

## Influence of CO<sub>2</sub> on melting of model granulite facies assemblages: a model for the genesis of charnockites

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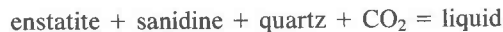
### Abstract

Partial melting studies at crustal pressures in SiO<sub>2</sub>-rich portions of the system KAlSiO<sub>4</sub>-Mg<sub>2</sub>SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> can be used to model the anatectic origin of charnockites. The univariant reaction



produces a SiO<sub>2</sub>-rich melt (granite analog) at 3 kbar; the vapor composition at the solidus is buffered to high H<sub>2</sub>O-contents by the coexistence of phlogopite with its breakdown products. At higher pressures, 8 and 15 kbar, the fluid phase is buffered to higher CO<sub>2</sub>-contents and the melt composition becomes enriched in K<sub>2</sub>O 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 CO<sub>2</sub>-rich fluid will be of an alkaline nature and will crystallize enstatite at lower pressures.

CO<sub>2</sub>-saturated melting of similar SiO<sub>2</sub>-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 CO<sub>2</sub>-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 CO<sub>2</sub> vapor (to a melt-crystal system) in sufficient amount to exhaust the vapor phase buffer will result in H<sub>2</sub>O 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 H<sub>2</sub>O (primarily CO<sub>2</sub>), and possibly occurring at high crustal levels (Smith *et al.*, 1979; Newton *et al.*, 1980).

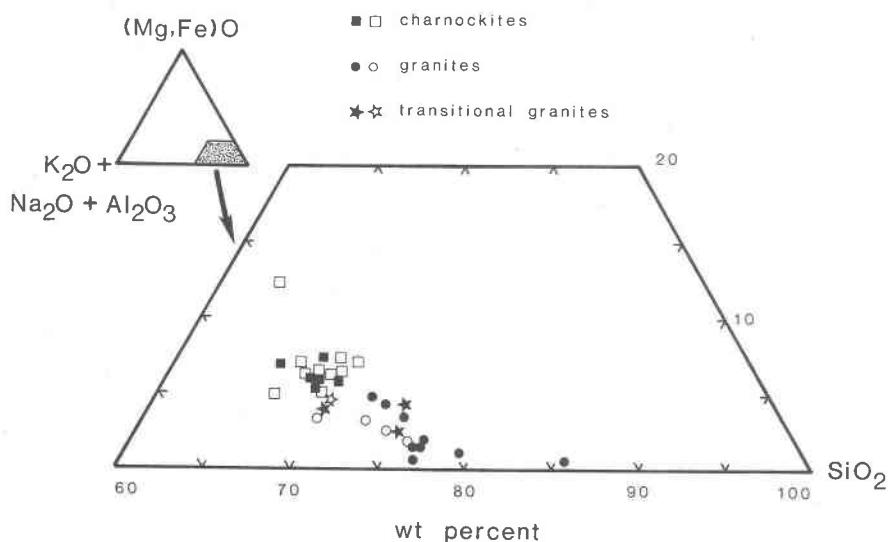
In this paper, experimental data on H<sub>2</sub>O-deficient melting of granulite facies assemblages are presented. It is not an objective of this paper to select between the alternative modes of origin, all models being conceivable, but rather, the data will be used to constrain all the models.

### 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 SiO<sub>2</sub> vs. (Mg,Fe)O vs. (Na,K)<sub>2</sub>O + Al<sub>2</sub>O<sub>3</sub> (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 H<sub>2</sub>O and CO<sub>2</sub>, 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 H<sub>2</sub>O-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



compiled from Letteney (1968), Hubbard & Whitley (1979)

Fig. 1. SiO<sub>2</sub> vs. MgO + FeO vs. K<sub>2</sub>O + Na<sub>2</sub>O + Al<sub>2</sub>O<sub>3</sub> 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 CO<sub>2</sub>-rich fluid inclusions occur in both charnockite (Ormaasen, 1977; Konnerup-Madsen, 1979) and granulite facies minerals (Touret, 1971b) suggesting high  $a_{\text{CO}_2}$ . Unfortunately, the interpretation of what these CO<sub>2</sub>-rich inclusions represent and how they originate is ambiguous. The proposed interpretations, summarized in Table 1, include suggestions that CO<sub>2</sub>-rich fluid inclusions may be unrelated to charnockite genesis, due instead to oxidation of graphite, loss of H<sub>2</sub> from H<sub>2</sub>O-CO<sub>2</sub> fluid inclusions by diffusion, or decarbonation of carbonate-bearing country rocks. A number of investigators contend, however, that the CO<sub>2</sub>-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 H<sub>2</sub>O-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 H<sub>2</sub>O-

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 SiO<sub>2</sub>-rich portion of the system KAlSiO<sub>4</sub>-Mg<sub>2</sub>SiO<sub>4</sub>-SiO<sub>2</sub> 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 CO<sub>2</sub> 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 H<sub>2</sub>O 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 H<sub>2</sub>O), phlogopite-sanidine-quartz. Both assemblages are models for simple granulite facies assemblages.

