

Influence of CO₂ on melting of model granulite facies assemblages: a model for the genesis of charnockites

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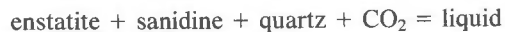
Abstract

Partial melting studies at crustal pressures in SiO₂-rich portions of the system KAlSiO₄-Mg₂SiO₂-H₂O-CO₂ can be used to model the anatectic origin of charnockites. The univariant reaction



produces a SiO₂-rich melt (granite analog) at 3 kbar; the vapor composition at the solidus is buffered to high H₂O-contents by the coexistence of phlogopite with its breakdown products. At higher pressures, 8 and 15 kbar, the fluid phase is buffered to higher CO₂-contents and the melt composition becomes enriched in K₂O and MgO (charnockite analog). Melting relations are controlled by the expansion of the quartz liquidus field relative to the enstatite and sanidine fields with increasing pressure. Partial melts generated at the base of the crust in the presence of a CO₂-rich fluid will be of an alkaline nature and will crystallize enstatite at lower pressures.

CO₂-saturated melting of similar SiO₂-rich bulk compositions (phlogopite-absent) by the reaction



occurs at temperatures in excess of 1000°C to about 15 kbar. Liquid compositions show analogous trends, however, with increasing pressure, to those observed in the 5-component system as a consequence of the expansion of the quartz liquidus surface relative to the enstatite surface.

This partial melting model for charnockite genesis satisfies the constraints of observed charnockite mineralogies, *P* and *T* estimations for charnockite assemblages (5–12 kbar and 750°–1000°C), and reports of high-temperature CO₂-rich fluid inclusions that are believed to approximate solidus vapor compositions (Ormaasen, 1977; Konnerup-Madsen, 1979). Also, observations of anatexis preceding granulite facies metamorphism are reconciled: Influx of CO₂ vapor (to a melt-crystal system) in sufficient amount to exhaust the vapor phase buffer will result in H₂O extraction from the melt and crystallization of the melt, although temperatures may continue to rise.

Introduction

Charnockites form a series of ultrabasic to felsic composition rocks, containing orthopyroxene, clinopyroxene, mesoperthite (or perthite), orthoclase, plagioclase, and quartz, as well as biotite, garnet, amphibole, olivine, or opaques, which crystallized (or recrystallized) during high-grade metamorphic conditions (Pichamuthu, 1969). They are often temporally and spatially associated with massif-type anorthosites. Models for the genesis of charnockites typically fall in 5 general categories:

(1) Intrusion of water-undersaturated magma in dry crust during, or with subsequent, granulite facies metamorphism (Martignole, 1979);

(2) *in situ* dry anatexis during granulite facies metamorphism (Martignole, 1979);

(3) charnockites are the residua after removal of granitic melt (Pride and Muecke, 1980; Nesbitt, 1980);

(4) charnockites are the cumulates of igneous fractionation (Field et al., 1980);

(5) granulite metamorphism involving volatiles

containing little H₂O (primarily CO₂), and possibly occurring at high crustal levels (Smith *et al.*, 1979; Newton *et al.*, 1980).

In this paper, experimental data on H₂O-deficient melting of granulite facies assemblages are presented. It is not an objective of this paper to select between the alternative modes of origin, all models being conceivable, but rather, the data will be used to constrain all the models.

Physical and chemical constraints on charnockite genesis

Observed mineralogies, measured and estimated volatile compositions, and thermobarometry estimates can be used to constrain conditions of charnockite genesis. The occurrence of orthopyroxene is an essential feature of the charnockite mineral assemblages (Pichamuthu, 1969). Its presence is reconciled in either of two ways: (a) by conditions of low $a_{\text{H}_2\text{O}}^{\text{melt}}$ (or low $a_{\text{H}_2\text{O}}^{\text{fluid}}$, if an occurrence is metamorphic in origin) resulting in orthopyroxene crystallization, whereas amphibole or biotite crystallization is favored by high $a_{\text{H}_2\text{O}}$, or (b) orthopyroxene crystallization may reflect more significant differences in composition between charnockites and granites than volatile content alone. In other words, charnockites may be compositionally dis-

tinct from granites giving rise to different mineralogies. Figure 1 shows SiO₂ vs. (Mg,Fe)O vs. (Na,K)₂O + Al₂O₃ (recalculated to 100%, wt.) for charnockites and granites from the Adirondacks (Letteney, 1968) and SW Sweden (Hubbard and Whitley, 1979). If considered as a quartz vs. pyroxene-component vs. feldspar-component pseudoternary diagram, then charnockites are noticeably enriched in both ferromagnesian and feldspathic components relative to granites. Whether this distinction relates to a difference in genetic mechanism as well, has not been determined; however, variation of relative proportions of volatiles, especially H₂O and CO₂, in the source regions may be a significant genetic variable inasmuch as volatile compositions have been shown to have a strong effect on melt compositions (*e.g.*, Mysen and Boettcher, 1975) and liquidus phase relations, in general (Eggler, 1974, 1975; Wyllie and Huang, 1975; Wendlandt and Eggler, 1980a,b).

