotite stability field scparated by a narrow mica transition zone between 2.4 and 2.6 GPa. At higher temperatures micas no longer exist and a silicate melt is produced, coexisting with clinopyroxene, kyanite and at higher temperatures with garnet and then corundum (Fig. 4.3B, D, F-H). Phengite is stable to 860 °C at 2.5 GPa and to 940 °C at 3.5 GPa. In this field, phengite is the only potassic phase present and coexists with clinopyroxene, zoisite, dolomite, kyanite, coesite/quartz and an excess H_2O-CO_2 fluid (Fig. 4.3A). Below the mica transition zone, phengite is absent and several biotite-present stability fields can be determined with slightly different coexisting phase assemblages (Fig. 4.2, 4.3C+E, Tab. 4.2). Together, these smaller stability fields constitute the P-T region at \leq 850 °C and 2.4 GPa.

4.4.1 Crystallization and phase compositions

Phengites typically form $\leq 15 \,\mu$ m laths or tabular grains, sometimes clustering in larger aggregates up to 40 μ m in size. Not all experiments have grains large enough to be analysed with a defocused beam, introducing potential for K-loss during microprobe analyses. The measured

potassium contents of the phengites, however, indicate less than 3 % K-loss (except run MC36 at 3 GPa and 900 °C). Phengites in the KCaMAS-HC system are mainly a solid solution between muscovite KIIAl₂[AlSi₃]O₁₀(OH)₂ and MgAl-celadonite KIIMgAl[Si₄]O₁₀(OH)₂, the inverse Mgtschermak's substitution (MgSiAl,) being the dominant exchange mechanism. For most of the analysed phengites (Tab. 4.3A), the sum of cations is close to the 7.0 apfu of ideal dioctahedral micas (Velde, 1965). Nevertheless, the magnesium content of the phengites, especially at ≤ 3.0

Table 4.3. Compositions of micas

A. Phengite co	omposition								
P(GPa) / T(°C)	2,4 / 850	2.5 / 800	2.5 / 850 ^h	2.7 / 800	2.7 / 850	3.0 / 850	3.0 / 900	3.5 / 850	5.0 / 1050'
No. analyses ^b	9	9	16	9	8	17	6	24	7
SiO ₂	49.51 (0.95)	50.71 (1.14)	49.95 (1.46)	50.03 (0.97)	50.60 (0.87)	51.36 (0.78)	48.88 (1.09)	52.52 (0.87)	54.16 (0.33)
Al ₂ O ₃	27.38 (1.36)	27.69 (1.00)	27.94 (1.64)	27.68 (0.41)	28.68 (0.65)	28.28 (0.66)	24.29 (1.11)	26.12 (0.89)	22.80 (0.28)
MgO	7.04 (0.39)	5.75 (0.43)	6.75 (0.63)	5.87 (0.43)	5.21 (0.24)	5.04 (0.20)	4.78 (0.41)	4.99 (0.32)	6.01 (0.27)
CaO	0,31 (0.09)	0.64 (0.48)	0.29 (0.30)	0.24 (0.12)	0.22 (0.09)	0.25 (0.19)	1.75 (0.75)	0.20 (0.11)	0.17 (0.09)
K ₂ O ^c	10.21 (0.52)	10.26 (0.32)	10.49 (0.58)	10,54 (0.28)	10.50 (0.25)	10.42 (0.68)	10.61 (0.36)	10.83 (0.31)	11.08 (0.18)
H ₂ O _(enic) ^d	4.49 (0.03)	4.53 (0.04)	4.54 (0.04)	4.49 (0.04)	4.54 (0.02)	4.56 (0.06)	4.27 (0.05)	4.52 (0.02)	4.50 (0.03)
Sum ^e	98.96 (0.53)	99.59 (0.73)	99.95 (0.70)	98.86 (0.73)	99.76 (0.42)	99.91 (0.83)	94.58 (1.01)	99.17 (0.38)	98.72 (0.64)
Si	3.303 (66)	3.354 (60)	3.307 (80)	3.338 (40)	3.338 (42)	3.378 (23)	3.435 (44)	3.485 (52)	3.611 (13)
Al [™]	0.697 (66)	0.646 (60)	0.693 (80)	0.662 (39)	0.662 (42)	0.622 (81)	0.565 (45)	0.515 (52)	0.389 (13)
AI ^{VI}	1.456 (45)	1.513 (41)	1.478 (67)	1.516 (22)	1.569 (21)	1.571 (97)	1.446 (73)	1.528 (28)	1.402 (15)
Mg	0.700 (41)	0.567 (46)	0.666 (65)	0.584 (44)	0.512 (24)	0.494 (15)	0.501 (49)	0,493 (32)	0.597 (24)
Са	0.022 (6)	0.046 (34)	0.023 (22)	0.017 (8)	0.016 (7)	0.017 (13)	0.132 (58)	0.014 (8)	0.012 (6)
к	0.869 (47)	0.865 (27)	0.881 (52)	0.897 (27)	0.884 (23)	0.875 (67)	0.951 (32)	0.916 (29)	0.942 (17)
н	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Tot. cations	7.048 (43)	6.991 (37)	7.047 (56)	7.014 (24)	6.981 (28)	6.957 (44)	7.031 (55)	6.951 (31)	6.954 (9)
Oct. vacancy	0.843	0.919	0.856	0.900	0.918	0.935	1.012	0.979	1.001

			Bioti	ites			Trans. mica
P(GPa) / T(°C)	2.0 / 850	2.3 / 750	2.3/800	2.3 / 850	2.4 / 750	2.4 / 800	2.5 / 750 ^h 2.5 / 85
No, analyses ^b	4	2	4	17	3	10	2
SiO ₂	43.44 (0.84)	44.48 -	46.86 (1.35)	42.97 (1.21)	47.16 (0.79)	44.81 (1.06)	50.57 46.8
Al ₂ O ₃	18.42 (1.47)	16.38 -	17.45 (0.25)	19.53 (0.95)	16.00 (0.70)	17.46 (0.49)	22.65 21.7
MaO	22.73 (1.26)	19,16 -	21.81 (0.48)	19.03 (0.91)	22.50 (0.62)	21.73 (0.51)	9.50 15.3
CaO	0.28 (0.09)	0.30 -	0.37 (0.12)	0.25 (0.23)	0.51 (0.20)	0.26 (0.17)	2.04 0.4
K ₂ Q ^c	9.93 (0.27)	8.86 -	8.91 (0.50)	9.63 (0.32)	8.29 (0.51)	10.12 (1.11)	8.54 10.4
H ₂ O _(reic) ^d	4.35 (0.02)	4,26 -	4.45 (0.06)	4.24 (0.06)	4.42 (0.04)	4.35 (0.03)	4,44 4.4
Sum ^e	99.14 (0.42)	93.43 -	99.86 (1.09)	95.64 (1.18)	98.89 (0.28)	98.73 (0.53)	97.72 99.1
Si	2.991 (46)	3.194 -	3.154 (58)	3.070 (75)	3,197 (102)	3.085 (61)	3.412 3.1
AI ^{/∨}	1.009 (26)	0.806 -	0.846 (58)	0.930 (75)	0.846 (58)	0.915 (61)	0.588 0.82
AI ^{VI}	0.486 (84)	0.518 -	0.539 (31)	0.657 (36)	0.539 (31)	0.503 (31)	1.212 0.93
Mg	2.332 (121)	2.033 -	2.188 (59)	2.004 (48)	2.274 (85)	2.230 (55)	0.957 1.5
Ca	0.021 (7)	0.023 -	0.027 (9)	0.028 (23)	0.037 (15)	0.019 (12)	0.147 0.03
к	0.819 (26)	0.775 -	0.765 (18)	0.862 (8)	0.717 (51)	0.889 (101)	0.734 0.9
н	2.000	2.000 -	2.000	2.000	2.000	2.000	2.000 2.0
lotal cations	7.658 (19)	7.348 -	7.520 (54)	7.551 (47)	7.610 (95)	7.642 (85)	7.051 7.4
Oct vacanced	0.182	0.449 .	0.273	0.339	0.251	0 267	0.831 0.5

 Oct. vacancy*
 0.102
 0.449
 0.273
 0.003
 0.001
 0.001
 0.001

 * Compositions in wt% and apfu based on 11 oxygens and 2 (OH). Numbers in parentheses are one standard deviation in wt% for weight fraction and in terms of last digit(s) for cations. Thus, for cations 3.354 (60) should be read as 3.354 ± 0.060 cat. ptu.
 0.000
 0.000
 0.000
 0.000
 0.000

^h Number of analysis considered as equilibrium phases and used in mass balance calculations. Standard deviations are reported only when there are at least three points to average.

^c Concentration of K2O corrected for potassium-loss during EMPA and used in mass balance calculations to achieve lowest possible residuals.

Calculated water contents.
 Calculated water contents.
 Analytical totals of oxide components including H₂O and corrected for K₂O due to mass balance calculations.

¹ Octahedral site vacancy calculated as: vacancy^{VI} = 7-(Si+AI+Mg) per 11 oxygens formula unit.

^h Mass balance not possible due to metastable phases (within mica transition zone).

GPa is slightly increased by up to 0.2 Mg pfu which implies a lower octahedral vacancy than for the ideal pseudobinary phengite solid solution (Fig. 4.4A). This feature is supported by a lower Al_{tot} and Si pfu content than for ideal phengites (Fig. 4.4B) and can be attributed to exchange along the dioctahedral-trioctahedral mica substitution (Mg₋₃Al₂□₁) between muscovite and phlogopite. From experiments at each side of the mica transition, just within the biotite and



Fig. 4.4. Composition of the biotites and phengites based on 11 oxygens. (A) Octahedral vacancy vs. Si diagram show the relation between phengite and biotite in terms of tschermak's and di-tri-octahedral mica exchange vectors (inset). (B) Si vs. Al diagram illustrating the close to ideal phengites and the non-ideal trioctahedral biotite behaviour. The net substitution vector between the biotites and phengites from each side of the mica transition is calculated to $Mg_{1.54}Si_{-0.23}Al_{-0.69}\Box_{-0.61}$. (C) shows phengite at 850 °C with a systematic increase in Si pfu towards higher pressure. (D) Decreasing K with increasing Si content indicates some solid solution of biotite towards talc. Diamonds = biotites, triangles = phengites, crosses = transitional micas.

phengite stability fields (i.e. at 2.3 and 2.7 GPa, respectively), the net exchange vector for phengite towards biotite is calculated to approximately $Mg_{1.54}Si_{.0.23}Al_{.0.69}\square_{.0.61}$. As expected, the silica content in the phengites increases with pressure, i.e. from 3.30 Si pfu at 2.4 GPa (850 °C) to 3.61 Si pfu at 5.0 GPa (1050°C) (isopleth for 850 °C in Fig. 4.4C), and Al_{tot} pfu decreases with increasing pressure. This is consistent with the results of previous studies in the KMASH (Massonne & Schreyer, 1987) and KCMASH systems (Hermann, 2002), and for phengites in general (Guidotti and Sassi, 1998, 2002; Velde, 1965, 1967). The difference in the location and slope of the phengite isopleths for the different chemical systems most likely reflects the various bulk compositions or, if present, the different buffering phase assemblages.

Similar to phengite, *biotites* forms small ($\leq 15 \,\mu$ m) laths. The compositions of the biotites (Tab. 4.3B) are more scattered than for the phengites, reflecting suboptimal analytical conditions. In a KCaMAS-HC system ideal biotite results from the Mg-tschermak's substitution (Mg, Si $_{1}Al_{2}$) within the solid solution phlogopite – castonite, i.e. $KMg_{3}[AlSi_{3}]O_{10}(OH)_{2} - KMg_{2}Al[Al_{2}Si_{2}]$ O₁₀(OH)₂. The sum of the cations for the analysed biotites varies between 7.35 and 7.66 apfu with octahedral occupancies from 2.55 to 2.82 pfu and interlayer cation vacancies of 0.11-0.28 pfu, suggesting non-ideal biotites with a cation-deficient interlayer and an octahedral vacancy of 0.18 to 0.45 pfu (Fig. 4.4A). With increasing pressure and decreasing temperature potassium contents decrease concomitant with an increase in silica contents, exceeding the upper limit of 3.0 Si pfu for ideal phlogopites. This results in a biotite stoichiometry, which can be understood as a result of a complex solid solution between the ideal biotite and phengite solid solutions, combined with a talc Mg₃[Si₄]O₁₀(OH)₂ component (Fig. 4.4B+D). The net exchange vector for the biotites is then a result of the dioctahedral-trioctahedral mica substitution (Mg_3Al,I],) and the Mg-tschermak's exchange (Mg_Si_Al_), joined with the K-edenitic substitution vector K_ ${}_{1}Al_{-1}Si$ towards talc. This complex substitution mechanism has recently been discussed by Comodi et al. (2004) for natural phlogopite and by Hermann (2002) for experimentally produced

Mg-biotites in the KCMASH system, suggesting that pressure favours the solid solution of phlogopite towards tale. Despite our limited P-T range yielding biotites, this effect is confirmed: the lowest silica content (2.99 Si pfu) is observed at 2.0 GPa (850 °C) increasing to 3.20 Si pfu at 2.4 GPa (750 °C).

Rare *transitional micas* with composition in between biotite and phengite are observed at 2.5 GPa within the mica transition zone, suggesting either the stable existence of such micas, polysomatic series, or sub-electron microscopic intergrowths of biotite and phengite.

Clinopyroxene forms compositionally homogeneous, $\leq 20 \,\mu m$ tabular to prismatic grains. At subsolidus conditions abundances of clinopyroxene and zoisite are inverse proportional, clinopyroxene dominating at higher pressures and temperatures. Clinopyroxenes contain very low contents of potassium (< 0.37 wt%), indicating insignificant incorporation of K in clinopyroxene at the investigated pressures. The normalisation scheme employed (Cawthorn and Collerson, 1974) allows for octahedral M2-site vacancies, representing the clinopyroxenes as a quaternary solid solution between diopside (CaMg[Si,]O₂), clinoenstatite (C-en, Mg,[Si,]O₂), Ca-tschermakite (Ca-Ts; CaAl[AlSi]O_s), and Ca-eskolaite (Ca-esk; Ca₀, []₀₅Al[Si₂]O_s) (Fig. 4.5A). Compositionally, the clinopyroxenes are Al-rich diopsides (Tab. 4.4), Al,O₃-contents increase with temperature from 4-5 wt% at 800-850 °C to almost 17 wt% at the highest temperature of 1200 °C (2.5 GPa). Above the solidus, silica contents decrease with temperature providing an increase in alumina on the tetrahedral site from 0.01 Al pfu at lower temperatures (850 °C) to 0.30 Al pfu at 1200 °C. Supported by the decrease in Mg with increasing temperature, this suggests an increase of tschermak's component (Mg, Si, Al₂) in clinopyroxenes with temperature (Fig. 4.5A). Calculated M2 site vacancies amount to 0.03-0.08 pfu corresponding to 6.3-16.2 mol% Ca-eskolaite, increasing with pressure at constant temperature. Experimentally produced clinopyroxenes with 4-9 mol% Ca-eskolaite (at 3.5 to 7.5 GPa and 740-1180 °C) were reported by Schmidt et al. (2004) in a pelite and greywacke bulk composition. For a KCMASH composition, Hermann (2002) reported Ca-



Fig. 4.5. (A) Clinopyroxene compositions with the endmembers diopside, clinoenstatite, Ca-tschermak and Ca-eskolaite. The Ca-tschermak's component increases with temperature and Ca-eskolaite with pressure. Note that the highest Ca-Eskolaite contents are at near-solidus temperatures. Typical standard deviation are indicated by the eclipse around the point closest to Ca-tschermak's component. (B) Garnet composition displaying an increase in grossular content with pressure.

cskolaite contents up to ~ 10 mol% at 4.5 GPa and 1100 °C, based on the correlation between the total cations and the excess Al pfu on the M1 site. The same relationship between M1, excess Al pfu, and total cation deficiency is observed in this study. In general, a comparison of Ca-eskolaite component in clinopyroxenes from this study with the experimental results of Hermann (2002), Schmidt et al. (2004), and natural clinopyroxenes from high pressure terrains (15-20% at 5.0 GPa and 1100 °C, Schultze et al., 2000; 8% at >3.3 GPa and 850 °C, Schmädicke & Müller, 2000; ~12% at 4.5 GPa and ~950 °C, Katayama et al., 2000) give comparable values. Nevertheless, in this study, the maximum Ca-eskolaite content at constant pressures are attained, not at the *highest* temperatures as in Hermann (2002) and Schmidt et al. (2004), but at *near-solidus* temperatures (850-950 °C) (Fig. 4.5A) similar to the experiments of Pertermann & Hirschmann (2003) at 3.0 GPa on quartz eclogites. Above the solidus, the Ca-eskolaite content is near-constant (at 2.0 GPa) or slightly reduced (at 2.5 and 3.5 GPa) with increasing temperature.

Garnets are generally idiomorphic, vary from < 5 to 100 μ m in size, and often contain

Table 4.4. Clino	oyroxene compo:	sition ^a											
P(GPa) / T(°C)	2.0 / 850	2.0/950	2.0 / 1050	2.3/800	2.3 / 850	2.3 / 900	2.4 / 850	2.4 / 800	2.5/800	2.5/850	2.5 / 900	2.5/950	2.5 / 1050
No. analyses ^b	80	10	7	16	14	7	80	14	Ģ	30	5	22	22
SIO ₂	53.67 (0.72)	53.10 (1.23)	50.55 (0.75)	54.43 (0.44)	54.26 (0.68)	54.28 (0.77) 54.55 (0.62)	54.04 (0.51)	54.72 (0.80)	54.56 (0.90)	53.29 (0.46)	52.94 (1.06)	51.79 (0.79)
Al ₂ O ₃	5.91 (0.58)	7.63 (1.04)	12.18 (0.53)	4.15 (0.40)	6.18 (1.35)	5.02 (1.09) 5.51 (0.83)	4.83 (1.04)	3.50 (0.53)	5.32 (1.28)	7.23 (0.62)	7.92 (1.39)	9.71 (0.95)
OBM	16.30 (0.36)	15.95 (0.79)	15.06 (0.36)	16.50 (0.43)	15.80 (0.79)	16.50 (0.51) 15.91 (0.56)	16.37 (0.84)	17.15 (0.45)	15.91 (0.59)	15.16 (0.29)	15.19 (0.73	15.08 (0.63)
cao	23.78 (0.37)	23.42 (0.43)	22.08 (0.31)	24.19 (0.42)	23.35 (0.84)	24.31 (0.54) 23.76 (0.57)	23.44 (0.38)	24.15 (0.34)	23.74 (0.52)	23.11 (0.24)	23.01 (0.57)	22.83 (0.44)
K20	0.08 (0.03)	0.13 (0.08)	0.19 (0.10)	0.06 (0.34)	0.07 (0.04)	0.14 (0.09) 0.18 (0.14)	0.08 (0.03)	0.25 (0.07)	0.07 (0.05)	0.15 (0.09	0.21 (0.15)	0.08 (0.04)
Sum ^c	99.84 (0.58)	100.23 (0.37)	100.06 (0.65)	99.89 (0.58)	99.74 (0.52)	100.24 (0.53) 99.90 (0.35)	99.06 (0.34)	99.78 (0.69)	99.60 (0.60)	98.94 (0.16)	99.27 (0.34)	99.51 (0.54)
si	1.921 (17)	1.889 (45)	1.796 (21)	1.959 (25)	1.937 (26)	1.937 (2:	() 1.947 (27)	1.951 (20)	1.963 (24)	1.952 (32)	1.917 (20)	1.898 (37)	1.852 (29)
AIN	0.079	0.111	0.204	0.041	0.063	0.063	0.053	0.049	0.037	0.048	0.083	0.102	0.148
АЙ	0.171	0.209	0.307	0.135	0.197	0.148	0.179	0.157	0.111	0.176	0.223	0.233	0.262
Мg	0.870 (14)	0.846 (44)	0.797 (21)	0.885 (18)	0.841 (43)	0.877 (23	 0.846 (27) 	0.881 (43)	0.917 (21)	0.848 (32)	0.813 (14)	0.812 (38)	0.804 (31)
Ca	0.912 (17)	0.893 (17)	0.840 (12)	0.932 (14)	0.893 (32)	0.929 (17	0:908 (20)	0.907 (14)	0.928 (11)	0.910 (21)	0.891 (10)	0.884 (22)	0.875 (17)
¥	0.004 (2)	0.006 (4)	0.009 (4)	0.003 (2)	0.003 (2)	0.006 (4	0.008 (6)	0.004 (2)	0.012 (3)	0.003 (2)	0.007 (4)	0.010 (7)	0.004 (2)
Total cations	3.956	3.954	3.953	3.955	3.934	3.961	3.941	3.948	3.969	3.938	3.934	3.939	3.945
Oct. vacancy	0.044	0.046	0.047	0.045	0.066	0.039	0.059	0.052	0.031	0.062	0.066	0.061	0.055
Ca-esc (mol%)	8.8	9.3	9.4	9.0	13.1	7.8	11.7	10.4	6.3	12.5	13.3	12.2	11.1

3.7 / 1100	14	52.70 (0.62)	8.87 (0.41)	14.83 (0.30)	22,68 (0.29)	0.12 (0.09)	99.39 (0.54)		1.887 (19)	0.113	0.261	0.792 (16)	0.870 (11)	0.005 (4)	3.929	0.071		14.30
3.5 / 1200	17	50.63 (0.66)	12.56 (1.05)	13.30 (0.62)	22.88 (0.23)	0.06 (0.02)	99.42 (0.40)		1.810 (21)	0.190	0.339	0.709 (32)	0.876 (11)	0.003 (1)	3.927	0.073		14.67
3.5 / 1150	~	51.49 (0.42)	10.46 (0.44)	14.20 (0.29)	22.63 (0.28)	0.07 (0.02)	99.06 (0.86)		1.851 (10)	0.149	0.294	0.761 (13)	0.871 (4)	0.003 (1)	3.929	0.071		14.16
3.5 / 950	16	54.68 (0.96)	6.41 (1.88)	15.23 (1.27)	22.63 (1.88)	0.37 (0.35)	99.56 (0.41)		1.954 (44)	0.046	0.224	0.811 (65)	0.866 (71)	0.017 (16)	3.919	0.081		16.17
3.5 / 850	7	55.48 (0.65)	3.92 (0.87)	16.05 (0.43)	23.83 (0.45)	0.09 (0.03)	99.38 (0.28)		1.988 (25)	0.012	0.154	0.857 (22)	0.915 (16)	0.004 (1)	3.931	0.069		13.86
3.0 / 950	19	53.63 (0.85)	6.48 (0.78)	15.18 (0.39)	23.88 (0.77)	0.12 (0.11)	99.47 (0.54)		1.927 (28)	0.073	0.201	0.813 (29)	0.919 (30)	0.006 (5)	3.939	0.061		12.25
3.0 / 900	9	54.21 (0.72)	6.08 (1.15)	15.54 (0.82)	23.45 (0.98)	0.15 (0.12)	99.48 (0.41)		1.941 (26)	0.059	0.198	0.829 (44)	0.900 (41)	0.007 (6)	3.934	0.066		13.22
3.0 / 850	22	54.59 (1.14)	4.78 (1.57)	16.28 (0.81)	23.90 (0.69)	0.11 (0.09)	99.65 (0.70	·	1.955 (35)	0.045	0.156	0.869 (45)	0.917 (28)	0.005 (5)	3.947	0.053		10.61
2.7 / 850	35	54.68 (0.90)	5.36 (1.49)	16.18 (0.83)	23.25 (0.94)	0.18 (0.11)	99.64 (0.61)		1.953 (33)	0.047	0.179	0.861 (41)	0.890 (33)	0.008 (5)	3.938	0.062		12.38
2.7 / 800	8	54.03 (0.74)	4.26 (0.86)	16.63 (0.63)	24.10 (0.49)	0.08 (0.04)	99.09 (0.49)		1.950 (27)	0.050	0.131	0.894 (33)	0.932 (17)	0.004 (2)	3.961	0.039	1	7.78
2.5 / 1200	13	47.43 (1.02)	16.98 (1.27)	12.54 (0.63)	22.45 (0.35)	0.06 (0.02)	99.46 (0.65)		1.697 (34)	0.303	0.414	0.669 (33)	0.861 (13)	0.003 (1)	3.946	0.054		10.81
2.5 / 1100	13	50.00 (0.64)	12.56 (1.09)	13.97 (0.68)	22.56 (0.39)	0.16 (0.14)	99.38 (0.26)		1.793 (23)	0.207	0.324	0.747 (36)	0.867 (15)	0.007 (6)	3.945	0.055		11.01
P(GPa) / T(°C)	No. analyses ^b	siO ₂	Al ₂ O ₃	MgO	CaO	K20	Sum ^c		Si	Al ^N	Al ^{vi}	Mg	Ca	×	Total cations	Oct. vacancy ^f		Ca-esc (mol%)

^a In wt% and cations ptu based on 12 charges (Cawthorn & Collerson, 1974). Numbers in parentheses are one standard deviation in wt%. (oxides) and in terms of last digit(s) (cations). Thus, 1:936 (22) is be read as 1:935 ± 0.022 cations ptu. ^b Number of analysis considered as equilibrium phases and used in mass balance calculations. Standard deviations are reported only when there are at least three points to average.