Volatile-absent, CO<sub>2</sub>-saturated, and H<sub>2</sub>O-under-

Table 1: Possible origins of CO<sub>2</sub>-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 <sub>2</sub> -H <sub>2</sub> O fluid by the reaction Pyroxene + (H <sub>2</sub> O-CO <sub>2</sub> ) <sub>f1</sub> = Hornblende + (CO <sub>2</sub> ) <sub>f1</sub>	Madsen (1977)
(6)	Diffusional loss of H <sub>2</sub> 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)

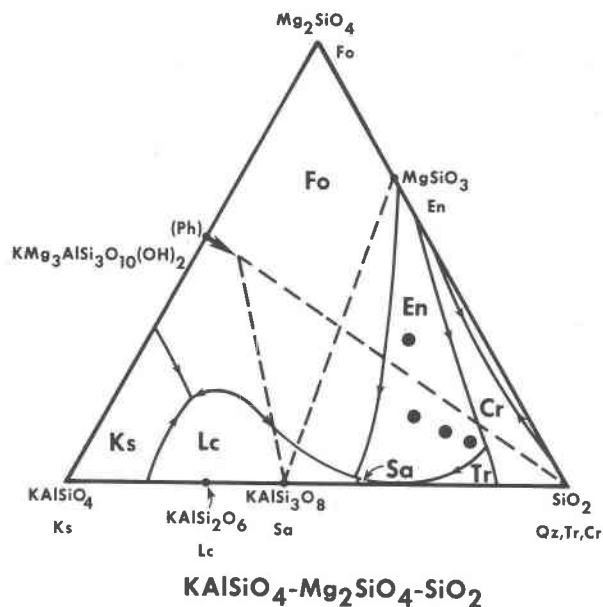


Fig. 2. Starting compositions (solid dots) as shown relative to the 1 atm liquidus surface (Schairer and Bowen, 1955; Luth 1966). Dashed lines show possible solidus assemblages (discussed in text).

saturated (mole fraction of H<sub>2</sub>O 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 CO<sub>2</sub>-saturated system melts at the temperature on the extreme left of the section. The addition of H<sub>2</sub>O 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 H<sub>2</sub>O/CO<sub>2</sub> 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 CO<sub>2</sub> 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 H<sub>2</sub>O relative to CO<sub>2</sub>; hence, if a volatile-rich fluid phase is present, then it is likely to be even more CO<sub>2</sub>-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 CO<sub>2</sub>-saturated solidus; and (2) the univariant solidus characterized by high X<sub>CO<sub>2</sub></sub> relative to H<sub>2</sub>O. 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*<sub>H<sub>2</sub>O</sub> conditions.

Existing experimental work applicable to this study include determinations of a CO<sub>2</sub>-saturated granite solidus at low pressures (less than 3 kbar) by Wyllie and Tuttle (1959) and a granite solidus for a range of CO<sub>2</sub>/H<sub>2</sub>O compositions at pressures less than 5 kbar by Novgorodov and Shkodzinskiy (1974).