Although some charnockite occurrences are believed to approach H₂O-saturation in the terminal stages of crystallization (Martignole, 1979), charnockites are thought to be the products of relatively dry processes. Mineral assemblages in both charnockites and granulites do not contain appreciable quantities of hydrous phases suggesting low $a_{\text{H}_2\text{O}}$. A

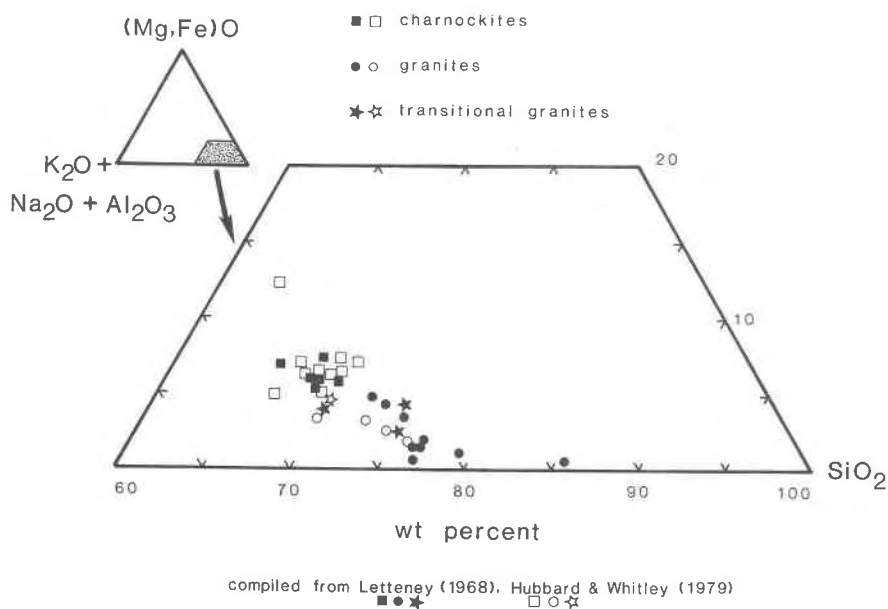


Fig. 1. SiO₂ vs. MgO + FeO vs. K₂O + Na₂O + Al₂O₃ for charnockites and granites from southwest Sweden (Hubbard and Whitley, 1979) and the Adirondack Mountains (Letteney, 1968). Transitional granites are intermediate in composition between granites and charnockites; they are charnockitic in mineralogy, and either spatially transitional into both granites and charnockites (Hubbard and Whitley, 1979) or spatially distinct from both homogeneous charnockite and granite (Letteney, 1968).

further observation, and one that deserves additional close scrutiny, is that high-temperature CO₂-rich fluid inclusions occur in both charnockite (Ormaasen, 1977; Konnerup-Madsen, 1979) and granulite facies minerals (Touret, 1971b) suggesting high a_{CO_2} . Unfortunately, the interpretation of what these CO₂-rich inclusions represent and how they originate is ambiguous. The proposed interpretations, summarized in Table 1, include suggestions that CO₂-rich fluid inclusions may be unrelated to charnockite genesis, due instead to oxidation of graphite, loss of H₂ from H₂O-CO₂ fluid inclusions by diffusion, or decarbonation of carbonate-bearing country rocks. A number of investigators contend, however, that the CO₂-rich inclusions are juvenile and their compositions may approximate peak metamorphic or magmatic fluid compositions. For the purposes of this study, it is assumed that the latter interpretation is correct at least in some instances.

Also bearing on the nature of volatiles associated with charnockite genesis is the observation of Blattner (1980) of high Cl and F contents in charnockites from Kondapalli, India.

Estimates of pressures and temperatures for the formation or crystallization of charnockites by igneous processes (Table 2) define a window from about 4 to 12 kbar and 750° to 1000°C; those by metamorphic processes may be formed at somewhat lower temperatures. The lowest estimated magmatic temperatures (*ca.* 750°C) are 100°–150°C above H₂O-saturated granite solidi for this pressure window (Tuttle and Bowen, 1958; Piwinski, 1968; Boettcher and Wyllie, 1968) implying $a_{\text{H}_2\text{O}}$ significantly less than unity.

Experiments were designed to test the hypothesis that compositional features of felsic charnockites may be generated by partial melting of a H₂O-

Table 2: Thermobarometry constraints on charnockite genesis

P, kbar	T, °C	Source of estimate
2-4	800-900	Saxena (1977)
7-10	800-900	Martignole (1979)
~12	~1000	Ormaasen (1977)
5-6	700-800	Konnerup-Madsen (1979)
	1000 ± 100	Bohlen and Essene (1978)
3-5	~600	Smith et al. (1979)
9-12	750-800	Jaffe et al. (1978)

undersaturated source over a P - T interval compatible with thermobarometry estimates.