^c Analytical totats of oxide components.

d Octahedral M1 site (apfu)

Octahedral M2 site including calculated vacancy (aptu).
¹ Octahedrat site vacancy in pfu calculated as: 4 - total cations.

inclusions of kyanite and quartz/coesite. Garnet is formed by incongruent melting of kyanite + clinopyroxene, is compositionally homogeneous in most experiments, and displays a systematic increase in grossular (22 to 46 mol%, Tab. 4.2B) with pressure, but no significant change with temperature (Fig. 4.5B).

Amphibole forms $\leq 20 \ \mu m$ laths or tabular grains occasionally including aggregates of kyanite and quartz inclusions. The analysed amphiboles contain 1.77-1.87 Ca pfu, 7.1 to 7.5 Si pfu, and are magnesio- to tremolitic hornblendes exhibiting tschermak's substitution and some minor Ca, Mg substitution. In the poorly developed amphibole grains in the run at 750 °C and 2.5 GPa, close intergrowths with clinopyroxene is inferred from a measured composition lying between amphibole and clinopyroxene.

Run no.	2.0 / 750	2.0 / 850	2.3 / 750	2.4 / 750
No. analyses ^b	4	16	10	4
SiO ₂	53.42 (2.18)	51.99 (0.79)	54.29 (0.99)	54.90 (0.70)
Al ₂ O ₃	9.74 (1.99)	11.65 (0.88)	7.52 (0.94)	7.59 (0.77)
MgO	^{20.07} (1.40)	20.48 (0.55)	21.27 (0.55)	20.65 (0.85)
CaO	12.26 (1.05)	12.15 (0.46)	12.29 (0.56)	12.39 (0.75)
K ₂ O	0.34 (0.03)	1.14 (0.30)	0.63 (0.18)	0.64 (0.30)
H₂O(calc) ^c	2.18 (0.01)	2.20 (0.01)	2.18 (0.01)	2.19 (0.02)
Sum ^d	98.00 (0.19)	99.61 (0.47)	98.17 (0.52)	98.34 (0.79)
Si	7.341 (269)	7.081 (89)	7.496 (126)	7.522 (98)
AI	0.659	0.919	0.504	0.478
AI ^{VI}	0.920	0.952	0.662	0.757
Mg	4.110 (285)	4.157 (109)	4.397 (124)	4.186 (159)
Ca	1.805 (160)	1.772 (71)	1.767 (69)	1.868 (103)
к	0.059 (5)	0.198 (51)	0.128 (27)	0.087 (53)
н	2.000	2.000	2.000	2.000
Sum	14.894 (137)	15.080 (57)	14.953 (101)	14.899 (61)

Table 4.5. Amphibole compositions^a

^a In wt% and cations pfu based on 46 charges. Numbers in parentheses are one standard deviation in wt% or in terms of last digit(s). Thus, for cations 7.341 (269) should be read as 7.341 ± 0.269 cations pfu.

^b Number of analysis.

^c Calculated water content in wt%.

^d Analytical totals of oxide components.

Zoisite forms ≤ 20 im prismatic or tabular grains often comprising small inclusions of clinopyroxene, mica or incompletely reacted starting material. No significant systematic compositional changes are detected. Careful analyses of large homogeneous grains reveal up to 1 wt% MgO, indicating Mg-incorporation of up to 0.13 Mg pfu into the zoisite structure (Tab. 4.2B). The structure of zoisite was confirmed (with respect to clinozoisite) by micro-Raman spectroscopy, which agrees with the results of Brunsmann et al. (2002) and Poli and Schmidt (1998, 2004), reporting zoisite as the stable high pressure polymorph up to ~7 GPa at 1070 °C in a CASH system.

Dolomite typically forms $\leq 10 \,\mu\text{m}$ subidiomorphic grains with X_{Mg} of 0.44 to 0.49, slightly more calcic than a stoichiometric composition (Tab. 4.2B).

Kyanite, *quartz/coesite* and *corundum* are pure in composition, generally forming ≤ 25 im laths, tabular, or prismatic grains, often with irregular inclusions of all the other phases present in the phase assemblage as well as of incompletely reacted starting material. *Corundum* is most probably a product of incongruent melting of kyanite.

The first produced *glass (quenched melt)* forms small interstitial pools less than 5-10 μ m in size. At all pressures investigated, clinopyroxene, kyanite, and quartz coexist with the initial liquids. At 2.0 GPa further coexisting phases are biotite, amphibole and zoisite, and at 2.5 GPa phengite (+ transitional mica), zoisite and dolomite, whereas at 3.0 GPa dolomite and at 3.5 GPa zoisite constitute the additional coexisting phases. The initial liquids are relatively rich in K₂O (9-11 wt%) and SiO₂ (71-74 wt%), but low in CaO (2-4 wt%) and MgO (< 1 wt%) (Tab. 4.5), are metaluminous (Al/(K+2*Ca)=0.66-0.98) granites (Na-free) with a Al/K of 1.0-1.4 (Fig. 4.6), reflecting the dominance of mica and quartz/coesite in the solidus reactions. Within a temperature increase of 100-250 °C above the solidus, the melts become enriched in Mg, Ca, and Al, due to melting of clinopyroxene and kyanite, thus producing slightly peraluminous or metaluminous ((Al/(K+2*Ca) ~ 0.98-1.04) granites. Further temperature increase results in garnet crystallization and meta-



luminous liquids with Al/(K+2*Ca) ratios near 0.9 at 2.5 GPa and ~0.7-0.75 at 3.5 GPa, representing granodioritic to tonalitic melts at 2.5 GPa, and quartz-monzonitic liquids at 3.5 GPa.

4.5. Phase relations and abundances

Mineral and melt proportions across the biotite to phengite reaction in a nearly isothermal section below the solidus at 750-850 °C and along isobaric sections at 2.5 and 3.5 GPa are presented in Fig. 4.7. We first discuss the biotite to phengite and amphibole to clinopyroxene

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P(GPa) / T(°C)	2.0 / 850	2.0 / 950	2.0 / 1050	2,3/900	2.5 / 850	2.5 / 950	2.5 / 1050	2.5 / 1100	2.5 / 1200
No. analyses ^b	3	6	25	4	12	11	27	23	28
SiO ₂	70.27 (0.34)	70.51 (1.02)	71.09 (1.10)	71.60 (1.19)	72.15 (0.93)	71.58 (0.99)	69.54 (1.02)	70.74 (0.95)	59.70 (0.49)
Al ₂ O ₃	13.12 (1.04)	16.23 (0.52)	16.23 (0.59)	15.44 (1.82)	13.43 (0.28)	15.66 (2.04)	17.03 (0.39)	16.19 (0.19)	21.63 (0.28)
MgO	1.77 (0.71)	1.12 (0.65)	1.31 (0.13)	0.85 (0.26)	0.71 (0.12)	0.78 (0.17)	1.27 (0.23)	1.49 (0.27)	4.08 (0.34)
CaO	5.18 (1.33)	4.31 (1.25)	4.47 (0.33)	3.62 (0.33)	3.40 (0.18)	3.29 (0.27)	5.56 (0.33)	5.39 (0.30)	11.75 (0.20)
K₂O [°]	9.66 (0.03)	7.83 (0.47)	6.89 (0.44)	8.50 (0.55)	10.32 (0.65)	8.70 (0.29)	6.60 (0.54)	6.19 (0.26)	2.84 (0.07)
Total ^d (wt%)	92.71	92.13	94.44	90.62	90.15	90.68	90.95	94.06	95.60
Si	3.157 (23)	3.116 (21)	3.125 (22)	3,164 (48)	3.219 (13)	3,162 (68)	3.070 (1(9	3.109 (17)	2 681 (19)
Altot	0.695 (60)	0.846 (20)	0.841 (29)	0.804 (88)	0.706 (9)	0.816 (101)	0.886 (15)	0.839 (10)	1.145 (17)
Mg	0.118 (48)	0.074 (33)	0.086 (9)	0.056 (18)	0.047 (8)	0.051 (11)	0.083 (15)	0.097 (19)	0.273 (23)
Ca	0.249 (64)	0.204 (13)	0.211 (17)	0.171 (18)	0.162 (8)	0.156 (14)	0.263 (16)	0.254 (15)	0.565 (7)
к	0.554 (2)	0.441 (33)	0.386 (25)	0.479 (36)	0.587 (36)	0.490 (18)	0.372 (30)	0.347 (14)	0.163 (3)
Tot. cat.	4.773	4.681	4.648	4.674	4,722	4.675	4.673	4.646	4.828
Al/(K+2*Ca) (apfu)	0.66	1.00	1.04	0.98	0.77	1.02	0.99	0.98	0.89
Al/K (apfu)	1.25	1.92	2.18	1.68	1.20	1.66	2.38	2.42	7.03
Qtz ^e	26.8	30.6	34.5	31.0	28.4	30.7	31.7	34.9	22.2
Plag ^e	8.3	21.8	23.1	17.5	6.6	16.7	27.9	27.0	58.4
Kfsn ^e	64.9	47.6	42.4	51.5	65.0	52.6	40.4	29.1	10.4

P(GPa) / T(°C)	2.5 / 1250	2.5 / 1300	3.0 / 950	3.5 / 950	3.5 / 1150	3.5 / 1200	3.5 / 1250	3.5 / 1300	3.7 / 1100
No. analyses ^b	13	12	7	11	10	12	17	24	11
SiOz	58.66 (0.27)	55.52 (0.36)	72.60 (0.87)	74.63 (1.34)	68.89 (0.34)	65.36 (0.67)	62.00 (0.36)	59.42 (0.28)	72.42 (1.58)
Al ₂ O ₃	21.43 (0.27)	22.38 (0.22)	13.10 (0.25)	13.38 (0.50)	15.31 (0.11)	17.12 (0.23)	19.08 (0.17)	19.51 (0.20)	15.15 (1.65)
MgO	4.41 (0.12)	7.55 (0.24)	0.49 (0.16)	0.49 (0.12)	1.73 (0.25)	2.47 (0.09)	3.32 (0.07)	4.82 (0.17)	0.59 (0.22)
CaO	12.76 (0.13)	12.46 (0.10)	2.58 (0.32)	2.45 (0.20)	7.98 (0.13)	10.82 (0.20)	12.14 (0.13)	13.31 (0.10)	3.95 (0.75)
K₂O [°]	2.75 (0.04)	2.09 (0.03)	11.22 (0.82)	9.05 (1.12)	6.09 (0.09)	4.23 (0.05)	3.45 (0.05)	2.95 (0.04)	7.88 (0.97)
Total ^d (wt%)	91.91	92.96	91.98	90.08	89.00	89.88	90.14	91.06	92.53
Si	2.648 (7)	2.516 (8)	3.244 (24)	3.280 (27)	3.064 (12)	2.922 (14)	2.788 (7)	2.691 (8)	3.187 (63)
Altot	1.140 (11)	1.195 (9)	0.690 (8)	0.693 (23)	0.803 (6)	0.902 (13)	1.012 (9)	1.041 (9)	0.786 (78)
Mg	0.296 (7)	0.510 (14)	0.033 (11)	0.032 (8)	0.115 (16)	0.165 (6)	0.222 (5)	0.325 (11)	0.039 (15)
Ca	0.617 (6)	0.605 (5)	0.124 (16)	0.115 (9)	0.380 (6)	0.518 (11)	0.585 (6)	0.646 (5)	0.186 (38)
ĸ	0.158 (2)	0.121 (2)	0.639 (48)	0.507 (62)	0.345 (5)	0.241 (3)	0.198 (3)	0.170 (2)	0.442 (54)
Tot. cat.	4.861	4.947	4.730	4.627	4.707	4.748	4.805	4.874	4.641
Al/(K+2*Ca) (apfu)	0.82	0.90	0.78	0,94	0.73	0.71	0.74	0.71	0.97
AI/K (apfu)	7.20	9.91	1.08	1.37	2.32	3.74	5.10	6.12	1.78
Qtz ^e	20.4	14.1	27.1	35.3	32.9	30.9	25.9	21.6	34.0
Plag ^e	60.2	70.1	2.8	10.0	26.7	39.9	49.8	56.3	18.5
Kfsp ^e	19.4	15.8	70.2	54.7	40.4	29.2	24.3	22.1	47.6

* In wt% and apfu based on 8 oxygens. Numbers in parentheses are one standard deviations in wt% (oxides) corrected to norm and for cations in terms of last digit(s). Thus, 3.018 (38) is read as 3.018 ± 0.038 cations pfu.

^b Number of analysis used in mass balance calculations.

Table 4.6 Melt compositions⁸

⁶ K₂O content adjusted for potassium loss from thermal diffusion during EMPA, K₂O concentrations are calculated from mass balanced fractions and bulk K2O.

^d Analytical sum including correction for calculated K2O content in ad. (c.

^e Normative composition in terms of the endmembers quartz, plagioclase and alkali-fledspar.

transformations, and then melting reactions, essentially reflecting the predominance of potassic phases on the high pressure phase relations of lithologies with an important pelitic component.

4.5.1. The transformation reaction of biotite to phengite.

The biotite to phengite transition is a key reaction in any crustal K-rich lithology and

has major implications for the melting behaviour in subduction zones. Micas are among the first

minerals that disappear through melting and host many key trace elements and isotopes such as LILE (K, Rb, Ba), Sr, B, ¹⁰Be and ²⁰⁷Pb (Dominak et al., 1993; Plank & Langmuir, 1998; Ishikawa & Nakamura, 1994). In this study, we have constrained the reaction from biotite to phengite taking place over a pressure range of 2.4 to 2.6 GPa at 750-850 °C (Fig. 4.2, 4.7A). Across the biotite to phengite transformation, the proportions of zoisite+quartz/coesite decrease and of clinopyroxene +kyanite increase, whereas the sum of biotite+phengite remains almost unchanged and close to the expected 20 wt%. This suggests a K₂O-conservative biotite to phengite reaction, buffered by zoisite, quartz/coesite, clinopyroxene and kyanite. The experiments allow quantification of the breakdown reaction from analysed phase compositions just within the stability field of phengite (at 2.7 GPa) and biotite (at 2.3 GPa) at 800 and 850 °C:

$$1.00bt + 0.79 zoi + 1.90 qtz/coe = 1.00 phe + 1.70 cpx + 0.59 ky + 0.40 H_{2}O$$
 (1)

(reaction coefficients are molar, melt being normalized to 8 oxygens). The reaction necessarily preserves K_2O as no other K-bearing phase is observed, but somewhat surprisingly, reaction (1) is not H_2O conservative. The amount of fluid produced from zoisite (~0.5 wt% H_2O in our experiments) would either cause a decrease of the X_{co_2} in the fluid, or some concomitant dolomite decarbonisation, however, the latter is within error in our mass balance.

4.5.2. The breakdown reaction of amphibole to clinopyroxene.

Amphibole is stable in the region below \sim 875 °C at 2.0 GPa to \sim 740 °C at 2.5 GPa. At higher pressures and above \sim 750 °C the calculated devolatilization reaction

$$1.00 \operatorname{amph} + 0.20 \operatorname{zoi} = 0.64 \operatorname{cpx} + 0.30 \operatorname{ky} + 0.26 \operatorname{H}_{2}O$$
 (2)

accounts for the replacement of amphibole by clinopyroxene, in addition it produces some minor biotite (~ 1.4 wt% in the experiments) proportional to the potassium content of the amphibole.



Fig. 4.7. Calculated phase proportions (wt%) for (A) 750-850 °C at 2.0-3.5 GPa (i.e. below the solidus), (B) 3.5 GPa, (C) 2.5 GPa. On (B) and (C) solidus and brackets are shown. The grey band in (A) represents the pressure range for the biotite to phengite transformation.

Both the amphibole to clinopyroxene and the biotite to phengite transformation reactions show, that zoisite is most abundant in the low temperature, low pressure portion of the P-T grid (from 40 wt% at 750 °C, 2.0-2.3 GPa down to 9 wt% at 850 °C, 2.5-3.5 GPa). In a first step, the zoisite abundance is reduced by ~ 10 % relative through the amphibole to clinopyroxene reaction, then, across the biotite to phengite transition zoisite is reduced to one fourth, and finally, at 5 GPa and 1050 °C (data from own experiments) zoisite is absent at subsolidus conditions, defining a wide P-T region of stepwise and progressive zoisite dehydration.

4.5.3. Initial melting reactions and relations (~ 850-950 °C)

The isobaric sections (Fig. 4.7B+C) illustrate the initial melting of a mica+zoisite+quartz/ coesite+dolomite assemblage. Melt proportions for the experiments first producing liquid at 2.0 and 2.5 GPa is 10 respectively 7 wt%, at 3.0 GPa ~ 19 wt% and at 3.5 GPa ~ 24 wt%. At 2.0 and 2.5 GPa, the persistence of mica (9 and 12 wt%), zoisite (22 and 9 wt%) and amphibole (8 wt%; only 2.0 GPa) indicate a wider temperature range for the multivariant solidus reaction, with more steadily increasing early melt fractions, than at 3.0 and 3.5 GPa, where no mica and only ~ 2 wt% zoisite (at 3.5 GPa) is left in each lowest temperature supersolidus experiment, thus producing larger apparent initial melt proportions. Melt proportions probably reflect the coexisting phase assemblage and the amount of overstepping of the solidus in temperature. The fluid-present solidus above 2.5 GPa is constrained to a narrow reaction band (\leq 50 °C), determined by the almost immediate breakdown of phengite, occurring at ~ 850 °C (2.5 GPa; Fig.4.3D), at ~ 900 °C (3.0 GPa) and < 950 °C at 3.5 GPa (Fig. 4.3B). Incongruent melting of phengite+zoisite+coesite producing silicate melt+clinopyroxene+kyanite occurs through the reaction

$$1.00 \text{ phc} + 0.32 \text{ zoi} + 1.14 \text{ coe} (+\text{fluid}) = 0.91 \text{ melt} + 0.51 \text{ cpx} + 1.04 \text{ ky}$$
 (3)

at 3.0 and 3.5 GPa. Due to the much larger solubility of H_2O vs. CO_2 in silicate melts (e.g. Papale, 1999; Dixon et al., 1997; Holloway & Blank, 1994; Hammouda, 2003; Wallace and Anderson, 1999), it is expected, that the fluid composition shifts drastically to a higher X_{CO_2} at the solidus, thus the reaction is calculated applying a low $X_{CO_2} = 0.02$ for the silicate melts.

Below 2.5 GPa initial melt is produced through incongruent melting of biotite (and amphibole) instead of phengite. At ~ 2.4 GPa (~860 °C) the breakdown of biotite and dolomite coincide. The solidus at 2.4 GPa is also the biotite-out, whereas zoisite and quartz melt out at ~ 50 °C higher. At 2.3 GPa and below, dolomite decarbonizes at subsolidus conditions. No other carbonate is formed, thus like at 2.5 to 3.5 GPa, the previously dolomite contained CO_2 enters the fluid. Similar to the melting reactions at \geq 2.5 GPa, the calculated solidus melting reaction at 2.3 GPa consumes mica (biotite)+quartz+zoisite to produce melt+clinopyroxene+kyanite through

$$1.00 \text{ bt} + 1.66 \text{ zoi} + 4.17 \text{ qtz} (+ \text{ fluid}) = 1.52 \text{ melt} + 3.07 \text{ cpx} + 2.24 \text{ ky}$$
 (4)

Complete decomposition of all reactants between 850 and 900 °C indicates that the overall solidus reaction (4) is composed by several melting reactions (see Fig. 2). Compared to the phengite-controlled solidus reaction (3), larger proportions of zoisite (35 wt%) and quartz (18 wt%) are consumed for the massive production of clinopyroxene (9 to 48 wt%) and kyanite (17 wt%) across the solidus. At 2.0 GPa the solidus reaction (~840 °C) involves amphibole together with biotite. A breakdown melting reaction could not be mass balanced with confidence, but from the near-solidus experiment at 850 °C (Fig. 4.3F) and Schreinemaker constraints, the qualitative melting reaction

$$bt + amph + zoi + qtz + fluid = cpx + ky + melt$$
 (5)

is most likely responsible for the first melt produced just below 850 °C.

4.5.4. Melting above 1000 °C

Towards higher temperatures, melt proportions increase only moderately, until substantial incongruent melting of elinopyroxene+kyanite begins (Fig. 4.7B+C), forming garnet through the reaction (at 2.0-2.5 GPa)

$$0.83 \text{ cpx} + 0.42 \text{ ky} = 1.00 \text{ melt} + 0.25 \text{ gt}$$
 (6)

which takes place from 950 to 1050 °C (Fig. 4.3G+H). At 1200 °C (2.5 GPa) kyanite disappears through the peritectic reaction

$$0.74 \operatorname{cpx} + 0.57 \operatorname{ky} = 1.00 \operatorname{melt} + 0.12 \operatorname{gt} + 0.19 \operatorname{cor}$$
(7)

producing a significant proportion of melt (Fig. 4.7C) and additional corundum (≤ 2 wt% in the experiments) just below the liquidus. Corundum was not observed at 3.5 GPa. At 2.5 and 3.5 GPa, clinopyroxene exhausts between 1200 and 1250 °C, and garnet is stable to the liquidus at 2.5 GPa.