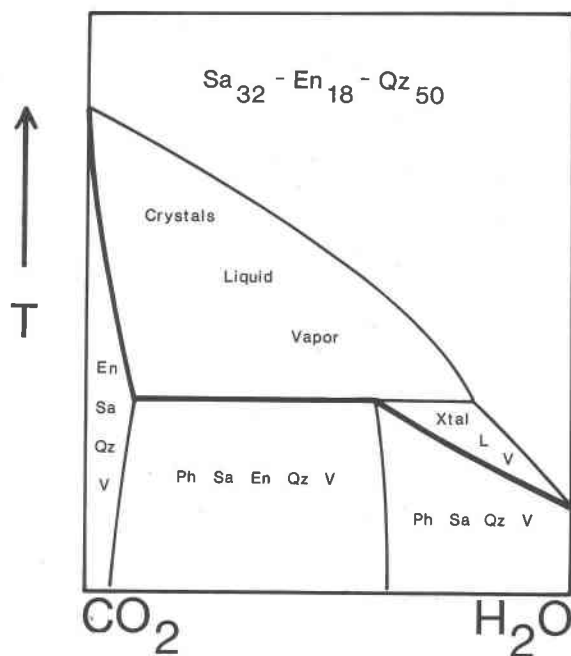


Fig. 3. Schematic *T-X* section for one of the starting compositions depicting the solidus configuration (heavy solid line) and subsolidus assemblages. Where phlogopite and enstatite coexist in the subsolidus, the vapor composition is buffered at a unique value for a given pressure and temperature and 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  $\pm 0.1$  kbar.

Temperatures were measured with Pt-Pt<sub>90</sub>Rh<sub>10</sub> 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-Pt<sub>90</sub>Rh<sub>10</sub> thermocouples and pressures were measured by strain gauge. Temperatures are precise to  $\pm 3^\circ\text{C}$  and pressures are precise to at least  $\pm 100$  bars.

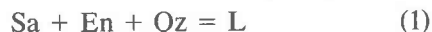
Starting materials were synthetic crystalline phlogopite (Ph), enstatite (En), sanidine (Sa), magnesite (Mag), and quartz (Qz). Anhydrous phlogopite component (Aph) consisted of crystalline forsterite, kalsilite, and leucite. Details of phase preparation have been reported elsewhere (Wendlandt and Eggler, 1980a). Starting mixtures were of the anhydrous compositions Sa<sub>26</sub>En<sub>14</sub>Qz<sub>60</sub>, Sa<sub>32</sub>En<sub>18</sub>Qz<sub>50</sub>, Sa<sub>40</sub>En<sub>22</sub>Qz<sub>38</sub>, and Sa<sub>36</sub>En<sub>42</sub>Qz<sub>22</sub> (wt). Two additional mixtures were used, (Ph<sub>15</sub>+Aph<sub>15</sub>)<sub>30</sub>Sa<sub>20</sub>Qz<sub>50</sub>, which is a partially hydrated equivalent of Sa<sub>40</sub>En<sub>22</sub>Qz<sub>38</sub>, and Sa<sub>30</sub>Mag<sub>30</sub>Qz<sub>40</sub>, which is the carbonated equivalent of Sa<sub>36</sub>En<sub>42</sub>Qz<sub>22</sub> (shown in Fig. 2). Carbon dioxide was added as Ag<sub>2</sub>C<sub>2</sub>O<sub>4</sub> or as MgCO<sub>3</sub>. A  $X_{\text{CO}_2} \approx 0.5$  (mol fraction) and a total volatile content of less than 10 wt.% (H<sub>2</sub>O+CO<sub>2</sub>) was found (by trial and error) to be optimal for investigating the H<sub>2</sub>O-undersaturated melting reaction; H<sub>2</sub>O and CO<sub>2</sub> were added as crystalline H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> · 2H<sub>2</sub>O.

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 H<sub>2</sub>O-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 H<sub>2</sub>O-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

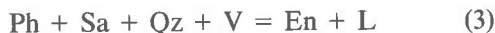
invariant point. Run durations ranged from 2.5 hours at 1600°C to 672 hours at 725°C. While temperature reversals were not accomplished, both water-undersaturated and CO<sub>2</sub>-saturated solidi were determined using different crystalline starting compositions: The former using both Ph + Aph + Sa + Qz + H<sub>2</sub>O + CO<sub>2</sub> and Sa + En + Qz + H<sub>2</sub>O + CO<sub>2</sub>, and the latter using Sa + En + Qz + CO<sub>2</sub> 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 CO<sub>2</sub>-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 CO<sub>2</sub>-saturated and the volatile-absent reactions become detectable. The H<sub>2</sub>O-undersaturated reaction occurs at about 750° C in the interval 5–10 kbar; H<sub>2</sub>O-saturated melting will occur at lower temperatures.