Experimental model

Most models for charnockite genesis invoke a crustal derivation from salic gneiss or granulite facies material of pelitic or greywacke composition (*e.g.*, Hubbard and Whitley, 1979). The SiO₂-rich portion of the system KAlSiO₄-Mg₂SiO₄-SiO₂ has been selected as a model for the volatile-absent source composition; a potassic phase in the source is assumed. In Figure 2, the starting compositions (solid dots) are shown relative to the 1-atm liquidus surface (solid lines) as determined by Schairer and Bowen (1955) and Luth (1966). All four compositions have protoenstatite as a liquidus phase at 1-atm. For anhydrous conditions, or when only CO₂ is present at crustal pressures, all compositions consist of orthopyroxene, feldspar and quartz, as shown by the 3-phase triangle, sanidine-enstatite-quartz. If any H₂O is present in the source composition, then phlogopite is stabilized as a solidus phase at pressures above about 0.5 kbar (Luth, 1967). This alternative assemblage is shown by the other 3-phase region (projected from H₂O), phlogopite-sanidine-quartz. Both assemblages are models for simple granulite facies assemblages.

Volatile-absent, CO₂-saturated, and H₂O-under-

Table 1: Possible origins of CO₂-rich fluid inclusions in charnockite and granulite minerals

(1)	Solidus vapor compositions	Ormaasen (1977), Konnerup-Madsen (1979)
(2)	Juvenile (upper mantle) origin	Hoefs and Touret (1975)
(3)	Oxidation of graphite or organic material in country rocks	
(4)	Decarbonation of carbonate-bearing country rocks	
(5)	Dehydration of CO ₂ -H ₂ O fluid by the reaction Pyroxene + (H ₂ O-CO ₂) _{f1} = Hornblende + (CO ₂) _{f1}	Madsen (1977)
(6)	Diffusional loss of H ₂ from mixed volatile inclusions	Hollister and Burruss (1976)
(7)	Evolved from proximal anorthosite or any basic magma body emplaced in the lower crust	Ashwal (1978), Smith <i>et al.</i> (1979)

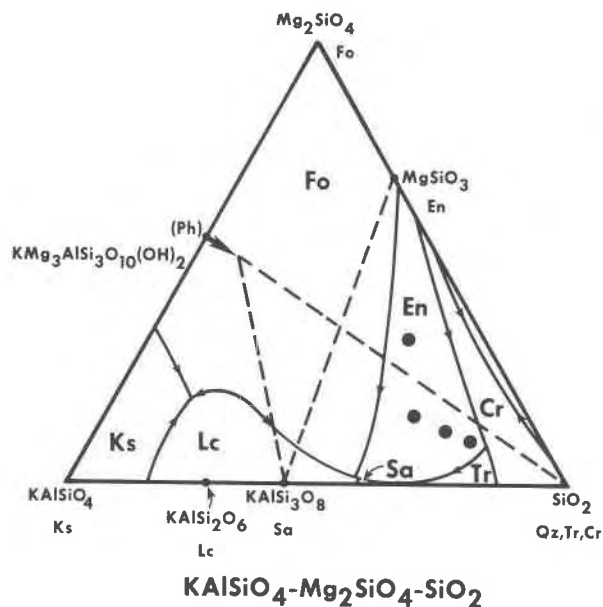


Fig. 2. Starting compositions (solid dots) as shown relative to the 1 atm liquidus surface (Schairer and Bowen, 1955; Luth 1966). Dashed lines show possible solidus assemblages (discussed in text).

saturated (mole fraction of H₂O in the vapor phase less than unity) melting relations have been determined for a pressure range corresponding to depths exceeding the thickness of the crust. Examples of the latter two types of reactions are shown schematically in Figure 3. This isobaric section depicts the solidus (heavy line) and subsolidus assemblages for one of the compositions. The CO₂-saturated system melts at the temperature on the extreme left of the section. The addition of H₂O stabilizes phlogopite, and where both phlogopite and enstatite coexist in the subsolidus, the phase rule predicts that univariant melting will occur. Furthermore, the vapor composition is buffered at a unique value for a given pressure and temperature in the region meaning that changing the H₂O/CO₂ ratio within this region changes the proportions of phases but not the assemblage or phase compositions. Two points are of interest:

(1) The interval of univariant melting expands to cover a wider range of volatile contents as the total amount of volatiles in the system decreases (Eggler, 1977b); and