Despite the temperature interval from 950 and 1100 °C at 3.5 GPa comprises the meltingout of zoisite and coesite, and the garnet-in reaction, only 0.8 wt% clinopyroxene and 1.8 wt% kyanite is consumed, and 1.7 wt% garnet and 3.2 wt% silicate melt produced (Fig. 4.7B). Above 1100 °C the melt fraction increases almost constantly by 2.3 wt% melt per 10 °C, reflecting a continuous melt generation within the garnet+kyanite+melt±clinopyroxene stability fields. At 3.5 GPa, clinopyroxene melts out through the reaction

$$0.77 \operatorname{cpx} + 0.38 \operatorname{ky} = 1.00 \operatorname{melt} + 0.15 \operatorname{gt}$$
 (8)

producing a small amount of additional garnet.

4.5.5. The liquidus surface

The melting relations define the liquidus surface of the KCaMAS-HC system, projected from quartz/coesite, kyanite, and fluid, thus leaving the principal components MgO, CaO and K_2O (Fig.4.6C). As to be expected, the lowest temperature liquid occurs close to the K_2O -corner, where peritectic melting (PM) takes place through reaction (3), (4) or (5) producing clinopyroxene. In our bulk composition, phengite melts out first, liquids then evolve along the peritectic line zoisite = clinopyroxene+liquid. Both the peritectic PM and the peritectic line at higher temperature shift towards K_2O with pressure, resulting in a clear difference of melt compositions between the experiments at 2.0-2.5 and at 3.5 GPa. When zoisite is exhausted with further increasing temperature, liquids leave the zoisite/clinopyroxene peritectic line and evolve on the clinopyroxene liquidus surface, simply consuming clinopyroxene. At 1050-1100 °C, liquids encounter the peritectic line clinopyroxene = garnet+liquid, and evolve on that line until clinopyroxene is exhausted. It should be noted, that both clinopyroxene becoming more aluminous through tschermaks exchange mainly with temperature (Fig. 5A) and garnet becoming more magnesian with pressure.

4.6. Comparison of the P-T grid to previous high pressure experimental studies.

Experimental studies of high pressure metasediments are mostly on natural CO_2 -free pelites and their simplified synthetic subsystems. First, we compare subsolidus phase relations, with emphasis on the biotite to phengite reaction, then melting reactions and melt compositions.

4.6.1. The biotite to phengite transformation and subsolidus phase relations.

The stability of biotite in KCaMAS-HC and subsystems is very much bulk composition dependent. Quartz+kyanite saturated bulk compositions more calcic than the tie-lines clinopyroxene-phengite (Fig. 4.8A) will have biotite reacting completely to phengite with pressure, bulk compositions in the triangle clinopyroxene-phengite-biotite will have phengite and biotite coexisting at high pressure, whereas less calcic but strongly magnesian compositions preserve biotite to high pressures without forming phengite.

Own unpublished experiments (2.5-6 GPa, 850-1100 °C) on a MgO-rich bulk composition (15.22 wt% MgO) with a molar Ca/(Ca+Mg) of 0.28 (MA in Fig. 4.8A) produced biotite with octahedral occupancies of 2.44-2.91 apfu up to 6 GPa and no phengite, indicating a bulk Ca:Mg control on the biotite to phengite transformation in KCaMAS-HC.

Experiments in KCMASH at 2.0-4.5 GPa, 680-1050 °C with 2-5 wt% H_2O (Hermann, 2002, 2003) produced biotite and phengite coexisting from 2.5 to 3.9 GPa at 780 °C. This pressure range narrows towards higher temperatures and terminates by melting near 900 °C at 3.0 GPa (Fig. 4.8 ad. 2). A phengite stability field above 2.5 GPa is consistent with our results. On the other hand, in Hermann's experiments biotite is stable to 1 GPa higher pressures and 50 °C higher temperatures (at 2.5 GPa) than in our study. This reflects the lower Ca/(Ca+Mg)=0.35 of Hermann's bulk composition compared to our experiments (=0.54), thus stabilizing biotite and forming phengite+orthopyroxene through the reaction

$$bt + ky + qtz = phe + opx$$
 (9)

Our higher Ca:Mg ratio stabilizes clinopyroxene+zoisite instead of clinopyroxene + orthopyroxene, buffering the biotite to phengite reaction (1). The higher Ca:Mg ratio also displaces the garnet stability field towards higher temperatures. In both studies, amphibole is stable only below 2.2 GPa at 800 °C to below 3.0 GPa at 750 °C, replacing clinopyroxene (Hermann, 2002).

In the KMASH experiments up to 4.5 GPa and 1100 °C of Massonne & Schreyer (1989), Massonne & Spzurka (1997) and Massonne (1992) on various Mg-rich, H_2O -saturated bulk compositions, the reaction

$$tlc + phe = bt + ky + qtz + H_2O \qquad (10)$$





- X (2) Average continental crust (P1; Hermann 2002, 2003)
- (5) Pelite (P) (CO821; Vielzeuf & Holloway 1988, Schmidt et al. 2004)
- (6) Greywacke (GW) (Auzanneau et al. 2006, Schmidt et al. 2004)
 - (8) Tonalite (RPR, RPR-a, RPR-c; Schmidt 1993)
 - 다 (9) Tonalite (Patiño Douce 2005)
- Phengite eclogites (BXLA, QL1, YK34) and average eclogite (E) from Dabie Suln (Nakamura 2003)



Fig. 4.8. Comparison of K-mica-producing bulk compositions from different studies in a CaO-MgO(+FeO₁₆₀)-1/3K₂O(+Na₂O) projection (A) and experimentally determined stability pelites (Vielzeuf & Holloway 1988). (6) Biotite and phengite-out and solidus in greywacke (Auzanneau et al. 2006). (7) Compiled schematic biotite to phengite reaction and fluidfields of biotite and phengite and loci of solidi in a P-T diagram (B). Quartz+kyanite saturated bulk compositions more calcic than the cpx-phe tie-line (thick dashed lines i A) will KMASH (Massonne and Schreyer 1989). (4) Phlogopite-out in KMASH (Massonne and Spzurka 1997). (5) Biotite to phengite reaction and mica-controlled melting in KFMASH stabilizes garnet and jadeitic cpx (instead of Al-diopside), thus virtually have no influence on the bulk phase assemblage buffering the biotite to phengite transformation reaction. have biotite decomposing with pressure to phengite, whereas compositions in the triangle cpx-biotite-phengite (e.g. ad. 2) have biotite and phengite coexisting at high pressures. (1) This study (see fig. 9). (2) Solidus, biotite and phengite stability in KCaMASH for average continental crust (Hermann 2002, Hermann & Green 2001). (3) Phengite-out in absent mica-controlled solidus based on pelites and greywackes (Schmidt et al. 2004). (8) Biotite-out through tonalite fluid-saturation melting (Schmidt 1993). (9) Biotite and addition of FeOtot (to the MgO apex) and Na₂O (to the ½K₂O apex) is indicated by the thin dashed lines i A. This compositional change does not produce any new phases, but Less calcic, but highly magnesium compositions (e.g. MA) preserve biotite to high pressure without forming phengite. The change in location of the natural compositions by shengite stability in fluid-absent tonalite (Patiño Douce 2005). (Massonne & Schreyer, 1989) was determined to define the lower pressure stability limit of phengite (+talc) at 1 GPa and 610 °C to 2.7 °C and 800 °C, crossing our mica transition field at 2.5 GPa and 770 °C (Fig. 4.8B ad. 3). In KMASH, the upper pressure stability limit of phlogopite+ kyanite+quartz is defined by

$$phl + ky + q = phe + pyrope$$
 (11)

This reaction is located at 2.5 GPa and 700 °C (Massonne, 1992) to 2.7 GPa and 810 °C (Massonne & Spzurka, 1997; Fig. 4.8B ad. 4), conditions surprisingly similar to our system.

Natural (CO₂-free) pelite and greywacke, at low pressures composed of biotite+ plagioclase+quartz±kyanite reacts to phengite+garnet+quartz±kyanite with increasing pressure. For pelite, Vielzeuf & Holloway (1988) determined the biotite to phengite reaction band to 1.8-2.0 GPa at 700-800 °C (Fig. 4.8 ad. 5), whereas Auzanneau et al. (2006) located this reaction band for a greywacke to 1.8-2.6 GPa at 800 °C, narrowing towards 2.2 GPa and 900 °C (Fig. 4.8 ad. 6).

For tonalites, the biotite to phengite reaction occurs at much lower pressures; in the H_2O -saturated tonalite melting experiments of Schmidt (1993) (Fig. 4.8 ad. 8) at ~1.3 GPa (and 650 °C) coexisting with amphibole+plagioclase+epidote+quartz and in the H_2O -undersaturated experiments of Patinõ Douce (2005) (Fig. 4.8 ad. 9) at 1.7-1.9 GPa (and 800-900 °C) coexisting with Kfsp+cpx+garnet+quartz+melt±kyanite.

The upper pressure stability limit of amphibole in our experiments is similar to experiments on fluid saturated mafic compositions, extending to no more than 2.5 GPa at 700 °C (summarized by Poli & Schmidt, 2002). Zoisite is generally limited to below 3 GPa in natural bulk compositions (Poli & Schmidt, 2002), the higher pressure stability limit of zoisite in our Fe-free experiments reflects the absence of garnet at subsolidus conditions and the high Ca:Mg ratio compared to most other bulk composition. P-T stability conditions of Mg-Ca-carbonates from several studies (Yaxley & Green, 1994; Molina & Poli, 2000; Kerrick & Connolly, 2001; Hammouda, 2003; Yaxley & Brey, 2004) indicate dolomite as the stable carbonate between 2 GPa at 600-750 °C and 3.0-5.0 at 900 °C relative to calcite, Mg-calcite, aragonite and magnesite, which is confirmed by our experiments.

4.6.2 Comparison of solidus, melting relations and melt compositions.

Initial melting begins at ~100 °C lower temperatures in the KCMASH experiments of Hermann & Green (2001) and Hermann (2002) than in our study (Fig. 4.8, ad. 2). This is due to the effect of CO₂, lowering $a_{\mu_2 0}$ in the fluid of our study. Phengite melts out at similar temperatures (at 2.5-3.5 GPa), but the upper thermal stability limit of biotite at 2.0-2.5 GPa is about 50 °C higher in Hermann's experiments which is caused by the differences in bulk composition. Initial liquids are slightly peraluminous granites, increasing in normative K-feldspar with temperature (Hermann & Green, 2001), whereas our experiments produce metaluminous granites increasing in normative plagioclase with temperature (Fig. 4.6A). This reflects a lower bulk SiO₂ and higher CaO content compared to Hermann & Green (2001). In both studies, initial melt compositions are almost invariable with pressure.

K-bearing eclogites composed of phengite+clinopyroxene+garnet+quartz/coesite±kyanite produce potassic Si-rich granites, comparable to our melts, through phengite-controlled initial melting at 4 GPa and 850-900 °C (Schmidt et al. 2004). Below 3.0 GPa, melt compositions represent granodiorite, tonalite or trondhjemite (Poli & Schmidt, 2002), and at ~ 2.0 GPa, the fluid-absent breakdown of phengite in pelites at ~ 825 °C produces granite melts (Fig. 4.8 ad. 5; Vielzeuf & Holloway 1988).

For tonalite, melting above 2.5 GPa is controlled by phengite (±zoisite) (Schmidt 1993, Patiño Douce 2005). In H₂O-undersaturated tonalite, phengitc breaks down at ~150 °C higher temperatures, reflecting a lower bulk a_{H_2O} than for our bulk composition (Patiño Douce 2005), whereas in H₂O-saturated bulk, the phengite-dominated solidus occurs at 600-700 °C (Schmidt,
1993), due to a higher a_{H_2O} . Biotite generally breaks down at lower pressures, in H₂O-undersaturated tonalite together with amphibole at ~ 900 °C (at 1.5 GPa) producing K-feldspar through

$$bt + amph + plag + qtz = cpx + gt + kfsp + mclt$$
(12)

In a H_2O -saturated bulk, K-feldspar is absent (Poli & Schmidt, 2002; Hermann, 2002; Boettcher, 1970), and epidote/zoisite stabilizes instead of plagioclase, resulting (for Na+Fe-free compositions) in a melting reaction comparable to our reaction (5).

Experiments at 1.5 to 3.5 GPa and 700-1000 °C on fluid-saturated carbonate-bearing cclogite (altered oceanic basalt) with 10 wt% calcite, (Yaxley & Green, 1994), produced just above the solidus at 700-750 °C, silicate melt and CO_2 -enriched fluid. Omphacite is omnipresent, whereas garnet is limited to < 1.5 GPa and 850-1000 °C, and amphibole to below 2.5 GPa and 950 °C. Thus, our petrogenetic grid is also comparable to mafic compositions, taking into account, that iron significantly enlarges the garnet stability field.

4.7. Discussion

4.7.1 The effect of Na and Fe in carbonate-saturated pelites

Natural compositions contain significant amounts of Na and Fc, which affect phase relations, but without producing further phases in the P-T region studied. Na is incorporated in the jadeitic component in clinopyroxene or in the albite component in plagioclase, both would not change the observed phase relations substantially as our experiments are at pressures above plagioclase stability, and the lowering of diopside activity in clinopyroxene would only have a minor effect. Na is a major component in barroisitic amphiboles which would be stable at 750 °C. Nevertheless, comparison to experiments of Poli & Schmidt (1995) show, that the effect of Na on the amphibole to clinopyroxene transformation pressure is small, barroisitic amphibole not

being stable above 2.5 GPa, compared to 2.4 GPa in our system (at 750 °C).

Fe partitions strongly into garnet, increasing the garnet stability field to much lower temperatures and the phase assemblage jadeitic cpx+garnet+phengite+carbonate (aragonite, dolomite or magnesite)±zoisite±quartz/coesite± kyanite is expected to be the dominant high pressure subsolidus phase assemblage for carbonate-saturated pelites above ~ 2.5 GPa and 750 °C in natural systems. The shift of garnet stability to higher pressures in Fe-free synthetic systems stabilizes zoisite, which decomposes with pressure to grossular+kyanite+coesite+H₂O in the CASH system (Poli and Schmidt 1998).

Addition of Fe and Na would also lower solidus temperatures slightly, mostly due to incorporation of Fe into micas and amphibolc which melt out at the solidus. The effect of Na in clinopyroxene on the melting temperature lessens with pressure as Na is partitioned into clinopyroxene and not into the melt (Schmidt et al. 2004).

4.7.2 The contribution from carbonaceous pelites to the recycling of H_2O and CO_3 at convergent margins

For the studied carbonate-saturated pelite composition, all decarbonation and melting reactions could only take place in very high temperature subduction zones (Kerrick & Connolly 2001; Kincaid & Sacks 1997). Consequently, (for closed-system behaviour) melting of subducted fluid-saturated carbonate-bearing pelites does not provide a significant volatile source for the generation of arc magmas at most subduction zone conditions. In terms of the global water and carbon cycle, this indicates that carbonate-bearing pelites will mostly be subducted to depths in excess of 120-150 km depth without releasing significant portions of their CO₂ or H₂O contained in carbonates and hydrates, carrying their CO₂ and H₂O into the deeper parts of the upper mantle. For the carbonate-bearing protolith considered here, the subsolidus reactions occurring at all P-T paths arc the biotite to phengite transformation, which releases H₂O through the partial

consumption of zoisite, and the decomposition of amphibole around 80 km dcpth (at 700 °C) producing approximately 0.5 wt% H₂O. Decarbonation of dolomite occurs at > 750 °C near 2.0 GPa, if dolomite survives 60 km depth, virtually no CO_2 will be released through subsolidus reactions during deeper subduction.

This agrees well with the model phase diagram calculations of subducted carbonatebearing marine sediments (e.g. clay-rich marl) of Kerrick & Connolly (2001), which predict that carbonate-bearing metascdiments are extremely volatile conservative. Our experiments demonstrate, that melting is necessary to liberate substantial amounts of their H_2O and CO_2 , however, necessary temperatures are exceedingly high in the subduction environment.

4.7.3 Terrains that may record devolatilization or melting reactions in carbonaceous pelites

Figure 4.9 compares geotherms from high pressure metamorphic terrains with carbonatepelite rocks to our P-T grid. The geotherms from Dora Maira (W. Alps), Western Gneiss Region (Norway), South Dabie Shan and Dabie Sulu (China) show peak P-T conditions of 3 to 4 GPa at 750-800 °C within the phengite stability field, and near-isothermal decompression through the biotite stability field. Consequently, carbonaceous pelites from these regions would not have undergone partial melting without external influx of H_2O -rich fluids, and are expected to show evidence of the phengite to biotite transformation (e.g. biotite overgrowth) and the clinopyroxene to amphibole transformation. Naturally, for the preservation or complete reequilibration of the high pressure phase assemblage during unloading, the amount of fluid present during decompression is an important mechanism (Heinrich, 1982). In contrast to the Dora Maira and South Dabie Shan, carbonaceous pelites from the Western Gneiss Region and Dabie Sulu are expected to loose their carbonates through decompression decarbonation at ~2 GPa. The geotherms from the Kokchetav Massif and Central Dabie Shan both cross the solidus in the petrogenetic P-T grid during their retrogressive stages. Thus, carbonaceous pelites from such



areas will most probably undergo phengite-controlled partial melting, as a result of near-isothermal decompression melting during their retrogression. Consequently, (and assuming complete reequilibration) phengite will decompose and any biotite that forms at lower P-T conditions cannot be a result of the decompression reaction of phengite to biotite.

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Fig. 4.9 (previous page). The petrogenetic grid (thin black lines with reactions) at 2.0-3.7 GPa and 700-1050 °C for carbonate-saturated pelite in KCaMAS-HC, based on the experimental results (Fig. 4.2) and chemographic analyses of phase relations (inset and Fig. 4.1). Large point denote invariant points. Changes due to the quartz/ coesite transformation (Bohlen & Boetcher, 1982) are not considered. Geotherms from high pressure metamorphic terrains with carbonate-bearing metasediments are inserted for comparison to the phase stability fields of the produced P-T-grid. Thick arrowed paths denote geotherms (1) Dabie Sulu (Nakamura & Hirajima 2000, Faure et al. 2003a+b; Wang et al. 1993). (2) Dabie Shan (Faure et al. 2003a).(3) Dora Maira (Schertl et al. 1991; Rubatto and Hermann 2001). (4) Kokchetav UHP Massif (Zhang et al. 1997, Shatsky et al. 1995). (5) Western Gneiss Region (Terry et al. 2000).

Chapter 5

Fluid-absent melting of fertile carbonate-saturated pelites at high pressures and silicate-carbonatite liquid immiscibility

Fluid-absent melting of fertile carbonate-saturated pelites at high pressures and silicate-carbonatite liquid immiscibility

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Abstract

Melting experiments on a Fe-rich carbonate-saturated pelite were performed at 850-1300 °C and 2.5-5.0 GPa to define the conditions to which carbonates remain residual to sediment melting. For this purpose, phase relations, melting conditions and melt compositions were determined. In this fertile bulk composition, 30 wt% potassic granite (2.5 GPa) to phonolite (5.0 GPa) are generated at the fluid-absent solidus. The latter is located at 900 °C, 2.4 GPa and 1070 °C, 5.0 GPa. Phengite+quartz/coesite control initial silicate melting and melt productivity through the reaction phengite+quartz/coesite+clinopyroxene+calcite = silicate melt+kyanite+garnet, which leaving most of the Fe-Mg-calcite in the residue. Fe-Mg-calcite disappears only through the formation of Ca-carbonatite at 1100 °C, 3.5 to 5.0 GPa. The experiments provide a possible source for Ca-carbonatites in combination with alkalinc granitic to phonolitic melts at temperatures unlikely to be achieved during ongoing subduction, but which can easily be obtained when burying rates slow down or subducted crust becomes incorporated into the mantle. Consequently, it is likely that carbonates will not be recycled extensively in a typical subarc region, thus extending and confirming earlier results from subsolidus studies (Connolly 2005), where >70-80% of the subducted carbonate will bypass the volcanic arc region and get buried to larger depths.

5.1. Introduction

A principal factor in the formation of arc magmas is the availability and composition of fluids or melts derived from the subducting crust through devolatilization or melting of carbonates and hydrous minerals (Gill 1981, Poli & Schmidt 2002). Furthermore, the deep burying rate vs. arc depth recycling rate of volatiles is one of the key parameters driving the secular geochemical evolution of the mantle, crust, and hydrosphere. Within the subducted oceanic crust, hydrated basalt and to a lesser extent hydrated gabbros constitute the major H2O source (Bebout 1996, Staudigl, 2005). Nevertheless, oceanic sediments play a significant role in the recycling of volatiles due to their high carbonate contents in combination with hydrous minerals driving metamorphic and melting reactions. Most prone for proliferating CO2-bearing fluids or melts are carbonaceous pelites as their high initial H2O and CO2 contents, in combination with quartz saturation and the highest K2O and Na2O contents in the subducting lithosphere cause large amounts of H2O-rich sheet silicates to be stable at subsolidus conditions and the lowest melting temperatures, compared to any other CO2-bearing subducted lithology. Carbonate-saturated pelites (protolith are carbonate-bearing clay, often with siliceous material and volcanic ash in addition, Plank & Langmuir 1998) are common shelf and platform sediments (Bucher & Frey 2002) being subducted in most modern subduction zones, and are common in most metamorphic high pressure terrains (Droop et al. 1990).

For CO₂-free pelite, greywacke and mafic compositions, experimental studies show that phengite (Si-rich white mica) and zoisite dominate fluid-present and -absent melting reactions in the subducted slab at pressures between 2.5 and 9 GPa (Nicolas et al. 1994, Schmidt et al. 2004, Auzanneau et al. 2006) and that complete devolatilization occurs at the solidus. For carbonate-bearing sediments, thermodynamic calculations (Kerrick & Connolly 2001, Connolly 2005), not including a melt phase, demonstrate that only minor decarbonation occurs through metamorphic

reactions at temperatures typical for subduction zones. Furthermore, even massive flushing of metasediments with aqueous fluid derived from the dehydration of underlying serpentinized oceanic mantle would not remove a large fraction of the CO_2 contained in the oceanic crust (Connolly 2005). One is thus left with the option of recycling CO_2 at are depth through melting processes.

In this study, we aim to understand which conditions are necessary for the complete recycling of CO_2 from subducted sediments. We thus study the phase petrology of a fertile, Ferrich carbonate-saturated pelite, determining the fluid-absent solidus, and focusing on initial melting reactions, conditions, and melt compositions.