The slope,  $dP/dT$ , of the CO<sub>2</sub>-saturated solidus (reaction 2) is approximately vertical. Novgorodov and Shkodzinskiy (1974) determined a slightly positive slope for the CO<sub>2</sub>-saturated solidus of a granite; they estimated a vertical slope for  $X_{\text{CO}_2} = 0.95$ . The possibility of generating small amounts of H<sub>2</sub>O ( $X_{\text{H}_2\text{O}} = 0.02$ ) by diffusion of H<sub>2</sub> 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-

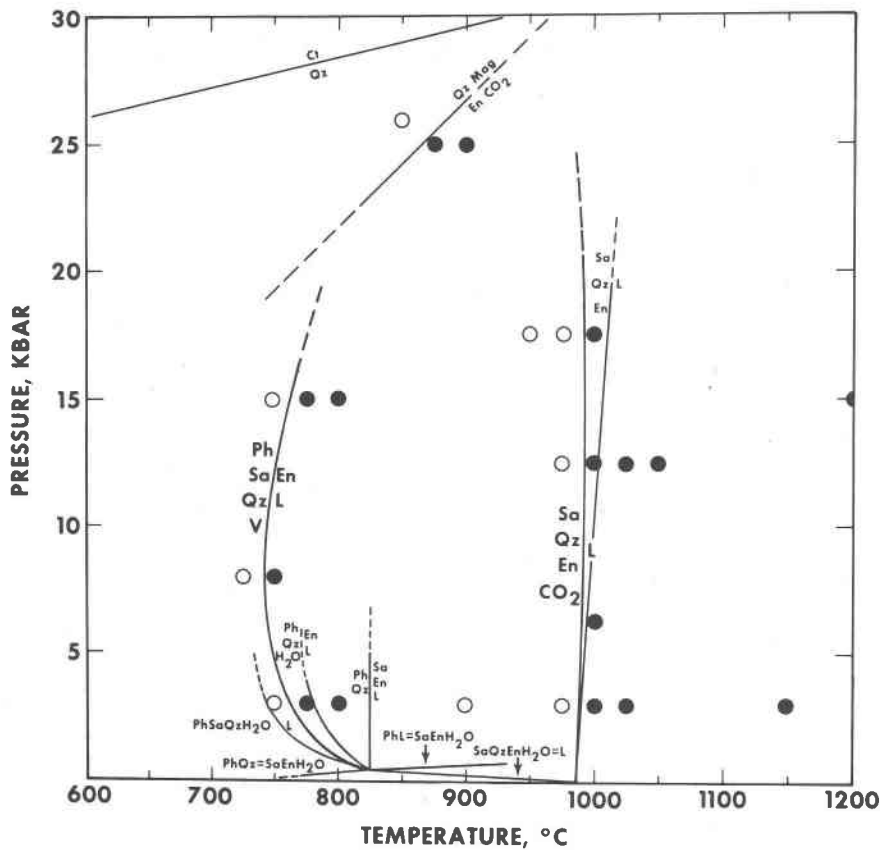


Fig. 4.  $P$ - $T$  projection of univariant melting reactions in the silica-rich portion of the system  $\text{KAlSiO}_4$ - $\text{Mg}_2\text{SiO}_4$ - $\text{SiO}_2$ - $\text{H}_2\text{O}$ - $\text{CO}_2$ . Open circles are subsolidus experiments; closed circles are runs in the melting intervals. The invariant point at approximately 0.5 kbar and 825°C is from Luth (1967). Numerous runs at temperatures above 1200°C are not shown (see Table 3).

creasing pressure for the  $\text{CO}_2$ -saturated system. The trend of liquid compositions for the  $\text{H}_2\text{O}$ -undersaturated melting reaction is approximately the same. This is because  $P_{\text{CO}_2}$  increases with increasing  $P_{\text{total}}$  in both reactions. In reality, the reaction involving small amounts of  $\text{H}_2\text{O}$  will have a slightly more siliceous melt composition than will the higher temperature  $\text{CO}_2$ -saturated reaction at a given pressure.

With increasing pressure, the liquidus stability field of quartz expands relative to enstatite, and, as a consequence, liquid compositions become enriched in potash, alumina and magnesia. The shift of the enstatite-quartz cotectic with increasing pressure (shown in Fig. 5) is constrained in part by observed liquidus phases for the compositions investigated. Unfortunately, electron microprobe analyses of quenched melt cannot be obtained near the solidus because the melt does not segregate into masses sufficiently large to analyze (quenched melt occurred as glass rims on stable crystals). Analyses of melts from runs at much higher temperatures are

possible, however, and have also been used to constrain the shift of the enstatite-quartz cotectic with increasing pressure. A glass analysis for a run at 1150°C and 3 kbar plots almost directly on the 1-atm curve; the analysis constraining the 15 kbar cotectic is at 1300°C, and the analysis along the 25 kbar cotectic is from a run at 1550°C.