(2) the vapor composition in the subsolidus is buffered to higher CO₂ contents with increasing pressure (Eggler, 1977b; Wendlandt and Eggler, 1980b). At temperatures above the solidus, for pressures corresponding approximately to the

crust, the melt preferentially dissolves H₂O relative to CO₂; hence, if a volatile-rich fluid phase is present, then it is likely to be even more CO₂-rich. Furthermore, the lower the amount of total volatiles, the greater the compositional difference between the dissolved and fluid components (Kadik and Lukanin, 1973; Eggler and Rosenhauer, 1978). The two melting reactions I have determined that are most applicable to charnockite genesis are: (1) The CO₂-saturated solidus; and (2) the univariant solidus characterized by high X_{CO₂} relative to H₂O. Water-saturated melting occurs at even lower temperatures than this univariant portion of the solidus but has not been determined as most evidence summarized previously indicates that charnockites were not produced at high *a*_{H₂O} conditions.

Existing experimental work applicable to this study include determinations of a CO₂-saturated granite solidus at low pressures (less than 3 kbar) by Wyllie and Tuttle (1959) and a granite solidus for a range of CO₂/H₂O compositions at pressures less than 5 kbar by Novgorodov and Shkodzinskiy (1974).

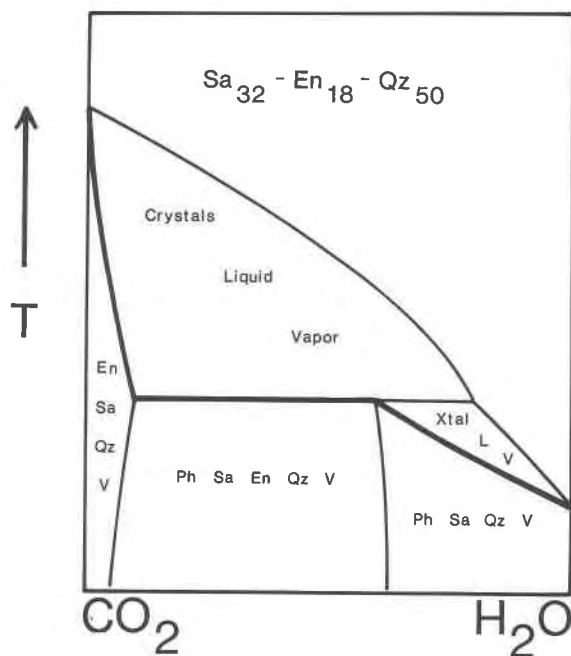


Fig. 3. Schematic *T-X* section for one of the starting compositions depicting the solidus configuration (heavy solid line) and subsolidus assemblages. Where phlogopite and enstatite coexist in the subsolidus, the vapor composition is buffered at a unique value for a given pressure and temperature and the solidus is isobarically invariant. The hypothetical pressure for this section is assumed to be greater than 0.5 kbar.

Methods

Experiments at pressures above 10 kbar were done with a solid-media, high-pressure apparatus (Boyd and England, 1960) using a "hot piston-out" technique without additional correction for the effect of friction on pressure. Talc-Pyrex furnace assemblies (1.27 cm diam) were used throughout. Nominal pressures were maintained at ± 0.1 kbar.

Temperatures were measured with Pt-Pt₉₀Rh₁₀ thermocouples and automatically controlled to $\pm 2^\circ\text{C}$. No corrections have been made for the effect of pressure on the emf output of the thermocouple.

Experiments at pressures below 10 kbar were done with an internally heated, gas-media apparatus. Temperatures were measured with Pt-Pt₉₀Rh₁₀ thermocouples and pressures were measured by strain gauge. Temperatures are precise to $\pm 3^\circ\text{C}$ and pressures are precise to at least ± 100 bars.

Starting materials were synthetic crystalline phlogopite (Ph), enstatite (En), sanidine (Sa), magnesite (Mag), and quartz (Qz). Anhydrous phlogopite component (Aph) consisted of crystalline forsterite, kalsilite, and leucite. Details of phase preparation have been reported elsewhere (Wendlandt and Eggler, 1980a). Starting mixtures were of the anhydrous compositions Sa₂₆En₁₄Qz₆₀, Sa₃₂En₁₈Qz₅₀, Sa₄₀En₂₂Qz₃₈, and Sa₃₆En₄₂Qz₂₂ (wt). Two additional mixtures were used, (Ph₁₅+Aph₁₅)₃₀Sa₂₀Qz₅₀, which is a partially hydrated equivalent of Sa₄₀En₂₂Qz₃₈, and Sa₃₀Mag₃₀Qz₄₀, which is the carbonated equivalent of Sa₃₆En₄₂Qz₂₂ (shown in Fig. 2). Carbon dioxide was added as Ag₂C₂O₄ or as MgCO₃. A $X_{\text{CO}_2} \approx 0.5$ (mol fraction) and a total volatile content of less than 10 wt.% (H₂O+CO₂) was found (by trial and error) to be optimal for investigating the H₂O-undersaturated melting reaction; H₂O and CO₂ were added as crystalline H₂C₂O₄ · 2H₂O.