5.2. Experimental and analytical methods

5.2.1 Starting material

The bulk composition (Tab. 5.1) corresponds to a Fe-calcarcous clay from the Antilles (Ant543, Plank & Langmuir 1998, their Tab.1) simplified in $K_2O-Na_2O-CaO-FeO-Fe_2O_3-MgO-Al_2O_3-SiO_2-H_2O-CO_2$ (KNCaFMAS-HC). The subsolidus phase equilibria and volatile content of this composition have been calculated by Kerrick & Connolly (2001). The carbonate-saturated bulk composition has an atomic K:H ratio of 1:2, as in K-micas, and is thus expected to be either fluid-absent at high pressure subsolidus conditions or at least have a tiny amount of H₂O-CO₂ fluid present. If all H₂O and K₂O are stored in mica and all CO₂ in carbonate, this bulk composition produces 26 wt% white mica and 11 wt% carbonate at subsolidus conditions. The starting material is made of powders of SiO₂, Al₂O₃, fayalite, diopside, albite and a synthetic KAl_{1.33}Mg_{0.5}Si_{3.5}O₁₀ glass, which were milled and grinded to < 5 µm, and then mixed with Al(OH)₃ and CaCO₃ to introduce the desired proportions of H₂O and CO₂.

Table 5.1	Bulk starting	composition	(wt%)
	Duik olarling	composition	(** L /0 <i>j</i>

	Bulk (AM)	Ant543 ^ª	calcschist ^b	Pelite ^c
SiO₂	47.6	46.6	44.5	64.4
Al ₂ O ₃	22.8	18.0	18.3	18.1
FeO _{tot}	9.2	7.4	4.8	6.3
MgO	2.0	1.6	2.8	2.4
CaO	6.8	5.5	9.7	1.5
Na ₂ O	2.4	1.9	1.4	1.7
K₂O	3.6	2.8	3.4	2.6
H₂O	1.1	12.0	2.8	2.1
CO2	4.8	3.8	10.7	-
SUM	100.3	99.5	98.4	99.1
Al/(Na+K+2*Ca) ^{molar}	0.70	0.69	0.44	0.50
Al/(Na+K) ^{molar}	2.91	2.90	3.06	0.72
K ₂ O/Na ₂ O	1.5	1.5	2.4	1.5
X _{Mg} (Fe _{tot}) (molar)	0.28	0.28	0.51	0.50
X _{CO2} molar	0.64	0.12	0.61	-

^a Fe-calcareous claystone, Antilles (p. 339 in Plank & Langmuir, 1998).

^b Calc-schist MF886 from the Alps (Frey, 1978).

^c Pelite CO821 (Vielzeuf & Holloway, 1988).

5.2.2 Experimental procedure

Experiments were carried out at ETH-Zürich (Switzerland), CNRS, Clermont-Ferrand (France) and ANU, Canberra (Australia). The 5.0 GPa experiments were performed in a Walkertype multi-anvil module with 25 mm edge length MgO octahedrons as pressure medium. At ETH-Zürich, 25 mm edge length WC-cubes with 12 mm truncation was employed, whereas 32 mm edge length WC-cubes with 17 mm truncation edge lengths was used at CNRS. Assemblies at ETHZ were composed of two graphite furnaces (one stepped), boron nitride powder, molybdenum end sleeves and internal MgO spacers. At CNRS, assemblies were composed of a ZrO_2 insulation sleeve, a stepped LaCrO₃ furnace with a graphite disc and ring between furnace and WC-cubes, and inner MgO cylinders. Two or three Au₁₀₀ or Au₅₀Pd₅₀ capsules of 1.6, 2.0 or 2.3 mm O.D. (length ~2.0 mm) were used in each experiment, placed on each side of the central thermocouple. Temperature gradients within the capsules were ±10 °C/2 mm (at 1000-1050 °C). Pressure calibration was against the quartz-coesite transformation at 3.1 GPa – 1000 °C (Bose & Ganguly 1995), the fayalite to γ -spinel reaction at 5.25 GPa – 1000 °C (Yagi et al. 1987) and the garnet-perovskite reaction at 6.1 GPa, 1200 °C (Susaki et al. 1985). Experiments below 5.0 GPa were conducted in end-loaded piston-cylinders with 14 mm (ETH) or 12.7 mm (ANU) bores. Capsules of Au₁₀₀ or Au₈₀Pd₂₀ were applied at \leq 1100 °C and Au₅₀Pd₅₀ capsules at > 1100 °C. The experimental approach and used assemblies is described in detail in Thomsen & Schmidt (in review, chapter 4). For all experiments, the temperature was controlled automatically by Eurotherm controllers within ±2 °C, using either a B-type (Pt₉₄Rh₆/Pt₇₀Rh₃₀) (ETH, ANU), or S-type (Pt₁₀₀/Pt₉₀Rh₁₀) thermocouple (CNRS). Quenching was done by turning off power to the furnace. Capsules were mounted longitudinally in epoxy resin, then polished to the centre of the capsule by a dry-polishing or a silica colloid wet-polishing method. Graphite was not produced in any of the experiments, suggesting oxygen fugacities (f_{O_2}) above the graphite-CO-CO₂ (CCO) buffer or even the graphite-H₂O buffer. Maximum oxidation of Fe²⁺ to Fe³⁺ from oxygen produced from complete diffusion of bulk hydrogen (in H₂O) through the capsule walls is calculated to 95 % relative (producing 9.6 wt% Fe₂O₃), corresponding to a Fc₂O₃/(Fe₂O₃+ FeO)=0.91.

5.2.3. Analytical methods

Experimental charges were analysed by a JEOL JXA8200 electron microprobe at ETH-Zürich using silicates, carbonates and oxide standards, 15 kV acceleration voltage, 20 nA beam currents for silicate minerals and 5-10 nA for carbonates and quenched glasses. For the carbonates and quenched carbonatites, Ca and C were standardized on calcite, Mg on magnesite and Fe on siderite, and the carbon content was measured with a precision of 1.5 to 4 wt% using a LDE2type crystal. Acquisition time was 10 or 20 seconds for all elements except carbon (40 s), measuring Na, K and C first to avoid most elemental loss. A fully focused beam was applied to most water-free crystalline phases providing totals close to 100 wt%. Mica, carbonate, quartz/coesite and glass exhibited electron beam damage at a diameter less than 5 μ m, thus a defocused beam (2-30 μ m) was applied whenever possible for these phases. After a first round of analyses, carbonatite-bearing samples were ground down a bit further and dry-polished with BN-powder on corundum or diamond coated sheets in order to avoid alkali-losses from the carbonatites when involving water or other solvents in the polishing process. A second round of analyses then yielded slightly higher Na₂O and K₂O concentrations. Textures were analysed from secondary and back-scattered electron images obtained by the microprobe or by a JEOL JSM6300 high field emission SEM at ETH-Zürich. Determination of carbonate polymorphs was done by micro-Raman spectroscopy.

5.3. Experimental results

Experimental run conditions, resulting phases and calculated phase proportions are listed in Tab. 5.2. A total of 21 experiments were performed in three pressure series at 2.5 GPa, 3.5-3.7 GPa and 5.0 GPa, defining phase stabilities and melting reactions in P-T space (Fig. 5.1).

5.3.1. Approach to equilibrium

All runs reported here are synthesis experiments. Textural equilibrium is indicated by generally well-crystallized grains (Fig. 5.2) and, at subsolidus conditions, 120° triple point junctions between the phases (Fig. 5.2A). Apart from garnets, which in a few runs exhibit Fe-Mg zonation (Fe-rich cores and Mg-rich rims or patchy Fe-Mg zoning), all phases are compositionally homogeneous. Regular compositional trends of minerals and melts throughout the experimental grid, and of calculated phase proportions (Fig. 5.3) and phase compositions suggest that equilibrium was generally reached. At \geq 1150 °C (3.5 and 5.0 GPa) and \geq 1100 °C (2.5 GPa), an FeO_{tot}-loss of 1-2 wt% compared to the bulk FeO_{tot} content occurred.

Run no.	P (GPa)	⊢ ()	Time (hours)	phengite	calcite	garnet	cpx	kyanite	corundum	silicate melt	carbonatite melt	qtz/coesite
AM-23 ^d	2.5	850	125	26.5 (2.1)	9.3 (1.1)	14.2 (1.4)	28.6 (2.0)	10.8 (1.3)	1	I	1	10.5 (1.6)
AM-19	2.5	006	285	4.0 (2.0)	9.0 (1.8)	19.0 (2.5)	21.3 (2.9)	12.1 (3.0)	I	32.2 (4.0)	I	2.2 (1.0)
AM-22	2.5	1000	70	1	8.7 (1.2)	19.6 (2.3)	19.6 (2.1)	10.9 (1.8)	I	41.2 (3.6)	I	I
AM-21 ^c	2.5	1100	88	I	I	I	22.0 (3.5)	9.0 (2.1)	2.3 (1.3)	66.7 (3.3)	I	ı
AM-13 ^{bc}	2.5	1200	86	ı	I	ı	I	I	3.3 (0.3)	96.6 (0.3)	I	I
AM-17 ^{bc}	2.5	1300	87	ł	I	1	I	I	2.2 (0.5)	97.8 (0.5)	I	ı
AM-03 ^d	3.7	006	334	26.1 (0.7)	10.1 (0.7)	22.8 (1.0)	21.0 (1.2)	9.1 (0.7)	I	1	I	11.0 (0.7)
AM-08 ^d	3.7	950	147	26.1 (0.7)	10.0 (0.6)	23.3 (0.8)	21.1 (1.1)	8.5 (0.6)	I	1	I	11.1 (0.6)
AM-07	3.7	1000	124	I	9.2 (0.5)	28.0 (2.1)	19.1 (2.7)	9.1 (0.9)	I	34.6 (2.4)	I	I
AM-02	3.7	1050	149	ı	8.7 (0.6)	26.6 (2.0)	17.9 (1.8)	9.8 (0.9)	1	37.1 (1.8)	I	l
AM-18	3.7	1100	146	I	8.3 (1.4)	27.6 (2.6)	7.0 (3.1)	9.6 (1.7)	I	47.6 (3.2)	I	ı
AM-04	3.7	1100	92	I	I	29.6 (3.8)	5.6 (2.6)	9.1 (2.9)	I	47.3 (4.6)	8.5 (2.2)	I
AM-24	3.7	1100	94	1	1	28.3 (3.2)	8.1 (3.5)	7.5 (2.1)	I	46.8 (3.7)	9.3 (2.6)	I
AM-10	3.5	1150	68	ı	5.6 (2.7)	29.6 (3.3)	6.0 (3.4)	4.0 (1.7)	I	54.9 (3.5)	1	1
AM-11 ^c	3.5	1200	06	I	1	28.5 (2.9)	4.4 (2.2)	0.6 (0.9)	5.0 (2.0)	61.6 (2.9)	ł	ı
AM-12 ^{bc}	3.5	1250	96	I	1	1	I	I	5.8 (0.3)	94.3 (0.3)	ŀ	ı
AM-16 ^{bc}	3.5	1300	72	I	I	1	1	I	4.0 (0.3)	96.0 (0.3)	1	1
ME-109 ^d	5.0	1000	48	25.3 (1.1)	6.0) 6.6)	24.5 (1.2)	22.4 (1.1)	9.1 (0.8)	I	I	I	8.8 (1.0)
AM-15 ^d	5.0	1050	58	25.6 (1.2)	9.5 (0.9)	22.7 (2.3)	21.4 (1.8)	11.1 (1.4)	I	I	I	9.6 (1.3)
ME-110	5.0	1100	24	I	I	29.1 (4.6)	20.0 (4.9)	12.2 (4.0)	I	29.7 (3.9)	8.9 (3.3)	I
ME-137 ^c	5.0	1150	75	ł	1	37.3 (1.7)	12.5 (2.3)	4.9 (2.9)	0.5 (1.5)	44.8 (1.2)	I	ł

Tab. 5.2. Experimental run conditions and calculated phase proportions (wt%) $^{
m a}$

^a Numbers in parantheses are one standard deviation (in wt%) calculated by Monte Carlo error propagation from phase composition inhomogeneities. ^b Phase proportions calculated excluding FeO due to significant Fe-loss to the capsule.

 $^{\circ}\,$ Experiments with carbonate or carbonatite melt include CO $_2\,$ as mass balance component.

 $^{\rm d}$ Subsolidus experiments include ${\rm H_2O}$ as mass balance component.



Fig. 5.1. P-T diagram of the experimental results with phase stability fields in KNCaFMAS-HC. Solid lines are determined reactions points denote individual experiments. Numbers denote the calculated proportions (Tab. 5.2) of silicate melt (black) and carbonatite melt (red). Quartz/coesite reaction from Bohlen and Boetcher (1982).

5.3.2. Phase stability and phase relations

Experiments below the solidus produce the expected phase assemblage carbonate+ phengite+clinopyroxene+garnet+kyanite+quartz/coesite from 2.5 to 5.0 GPa. More surprisingly, the stable carbonate in our bulk composition is always Fe-Mg-calcite, which is different from basaltic compositions, in which calcite is replaced by dolomite in turn by magnesite (or aragonite) with increasing pressure (Dasgupta et al. 2004, Molina and Poli 2000). The solidus is confined to 1050-1100 °C at 5.0 GPa (Fig. 5.2B), 950-1000 °C at 3.7 GPa (Fig. 5.2D), and near 900 °C at 2.5 GPa (Fig. 5.2G). At the solidus, phengite and quartz/coesite disappear concomitantly. Experiments just above the solidus have rounded vesicles in the silicate glass (Fig. 5.2B-I), indicating the presence of some fluid at supersolidus conditions. Fe-Mg-calcite is stable to < 1100 °C at 2.5 GPa and to 1150 °C at 3.5 GPa (Fig. 5.2D+G), coexisting with silicate melt above the solidus. At 5.0 GPa, calcite does not occur above the solidus. Coexisting silicate and carbonatite liquids form in 3 experiments at 1100 °C (AM-04 and AM-24 at 3.7 GPa and ME-110 at 5.0 GPa), the carbonatite melt replacing calcite in the phase assemblage (Fig. 5.2B+E+F). Experiments are kyanite-saturated and contain clinopyroxene and garnet to ≥ 1150 °C at 5 GPa, to 1200 °C at 3.5 GPa and to <1000 °C at 2.5 GPa. At this latter pressure, garnet exhausts at 1100 °C before clinopyroxene and kyanite (Fig. 5.2H), while all three of them melt out between 1200 and 1250 °C at 3.5 GPa.

Fig. 5.2 (next page). BSE-images of run products with pressure and temperature (GPa/ °C). (A) The subsolidus phase assemblage phe+gt+cpx+cc+coe. (B) Initial melting at 5.0 GPa forms immiscible silicate and carbonatite melts with gt+cpx+ky, whereas at 1150 °C (C) a single silicate melt occur. (D) Initial silicate melt at 3.7 GPa coexists with rounded Fe-Mg-calcite, the latter being replaced by carbonatite melt at 1100 °C (E+F). (G) Initial melting at 2.5 GPa with possible fluid present. (H) Rounded bubble in the calcite-free silicate melt+gt+ky/cor stability field. (I) Dissolution of a Ca-rich quench phase (< 0.5 µm white blebs) in the silicate melt matrix and concentrated at rims of vesicles.All melting experiments at 3.5 to 5.0 GPa includes numerous, < 0.5 µm (white) blebs (e.g. C+I) of a Ca-rich quench phase, whereas at 2.5 GPa this quench phase is sparse or absent (H).





Fig. 5.3. Calculated modes as weight fractions (Tab. 5.2) of observed phases for the three pressure series at 5.0 GPa, 3.7 GPa (900-1100 °C) to 3.5 GPa (1150-1300 °C) and 2.5 GPa. Carbonatite melt has (yet) not been detected at 2.5 GPa.

5.3.3. Silicate melt composition

The first produced silicate melt occurs as small interstitial pools of $< 10 \,\mu\text{m}$ in size (Fig. 5.2B+D+G). Numerous speckles of a Ca-rich phase typically $\le 0.5 \,\mu\text{m}$ in size are dispersed throughout the silicate melt (Fig. 5.2C+1), probably representing quench carbonates exsolved from the silicate melt. The speckles are too small to analyse individually and too abundant to analyze speckle-free silicate melt. Silicate melt compositions (Tab. 5.3A) are thus average melt compositions including the quench speckles. Melts just above the solidus are rich in K₂O and SiO₂, and low in CaO, MgO, FeO_{tot} and Na₂O, indicating a dominance of phengite+quartz/coesite in the initial melting reaction and a minor role of jadeite component in clinopyroxene. At 2.5 and

Table 5.3A. Silicate melt c	ompositions ^a									
Run no.	AM-19	AM-22	AM-21	AM-13	AM-17	AM-07	AM-02	AM-18	AM-04	AM-24
P (GPa) / T (°C)	2.5 / 900	2.5 / 1000	2.5 / 1100	2.5/1200	2.5 / 1300	3.7 / 1000	3.7 / 1050	3.7 / 1100	3.7 / 1100	3.7 / 1100
No. analyses	7	8	13	10	18	ê	6	13	22	10
SiO ₂ (wt%)	66.9 (1.7)	62.7 (0.7)	60.6 (0.4)	50.5 (0.5)	50.8 (0.7)	64.9 (1.1)	63.5 (1.2)	60.0 (1.8)	59.6 (1.0)	60.9 (1.5)
Al ₂ O ₃	19.0 (1.2)	20.4 (0.9)	20.7 (0.1)	21.1 (0.2)	22.2 (0.4)	20.3 (1.0)	20.1 (0.2)	20.1 (0.6)	19.9 (0.6)	21.7 (0.8)
Feo	0.72 (0.40)	1.31 (0.21)	1.69 (0.12)	9.85 (0.15)	9.75 (0.24)	1.09 (0.09)	1.76 (0.36)	2.46 (0.14)	2.39 (0.27)	1.74 (0.61)
OBM	0.07 (0.28)	0.55 (0.19)	0.94 (0.05)	2.20 (0.09)	2.16 (0.12)	0.13 (0.04)	0.25 (0.09)	0.79 (0.08)	0.52 (0.07)	0.21 (0.12)
CaO	0.70 (0.89)	2.49 (0.45)	4.32 (0.05)	8.25 (0.15)	7.40 (0.17)	0.46 (0.07)	0.90 (0.26)	2.86 (0.28)	2.79 (0.26)	1.09 (0.62)
Na ₂ O	1.71 (0.60)	2.49 (0.23)	3.56 (0.27)	3.06 (0.07)	2.79 (0.13)	1.37 (0.14)	1.84 (0.41)	2.93 (0.45)	4.42 (0.32)	3.32 (0.41)
K ₂ 0	10.9 (1.1)	10.1 (1.0)	8.22 (0.10)	4.99 (0.04)	4.90 (0.07)	11.7 (0.9)	11.7 (0.5)	10.9 (0.7)	10.4 (0.3)	11.0 (0.9)
Sum	100	100	100	100	100	100	100	100	100	100
Totmessured (wt%)	91.8 (1.3)	90.7 (0.6)	90.7 (0.3)	89.1 (0.6)	92.6 (1.2)	90.1 (0.8)	91.7 (1.5)	89.4 (1.3)	88.2 (0.8)	94.0 (1.2)
H ₂ O _{cak} ^b (wt%)	3.4	2.7	1.7	1.1	1.1	3.2	3.0	2.3	2.3	2.4
CO _{2cale} ^b (wt%)	2,4	2.2	7.2	5.0	4.9	2.2	2.6	2.4	1.5	0.5
Si ^c (apfu)	3.016 (56)	2.868 (47)	2.788 (10)	2.451 (10)	2.448 (9)	2.949 (42)	2.910 (16)	2.796 (25)	2.786 (27)	2.811 (40)
Al _{lot}	1.009 (58)	1.099 (33)	1.121 (6)	1.208 (8)	1.262 (10)	1.087 (53)	1.085 (25)	1.102 (24)	1.095 (31)	1.179 (39)
Fetrot	0.027 (15)	0.050 (9)	0.065 (5)	0.400 (1)	0.393 (5)	0.042 (3)	0.068 (14)	0.096 (5)	0.094 (11)	0.067 (25)
Mg	0.005 (19)	0.038 (22)	0.065 (3)	0.159 (6)	0.156 (6)	0.009 (3)	0.017 (6)	0.055 (6)	0.036 (5)	0.014 (9)
Ca	0.034 (43)	0.122 (10)	0.213 (3)	0.429 (7)	0.382 (6)	0.022 (4)	0.044 (12)	0.143 (14)	0.140 (14)	0.054 (39)
Na	0.149 (52)	0.221 (31)	0.317 (24)	0.287 (6)	0.261 (12)	0.120 (15)	0.163 (34)	0.266 (46)	0.401 (30)	0.297 (39)
×	0.628 (26)	0.592 (37)	0.482 (6)	0.309 (4)	0.301 (3)	0.679 (66)	0.684 (40)	0.650 (52)	0.621 (21)	0.650 (61)
Total cations	4.868 (70)	4.989 (48)	5.051 (22)	5.243 (8)	5.203 (10)	4.908 (57)	4.971 (26)	5.108 (69)	5.173 (37)	5.073 (72)
								·		
K ₂ O/Na ₂ O (wt%)	6.39	4.07	2.31	1.63	1.75	8.59	6.36	3.72	2.36	3.32
Al/(Na+K+2*Ca) (molar)	1.19	1.04	0.91	0.83	0.95	1.29	1.16	0.92	0.84	1.12
D _{Na} (cpx/melt) (wt%)	3.10	1.48	0.55	1	I	7.32	5.35	2.39	1.84	2.66
X _{Mg} (Fe _{tot}) (molar)	0.15	0.43	0.50	0.28	0.28	0.17	0.20	0.36	0.28	0.17
CIPW (wt%)										
Quartz	12.9	2.2	0.0	0.0	0.0	10.0	4.3	0.0	0.0	0.0
Plagioclase	17.9	33.4	42.7	36.4	45.4	13.9	20.0	21.0	14.4	25.1
Orthoclase	64.5	59.9	48.6	29.5	29.0	69.3	69.1	64.5	61.5	65.2
Nepheline	0.0	0.0	2.0	10.1	6.4	0.0	0.0	7.1	14,4	4.6
Leucite	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Corundum	3.1	0.8	0.0	0.0	0.0	4.5	2.8	0.0	0.0	2.3
Diopside	0.0	0.0	4.4	10.1	2.7	0.0	0.0	4.1	8.8	0.0
Hypersthene	1.5	3.8	0.0	0.0	0.0	2.3	3.9	0.0	0.0	0.0
Olivine	0.0	0.0	2.4	13.9	16.6	0.0	0.0	3.3	0.9	2.8
Na ₂ SiO ₃	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0