The melt compositions of most interest are those generated at the solidi of the melting reactions. Although melt compositions near the solidus cannot be determined directly, the *trend* of evolution of liquid compositions with increasing  $P_{\text{CO}_2}$  can be established: At 1 atm, the eutectic involving  $\text{Sa} + \text{En} + \text{Qz} + \text{L}$  is labelled P (Fig. 5), and, it can be demonstrated that with increasing  $P_{\text{CO}_2}$ , the liquid composition represented by this point shifts away from the  $\text{SiO}_2$  apex toward higher alkali, magnesia and  $\text{CO}_2$  contents. In the end member system,  $\text{MgO}$ - $\text{SiO}_2$ - $\text{CO}_2$ , as presented by Wyllie and Huang (1976) and Egger (1974, 1975), the  $\text{CO}_2$ -saturated quartz liquidus surface is shown to intersect the enstatite- $\text{CO}_2$  join at a pressure between 42 and 55

Table 3: Results of experiments

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

\*\*  $X_{CO_2}$  is slightly less than 1 due to H<sub>2</sub>O 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 K<sub>2</sub>O + Al<sub>2</sub>O<sub>3</sub>, 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 + CO<sub>2</sub> will intersect the Sa-En-CO<sub>2</sub> plane at

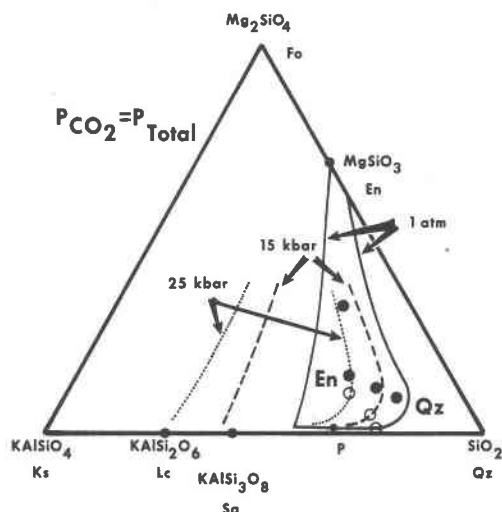


Fig. 5. Evolution of the liquidus surface with increasing pressure for CO<sub>2</sub>-saturated melting. Solid circles show the starting compositions. Open circles denote liquid compositions (analysed by electron microprobe) in equilibrium with quartz and enstatite at high temperatures and 3, 15, and 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 + CO<sub>2</sub>. 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–SiO<sub>2</sub>–CO<sub>2</sub>, is a consequence of the much lower melting temperatures (600°–700°) of the assemblage Sa + En + Qz + CO<sub>2</sub> as opposed to the assemblage En + Qz + CO<sub>2</sub>. Because the H<sub>2</sub>O-undersaturated reaction is also characterized by increasing  $P_{\text{CO}_2}$  (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 SiO<sub>2</sub> contents). Analogous phase relations involving both CO<sub>2</sub>-saturated and H<sub>2</sub>O-undersaturated melting reactions in the silica-undersaturated portion of the system KAISiO<sub>4</sub>–Mg<sub>2</sub>SiO<sub>4</sub>–SiO<sub>2</sub>–

H<sub>2</sub>O–CO<sub>2</sub> 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 CO<sub>2</sub> 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 SiO<sub>2</sub> 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 SiO<sub>2</sub> contents than melts generated at higher pressures. At a given pressure, the melt generated by reaction 3 will have higher SiO<sub>2</sub> 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 CO<sub>2</sub> relative to H<sub>2</sub>O 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 CO<sub>2</sub>-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 CO<sub>2</sub>-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 H<sub>2</sub>O transfers to an increasing fraction of melt. Weaver, on the other hand, suggested that fluctuations in the composition of the metamorphic fluid, from H<sub>2</sub>O-rich to CO<sub>2</sub>-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 CO<sub>2</sub>-rich vapor phase will commence at approximately 750°C. The assemblage of liquid + crystals (including biotite) will persist with continuing CO<sub>2</sub> influx until the biotite is exhausted by H<sub>2</sub>O extraction, at which point the vapor phase composition will be no longer buffered. Extraction of H<sub>2</sub>O 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 CO<sub>2</sub>-saturated and H<sub>2</sub>O-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 CO<sub>2</sub>-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 H<sub>2</sub>O and CO<sub>2</sub>, pressures corresponding to the deep crust are required to generate a melt enriched in pyroxene and feldspar components. Melting in the presence of pure CO<sub>2</sub> 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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