Approximately 10 mg of the reactants, encapsulated in 3 mm Pt capsules by arc-welding both ends, were run at the pressure and temperature of interest. The solidi for all the reactions were determined by the presence of glass which is assumed to be quenched liquid. The H₂O-undersaturated reaction was located by confirming the presence of both phlogopite and enstatite in the subsolidus; reaction stoichiometry was determined by the location of the solidus relative to the low pressure H₂O-saturated univariant reactions determined by Luth (1967). The present data are not inconsistent with the topology of Luth's forsterite-, kalsilite-, and leucite-absent invariant point (labelled (v) in Fig. 4; Luth 1967), but do not constrain the location of the

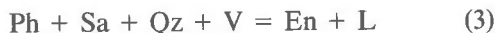
invariant point. Run durations ranged from 2.5 hours at 1600°C to 672 hours at 725°C. While temperature reversals were not accomplished, both water-undersaturated and CO₂-saturated solidi were determined using different crystalline starting compositions: The former using both Ph + Aph + Sa + Qz + H₂O + CO₂ and Sa + En + Qz + H₂O + CO₂, and the latter using Sa + En + Qz + CO₂ and Sa + Mag + Qz mixtures. A close approach to equilibrium is inferred from the agreement of different starting compositions and from the lengthy run durations. Phases were detected by optical and X-ray diffraction techniques; segregations of glass sufficiently large to be analyzed by electron microprobe existed only at temperatures 100°–300°C above the solidus.

Results

Table 3 summarizes the experiments defining the melting reactions



and,



In Figure 4, these reactions are shown in *P-T* projection. The CO₂-saturated assemblage melts at about 1000° C over a considerable pressure interval. Only at pressures of about 15 kbar and higher does the difference between melting points for the CO₂-saturated and the volatile-absent reactions become detectable. The H₂O-undersaturated reaction occurs at about 750° C in the interval 5–10 kbar; H₂O-saturated melting will occur at lower temperatures.

The slope, dP/dT , of the CO₂-saturated solidus (reaction 2) is approximately vertical. Novgorodov and Shkodzinskiy (1974) determined a slightly positive slope for the CO₂-saturated solidus of a granite; they estimated a vertical slope for $X_{\text{CO}_2} = 0.95$. The possibility of generating small amounts of H₂O ($X_{\text{H}_2\text{O}} = 0.02$) by diffusion of H₂ into the experimental charges of this investigation cannot be dismissed (Eggler, Mysen, and Hoering, 1974), and may be affecting the solidus determination in this study.

Discussion

Melt compositions and high pressure phase relations

Figure 5 summarizes the changes in the liquidus surface and, thus, in liquid compositions with in-