Table 5.3A. Silicate melt c	composition (con	tinued).								
Run no.	AM-10	AM-11	AM-12	AM-16	ME-110	ME-137	pelite ^d	pelite ^d	greywacke ^d	greywacke ^d
P (GPa) / T (°C)	3.5 / 1150	3.5 / 1200	3.5 / 1250	3.5 / 1300	5.0 / 1100	5.0 / 1150	4.07850	5.0 / 950	4.0 / 900	5.0 / 950
No. analyses	15	14	15	15	4	14				
'SIO ₂ (wt%)	60.0 (1.0)	59.2 (1.0)	52.2 (0.4)	51.5 (0.5)	59.2 (1.3)	56.0 (0.7)	76.8	72.0	75.2	71.0
Al ₂ O ₃	20.5 (0.6)	20.3 (0.6)	19.5 (0.2)	20.7 (0.3)	18.4 (1.5)	19.6 (0.4)	13.4	15.0	13.5	15.6
FeO	1.65 (0.15)	2.71 (0.64)	9.96 (0.13)	9.66 (0.10)	3.06 (0.76)	4.65 (0.40)	0.81	1.14	0.84	0.88
OgM	0.72 (0.08)	1.02 (0.15)	2.19 (0.08)	2.16 (0.05)	0.50 (0.21)	0.88 (0.13)	0.32	0.28	0.28	0.30
CaO	3.04 (0.30)	5.27 (0.09)	7.43 (0.11)	8.09 (0.12)	2.45 (0.54)	5.21 (0.56)	0.85	0.87	0.56	0.52
Na ₂ O	3.45 (0.28)	3.64 (0.23)	3.28 (0.10)	3.00 (0.11)	2.44 (0.20)	4.62 (0.11)	2.36	4.00	2.30	3.48
K20	10.7 (0.2)	7.86 (0.22)	5.38 (0.06)	4.89 (0.06)	14.0 (0.8)	9.00 (0.25)	5.12	6.31	6.94	7.87
Sum	100	100	100	100	100	100	99.7	9.66	9.66	99.7
Tot _{measured} (wt%)	88.2 (1.1)	89.4 (0.52)	88.6 (0.36)	88.3 (0.69)	87.0 (1.42)	87.7 (0.40)	88.0	95.8	89.2	96.0
H ₂ O _{calc} ^b (wt%)	2.0	1.8	1.2	1.1	3.7	2.5	15.4	5.1	8.4	4.6
CO _{2calc} ^b (wt%)	4.3	7.8	5.0	4.9	2.2	10.7	I	ı	,	,
Si ^c (apfu)	2.789 (8)	2.747 (30)	2.530 (12)	2.488 (7)	2.813 (55)	2.670 (16)	3.314	3.177	3.283	3.153
Altor	1.121 (8)	1.112 (35)	1.115 (14)	1.179 (10)	1.033 (73)	1.103 (15)	0.683	0.779	0.692	0.815
Feloc	0.064 (2)	0.105 (6)	0.403 (4)	0.390 (2)	0.122 (31)	0.185 (17)	0.029	0.042	0.031	0.033
Mg	0.050 (6)	0.071 (7)	0.158 (6)	0.155 (4)	0.035 (15)	0.063 (9)	0.021	0.018	0.018	0.020
Ca	0.151 (3)	0.262 (13)	0.385 (5)	0.419 (5)	0.125 (28)	0.266 (30)	0.039	0.041	0.026	0.025
Na	0.311 (24)	0.328 (21)	0.308 (9)	0.281 (9)	0.225 (20)	0.427 (11)	0.197	0.342	0.195	0.299
×	0.632 (11)	0.466 (14)	0.332 (4)	0.301 (4)	0.847 (54)	0.547 (13)	0.282	0.355	0.387	0.446
Total cations	5.119 (17)	5.090 (21)	5.233 (11)	5.214 (8)	5.200 (22)	5.262 (13)	4.575	4.769	4.647	4.803
K20/Na20 (wt%)	3.09	2.16	1.64	1.63	5.73	1.95	2.17	1.58	3.02	2.26
Al/(Na+K+2*Ca) (molar)	0:00	0.84	0.79	0.83	0.78	0.73	1.22	1.00	1.09	1.03
D _{Na} (cpx/melt)	1.84	1.42	I	ı	3.58	1.41	4.30	1	4.35	2.96
X _{Mg} (Fe _{tot}) (motar)	0.44	0.40	0.28	0.28	0.23	0.25	0.41	0.30	0.37	0.38
Outartz			00	00	ŰŰ	00	40.7	217	53.9	18 J.
Distington		41.0	0.00	5 0		2 C		1 00	4 C C	
ridgiuciase	7.07	0.10	0,00	0. 0 0. 0	0.0	ο c ο c	7 4 V	- 0	7.77	0 I G
	03.1	0.04	0.10	£'07		7.66	0.00	C. / C	4	40.0
Nepheline	9.4	4.9	0.6	7.6	6.9	20.1	0.0	0.0	0.0	0.0
Leucite	0.0	0.0	0.0	0.0	15.2	0.0	0.0	0.0	0.0	0.0
Corundum	0.0	0.0	0.0	0.0	0.0	0.0	2.5	0.0	1.1	0.4
Diopside	5.2	8.7	12.2	9.9	10.5	16.9	0.0	0.0	0.0	0.0
Hypersthene	0.0	0.0	0.0	0.0	0.0	0.0	ر 8.	2.2	1.6	2.0
Olivine	1.6	2.3	13.2	13.6	1.1	1.5	0.0	0.0	0.0	0.0
Na ₂ SiO ₃	0.0	0.0	0.0	0.0	0.8	0.0	0.0	0.0	0.0	0.0

^a Parentheses denote one standard deviation. ^b H_2O and CO_2 content calculated from bulk and melt fraction. ^c Cations calculated on the basis of 8 oxygens. ^d Melt compositions produced from pelite and greywacke (Schmidt et al. 2004)

3.7 GPa, the first liquids are peraluminous potassic granites, at 5.0 GPa, a slightly peralkaline phonolite is produced (Fig. 5.4). With increasing temperature, SiO₂ and K₂O decrease, whereas CaO, MgO, FeO_{tot} and to a lesser extent Na₂O increase, resulting at all pressures in metaluminous phonolitic melts at \geq 1100 °C. Along the solidus, K₂O contents in melts increase (from 8.2 to 14.0 wt%) with pressure and SiO₂ contents decrease (from 66.9 to 59.2 wt%). All other trends are overruled by the lack of calcite saturation in the first supersolidus melt at 5.0 GPa, which has significantly increased CaO, MgO, FeO and Na₂O, compared to the solidus melts at 2.5 and 3.7 GPa.

The CO_2 content of the silicate melts is not quenchable and could not be directly measured. Hence, CO_2 was calculated from mass balanced phase proportions and bulk composition, yielding 1.5-2.6 wt% CO_2 (Tab. 5.3A) for experiments near the solidus, either saturated in calcite or carbonatite melt. With temperature, calculated CO_2 concentrations peak at 7.2-10.7 wt% just after the calcite- or carbonatite-out and then decrease with the increasing degree of melting. The latter values are comparable to CO_2 solubilities of natural and synthetic silicate melts at high pressures (c.g. King & Holloway 2002, Blank and Brooker 1994).

The clinopyroxene/silicate melt partitioning of Na along the solidus increases from 2.5 to 3.7 GPa with $D_{Na}^{opx/melt} = 3.1$ to 7.3, respectively; but is somewhat lower in the carbonatite-bearing near-solidus experiment at 5.0 GPa with $D_{Na}^{opx/melt} = 3.6$. The silicate melts coexist with clinopyroxenes having jadeite contents of Jd_{38} (2.5 GPa) to Jd_{68-61} (3.7 and 5.0 GPa) near the solidus. The highest partition coefficients are measured from calcite-saturated liquids, with melt fractions (F) ranging from 32 to 41 wt%. $D_{Na}^{opx/melt}$ remains between 1.8 and 1.4 with F ranging from 45 to 62, as long as garnet and kyanite coexist with clinopyroxenes of $Jd_{70.67}$ compositions for a CO₂-free pelite at 4 GPa (Schmidt et al. 2004). CO₂ obviously decreases the solubility of Na₂O in the silicate liquid at high pressures, making Na a quite incompatible element mostly stored in the residual clinopyroxene.



Fig. 5.4. Silicate melt compositions. Solidus melts are strongly potassic (A), peraluminous (B), silica-saturated granites (C). The Ca+Naenrichment with increasing temperature occurs through melting of carbonate, garnet and cpx, producing metaaluminous (B) phonolites (C). Brown arrow in (A) denote the compositional path with increasing temperature for melts produced from pelite and greywacke (Schmidt et al. 2004). Grey, dashed field in (C) is the compositional space of natural granites to phonolites/nephelinesyenites (Hamilton and MacKenzie 1965). The high-pressure minimum melts field in (C) represents the compositional range of initial melts produced from pelite (Schmidt et al. 2004), greywacke (Auzanneau et al. 2006), muscovite-granite (Huang & Wyllie 1973) and a KCMASH crust composition (Hermann & Green 2001).

Legend

■ 2.5 GPa
 ● 3.5-3.7 GPa
 ▲ 5.0 GPa

5.3.4. Carbonatite melt composition

Modal abundances of 9 wt% carbonatite liquid are produced in three experiments at 1100 °C, 3.7 GPa (AM-04, AM-24) and 5.0 GPa (ME-110), coexisting with 47 and 30 wt% silicate melt, respectively. The carbonatite melt forms < 20 μ m, rounded drops with wrinkly textures (Fig. 5.2B+E+F), similar to the carbonatites produced by Kjarsgaard (1998), Lee & Wyllie (1996, 1997), Kjarsgaard & Peterson (1991) and Wyllic & Tuttle (1960). The wrinkly texture probably indicates some exsolution of silicate and carbonate components to occur during quench. Liquids are CaO-rich (31 wt%) ferro-carbonatites (10-12 wt% FcO_{tot}), low in SiO₂ and Al₂O₃ (both ≤ 1 wt%), and contain some Na₂O (2 wt%) (Tab. 5.3B, Fig. 5.6). K₂O contents vary from 0.7 wt% K₂O at 3.7 GPa to 4.2 wt% at 5 GPa. The Ca# (i.e. Ca/(Ca+Mg+Fe) ratio) of 0.67-0.72 and X_{Mg} of 0.36-0.44 is lower

Table 3B. Carbonatite melt compositions

Run no.	AM-04	AM-24	ME-110
P (GPa) / T (°C)	3.7 / 1100	3.7 / 1100	5.0 / 1100
No. analyses	19	12	7
SiO ₂ (wt%)	1.01 (0.46)	0.91 (0.73)	0.62 (0.40)
Al ₂ O ₃	1.04 (0.21)	0.97 (0.53)	0.87 (0.26)
FeO(tot)	10.0 (0.5)	8.76 (0.76)	11.9 (0.7)
MgO	4.32 (0.49)	3.62 (0.28)	3.76 (0.36)
CaO	32.3 (2.6)	30.8 (2.1)	30.1 (1.7)
Na ₂ O	2.62 (1.42)	4.01 (2.10)	1.97 (0.61)
K₂O	0.67 (0.17)	0.71 (0.21)	4.21 (0.73)
CO ₂ (measured)	47.6 (1.8)	48.9 (2.4)	46.7 (4.4)
Sum (wt%)	99.6 (2.1)	98.6 (3.1)	100.2 (4.0)
Si ^a (apfu)	0.033 (15)	0.029 (22)	0.020 (14)
Altot	0.039 (8)	0.037 (21)	0.034 (10)
Fe ²⁺ tot	0.270 (11)	0.235 (30)	0.327 (13)
Mg	0.207 (19)	0.173 (17)	0.184 (14)
Са	1.114 (56)	1.056 (55)	1.058 (46)
Na	0.164 (92)	0.249 (95)	0.125 (39)
к	0.028 (8)	0.029 (37)	0.176 (31)
с	2.094 (204)	2.142 (233)	2.095 (353)
$X_{Mg}(Fe_{tot})$ (molar)	0.43	0.42	0.36
Ca/(Ca+Mg+Fe) (molar)	0.70	0.72	0.67
Al/(Na+K+2*Ca) (molar)	0.016	0.015	0.014
K ₂ O/Na ₂ O	0.26	0.18	2.14

^a Cations calculated on the basis of 6 oxygens.

than for the calcites (Ca# = 0.70-0.90 and $X_{Mg} = 0.50-0.74$). Calculated CO₂ contents, based on measured carbon concentrations, amount to 47(±4) wt%, resulting in analytical totals close to 100 wt%, however the analytical error on CO₂ still allow for up to 4 wt% H₂O in the carbonatite melt. Above 1100 °C (at 3.7-5.0 GPa), the carbonatite melt dissolves into the silicate melt.

5.3.5. Mineral composition and crystallization.

Garnet forms subidiomorphic, 5-90 μ m large crystals, frequently with inclusions of other phases. Close to the upper temperature limit more rounded crystals occur. In four experiments, garnet exhibits growth zonation in Fe-rich cores and Mg-rich rims or patchy Fe-Mg zonation. With temperature, grossular contents increase from 28 to 38 mol% and pyrope from 10 to 23 mol% (Tab. 5.5A) (X_{Mg} increases from 0.15 to 0.38; Tab. 5.4). Significant compositional changes with pressure are not observed.

Clinopyroxenes form tabular to prismatic grains of $\leq 20 \,\mu$ m in size. Generally, Ca-eskolaite component (Tab. 5.5) decreases with increasing melt fraction from maximum Ca-eskolaite contents of 6.7-11.8 mol% at near-solidus temperatures to 0 mol% at 1200 °C (Fig. 5.5B), in agreement with Ca-eskolaite trends from comparable bulk compositions (e.g. Schmidt et al. 2004, Hermann 2002, Schultze et al. 2000, Schmädicke & Müller 2000, Katayama et al. 2000), own experiments in KCaMAS-HC (Thomsen & Schmidt, submitted), and from basaltic compositions (Schmidt et al. 2004, Pertermann and Hirschmann 2003). Jadeite contents decrease from Jd₆₈₋₇₂ (900-1000 °C) to Jd₃₇₋₄₆ (1150-1200 °C) at 3.5 and 5.0 GPa, and from Jd₄₇ (850 °C) to Jd₁₄ (1100 °C) at 2.5 GPa. Across the solidus, the small decrease in jadeite and Ca-Tschermak contents suggests that clinopyroxene plays a minor role in initial melting reactions, in particular at the two higher pressures studied. Above the solidus, tetrahedral alumina increases with temperature (0.02 to 0.25 Al pfu, 850-1200°C and 3.5-5.0 GPa, and 0.14 to 0.35 Al pfu, 850 to 1100 °C at 2.5 GPa), which, combined with increasing CaO and MgO, yields increasing diopside and Ca-Tschermak contents in clinopyroxene. From 2.5 to 3.7 GPa, jadeite content increases and Ca-Tschermak component decreases at the solidus, whereas no significant compositional changes is observed from 3.7 to 5.0 GPa.

Table 5.4. Garnet	composition							
Run no.	AM-23	AM-19	AM-22	AM-03	AM-08	AM-07	AM-02	AM-04
P (GPa) / T (°C)	2.5 / 850	2.5 / 900	2.5 / 1000	3.7 / 900	3.7 / 950	3.7 / 1000	3.7 / 1050	3.7 / 1100
No. analyses	4	10	7	8	10	5	13	11
SiO ₂ (wt%)	37.8 (0.9)	38.5 (0.3)	38.7 (05)	37.9 (0.3)	38.0 (0.2)	39.0 (0.3)	38.7 (0.3)	38.6 (0.5)
Al ₂ O ₃	21.7 (0.6)	21.4 (0.4)	20.1 (0.3)	21.3 (0.1)	21.2 (0.2)	21.8 (0.2)	21.5 (0.4)	21.7 (0.6)
Fe ₂ O ₃	1.24 (0.96)	0.92 (0.44)	1.93 (1.17)	0.82 (0.33)	0.78 (0.52)	0.00 -	1.09 (0.57)	0.87 (0.72)
FeO	24.7 (0.7)	23.3 (0.8)	20.8 (1.0)	26.1 (0.48)	25.1 (0.4)	23.4 (1.3)	23.2 (1.6)	21.2 (2.1)
MgO	2.95 (0.24)	3.57 (0.51)	4.51 (0.38)	2.64 (0.3)	3.57 (0.42)	4.59 (0.78)	4.67 (0.55)	5.05 (0.75)
CaO	11.3 (0.2)	12.6 (0.4)	13.0 (0.5)	10.8 (0.6)	10.2 (0.6)	10.6 (0.7)	10.9 (1.1)	11.7 (1.5)
Na ₂ O	0.09 (0.08)	0.03 (0.02)	0.12 (0.04)	0.12 (0.05)	0.12 (0.05)	0.09 (0.02)	0.11 (0.05)	0.12 (0.06)
K₂O	0.11 (0.03)	0.02 (0.01)	0.05 (0.03)	0.03 (0.04)	0.07 (0.02)	0.10 (0.04)	0.09 (0.07)	0.11 (0.11)
Sum°	100.0 (0.8)	100.4 (0.2)	99.3 (0.6)	99.8 (0.4)	99.1 (0.3)	99.5 (0.3)	100,2 (0.6)	99.4 (0.9)
Si ^a (apfu)	2.970 (43)	2.992 (22)	3.027 (45)	2.993 (11)	3.002 (11)	3.038 (14)	2.998 (22)	2.992 (26)
Al _{to1}	2.010 (52)	1.966 (27)	1.855 (36)	1.977 (10)	1.975 (11)	2.000 (22)	1.963 (29)	1.989 (35)
Fe ³⁺	0.073 (54)	0.054 (29)	0.114 (79)	0.049 (19)	0.047 (31)	0.000	0.064 (33)	0.051 (43)
Fe ^{2*}	1.625 (45)	1.517 (57)	1.363 (68)	1.725 (35)	1.663 (31)	1.522 (89)	1.504 (107)	1.376 (153)
Mg	0.345 (20)	0.413 (51)	0.526 (50)	0.311 (32)	0.420 (48)	0.533 (89)	0.539 (61)	0.583 (81)
Са	0.952 (19)	1.051 (32)	1.093 (78)	0.916 (51)	0.867 (50)	0.884 (57)	0.903 (94)	0.974 (116)
Na	0.013 (13)	0.004 (3)	0.017 (7)	0.018 (8)	0.019 (8)	0.013 (2)	0.017 (7)	0.018 (8)
X _{Mg} (Fe _{tot}) (molar)	0.17 (11)	0.21 (3)	0.26 (6)	0.15 (13)	0.20 (2)	0.26 (4)	0.26 (3)	0.29 (5)

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Run no.	AM-18	AM-24	AM-10	AM-11	ME-109	AM-15	ME-110	ME-137
P (GPa) / T (°C)	3.7 / 1100	3.7 / 1100	3.5 / 1150	3.5 / 1200	5.0 / 1000	5.0 / 1050	5.0 / 1100	5.0 / 1150
No. analyses	10	10	34	37	4	5	13	12
SiO ₂ (wt%)	38.8 (0.7)	38.0 (0.8)	38.7 (0.7)	39.1 (0.5)	38.4 (0.3)	38.4 (0.9)	38.5 (0.5)	37.9 (0.4)
Al ₂ O ₃	20.7 (0.5)	21.1 (0.6)	21.7 (0.7)	21.4 (0.7)	21.5 (0.1)	20.2 (0.7)	21.7 (0.2)	21.5 (0.5)
Fe ₂ O ₃	2.07 (1.36)	1.83 (1.01)	1.35 (0.74)	1.51 (0.88)	1.47 (0.28)	2.81 (1.55)	4.60 (1.19)	3.23 (0.77)
FeO	19.6 (1.3)	23.6 (1.7)	18,7 (2.7)	16.9 (2.0)	24,9 (0.2)	23.3 (1.7)	15.2 (1.3)	19.0 (1.5)
MgO	5.27 (0.20)	4.55 (1.48)	5.43 (1.46)	6.22 (1.00)	3.68 (0.74)	3.84 (0.16)	6.27 (1.08)	5.06 (1.46)
CaO	13.2 (0.4)	10.4 (0.5)	13.6 (1.8)	14.3 (1.1)	10.9 (1.0)	11.0 (0.8)	13.1 (1.2)	12.9 (1.3)
Na ₂ O	0.07 (0.02)	0.07 (0.04)	0.06 (0.03)	0.09 (0.03)	0.05 (0.02)	0.16 (0.16)	0.26 (0.10)	0.14 (0.14)
K₂O	0.04 (0.01)	0.02 (0.01)	0.08 (0.02)	0.04 (0.02)	0.12 (0.05)	0.13 (0.03)	0.57 (0.28)	0.07 (0.07)
Sum ^c	99.8 (0.5)	99.7 (0.8)	99.6 (0.5)	99.5 (0.4)	100.9 (0.2)	99.8 (0.6)	100.1 (0.6)	99.8 (0.5)
Si ^a (apfu)	3.002 (44)	2.977 (20)	2.983 (19)	2.996 (11)	2.983 (14)	3.018 (55)	2.939 (19)	2.934 (12)
Al _{tot}	1.890 (43)	1.950 (30)	1.972 (44)	1.932 (41)	1.966 (11)	1.871 (59)	1.949 (22)	1.965 (25)
Fe³⁺	0.121 (80)	0.108 (61)	0.078 (44)	0.087 (51)	0.086 (16)	0.129 (92)	0.264 (69)	0.188 (36)
Fe ²⁺	1.269 (82)	1.548 (126)	1.205 (263)	1.082 (140)	1.615 (13)	1.570 (101)	0.968 (82)	1.232 (72)
Mg	0.608 (23)	0.529 (167)	0.624 (158)	0.710 (107)	0.426 (84)	0.449 (19)	0.713 (119)	0.582 (39)
Ca	1.095 (31)	0.876 (49)	1.121 (133)	1.174 (86)	0.905 (87)	0.925 (73)	1.071 (101)	1.068 (59)
Na	0.010 (3)	0.010 (6)	0.009 (4)	0.013 (4)	0.007 (2)	0.024 (24)	0.038 (15)	0.021 (29)
X _{Mg} (Fe _{tot}) (molar)	0.30 (1)	0.24 (8)	0.33 (10)	0.38 (7)	0.20 (3)	0.21 (9)	0.37 (4)	0.29 (1)

* Cations calculated on the basis of 8 cations and 12 oxygens.



Fig. 5.5. Composition of garnet, clinopyroxene, and phengite. (A) Garnet composition show a general decrease in almandine and increase in grossular and pyrope contents. At 3.5-3.7 GPa, subsolidus garnet is enriched in pyrope only, whereas supersolidus garnets with T increase in grossular and pyrope content. (B) Clinopyroxene compositions show the highest Caeskolaite content at sub- and nearsolidus temperatures. With pressure, jadeite content increases. (C) Phengites show increasing celadonite content with P due to tschermak's substitution (inset) along the dioctahedral muscoviteceladonite solid solution.