Table 3: Results of experiments

Run number	Crystalline starting composition	P (kbar)	T (°C)	Mole Fraction CO ₂	CO ₂ added (wt%)	CO ₂ +H ₂ O added (wt%)	duration (hrs)	Final assemblage
694	(Ph _{1.5} APh _{1.5}) ₃₀ Sa ₂₀ Qz ₅₀	3	750	0.5*	-	10.55	164	Qz,Sa,En,Ph,V
698	(Ph _{1.5} APh _{1.5}) ₃₀ Sa ₂₀ Qz ₅₀	3	775	0.5*	-	9.45	167	Qz,Sa,En,Ph,L(tr),V
682	(Ph _{1.5} APh _{1.5}) ₃₀ Sa ₂₀ Qz ₅₀	3	800	1.0**	20.58	-	262	Qz,Sa,En,V
706	Sa ₄₀ En ₂₂ Qz ₃₈	3	800	0.5	-	8.85	168	Qz,Sa(q),En,L,V
681b	Sa ₄₀ En ₂₂ Qz ₃₈	3	900	1.0	19.27	-	72	Qz,Sa,En,V
726a	Sa ₄₀ En ₂₂ Qz ₃₈	3	975	-	-	-	168	Qz,Sa,En
726b	Sa ₃₀ Mag ₃₀ Qz ₄₀	3	975	1.0	15.66	-	168	Qz,Sa,En,V
696a	Sa ₄₀ En ₂₂ Qz ₃₈	3	1000	-	-	-	95	Qz,Sa,En,L
696b	Sa ₄₀ En ₂₂ Qz ₃₈	3	1000	1.0	15.77	-	95	Qz,Sa,En,L,V
688	Sa ₄₀ En ₂₂ Qz ₃₈	3	1025	1.0	19.35	-	116	Qz,En,L,V
723a	Sa ₄₀ En ₂₂ Qz ₃₈	3	1150	-	-	-	96	Qz(tr),En,L
723b	Sa ₃₀ En ₁₈ Qz ₅₀	3	1150	1.0	28.22	-	96	Qz,En,L,V
723c	Sa ₂₆ En ₁₄ Qz ₆₀	3	1150	1.0	34.28	-	96	Qz,En,L,V
703a	Sa ₄₀ En ₂₂ Qz ₃₈	6.3	1000	-	-	-	98.5	Qz,Sa,En,L(tr)
703b	Sa ₄₀ En ₂₂ Qz ₃₈	6.3	1000	1.0	14.81	-	98.5	Qz,Sa,En,L(tr),V
712	Sa ₄₀ En ₂₂ Qz ₃₈	8	725	0.5	-	7.53	672	Qz,Sa,En,Ph,V
700a	Sa ₄₀ En ₂₂ Qz ₃₈	8	750	0.5	-	6.36	186	Qz,Sa,En,Ph,L(tr),V
700b	(Ph _{1.5} APh _{1.5}) ₃₀ Sa ₂₀ Qz ₅₀	8	750	0.5*	-	19.77	186	Qz,Sa,En(tr),L,V
713a	Sa ₄₀ En ₂₂ Qz ₃₈	12.5	975	-	-	-	24.75	Qz,Sa,En
713b	Sa ₃₀ Mag ₃₀ Qz ₄₀	12.5	975	1.0	15.66	-	24.75	Qz,Sa,En,V
711a	Sa ₄₀ En ₂₂ Qz ₃₈	12.5	1000	-	-	-	24	Qz,Sa,En,L(?)
711b	Sa ₃₀ Mag ₃₀ Qz ₄₀	12.5	1000	1.0	15.66	-	24	Qz,En,L,V
708a	Sa ₃₀ Mag ₃₀ Qz ₄₀	12.5	1025	1.0	15.66	-	24.5	Qz(tr),En,L,V
708b	Sa ₄₀ En ₂₂ Qz ₃₈	12.5	1025	-	-	-	24.5	Qz,Sa,En,L(tr)
715a	Sa ₄₀ En ₂₂ Qz ₃₈	12.5	1050	1.0	13.57	-	25	Qz,En,L,V
704	Sa ₄₀ En ₂₂ Qz ₃₈	15	750	0.5	-	5.69	22.5	Qz,Sa,En,Ph,V
702	Sa ₄₀ En ₂₂ Qz ₃₈	15	775	0.5	-	9.23	26.75	Qz,Sa(?),En(tr),L,V(?)
707	Sa ₄₀ En ₂₂ Qz ₃₈	15	800	0.5	-	8.08	23.5	Qz,Sa(?),En(?),Ph(q),L,V(?)
722	Sa ₃₂ En ₁₈ Qz ₅₀	15	1200	1.0	30.84	-	10	Qz,En,L,V(?)
725	Sa ₃₂ En ₁₈ Qz ₅₀	15	1300	1.0	39.06	-	7.3	Qz,En,L,V
728	Sa ₃₂ En ₁₈ Qz ₅₀	15	1400	1.0	60.56	-	7	Qz,En,L,V
729	Sa ₃₂ En ₁₈ Qz ₅₀	15	1475	1.0	49.12	-	6	Qz,En,L,V
731	Sa ₄₀ En ₂₂ Qz ₃₈	15	1500	1.0	9.07	-	5	En,L,V
732	Sa ₃₂ En ₁₈ Qz ₅₀	15	1525	1.0	70.02	-	5	En,L,V
730	Sa ₂₆ En ₁₄ Qz ₆₀	15	1550	1.0	29.95	-	5.5	Qz,L,V
718	Sa ₃₀ Mag ₃₀ Qz ₄₀	17.5	950	1.0	15.66	-	63.5	Qz,Sa,En,V
716a	Sa ₃₀ Mag ₃₀ Qz ₄₀	17.5	975	1.0	15.66	-	45.5	Qz,Sa(?),En,V
724	Sa ₃₀ Mag ₃₀ Qz ₄₀	17.5	1000	1.0	15.66	-	21	Qz,En,L,V
705	Sa ₃₀ Mag ₃₀ Qz ₄₀	25	875	1.0	15.66	-	26	Qz,Sa,En(tr),Mag,L(?)
701	Sa ₃₀ Mag ₃₀ Qz ₄₀	25	900	1.0	15.66	-	18	Qz,Sa,En,Mag,L(?)
738	Sa ₄₀ En ₂₂ Qz ₃₈	25	1550	1.0	27.54	-	5.5	Qz,En,L,V
739	Sa ₄₀ En ₂₂ Qz ₃₈	25	1600	1.0	37.34	-	2.5	Qz(tr),En,L,V
699	Sa ₃₀ Mag ₃₀ Qz ₄₀	26	850	1.0	15.66	-	20.75	Qz,Sa,Mag

Abbreviations: Sa, sanidine; En, enstatite; Qz, quartz; Mag, magnesite; Ph, phlogopite; APh, anhydrous phlogopite; L, liquid; V, vapor; (q), phase interpreted as quench; (tr), trace amounts; (?), phase believed to be present.

* X_{CO_2} is a bit less than 0.5 due to small amounts of H₂O in the phlogopite.

** X_{CO_2} is slightly less than 1 due to H₂O in the phlogopite.

kbar, and intersect the carbonate stability surface at a pressure surmised to be about 60 kbar. That is, Wyllie and Huang propose that the melting reaction $En + CO_2 = Qz + L$ intersects the decarbonation reaction $En + CO_2 = Qz + Mag$ at about 60 kbar and about 1600° C. In the system investigated in

this work, containing the additional component of K₂O + Al₂O₃, the quartz stability volume will also expand with increasing P_{CO_2} relative to the enstatite stability volume. It can be reasonably inferred that the liquid composition in equilibrium with Sa + En + Qz + CO₂ will intersect the Sa-En-CO₂ plane at

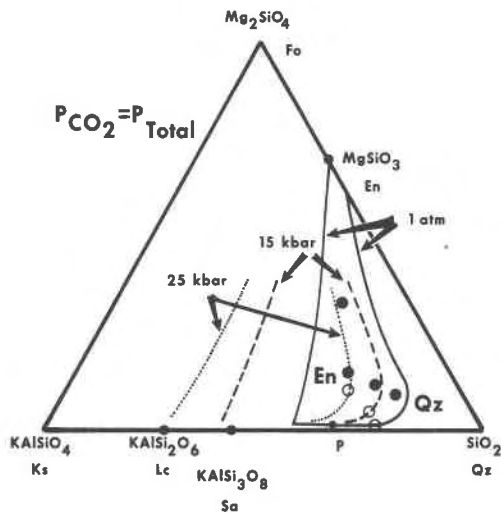


Fig. 5. Evolution of the liquidus surface with increasing pressure for CO₂-saturated melting. Solid circles show the starting compositions. Open circles denote liquid compositions (analysed by electron microprobe) in equilibrium with quartz and enstatite at high temperatures and 3, 15, and 25 kbar. P indicates the 1 atm eutectic involving quartz, sanidine, enstatite and liquid. The cotectics bounding the enstatite liquidus surface at low silica contents are taken from Schairer and Bowen (1955) for the 1 atm data, and from Wendlandt and Egger (1980a) for the 15 and 25 kbar data.

a pressure near 25 kbar because the melting reaction involving that assemblage (reaction 2) must intersect the same decarbonation reaction (shown in Fig. 4) as did the assemblage En + Qz + CO₂. Three experiments were made at 25–26 kbar and 850°–900°C to locate this decarbonation reaction (see Fig. 4); in the two higher temperature runs quenched liquid (mixed silicate and carbonate) was observed suggesting that reaction 2 may intersect the decarbonation reaction at pressures a bit below 25 kbar. This lower pressure of intersection, contrasted with 60 kbar in the system MgO–SiO₂–CO₂, is a consequence of the much lower melting temperatures (600°–700°) of the assemblage Sa + En + Qz + CO₂ as opposed to the assemblage En + Qz + CO₂. Because the H₂O-undersaturated reaction is also characterized by increasing P_{CO_2} (relative to $P_{\text{H}_2\text{O}}$) with increasing total pressure, similar evolution of liquid compositions can be inferred (toward higher feldspar and pyroxene components and lower SiO₂ contents). Analogous phase relations involving both CO₂-saturated and H₂O-undersaturated melting reactions in the silica-undersaturated portion of the system KAISiO₄–Mg₂SiO₄–SiO₂–

H₂O–CO₂ have been discussed in greater detail elsewhere (Wendlandt and Egger, 1980a,b).

Conditions of charnockite genesis

The formation of silicic partial melts enriched in feldspar and orthopyroxene components (which may be defined as protocharnockitic) is enhanced by low $a_{\text{H}_2\text{O}}$. The physical conditions of partial melting to produce such melts are in concert with thermobarometry estimates for the genesis of natural charnockite occurrences (Table 2). Melting may be initiated in the pressure interval 4–12 kbar at temperatures near 750°C by reaction 3, or, in the presence of pure CO₂ at temperatures of approximately 1000°C for the same pressure interval by reaction 2. Melting by reaction 3 at pressures less than 4 kbar will produce melts with high SiO₂ contents (granite analogs) because the composition of the volatile-rich fluid phase at the solidus will be buffered at high $X_{\text{H}_2\text{O}}$. Similarly, melts generated at low pressures by reaction 2 will have higher SiO₂ contents than melts generated at higher pressures. At a given pressure, the melt generated by reaction 3 will have higher SiO₂ content than the melt generated by reaction 2 at the same pressure.