Table 5.5. Clinop	yroxene compos	ition							
Run no.	AM-23	AM-19	AM-22	AM-21	AM-03	AM-08	AM-07	AM-02	AM-18
P (GPa) / T (°C)	2.5 / 850	2.5 / 900	2.5 / 1000	2.5/1100	3.7 / 900	3.7 / 950	3.7 / 1000	3.7 / 1050	3.7 / 1100
No. analyses	4	2	5	9	8	11	3	15	6
SiO ₂ (wt%)	52.4 (0.8)	51.3	48.1 (0.7)	44.6 (0.9)	57.4 (0.5)	56.8 (0.3)	56.3 (0.4)	55.4 (0.7)	51.6 (0.7)
Al ₂ O ₃	17.9 (0.5)	17.2	18.0 (0.5)	18.6 (0.6)	20.8 (0.8)	21.0 (0.5)	21.7 (0.2)	20.4 (0.6)	20.3 (0.6)
FeOtot	10.1 (0.17)	10.20	8.33 (0.24)	6.53 (0.19)	4.08 (0.88)	3.81 (0.27)	3.57 (0.06)	3.98 (0.68)	5.17 (1.04)
MgO	3.61 (0.21)	3.92	5.61 (0.37)	7.32 (0.24)	2.13 (0.39)	2.06 (0.23)	2.33 (0.39)	3.25 (0.33)	4.33 (0.33)
CaO	9.01 (0.32)	11.9	16.0 (0.5)	20.6 (0.2)	5.15 (1.04)	5.01 (0.49)	5.33 (0.52)	6.90 (0.79)	11.3 (0.2)
Na ₂ O	6.78 (0.45)	5.30	3.69 (0.35)	1.96 (0.10)	10.7 (0.5)	10.6 (0.3)	9.99 (0.42)	9.85 (0.54)	7.01 (0.83)
K₂O	0.07 (0.03)	0.10	0.12 (0.07)	0.06 (0.03)	0.04 (0.06)	0.09 (0.02)	0.11 (0.01)	0.13 (0.05)	0.21 (0.11)
Sum	99.9 (0.8)	99.9	99.8 (1.0)	99.7 (0.8)	100.3 (0.7)	99.3 (0.4)	99.3 (0.5)	99.9 (0.6)	99.9 (0.3)
Si ^a (aptu)	1.887 (54)	1.862	1.757 (14)	1.647 (43)	1.978 (7)	1.973 (5) 0.861 (17)	1.953 (11)	1.935 (15)	1.834 (22)
7ºtot	0.700 (49)	0.730	0.777 (29)	0.009 (02)	0.044 (20)	0.001 (17)	0.003 (3)	0.040 (13)	0.0463 (27)
re	0.305 (24)	0.310	0.255 (10)	0.202 (27)	0.118 (18)	0.111 (8)	0.104 (2)	0.116 (20)	0.155 (62)
Mg	0.194 (18)	0.212	0.306 (19)	0.403 (20)	0.110 (16)	0.107 (12)	0.120 (20)	0.169 (18)	0.229 (17)
Ca	0.348 (30)	0.463	0.627 (25)	0.817 (19)	0.190 (31)	0.187 (19)	0,198 (20)	0.258 (31)	0.431 (9)
Na	0.474 (25)	0.373	0.262 (16)	0.141 (14)	0.717 (32)	0.712 (17)	0.672 (28)	0.647 (33)	0.483 (58)
ĸ	0.003 (1)	0.005	0.006 (2)	0.003 (1)	0.002 (2)	0.004 (1)	0.005 (1)	0.006 (2)	0.010 (5)
Total cations	3.971 (47)	3.959	3.988 (12)	4.021 (54)	3.959 (10)	3.954 (6)	3.941 (3)	3.971 (7)	3.988 (38)
$X_{Mg}(Fe_{tot})$ (molar)	0.39 (21)	0.41	0.55 (23)	0.67 (11)	0.48 (21)	0.49 (15)	0.54 (44)	0.59 (27)	0.60 (55)
Oct. Vacancy ^b	0.029 (9)	0.041	0.012 (11)	0	0.041 (10)	0.046 (6)	0.059 (3)	0.029 (7)	0.012 (8)
Jadeite (mol%)	47.7 (3.1)	37.7	26.7 (3.3)	14.2 (0.6)	71.9 (3.2)	71.6 (1.8)	67.7 (2.9)	65.2 (3.5)	49.3 (2.1)
Ca-eskolaite	5.7 (2.3)	8.2	2.4 (1.3)	0.0 -	8.2 (1.4)	9.2 (0.9)	11.8 (0.8)	5.7 (1.5)	2.3 (1.8)
Ca-Tschermak	11.3 (2.9)	13.8	24.3 (2.7)	30.9 (1.5)	2.2 (0.7)	2.7 (0.5)	4.7 (1.0)	6.5 (1.8)	16.6 (1.6)

Run no.	AM-04	AM-24	AM-10	AM-11	ME-109	AM-15	ME-110	ME-137
P (GPa) / Ť (°C)	3.7 / 1100	3.7 / 1100	3.5 / 1150	3.5 / 1200	5.0 / 1000	5.0 / 1050	5.0 / 1100	5.0 / 1150
No. analyses	13	12	11	9	5	6	9	9
SiO ₂ (wt%)	53.1 (0.8)	53.6 (0.8)	50.2 (0.6)	48.2 (0.5)	56.7 (0.3)	56.6 (0.5)	55.0 (0.5)	49.6 (0.6)
Al ₂ O ₃	20.5 (0.7)	20.5 (0.5)	20.9 (1.7)	20.1 (0.6)	21.0 (0.8)	20.1 (0.6)	20.0 (1.0)	20.5 (0.2)
FeO _{tot}	4.03 (0.22)	3.97 (0.26)	3.96 (0.29)	6.02 (0.93)	3.65 (0.68)	4.03 (0.33)	4.23 (0.90)	6.60 (0.19)
MgO	3.96 (0.43)	3.50 (0.36)	4.90 (0.75)	4.79 (0.75)	2.39 (0.29)	2.54 (0.22)	3.56 (0.33)	4.16 (0.20)
CaO	9.55 (0.48)	8.63 (0.38)	13.1 (0.7)	14.8 (0.9)	5.20 (0.62)	5.60 (0.43)	8.11 (0.57)	12.0 (0.3)
Na₂O	8.12 (0.32)	8.84 (0.37)	6.34 (0.35)	5.16 (0.45)	10.7 (0.6)	10,3 (0.59)	8.73 (0.42)	6.50 (0.18)
K20	0.10 (0.05)	0.08 (0.08)	0.11 (0.03)	0.04 (0.02)	0.06 (0.05)	0.28 (0.13)	0.46 (0.22)	0.12 (0.09)
Sum	99.39 (1.0)	99.06 (0.9)	99.55 (0.2)	99.12 (0.3)	99.68 (0.1)	99.42 (0.2)	100.08 (0.7)	99.54 (0.4)
Si ^a (apfu)	1.875 (14)	1.894 (19)	1.791 (12)	1.752 (16)	1.968 (4)	1.974 (10)	1.924 (15)	1.789 (13)
∧l _{tot}	0.854 (31)	0.853 (21)	0.878 (48)	0.862 (24)	0.858 (28)	0.827 (21)	0.822 (39)	0.871 (11)
Fe	0.119 (7)	0.117 (13)	0.118 (9)	0.183 (29)	0.106 (20)	0.118 (12)	0.124 (27)	0.199 (16)
Mg	0.208 (22)	0.184 (20)	0.260 (41)	0.259 (41)	0.124 (15)	0.132 (12)	0.186 (17)	0.224 (10)
Ca	0.361 (19)	0.327 (15)	0.501 (29)	0.577 (34)	0.193 (23)	0.209 (18)	0.304 (20)	0.463 (14)
Na	0.556 (18)	0.606 (23)	0.438 (23)	0.364 (32)	0.707 (37)	0.690 (41)	0.591 (33)	0.454 (13)
к	0.005 (2)	0.004 (4)	0.005 (1)	0.002 (1)	0.003 (2)	0.012 (6)	0.021 (10)	0.006 (4)
Total cations	3.978 (13)	3.985 (21)	3.992 (9)	4.000 (8)	3.958 (10)	3.963 (26)	3.971 (19)	4.006 (9)
X _{Mg} (Fe _{tot}) (molar)	0.637 (23)	0.611 (20)	0.688 (37)	0.586 (75)	0.539 (19)	0.529 (16)	0.600 (46)	0.529 (15)
Oct. Vacancy ^b	0.022 (12)	0.015 (9)	0.008 (7)	0	0.042 (10)	0.037 (34)	0.029 (18)	0
Jadeite (mol%)	67.2 (1.9)	61.0 (2.5)	AA A 12 31	36.6 /3.0\	72.2 (3.5)	70.0 (3.2)	61.2 (2.7)	45 9 (1 2)
Ca askalaita	4.2 (2.4)	01.0 (2.3)	16(15)	0.0 (1.4)	67 (17)	70.9 (3.2) 6 A (3.0)	E R (2 E)	40.8 (1.2)
Ca-Tschermak	4.3 (2.4) 12.5 (1.6)	3.1 (1.5) 10.6 (1.9)	20.9 (2.8)	24.8 (2.3)	3.4 (0.7)	2.7 (1.2)	5.6 (2.5) 7.6 (1.6)	20.0 (1.0)
roononnak		10.0 (1.0)	2010 (2.0)	27.0 (2.0)	0.1(0.1)	(,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	1.0 (1.0)	20.0 (1.0)

^a Cations calculated on the basis of 12 charges (Cawthorn and Collerson, 1974).

^b Octahedral site vacancy calculated as 4 - total cations.

Below the solidus, *Fe-Mg-calcites* form 5-25 μ m, polyhedral grains. Above the solidus the calcites become rounded (Fig. 5.2D) or dumbbell-shaped, similar to the supersolidus calcites of Kjarsgaard (1998), Lee & Wyllie (1994, 1996) and Wyllie & Tuttle (1960). The Fc-Mg-rich calcites (Tab. 5.6, Fig. 5.6A) have molar Mg# of 0.48-0.74, increasing with temperature, and do not show any significant compositional variation with pressure.

Table 5.6. Carbonate composition

Run no.	2.5 / 850	2.5 / 900	2.5 / 1000	3.7 / 900	3.7 / 950	3.7 / 1000
No. analyses	4	5	4	3	4	4
FeO _{tot} (wt%)	8.06 (0.44)	3.69 (1.30)	2.96 (0.14)	9.96 (0.41)	9.11 (0.48)	7.56 (0.32)
MgO	5.25 (0.37)	3.75 (0.97)	3.55 (0.14)	5.55 (0.19)	5.39 (0.71)	5.30 (0.29)
CaO	40.8 (0.9)	47.9 (1.0)	49.5 (1.0)	38.8 (1.0)	40.0 (1.5)	41.6 (0.3)
Na ₂ O	0.15 (0.07)	0.10 (0.05)	0.11 (0.09)	0.15 (0.06)	0.07 (0.08)	0.12 (0.05)
K₂O	0.17 (0.12)	0.19 (0.06)	0.15 (0.07)	0.17 (0.05)	0.20 (0.05)	0.21 (0.03)
CO2 ^a	43.5 (0.5)	44.8 (0.7)	45.2 (0.6)	43.4 (0.7)	43.4 (1.3)	43.9 (0.4)
Total	97.9 (1.5)	100.5 (1.0)	101.5 (1.8)	98.0 (1.3)	98.2 (1.9)	98.7 (1.0)
calcite (mol%)	0.747 (11)	0.852 (4)	0.869 (10)	0.711 (5)	0.730 (9)	0.755 (4)
siderite	0.115 (9)	0.052 (19)	0.041 (5)	0.143 (2)	0.130 (11)	0.107 (4)
magnesite	0.134 (10)	0.092 (22)	0.087 (6)	0.142 (3)	0.137 (17)	0.134 (7)

Run no.	3.7 / 1050	3.7 / 1100 ^b	3.5 / 1150	5.0 / 1 000	5.0 / 1050
No. analyses	10	5	5	10	4
FeO _{tot} (wt%)	6.16 (0.26)	2.26 (0.14)	1.36 (0.09)	8.23 (0.80)	7.83 (1.96)
MgO	4.75 (0.18)	3.16 (0.06)	2.17 (0.07)	6.40 (0.49)	5.50 (0.98)
CaO	43.3 (0.3)	49.1 (0.7)	50.8 (0.4)	39.7 (1.0)	40.9 (0.4)
Na₂O	0.12 (0.05)	0.11 (0.04)	0.08 (0.04)	0.47 (0.17)	0.08 (0.06)
K ₂ O	0.19 (0.06)	0.22 (0.04)	0.27 (0.02)	0.68 (0.25)	0.44 (0.17)
CO ₂ ^a	43.8 (0.4)	44.2 (0.6)	44.2 (0.3)	44.9 (0.9)	44.8 (1.2)
Total	98.4 (0.7)	99.1 (1.4)	98.9 (0.7)	100.3 (1.0)	99.4 (2.5)
				:	
calcite (mol%)	0.788 (3)	0.883 (2)	0.922 (2)	0.723 (18)	0.744 (12)
siderite	0.087 (4)	0.031 (2)	0.019 (1)	0.116 (14)	0.111 (25)
magnesite	0.120 (4)	0.082 (1)	0.055 (2)	0.161 (10)	0.139 (21)

^a Calculated CO₂ content from norm.

^b Experiment AM-18.

Phengite (Si-rich white mica) occurs as subidiomorphic, tabular grains of 5-20 μ m in size. Total cations contents are 6.91-6.99 apfu (Tab. 5.7), thus phengites are almost ideal dioctahedral micas along the muscovite–celadonite solid solution (Fig. 5.5C), the (Mg,Fc)-tschermak's substitution being the dominant exchange mechanism. Si increases with pressure from 3.1 Si pfu to 3.4 Si pfu (2.5 to 5.0 GPa). Generally, phengites and carbonates are the most magnesium-rich phases in the assemblage with X_{Mg} (phe) ~ X_{Mg} (cc) > X_{Mg} (cpx) > X_{Mg} (gt).

Quartz/coesite are pure in composition, forming anhedral grains $\leq 10 \ \mu\text{m}$ in size. *Ky-anite* and *corundum* contain 0.5-2.2 wt% FeO_{tot} and form $\leq 20 \ \mu\text{m}$ (up to 100x30 $\ \mu\text{m}$) laths or prismatic grains, frequently with inclusions of other phases in the phase assemblage.

P (GPa) / T (°C)	2.5 / 850	2.5 / 900	3.7 / 900	3.7 / 950	5.0 / 1000	5.0 / 1050
No. analyses	4	8	4	5	9	5
SiO ₂ (wt%)	46.6 (0.4)	46.8 (0.6)	48.8 (0.3)	48.2 (0.6)	48.1 (0.6)	51.3 (0.8)
Al ₂ O ₃	32.7 (1.0)	32.4 (1.2)	30.6 (0.5)	31.1 (0.4)	29.1 (1.1)	27.3 (0.3)
FeO	3.41 (0.54)	1.63 (0.70)	2.63 (0.29)	2.76 (0.18)	3.93 (0.62)	2.64 (0.43)
MgO	1.84 (0.19)	1.94 (0.28)	1.99 (0.15)	1.86 (0.02)	2.35 (0.27)	3,11 (0.22)
CaO	0.11 (0.05)	0.14 (0.06)	0.05 (0.03)	0.08 (0.02)	0.11 (0.05)	0.16 (0.07)
Na ₂ O	0.48 (0.09)	0.60 (0.12)	0.33 (0.03)	0.26 (0.04)	0.25 (0.06)	0.01 (0.01)
K₂O	10.1 (0.7)	9.7 (0.59)	10.5 (0.1)	10.5 (0.1)	11.2 (0.1)	10.7 (1.1)
H ₂ O _{calculated}	4.46 (0.04)	4.42 (0.03)	4.47 (0.03)	4.46 (0.04)	4.41 (0.05)	4.49 (0.03)
Total	99.8 -0.6	97.5 (0.6)	99.3 (0.6)	99.2 (0.8)	99.5 (1.2)	99.7 (0.9)
Si ^a (apfu)	3.131 (52)	3.179 (47)	3.275 (9)	3.242 (21)	3.266 (47)	3.427 (41)
Al [™]	0.869 (46)	0.821 (20)	0.725 (10)	0.758 (10)	0.734 (21)	0.573 (41)
AI ^{VI}	1.724 (41)	1.769 (63)	1.695 (18)	1.710 (25)	1.596 (49)	1.574 (37)
Fe _{tot}	0.192 (41)	0.093 (36)	0.147 (14)	0.155 (9)	0.223 (31)	0.147 (21)
Mg	0.184 (33)	0.197 (28)	0.199 (15)	0.187 (10)	0.238 (28)	0.310 (20)
Са	0.008 (4)	0.010 (4)	0.004 (2)	0.006 (2)	0.008 (4)	0.011 (5)
Na	0.062 (10)	0.079 (16)	0.043 (4)	0.034)6)	0.032 (8)	0.001 (1)
к	0.868 (72)	0.837 (54)	0.899 (10)	0.899 (4)	0.974 (11)	0.913 (46)
Total cations	7.037 (87)	6.984 (43)	6.986 (8)	6.990 (7)	7.072 (14)	6.957 (47)
X _{M0} (Fe _{tot}) (molar)	0.49	0.68	0.57	0.55	0.52	0.68
Octahedral vacancy	0.901	0.942	0.959	0.948	0.942	0.969

Table 5.7. Phengite composition

^a Cations calculated on the basis of 12 oxygens including 2 (OH).

5.4. Solidus and melting reaction

The subsolidus mode of the selected carbonaceous metapelite is $27 \rightarrow 25$ wt% phengite, 11 \rightarrow 9 wt% quartz/cocsite, $29\rightarrow$ 21 wt% clinopyroxene, 9-10 wt% calcite, 9-11 wt% kyanite and 14 \rightarrow 23 wt% garnet (at 2.5 \rightarrow 5.0 GPa). The variations with pressure along the solidus arc (i) an increase of the equilibrium concentration of jadeite in clinopyroxene resulting in a decrease of the absolute amounts of all other clinopyroxene components as, at subsolidus conditions, the total amount of jadeite is fixed by the bulk composition, (i) a decrease of tschermak's exchange (*tk*) in clinopyroxene (and phengite) with pressure, and (iii) consequently a reaction of the type: 2 diopside + 1 *tk* = 1 garnet, causing the observed strong increase of garnet mode with pressure.

5.4.1. The silicate melting reaction

The rapid generation of large amounts of silicate melt (30-35 wt%) within < 50 °C is controlled by melting out of phengite and quartz/coesite (Fig. 5.3). The reaction responsible for the production of the first observed silicate melt (within error identical at 2.5 and 3.7 GPa) is

$$0.73 \text{ phe} + 0.29 \text{ qtz/coe} + 0.14 \text{ cpx} + 0.02 \text{ cc} =$$

$$1.00 \text{ silicate melt} + 0.14 \text{ gar} + 0.03 \text{ ky}$$
 (1a)

in weight proportions. The educt phengite:quartz/coesite ratio of reaction (1b) is close to our subsolidus mode, which explains the large proportion of melt and the subsequent disappearance of both phases at the solidus. At 5 GPa, the solidus reaction is a combined reaction that produces silicate and carbonatite melt. Subtracting a simplified Fe-Mg-calcite = carbonatite melting reaction, as justified by the carbonatite melt composition, the resulting silicate melting reaction is

0.85 phe + 0.30 coe + 0.08 cpx + 0.03 cc =

$$1.00 \text{ silicate melt} + 0.16 \text{ gar} + 0.10 \text{ ky}$$
 (1b)

Reaction (1b) is similar to the 2.5-3.7 GPa reaction (1a), but slightly more peritectic in character, consuming less clinopyroxene, and producing more garnet and kyanite. Reaction (1a) compares to

$$0.50 \text{ phe} + 0.88 \text{ qtz/coe} + 0.10 \text{ cpx} + \text{H}_2\text{O} =$$

1.00 silicate melt + 0.35 gar + 0.12 ky (2)

the H_2O -saturated melting reaction of a pelite located between 790 and 850 °C at 4 GPa (calculated from Schmidt et al. 2004, their table 2). Reaction (2) produces highly siliceous granite with 76 wt% SiO_2 , 13 wt% Al_2O_3 , and a K_2O/Na_2O wt-ratio of 2.2, whereas the melt produced through reaction (1) is a potassic granite with 65 wt% SiO_2 , 20.3 wt% Al_2O_3 and a K_2O/Na_2O wt-ratio of 8.6.

5.4.2. Discussion of the solidus

Melt was not observed at temperatures below the massive production through reaction (1) as defined above, making reaction (1) our apparent solidus. However, as the experimental system contains two volatile components, H_2O and CO_2 , and four major solid solutions (phengite, clinopyroxene, garnet, and Fe-Mg-calcite), it is virtually impossible that for any P-T condition our bulk composition corresponds to exactly the sum of equilibrium mineral compositions with the exact amount of H_2O and CO_2 that can be stored in these solid solutions. As there is no sign for fluid undersaturation (e.g. the appearance of K-feldspar), we have to assume that some fluid was present at subsolidus conditions. The observed large vesicles in the melt indicate the presence of fluid at supersolidus conditions and this may be taken as evidence that fluid was also present in the subsolidus. The increase of approximately 150 °C (at 3.7-4.0 GPa) of our apparent solidus temperature with respect to CO_2 -free compositions (Schmidt et al. 2004) cannot be attributed to the effect of lowering H_2O activity through CO_2 in the fluid. Equilibrium fluid compositions have > 85 mol% H₂O (Kerrick and Connolly 2001), resulting in a shift of the fluid-

saturated melting reaction by < 30 °C. We thus argue, that the only plausible scenario is, that minor melting occurs approximately 150 °C below reaction (1), probably through the same eutectic minimum melting reaction phengite+quartz/coesite+clinopyroxene+fluid = silicate melt as defined by Schmidt et al. (2004) for H₂O-saturated pelite and greywacke. With a two component fluid, this reaction must not necessarily consume an educt phase, but may continue to produce minuscule amounts of melt with increasing temperature, while the fluid composition and melt volatile content adjust with temperature. The massive appearance of melt then occurs through melting reaction (1), which would be located at the fluid-absent solidus.

5.4.3. Discussion of melt compositions and relations, and previous experimental studies

Our composition was chosen for its potential fertility in melt production. In fact, a low $X_{M_{\rm R}}$ and optimal proportions of quartz and phengite with respect to reaction (1) lead to the sudden appearance of large amounts of melt through a "muscovite+quartz"-type melting reaction adapted for natural bulk compositions. Our experiments define the melting reaction for a fluid-absent carbonate-saturated pelite. Reaction (1) is qualitatively similar to melting reactions for initially H₂O-saturated greywacke (at 2.5 to 5.0 GPa, Auzanneau et al. 2006), pelite (at 4 and 5 GPa, Schmidt et al. 2004), and to muscovite-granite (at 2.5 to 3.5 GPa, Huang & Wyllie 1973), however, the role of fluid is fundamentally different. While the presence of 1 wt% of aqueous fluid causes a moderate amount of melt (8 wt%) to be produced at a granite-minimum in the pelite of Schmidt et al. (2004), the diminutive amount of free fluid in this study does not result in any appreciable quantity of melt at the fluid-saturated solidus. Instead, melting is retarded by about 150 °C to the sudden appearance of 30-35 wt% melt at the peritectic reaction (1). As pointed out above (and in Fig. 5.4C), the melts in the CO₂-bearing system are more potassic and less siliceous, and have less Na₂O and CaO than in the CO₂-free system (at 3.7-4.0 GPa). At 5 GPa, these melts become potassic phonolites in the CO2-bearing system, whereas they remain granitic in the CO₂-free system.