A possible scenario for which the data of this study might be applicable is as follows: Emplacement of an anorthosite or mafic magma in the lower crust preferentially releases CO₂ relative to H₂O during crystallization (Kadik and Lukanin, 1973; Egger and Rosenhauer, 1978), or promotes decarbonation of carbonate-bearing country rocks, fluxing partial melting of the country rocks. This partial melt solidifies at high grade metamorphic conditions as the charnockite rock suite. A partial melt generated in the presence of CO₂-rich fluids at some pressure, perhaps 8–10 kbar, which crystallizes at some lower pressure, 5–8 kbar, will initially separate orthopyroxene and feldspar, followed by quartz. Differences in bulk composition of observed charnockites may have arisen from variations in depth of genesis (melting and crystallization), degree of partial melting, or the composition of the source material.

This model is analogous to that presented by Emslie (1978) for derivation of essentially bimodal anorthosite–granite suites. Emslie stressed the alkaline nature of the granitic rocks, including charnockites and rapakivi granites, associated with Grenville anorthosite massifs, and the relation of the suite to anorogenic magmatic processes. The reactions presented in this study reinforce his ob-

servations by predicting the alkaline, as opposed to calc-alkaline, nature of the granitic fractions. The compositions of partial melts generated near the base of the crust, in the presence of a CO₂-rich vapor phase, will be controlled by the expansion of the primary quartz field and characterized by enrichment of alkalis in the melt fractions.

A further application of the data of this study regards the common association of migmatites and felsic melts with charnockites (*e.g.*, Quensel, 1950; Touret, 1971a; Sen, 1974; Weaver, 1980). Weaver (1980) and Phillips (1980) suggested that partial fusion may be a logical precursor to granulite facies metamorphism. Phillips argued that the reduced $a_{\text{H}_2\text{O}}$ necessary for granulite metamorphism may be due to partial melting (probably by biotite breakdown) with $a_{\text{H}_2\text{O}}$ decreasing with increasing temperature as H₂O transfers to an increasing fraction of melt. Weaver, on the other hand, suggested that fluctuations in the composition of the metamorphic fluid, from H₂O-rich to CO₂-rich, correspond with initial production of anatectic melt followed by high-grade metamorphism at low $a_{\text{H}_2\text{O}}$. Elaboration on these models is possible in light of melting reaction 3 that has been presented here. Anatexis in the presence of an incoming CO₂-rich vapor phase will commence at approximately 750°C. The assemblage of liquid + crystals (including biotite) will persist with continuing CO₂ influx until the biotite is exhausted by H₂O extraction, at which point the vapor phase composition will be no longer buffered. Extraction of H₂O from the silicate melt will then occur, promoting melt crystallization despite temperatures which may continue to increase (Fig. 3). The resultant mineralogy of the quench melt is likely to be devoid of volatile-bearing minerals and more felsic (perhaps aplitic) than the surrounding terrain.

Effect of Fe on the phase relations

It is likely that the inclusion of additional components to the system investigated will result in depression of the melting temperatures. The most significant component is likely to be iron; charnockites have Fe/(Fe+Mg) (oxide wt) ratios on the order of 5–15. In this study, the objective was to present the phase relations of CO₂-saturated and H₂O-undersaturated melting in the most simple way possible, consequently, the added complexity of (Fe,Mg)O solid solutions was neglected. Some general observations may be in order, however. The melt fraction separating from a metapelite or meta-

greywacke source will be enriched in Fe relative to Mg (MacRae and Nesbitt, 1980), and thus it is likely that melting temperatures will occur at lower temperatures than those determined in this study. Saxena (1969), however, analyzed coexisting biotite and orthopyroxene in charnockites and observed that the distribution coefficient for Fe/Mg between the two phases was approximately unity. He projected that a substantial shift of melting equilibria in systems involving (Fe,Mg)O solid solutions in both mica and orthopyroxene was unlikely. Accordingly, it is expected that the equilibrium temperature of reaction 2 will be shifted to lower temperatures by the addition of Fe, while the temperature for reaction 3 will decrease to a lesser degree.

Conclusions

A model has been presented for the melting of a simple granulite assemblage in the presence of CO₂-rich fluid phases. Melting can occur between 750°–1000°C at crustal pressures, and these temperatures are well within the range estimated for regional metamorphism in, for example, the Adirondacks (Bohlen and Essene, 1977; Jaffe *et al.*, 1978; Valley and Essene, 1980). For melting occurring at about 750°C in the presence of both H₂O and CO₂, pressures corresponding to the deep crust are required to generate a melt enriched in pyroxene and feldspar components. Melting in the presence of pure CO₂ at about 1000°C generates analogous melt compositions at lower pressures. The experimental melting reactions are in agreement with a number of observations constraining charnockite occurrences: Pressure and temperature constraints, mineralogical constraints, and constraints on the compositions of volatiles associated with peak conditions of charnockite formation.

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