In anhydrous K-free basaltic eclogite with 5-15 wt% CO_2 (Dasgupta et al. 2006, 2004, Yaxley & Brey 2004), silicate melts appear at ~300 °C higher temperature (at 2.5-5.0 GPa) than in our study. Fluid-saturated experiments in KCaMAS-HC with a carbonate-saturated pelite, containing 2.1 wt% CO_2 and 3.6 wt% H₂O, yield a solidus at 850 to 900°C, 2.5 to 3.5 GPa (Thomsen & Schmidt, submitted). Furthermore, the location of our solidus is 50-100 °C higher compared to the H₃O-saturated solidus in KCMASH of Hermann (2002) and Hermann and Green (2001).

5.5. The formation and stability of carbonatite liquid

Three of the experiments produced coexisting silicate and carbonatite liquids, viz. two experiments at 1100 °C, 3.7 GPa (AM-04, AM-24) and one at 1100 °C, 5.0 GPa (ME-110). At 1100 °C, 3.7 GPa, a total of three experiments were performed, of which two produced carbonatitc liquid, whereas the third formed Fe-Mg-calcite, indicating that these experiments are near the closure of the two-liquid silicate+carbonatite solvus. All three experiments at 1100 °C wcrc performed at the same experimental conditions, however, the calcite-producing experiment at 3.7 GPa, 1100 °C (AM-18) probably had a slightly lower oxygen fugacity and higher H₂O-content than the other two experiments producing carbonatite liquid. For experiment AM-18, we did not dry the entire assemblage with the capsule loaded for 24 hours at 120 °C (otherwise our standard procedure), thus leaving some humidity and absorbed H₂O which causes a partial H₂-pressure outside the capsule.

On the pseudo-ternary projection (Fig. 5.6B, Freestone & Hamilton 1980), our carbonatite melts plot close to sövites near the CaO+MgO+FeO_{tot} apex, comparable to near-solidus Cacarbonatites from Dasgupta et al. (2006), Yaxley & Brey (2004) and Wallace & Green (1988). The coexisting silicate melts are olivine and nepheline normative but poor in FeO+MgO+CaO. In Fig. 5.6B, the carbonatite-phonolite liquid miscibility gap is depicted according to our experiments. The stable part of the miscibility gap, i.e. the portion of the miscibility gap rising above the calcite-saturation surface, is small in P-T space. The solvus is expected to disappear below the calcite saturation surface, and thus become metastable not far above 5 GPa, as the increase of CO_2 -solubility in silicate melts with pressure (Mysen et al. 1975) should further reduce the solvus width.



Fig. 5.6. (A) Compositions in CaCO₃-MgCO₃-FeCO₃ space of carbonates and carbonatite melts produced in the current experiments, compared to those produced in carbonated eclogite (D06, Dasgupta et al. 2006, YB04, Yaxley & Brey 2004) and carbonated peridotite (WG88, Wallace & Green 1988). (B) Pseudo-ternary projection (Freestone & Hamilton 1980) with the produced carbonatite and silicate melts, defining a silicate-carbo-natite liquid miscibility gap at 1100 °C (3.7 and 5.0 GPa), compared to the solvus of Dasgupta et al. (2006) and the carbonatite melt compositions produced in Yaxley & Brey (2004) and Wallace & Green (2004). Dashed line are the twoliquid solvus of the melts from Dasgupta et al. (2006).

The convergence of reaction (1) with a Clapeyron slope of 70 °C/GPa with the nearly temperature independent calcite to carbonatic phase boundary (Fig. 5.1) further suggests that the carbonate melting reaction will cross the fluid-absent solidus at pressures not much higher than 5 GPa. Hence, at higher pressures, melting will commence through carbonate melting, silicate melts will then only form at higher temperatures, as this is the case already at \geq 2.5 GPa in the K-free basalt systems (Yaxley and Brey 2004, Dasgupta et al. 2004, 2006).

Although our composition has an optimized fertility with respect to its silicate components, this is not necessarily the case for its carbonate component. As the carbonatite melt compositions imply (Tab. 5.3B), carbonatite generation in the present sedimentary and also in basaltic systems (Yaxley and Brey 2004, Dagupta et al. 2005, 2006) can be approximated in the (Fe,Mg,Ca)CO₃-system (Fig. 5.6A). This system is eutectic at 2.7 and 6.0 GPa (Irving and Wyllie 1975, Buob et al. 2006) for compositions with a $X_{ca} = Ca/(Ca+Fe+Mg) = 0.4$ and 0.5, respectively. Dolomite-bearing lithologies can thus be expected to yield the lowest carbonate melting temperatures, whereas our carbonate composition with an X_{ca} of 0.75-0.85 may lead to 70-100 °C higher melting temperatures.

5.6. Carbonate recycling during subduction and concluding remarks

Carbonate-saturated pelitic lithologies of the subducting crust are composed of an eclogitic phengite+garnet+clinopyroxene+kyanite+Fe-Mg-calcite+quartz/coesite subsolidus phase assemblage at depths between 75 and 150 km. Fluid-absent partial melting of such lithologies at high pressure would occur at 900 to 1050 °C, 2.5 to 5.0 GPa, i.e. at temperatures unrealistic for most subduction zones. To remove Fe-Mg-calcite from the residue and quantitatively recycle CO_2 from such sediments at moderate pressures (2.5-3.7 GPa), an additional 100-150 °C are required. We thus argue that in most subduction zones quantitative recycling of carbonates does not take place at typical subarc depth. Instead, confirming earlier arguments by Kerrick and

Connolly (2001) and by Connolly (2005), only relatively small amounts of the total subducted CO_2 are expected to be released, viz. only <5 % of the total CO_2 , through metamorphic reactions, because of the low X_{co_2} of 0.05-0.15 in metamorphic fluids at low temperature, high pressure conditions (Kerrick & Connolly 2001, Connolly 2005). If temperatures are high enough, about 10-20 % of the total CO_2 is flushed out through infiltration driven decarbonation with aqueous fluids released from serpentine below the sediment layer (Connolly 2005), and in extremely hot cases, up to 1 wt% bulk CO_2 is dissolved in the silicate melt when crossing the fluid-absent silicate solidus. It should be noted, that flush-melting of such carbonate-rich lithologies is difficult to achieve. In a fast spreading pacific-type stratified oceanic lithosphere, temperature gradients in the oceanic lithosphere predict the uppermost partly serpentinized peridotite to be 100-200 °C colder than the sediment layer. Thus, serpentine would have dehydrated before the carbonate-bearing sediments reach their solidus temperature.

Regarding the fertility of a sediment composition, our investigated pelite proved to be at an optimum quartz:phengite wt-ratio near 2:1, a composition close to the peritectic, exhausting both of these phases.

Finally, carbonate recycling from subducting crust becomes more likely with increasing pressure, because the calcite to carbonatite reaction has a steep slope in P-T space, and crosses below the silicate solidus not far above 5 GPa. We thus expect that carbonaceous pelites will begin to melt whenever they become incorporated into the mantle, and the subduction-caused temperature anomaly begins to relax towards an adiabatic temperature gradient. The resulting carbonatite melts are surprisingly calcic with minor Na₂O and K₂O, similar to those from metabasalts, and apart from a much lower X_{Mg} , are not far from equilibrium with mantle peridotite (Wallace & Green 1988), whereas possible coexisting potassic phonolites would react with the mantle and probably develop towards melilitic compositions.
Chapter 6

The stability of biotite (phlogopite) to 6 GPa in carbonate-saturated, Mg-rich pelites

The stability of biotite (phlogopite) to 6 GPa in carbonate-saturated, Mg-rich pelites:

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Data from this chapter is included in the chapter 4 manuscript to *Journal of Petrology* for comparison of the results.

Abstract

In experiments from 2.5 to 6.0 GPa and 850 to 1100 °C in KCaMAS-HC on a carbonatc+kyanite-saturated, Mg-rich pelite (i.e. carbonated whiteschist) with 0.74 wt% H₂O and 6.6 wt% CO₂, biotite is stable to 6.0 GPa (at 950 °C) and to 1100 °C (at 3.0 GPa) in a phase assemblage composed among kyanite, carbonates (dolomite, aragonite or magnesium calcite), garnet, corundum, clinopyroxene (aluminium-diopside), zoisite, spinel and silicate liquid. Biotite most probably controls initial melting, defining the solidus to 950-1050 °C. The stability of biotite is very much bulk composition dependent, demonstrated from comparison to other studies, in KCaMAS-H(C) especially shown by the lower Ca/(Ca+Mg) ratio of our bulk composition (~0.28) compared to compositions with higher Ca/(Ca+Mg) ratios, which produced biotite at lower pressures (and phengite at higher pressures).

6.1. Introduction

The stability of biotite has been the target of many recent studies, because it's potential to influence mass transport and metasomatism in subducting slabs and mantle wedges. Phengite (i.e. Si-rich white mica) is the predominant potassic mica controlling fluid-absent melting in pelite, greywacke and basalt from ~3 GPa to ~9-10 GPa (Ono 1998, Dominak & Holloway 1996, 2000, Schmidt 1996, Ogasawara et al. 2000, Schmidt et al. 2004), whereas biotite usually is restricted to pressures below ~3 GPa (Vielzeuf & Holloway 1988, Patiño Douce & Beard 1995, Spear 1995, Bucher & Frey 2002, Schmidt et al. 2004, Auzanneau et al. 2006). However, in bulk compositions poor in Fe and Al, biotite (phlogopite) is a major potassium phase stable to ~7-8 GPa (Konzett 1997, Konzett et al. 1997), and experiments of Trønnes (2002) show that pure phlogopitc is stable to 8-9 GPa. Starting with a natural 1M phlogopite (Cruciani & Zanazzi 1994), Comodi et al. (2004) produced increasingly K-deficient and Si-enriched phlogopites to ~6.5 GPa. For natural phlogopite and phlogopite+enstatite, Sato et al. (1997) suggested phlogopite stability to 5 GPa, whereas phlogopite coexisting with diopside± enstatite is stable to 6-7 GPa (Sudo & Tatsumi 1990), and to 6.0-6.5 GPa (at 1100 °C) for phlogopite in experiments with K-doped lhcrzolite (Konzett & Ulmer 1999). In a KNCFMASH lher-zolite, Fumagalli (2004) reported non-ideal phlogopite to 6.0 GPa (at 700-800 °C) involving a complex solid solution with tale. For a quartz+kyanite-saturated crustal composition in KCMASH, biotite is stable to 3.9 GPa at ~780 °C coexisting with different phase assemblages composed among clinopyroxene, zoisite, kyanite, quartz/coesite, phengite, amphibolc, talc or silicate liquid (Hermann 2002, 2003). In the Kokchetav Massif, Sobolev & Shatsky (1990) found biotite intergrowths with micro-diamond in garnetbiotite gneiss, indicating biotite stability to ~5 GPa, and in the Western Gneiss Region, biotite is present at 2.7-4.3 GPa and 780-850 °C in kyanite-free, picrite basaltic eclogite with CaO/MgO (wt%) ratio of ~0.5-0.7 (Lappin & Smith 1978, Smith 1988, Wain et al. 2000, Cuthbert et al. 2000,

Nakamura 2003). In the North-east Greenland Eclogite Province (NEGEP) biotite-bearing eclogites formed at > 1.5 GPa and 700-780 °C are rich in MgO and CaO but very poor in Al₂O₃ (Brueckner et al. 1998). Thus, the occurrence of biotite above ~3 GPa in basaltic and ultrabasic rocks is generally restricted to compositions with a high MgO (and X_{Mg}) and low Al₂O₃ and CaO content. For magnesium-rich metasediments with a higher Al₂O₃ content (e.g. whiteschist, Schreyer 1973, 1977), phengite+tale is the predominant phase assemblage above 3 GPa, whereas for carbonatebearing Mg-rich sediments with significant proportions of CaO and CO₂ (e.g. carbonated whiteschist), the relationship between bulk composition and phase stabilities is less clear. Hence, in this reconnaissance study, we investigate experimentally the high pressure phase petrology of carbonate-saturated, Mg-rich (and Fe-free) pelites, focusing on the stability of K-micas and in particular biotite.

6.2. Experimental and analytical techniques

Experiments were performed in the model system $K_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O-CO_2$ (KCaMAS-HC), constituting the simplest system reproducing the mineralogy of carbonate saturated Mg-rich pelites. The major differences of this simplified system with respect to the natural system are the lack of iron and sodium. The absence of Na₂O suppresses crystallization of jadeitic or omphacitic clinopyroxene and of sodic amphiboles, whereas FeO is distributed among the MgO-bearing phases, thus not producing any additional phases. Nevertheless, the stability of garnet is generally shifted to higher pressures by the absence of FeO.

6.2.1 Experimental apparatus

For the 5 and 6 GPa experiments, a Walker-type multi-anvil module employing 25 mm edge length WC-cubes with 12 mm truncation was applied, using a cast, sintered MgO octahe-

dron as pressure medium, a stepped graphite furnace, boron nitride powder, molybdenum end disks and MgO spacers. Pressure was calibrated against the quartz-coesite transformation at 3.1 GPa and 1000 °C (Bose & Ganguly 1995), the fayalite to y-spinel reaction at 5.25 GPa and 1000 °C (Yagi et al. 1987) and the garnet-perovskite reaction at 6.1 GPa and 1200 °C (Susaki et al. 1985). The oil pressure was controlled automatically by Eurotherm controllers within ± 1 bar, corresponding to ± 0.2 GPa. Experiments at 2.5 to 3.5 GPa were conducted in an end-loaded 14 mm bore piston-cylinder apparatus. Assemblics below 1000 °C were composed of an outer NaCl sleeve, a straight graphite heater, a corundum disc between thermocouple and capsule and cylinders of NaCl inside the furnace. For the experiments at 1050 °C, a pyrex glass sleeve between the outer NaCl sleeve and the graphite furnace was used and the internal NaCl cylinders was replaced by MgO liners. A friction correction of 2 % for full salt assemblies and 3 % for NaCl-Pyrex-MgO assemblies was applied to the nominal pressure, obtained by calibration against the quartzcoesite transition (Bose & Ganguly 1995). In all experiments, the hydraulic pressure was controlled automatically by a spindle element with a relative precision better than 1 Pa. Temperatures was regulated by a automatic Eurotherm temperature controller within ± 2 °C using either S-type (Pt₁₀₀/Pt₉₀Rh₁₀) or B-type (Pt₉₄Rh₆/Pt₇₀Rh₃₀) thermocouples. Gold capsules were welded at one end, fired and filled with starting material dried at 110 °C, and then welded shut. For the piston cylinder experiments one capsule of 3 mm O.D. and 3-5 mm long were used. The capsules were control at the hot spot to within ± 0.7 mm, the thermocouple tip in the piston cylinder experiments thus recording the coldest temperature in the capsule. Thermal gradients across the length of the capsules were estimated to 10-20 °C at 1050-1300 °C and 2.0 GPa. In the multi-anvil experiments a capsule of 2.3 mm O.D. and 2.5 mm length was placed on each side of the central thermocouple. Quenching was done by turning off power to the furnace. The capsules were mounted longitudinally in epoxy resin, then ground to approximately the centre of the capsule and fine polished using a wet-silica colloid lapping method.

6.2.2 Starting material

The bulk composition (Tab. 6.1) employed in this study corresponds to a Mg-rich pelite (e.g. carbonated whiteschist) with a molar Ca/(Ca+Mg)~0.28, saturated in carbonate, kyanite and fluid (but slightly undersaturated in H_2O) at subsolidus conditions. The composition produces ~16.5 wt% K-mica and ~13.9 wt% carbonate, if all H_2O and CO_2 are stored in mica and carbonate, respectively. The base of the starting material was a synthetic glass made of the oxides SiO₂, Al₂O₃, MgO, CaO mixed with natural alkali feldspar. The glass was fine grinded to < 5 µm employing agate mortars with ethanol, then remolten at 1100-1200 °C during 30-45 minutes in a new Pt-crucible. Milling, grinding and firing was repeated three times to ensure homogeneity of the glass (controlled by microprobe using a defocused beam). The final glass was then pulverized and mixed with Al(OH)₃ and CaCO₃ to introduce the desired proportions of H₂O and CO₂. Free water or CO₂ was not added to have a precise control of the fluid content and to prevent fluid-loss during welding.

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	MA ^a	K-AO15 ^b	A42 ^c	Z234 ^d	P1 ^e
SiO ₂	40.76	56.10	56.20	57.20	61.50
Al ₂ O ₃	24.30	19.40	16.00	16.20	21.00
FeO _{tot}	0	2.68	0.37	5.38	0
MgO	15.22	17.80	22.90	11.40	8.00
CaO	8.44	0.50	0.10	0.20	6.00
Na ₂ O	0	0.10	0.60	5.30	0
K ₂ O	3.91	2.30	0.20	0.70	3.00
H₂O	0.74	1.02	3.50	2.30	2.2-10
CO2	6.62	0	0.17	0.09	0
Sum	100.00	99.90	100.04	98.77	99.50
Ca/(Ca+Mg) ^f	0.29	0.02	0.00	0.01	0.35
Al/(K+Na+2*Ca) ^{molar}	0.70	4.34	10.21	1.59	0.84
Al/Na+K ^{molar}	5.74	7.79	73.92	21.44	6.47
v g	0.79	_	0.02	0.02	-

Tab. 6.1. Bulk starting composition (wt%) compared to carbonate-free
whiteschists, mudstone and average continental crust.

^a Bulk composition used in this study

^b Evaporitic mudstone, Sahara Atlas (Kulke, 1976)

^c Whiteschist (McKie, 1959)

^d Whiteschist (Schreyer and Abraham, 1977)

^e Average continental crust (Hermann, 2002)

f molar Ca/(Ca+Mg)

^g molar CO₂/(CO₂+H₂O)

6.2.3 Analytical techniques

Experimental charges were analysed by a Cameca SX50 or a JEOL JXA8200 electron microprobe using silicates, carbonates and oxide standards, 15 kV acceleration voltages, a beam current of 20 nA for silicate minerals and 5-10 nA for carbonates and quenched glasses. Acquisition time was 10-20 seconds for all elements, measuring potassium first for 10 seconds to avoid diffusive loss. A focused beam was applied to water-free solid phases, whereas a defocused beam of 2-30 μ m was used for micas, carbonates and glasses whenever possible. Textural phase relations were analysed from secondary and back-scattered electron images (BSE) obtained from the microprobes and a Camscan CS44LB scanning electron microscope equipped with an EDS. Polymorph phases of carbonate were determined by micro-Raman spectroscopy using an argon laser of 488 nm.

3. Experimental results

Run conditions and resulting phase assemblages for the eleven synthesis experiments from 2.5 to 6 GPa at 850 to 1100 °C are listed in Tab.6.2 and presented in Fig. 6.1. In 6 of the 11 experiments, reaction rims are produced, typically involving carbonate, Ca-Mg silicates (garnet, clinopyroxene or zoisite) and silicate melt or biotite, indicating that complete chemical equilibrium was generally not reached. Further, several phases developed only very small crystals (< 1 μ m), resulting in sub-optimal analytical conditions. Hence, the experiments did most probably not attain chemical equilibrium, and phase composition changes with pressure and temperature are generally inconsistent, thus mass balance calculations were not performed. Nevertheless, all experiments produced well-crystallized biotite grains of > 10 μ m in size, indicating that biotite is the stable K-mica in the entire experimental grid, i.e. to at least 6.0 GPa (at 950 °C) and to 1150 °C (at 3.0 GPa). Furthermore, the approximate location of several reactions can be established from the experiments. The solidus is determined to between 950 and 1050 °C, most probably resulting



Fig. 6.1. Pressure-temperature diagram with experimental results and tentative phase stability fields for the MA bulk composition. Biotite is omnipresent, and the dominant carbonate polymorph for each experiment (dots) is marked in blue (dol = dolomite, Mg-cc =magnesian calcite, arag = aragonite). Solid lines mark experimentally determined reactions, and dashed lines are inferred brackets based on experiments not fully equilibrated. Calcite/aragonite reaction from Carlsson (1980).

Tab. 6.2. A. Experimental run conditions and resulting phase assemblages for the MA bulk composition

Run no.	P (GPa)	T (°C)	Run time (hours)	Phase assemblage
MA-01 ^a	2.5	850	94	bt + dol + ky (+ spl) +/- zoi
MA-02 ^a	2.5	950	112	bt + gt + dol + ky +/- zoi
MA-03	2.5	1050	116	bt + silicate melt + gt + cor
MA-06	3.0	850	120	bt + gt + dol + ky + zoi (+/- cpx?)
MA-05 ^ª	3.0	950	108	bt + gt + cpx + dol + ky
MA-07	3.0	1050	118	bt + silicate melt + gt + cor + dol
MA-08	3.0	1100	60	bt + silicate melt + gt + cor
MA-10 [®]	3.5	950	113	bt + gt + dol + ky (+/- cpx?)
MA-09 ^a	3.5	1050	108	bt + silicate melt + gt + Mg-cc + ky + cor
MA-11 ^a	5.0	950	88	bt + gt + arag + spl (+/- melt +/- ky/cor?)
MA-12 ^ª	6.0	950	121	bt (low-K) + gt + arag + spl (+/- silicate melt)

^a Experiment did not attain complete chemical equilibrium (reaction rims are present).

B. Composition of carbonate, garnet,

ciinopyroxe	ene and	zoisite^	
Carbonate	Garnet	Clinopyroxene	Zoisite
X _{ca} ^b	X _{gros} ^b	X _{ca} ^b Al (pfu) ^c	Mg (pfu)
0.485	Ŧ	-	?
0.483	?	-	?
-	0.350	any?	-
0.471	0.291	any?	0.103
0.495	?	0.495 0.875	-
0.490	0.326	-	-
-	0.323	-	-
0.481	0.472	any?	-
0.354	0.497		-
0.008	?	-	-
0.001	?	-	-

^b molar XCa = Ca/(Ca+Mg).

^c Normalization on 4 cations & 12 charges

from the decomposition of biotite (±quartz/coesite). Corundum first appears at > 950 °C and is stable to 1150 °C, whereas kyanite is stable from subsolidus conditions to 1050 °C at 3.5 GPa and to ~1050 °C at 2.5-3.0 GPa. Dolomite is the dominant carbonate from 2.5 to 3.5 GPa (at 1050-1100 °C), whereas aragonite occurs at 5 and 6 GPa (Tab. 2B). Zoisite is found in one sample at 850 °C and 3.0 GPa, clinopyroxene (aluminium-diopside) in another sample at 950 °C and 3.0 GPa, and from 850 to 950 °C at 2.5 GPa garnet is absent. In the two experiments at 5.0 and 6.0 GPa, spinel (MgAl₂O₄) is observed.

3.1 Biotite composition

Composition of the analysed biotites are shown in Fig.6.2 and given in Fig. 6.3. For KCaMAS-HC, the ideal biotite solid solution results from the Mg-tschermak's substitution (Mg₁Si_{.1}Al₂) between the endmembers phlogopite $KMg_3[AlSi_3]O_{10}(OH)_2$ and eastonite $KMg_2Al[Al_2Si_2]O_{10}(OH)_2$. However, the sum of the cations for the analysed biotites varies between 7.13 and 7.87 apfu with octahedral occupancies from 2.44 to 2.91 pfu and interlayer cation vacancies of 0.05-0.62 pfu. These non-ideal biotites have a cation-deficient interlayer and an



Fig. 6.2. Si vs. Al diagram with nonideal trioctahedral biotites, indicating substitution towards the phengite solid solution series. Solid solution through the K-edenite-type exchange towards talc is difficult to determine for the MA biotites. A continious increase in silica content with pressure (numbers in GPa at each point) can also not be determined, though indicated. Dashed area denoted MC represent the compositional range of biotites from Thomsen & Schmidt (in review). Normalization on 11 oxygens and 2(OH).

mposition ^a
8
Biotite
6.3
Table

P(GPa) / T(°C)	2.5 / 850	2.5/950	2.5 / 1050	3.0 / 850	3.0 / 950	3.0 / 1050	3.0 / 1100	3.5 / 950	3.5 / 1050	5.0 / 950	6.0 / 950
No. analyses ^b	ы	N	4	-	7	ç	7	e	2	2	10
SiO ₂	44.72 -	43.80 -	39.86 (0.55)	43.33 -	44.96 -	41.28 (0.45)	39.51 (0.57)	44.45 (2.08)	47.19 -	48.78 -	48.04 (0.85)
Al ₂ O ₃	26.86 -	26.30 -	20.78 (0.56)	19.41 -	24.26 -	22.11 (0.27)	21.38 (1.59)	24.68 (1.10)	24.67 -	23.00 -	25.52 (0.80)
MgO	17.54 -	16,49 -	23.64 (0.18)	22.08 -	15.18 -	20.93 (0.19)	23.48 (0.83)	16.99 (1.54)	13.88 -	13.07 -	17.56 (0.61)
CaO	0.10 -	0.36 -	0.05 (0.03)	0.39 -	1.03 -	0.01 (0.03)	0.02 (0.02)	0.38 (0.44)	0.10 -	1.06 -	0.47 (1.15)
K20°	6.85 -	9.53 -	10.73 (0.05)	9.95 -	9.55 -	10.83 (0.16)	10.78 (0.42)	9.06 (0.50)	8.73 -	9.33 -	4.64 (0.22)
H ₂ O _{{calc)} ^d	4.57 -	4.50 -	4.32 (0.03)	4.38 -	4.43 -	4.35 (0.02)	4.33 (0.04)	4.47 (0.05)	4.48 -	4.49 -	4.66 (0.05)
Sum	100.61 -	100.98 -	99.38 (0.70)	99.54 -	99.40 -	99.51 (0.36)	99.49 (0.58)	100.03 (0.92)	- 50,66	99.73 -	100.89 (0.57)
Si	2.936 -	2.918 -	2.765 (34)	2.967 -	3.041 -	2.842 (25)	2.738 (56)	2.981 (107)	3.158 -	3.256 -	3.093 (30)
AIN	1.064 -	1.082 -	1.235 (34)	1.033 -	0.959 -	1.158 (25)	1.262 (56)	1.019 (107)	0.842 -	0.744 -	0.907 (30)
AI ^{VI}	1.015 -	0.983 -	0.463 (14)	0.533 -	0.975 -	0.637 (12)	0.485 (94)	0.931 (119)	1.105 -	1.066 -	1.030 (38)
Mg	1.716 -	1.637 -	2.444 (23)	2.253 -	1.530 -	2.148 (15)	2.425 (103)	1.698 (95)	1.384 -	1.300 -	1.686 (60)
Ca	0.007 -	0.025 -	0.004 (2)	0.029 -	0.074 -	0.001 (13)	0.001 (2)	0.028 (31)	0.007 -	0.075 -	0.033 (81)
×	0.573 -	0.810 -	0.950 (3)	0.869 -	0.824 -	0.951 (67)	0.953 (45)	0.775 (37)	0.745 -	0.794 -	0.381 (18)
I	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000	2.000
Total cations	7.311 -	7.455 -	7.861 (18)	7.684 -	7.404 -	7.736 (22)	7.865 (51)	7.432 (85)	7.241 -	7.236 -	7.129 (44)
Oct. vacancy [†]	0.269	0.380	0.092	0.213	0.495	0.216	0.089	0.371	0.511	0.634	0.285
:		•	:								

Representative compositions in wt% and apfu based on 11 oxygens and 2 (OH).

 $^{\rm b}$ Number of analysis considered as equilibrium phases. $^{\rm c}$ Measured concentration of K_2O, not corrected for K-loss during EMPA.

 d Calculated water content. e Analytical total of oxide components including ${\rm H_2O}.$

^f Octathedrał site vacancy całculated as: vacancy^M = 7-(Si+Al+Mg) per 11 oxygens formula unit.

octahedral vacancy of 0.09 to 0.46 pfu. The highest Si content of 3.1 to 3.3 Si pfu occurs in the highest pressure and temperature experiments. The composition of the biotites arc comparable to the biotites of Hermann (2002, 2003) in KCaMASH, and own experiments in KCaMAS-HC on a quartz+kyanite+carbonate-saturated pelite higher in CaO (11.79 wt% instead of 8.44 wt%) and lower in MgO (7.36 wt% instead of 15.22 wt%), but exhibit larger compositionally variations as a result of limited equilibration in the present experiments.

6.4. Discussion

6.4.1 Biotite stability

The stability of biotite in KCaMAS-HC and subsystems is bulk composition dependent. In quartz+kyanitc-saturated, magnesian bulk compositions less calcic than the tie-lines cpxphengite or garnet-phengite (Fig. 6.1 inset), biotite is preserved to high pressures without forming phengite, whereas for more calcic compositions, biotite decomposes with increasing pressure, producing phengite (±cpx, ±garnet, ±zoisite). In this study biotite is stable to at least 6.0 GPa, i.e. to much higher pressures compared to the experiments with the KCaMAS-HC bulk composition in chapter 4 (MC), which yielded phengite replacing biotite at > 2.6 GPa. Hermann (2002, 2003) obtained coexisting biotite and phengite between 2.5 and 3.9 GPa at 780 °C in KCaMASH (at higher pressure biotite was absent), which is at 2 GPa lower pressures than in this study. The stability of biotite to higher pressure reflects the lower Ca/(Ca+Mg)=0.29 of our bulk composition (MA in fig. 1 inset) compared to 0.35 of Hermann's bulk composition (P1 in Fig. 6.1 inset and Tab. 6.1) and to 0.54 of own parallel KCaMAS-HC experiments (MC in fig. 1, described in chapter 4). This supports the argument of bulk Ca:Mg control on the pressure stability of biotite and thus on the biotite to phengite transformation in KCaMAS-HC and KCaMASH. The lower Ca:Mg ratio also displaces the garnet stability field towards higher temperatures.

6.4.2 Non-ideality of biotites at high pressures

Exchange mechanisms in the ideal biotite solid solution series and main crystallochemical variations are described in chapter 2.2. In terms of crystallochemical effects, deviation from ideal biotite solid solution towards phengite solid solution series at high pressures occur mainly through the coupled *di-tri-octahedral substitution* $2^{VI}(Al^{3+}) + {}^{VI}\Box \leftrightarrow 3^{VI}(Fe^{2+}, Mg^{2+})$, resulting in a lower octahedral occupancy for biotites. For biotites, the extent of the *ferri-muscovite ex* $change^{VI}(Fe^{3+}) \leftrightarrow^{VI}(Al^{3+})$ substitution mechanism is virtually unknown, but the *K*-edinite-type substitution $K^+ + {}^{IV}(Al^{3+}) \leftrightarrow \square + {}^{IV}(Si^{4+})$ for biotites towards tale was recently suggested by Hermann (2002) and Wunder & Melzer (2002), and discussed by Comodi et al. (2004) as a significant exchange vector for high pressure biotites. Increasing pressure (and decreasing temperature) favours the K-edinite-type substitution $K^+ + {}^{\gamma\nu}(A1^{3+}) \rightarrow \Box + {}^{\gamma\nu}(S1^{4+})$ in biotites, resulting in a larger talc component Mg₃[Si₄O₁₀](OH)₂, essentially due to a decrease in size of the tetrahcdral sheet, coupled in the alumino-celadonite substitution by an increase of the octahedral sheet dimensions (Comodi et al. 2004). This decrease in potassium with increasing pressure contrasts with the general K increase over Na with increasing pressure, mainly reflecting pressure effects on the octahedral and tetrahedral substitutions on the degree of (non-)ideality for the Na-K exchange (Guidotti and Sassi 2002). For biotites, increasing $Fe^{2+} \rightarrow Fe^{3+}$ oxidation is thought to be common in some bulk rock compositions, but has not been quantitatively established (discussed further in Eugster & Woones 1962).

6.4.2 The stability of carbonates compared to previous studies

Fig. 6.3 compares the pressure-temperature stability of carbonate polymorphs from this study to previous investigations on the stability of carbonates in the CaCO₃-MgCO₃ solid solution, clearly showing a significant discrepancy in the pressure-temperature stability conditions, which is dependent on bulk and C-O-H fluid composition. Nevertheless, the consistent



Fig. 6.3. Pressure-temperature diagram with stability fields of carbonate polymorphs from different studies compared to our results, showing that carbonate stability and polymorphism is very much dependent on bulk and C-O-H fluid composition. In general, calcite (cc) occurs at low P-T, Mg-calcite (Mgcc) at the highest temperatures, dolomite (dol) and in turn aragonite (arag) at increased P-T, whereas magnesite (mgs) occurs at very high P. (1) this study. (2) Thomsen and Schmidt (in review). (3) Kerrick & Connolly (2001). (4) Yaxley & Green (1994). (5) Molina & Poli (2000). (6) Yaxley & Brey (2004). (7) Hammouda (2003). (8) Experimentally determined reaction dolomite=aragonite+magnesite (Buob et al. 2006, Luth 2001).

trend with low pressure calcite and Mg-calcite present at the highest temperatures, and dolomite in turn aragonite and magnesite forming with increasing pressure, is similar to our results, where Mg-calcite is found only at $1050 \,^{\circ}\text{C} - 3.0 \,\text{GPa}$, and dolomite is stable from 2.5 to 3.5 GPa (at 1050- $1100 \,^{\circ}\text{C}$), whereas aragonite stabilize at 5 and 6 GPa. The stability of dolomites from this study overlap with the dolomites of Thomsen & Schmidt (in review), Yaxley & Green (1994) and most probably also Kerrick & Connolly (2001). Mg-calcite overlap with the Mg-calcites stability field in Yaxley & Green (1994) and Yaxley & Brey (2004), whereas the lower limit of our aragonite stability field is located at slightly lower pressures than most other studies producing aragonite.

6.5. Concluding remarks

This study indicates biotite (phlogopite) as a stable phase to at least 6.0 GPa in carbonate+kyanite-saturated, Mg-rich pelites, coexisting with different phase assemblages composed among carbonate (aragonite, dolomite, calcite), kyanite, corundum, garnet, clinopyroxene (Al-diopside), zoisite, spinel or silicate liquid. Thus, subduction even along fairly hot geotherms of such metasediments may preserve H_2O in biotite and CO_2 in aragonite to at least ~180 km depths, i.e. into the upper mantle. However, it must be stressed that the results are only suggestive, as complete equilibrium clearly were not attained for all experiments, most likely resulting in considerable uncertainties in phase stability fields and phase compositions.

Chapter 7

Summary, On-going work and Outlook

7. Summary, On-going work and Outlook

Piston-cylinder and multi-anvil experiments have been carried out to determine the pressure-temperature phase relations for carbonate-saturated pelites in the systems KCaMAS-HC and KNCaFMAS-HC. This research project lays an experimental basis for further investigations of carbonate-saturated pelites, and more generally for the study of high-pressure metasediments. The following sections gives a brief summary of the results of this thesis, ongoing work and suggestions for future research are outlined.

7.1 Summary of the major results of this thesis

With the characterization of carbonatc-saturated pelites in the KCaMAS-HC model system and the KNCaFMAS-HC pseudo-natural system, subsolidus and melting reactions are determined. For the MC bulk composition in KCaMAS-HC (chapter 4), the biotite to phengite transformation takes place with increasing pressure between 2.4 and 2.6 GPa, whereas the amphibole to elinopyrorxene (aluminium-diopside) reaction occurs from ~875 °C at 2.0 GPa to ~740 at 2.5 GPa. Both reactions conserve K_2O and CO_2 with pressure, but not H_2O , which is produced from the decomposition of zoisite and amphibole. The H_2O stored in the micras is conserved during pressurizing. Dolomite constitutes the carbonate throughout the studied P-T grid, and is stable to higher temperatures at higher pressures, that is 950 °C at 3.5 GPa compared to 850 °C at 2.3 GPa. The solidus is constrained to between 850-950 °C and produces 7-24 wt% K-rich granite melts through the melting reaction phengite+zoisite+cocsite = silicate melt+clinopyroxene+kyanite above ~2.5 GPa. The liquidus surface is dominated by the melting of zoisite and then clinopyroxene with increasing temperature.

The reaction phengite+coesite+clinopyroxenc = silicate melt+kyanite+garnet defines the initial fluid-absent melting (solidus) for carbonate-saturated pelites of AM bulk composition in the KNCaFMAS-HC system (chapter 5). Thus, such compositions provide a solidus reaction similar to initial silicate melt producing reactions for typical high-pressure pelites, greywackes and K-rich granites, though larger melt fractions of 30-35 wt% are produced in the AM composition. The silicate melt forming reactions do not include carbonate, thus the Ca-rich ferrocarbonatite produced at 1100 °C is controlled by the degree of CO_2 -saturation of the coexisting silicate melt and the stability of Fe-Mg-calcite. The results indicate that carbonate-saturated pelite compositions provide a potential source for carbonatite formation through liquid immiscibility with a Si-undersaturated phonolitic melt.

In the KCaMAS-HC experiments with a carbonate-saturated Mg-rich pelite composition (carbonated whiteschist) having 0.74 wt% H_2O (chapter 6), biotite is stable to 6 GPa (950 °C) and to 1100 °C (at 3.0 GPa). The stability of biotite is very much bulk composition, and for KCaMAS-HC especially the Ca/(Ca+Mg)-ratio demonstrate that biotite is more stable in bulk compositions with a low Ca/(Ca+Mg) ratio, than in compositions with a high Ca/(Ca+Mg) ratio.

7.2 Thermodynamic modelling of high-pressure KCaMAS-HC carbonate-saturated pelites employing a modified solid solution mixing model for K-micas

In collaboration with Dr. Marc Caddick, a thermodynamic treatment of the data obtained from the subsolidus experiments in chapter 4 is employed for the calculation of a thermodynamic model, producing an empirical pressure-temperature grid consistent with the results obtained from the experiments. However, as this work is in progress and being prepared for future publication, it does not constitute a complete chapter in the thesis. The following sections provide a brief summary of this work and the preliminary results.

7.2.1 Introduction

The experiments in the model system KCaMAS-HC ($K_2O-CaO-MgO-Al_2O_3-SiO_2-H_2O-CO_2$, chapter 4), which constitutes the simplest system able to generate the mineralogy of carbonate-saturated pelites, produced phase assemblages composed among biotite, phengite, dolomite, clinopyroxene (aluminium-diopside), zoisite, garnet, kyanite, quartz/coesite, silicate melt and a mixed H_2O-CO_2 fluid. Based on this study, we have calculated a pressure-temperature petrogenetic grid for carbonate-saturated pelites in KCaMAS-HC from 2 to 4 GPa, 700 to 950 °C, employing the bulk composition MC (see Tab. 4.1, p.32) and previously published, internally consistent thermodynamic datasets and updated models of activity-composition relations for the solid solutions produced in the experiments.

7.2.2 Software, input parameters and models employed

Preliminary calculations with the program Perplex_06 (Connolly, 2005) utilised the 2002 update of the Holland and Powell (1998) thermodynamic database. Activity composition models were taken from the Perplex solution file (i.e. amphibole after Dale et al., 2005, calcite-dolomite-magnesite after Holland and Powell, 2003, and end-member compositions for kyanite, zoisite, quartz, coesite, diopside and talc), with the exception of mica that was modelled as follows. As a starting point for future calculations, a simple "ternary" mica model was developed to simulate mixing between phlogopite, castonite and muscovite end-members. Thus, the celadonite end-member was not included (i.e. no phengite) in the calculations. Interaction energy parameters for muscovite-eastonite and muscovite-phlogopite solutions are essentially unknown, so were set at arbitrarily high values ($W_{east-mu} = W_{phl-mu} = 1000 \text{ kJ/mol}$) to minimise mixing between di- and trioctahedral micas. Naturally, using such high interaction energy parameters, the risk of no di- and trioctahedral mica mixing is possible, which will provide a mica model with a binary phlogopite-eastonite solid solution and muscovite as end-member, and not a true ternary mica model. W_{phl}





Fig. 7.1. (A) Pressure-temperature equilibrium phase diagram computed in KCaMAS-HC for a carbonate-saturated pelite with bulk composition MC (see Tabs. 3.1 or. 4.1). The calculated P-T diagram provides a reasonable approximation for the biotite-phengite, amphibole-clinopyroxene and dolomite-out reactions, compared to the experimentally based petrogenetic grid (red dashed lines, see Fig. 4.9), considering the simple setup parameters for the calculation. (B) Calculated Si/ (Si+Al) cation ratios for micas. (C) Calculated Mg/(Mg+Al) cation ratios for biotites. (D-G) Calculated proportions (in vol%) of diopside (D), dolomite (E), mica (F) and amphibole (G).

 $_{east}$ (10 kJ/mol) was taken from the Thermocale website of T.J.B. Holland (http://www.esc.cam.ac.uk/ astaff/holland/ds5/biotites/biotite.html). Calculations modelled the bulk composition MC with the CORK (compensated Redlich-Kwong) fluid model (Holland & Powell, 1991) and a X_{co_2} (fluid) of 0.14, as applied in the experimental mass balance calculations.

Obviously, several over-simplifications are made in this first model that must be improved in future calculations. Most important is the lack of the celadonite end-member component in the phengite solid solution series (see Fig. 2.4), setting muscovite to a fixed end-member composition, which has the effect of muscovite not becoming celadonite-enriched with increasing pressure. Biotite is modelled as a simple phlogopite-eastonite binary, which does not account for any non-ideal behaviour in terms of exchange mechanisms towards dioetahedral micas or tale. Furthermore, the interaction parameters were guessed, and thus have no pressure or temperature dependence. A next step is to implement a phengite composition into the model.

Additionally, the micas in this study do not contain Fe, Ti or Na, which generally is present in significant amounts in natural mica compositions. This is similar for other minerals at high pressures, where the absence of Na suppresses crystallization of jadcitic/omphacitic clinopyroxene and of sodic amphiboles, whereas addition iron is distributed among the magnesian phases, not producing additional phases, however greatly shifts the stability field of e.g. garnet to lower pressures and temperatures.

7.2.3 Preliminary results

In Fig. 7.1A, the calculated petrogenetic diagram is compared to reactions determined from the experiments (red dashed lines, Fig. 4.9). Considering the over-simplifications mentioned above, the petrogenetic diagrams show surprisingly good consistency of the biotite to phengite (muscovite), the amphibole to clinopyroxene and the dolomite-out reactions. Note, that because the celadonite component is not included in the modelling, phengite is interpreted as the high pressure stable white mica phase (over muscovite), which is supported by the experimental study and literature. The calculated cation ratios in Fig. 7.1B+C show increasing Mg and Si in biotite with pressure, indicating the tschermak's exchange in biotite. Calculated proportions (in vol%) for mica, amphibole, clinopyroxene and dolomite is shown in Fig. 7.1D-G, which also fits surprisingly well with the calculated proportions (by mass balance) from the experiments (see Tab. 4.2). In conclusion, this first attempt to model the subsolidus phase assemblage of a simplified carbonate-saturated pelite bulk composition give consistent results compared to the experimental study, providing a solid base for future model calculations.

7.3 Recommendations for future scientific work

The amount of work performed on carbonaceous pelites is small at all conditions, dcspite the common occurences of such lithologies. While this thesis has focused on the experimental determination of subsolidus and melting reactions and phase compositions in model carbonate-saturated pelites in the vicinity of the solidus, several important aspects of such compositions are yet to be explored. Below are outlined some recommendations for future research.

7.3.1 Field study of carbonaceous pelites from high-pressure terrains

Petrological experiments simulating reactions occuring in natural rock compositions should be compared to alike natural compositions. In this study, the subsolidus reaction biotite to phengite was the major focus, thus an investigation to identify metamorphic units, where carbonaceous pelites are well described and metamorphic conditions were possible to deduce were initiated. However, it soon became clear that research on high-pressure carbonaceous pelites or akin compositions are scarce, as most research on such compositions are at much lower pressures than in this study. Nevertheless, it was possible to locate a few high-pressure terrains, which contain carbonaceous pelites or pelitic marbles that show, or most likely will have, indications of the phengite to biotite (or vice versa) transformation: (A) Eclogite Zone, Austria. Permomesozoic carbonaceous and pelitic metasediments of the Penninic series, south of the Gross Grossvenediger, Tauern Window, show high-pressure Alpine phase assemblages with phengite overprinted by lower pressure biotite-bearing greenschist-amphibolite facies assemblages. The phengite-biotite transformation was determined to Dachs (1986, 1990) to 0.6-2.0 GPa at a T_{max} of 550-600 °C. Potential field in Dorfertal and Timmeltal, north of the Virgenthal. The results from a reconnaissance field work combined with this study is not included in the thesis.

(B) The Eide area, Romsdalshalvöya and Straumen eclogite pod, Western Norway. Eclogite facies overprint of granulite facies metasediment including pelites, cale-pelites and marbles at higher temperatures than in (A). Reksten (1985) and Smith (1998).

(C) Carbonate-bearing politics and marbles, Western Gneiss region, Norway. Precambrian granulite facies (800-900 °C, <1.1 GPa) to eclogite facies (700 °C, >1.8 GPa) transition.

7.3.2 Partitioning of trace elements between solids, melts and fluid

In experimental studies of trace element partitioning among the minerals, melts and fluid produced by carbonate-saturated bulk compositions, the primary goal would be to establish the nature of trace element partitioning between potassic micas and silicate melt, because micas have major implications for melting behaviour (and host many key trace elements such as Rb, B, Be, Ba; Domanik et al. 1993), as they are among the phases that disappear first during melting, thus influencing the geochemistry of recycling into the global cycle (i.e. into the mantle).

7.3.3 Carbonatites originating from metasedimentary rocks

In chapter 5, it is shown that carbonatics can be produced from carbonate-saturated pelites as a concequence of liquid immiscibility during partial melting. A follow up upon these experiments and comparison to natural low-alkali carbonatite compositions would further constrain P-T-Xco, conditions for carbonatics produced from melting of carbonated pelites.

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