



# Fluids and H<sub>2</sub>O activity at the onset of granulite facies metamorphism



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## ABSTRACT

Evidence is accumulating from experimental petrology and thermodynamic calculations based on detailed descriptions of key natural occurrences that H<sub>2</sub>O activity at the regional amphibolite facies–granulite boundaries in high-grade Precambrian gneiss terranes (coincident with the orthopyroxene isograd) is considerably higher (0.3–0.6) than previously thought (0.15–0.3). This revision provides insight into the significance of fluid inclusions in minerals of the incipient charnockites characteristic of the granulite facies transitions in several Precambrian gneiss terranes. Observations on NaCl-dominated brine inclusions in minerals, including some new data in this paper, in rocks from such places as the Kabbal–Satnur–Halagur area of the Archean Shield of South India have salt concentrations consonant with the stabilization of orthopyroxene relative to calcic amphibole and biotite; closely associated CO<sub>2</sub>-dominated fluid inclusions can have substantial H<sub>2</sub>O contents at typical incipient granulite facies conditions (700–750 °C and 0.5–0.7 GPa) and can thus have been in equilibrium with the associated brines as immiscible metamorphic fluids. Observed densities of the best-preserved CO<sub>2</sub>-rich fluid inclusions in quartz are consistent with those expected from the equation of state of CO<sub>2</sub> at incipient granulite facies pressure–temperature conditions.

It seems likely that the role of fluids in granulite facies metamorphism of the deep crust has been considerably underemphasized in discussions, still prevalent, which concentrate on the role of fluid-deficient partial melting as the primary agent, to the exclusion of a possible role of metamorphic fluids and metasomatism.

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## 1. Introduction

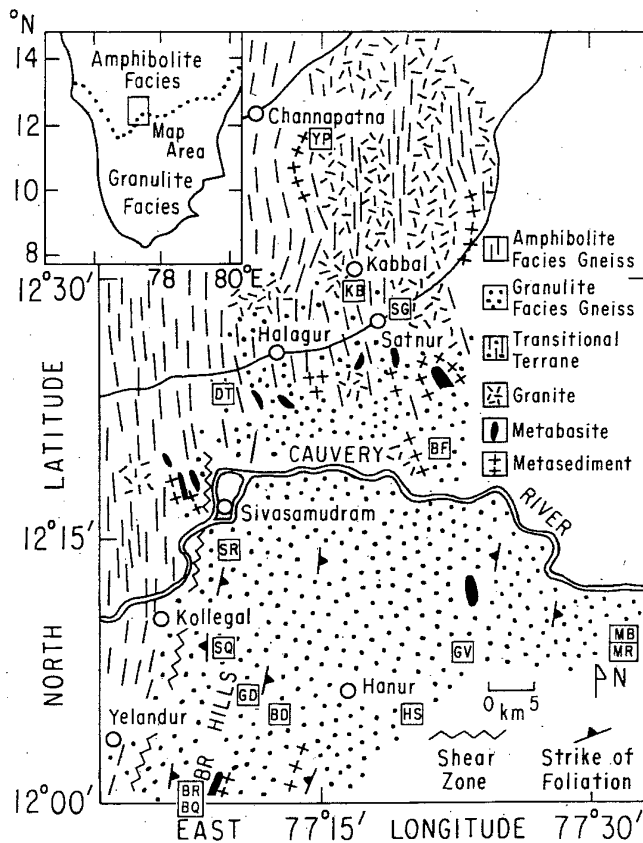
Orthopyroxene in quartzofeldspathic metamorphic rocks is the definitive mineral of the granulite facies. The origin of granitic rocks with orthopyroxene is an on-going controversy, more than a century after Holland (1900) first described the rock he called charnockite in southern India. Charnockite is now known to be a characteristic feature of crystalline terranes of deep-seated origin on all continents.

The simplest proposed origin of charnockite is direct crystallization from mantle-derived very dry felsic magmas (Drury, 1980; Wells, 1978). Supporting this concept are the plutonic character of many large “massif” charnockitic bodies and the fact that

charnockite is an important component of some mantle-derived layered magmatic complexes, as in SW Norway (Demaiffe and Hertogen, 1981). In support of a metamorphic origin of charnockite (Cooray, 1969) is its gradual or abrupt appearance in rocks of suitable composition (orthogneiss or paragneiss) in a progressive metamorphic terrane like the Late Archean Dharwar Craton of South India. There the granulite facies appears to be an overprint on rocks of demonstrably upper-crustal origin, such as metapelites and marbles, as well as on the dominant felsic orthogneiss. A regional orthopyroxene-in isograd may be present, like the “Fermor Line” of southern India (Devaraju and Sadashivaiah, 1969), or those in southern Norway (Touret, 1971), SW Finland (Schreurs, 1985) and SW Greenland (McGregor and Friend, 1992). The Nagercoil charnockitic batholith at the southern tip of India has traditionally been regarded as a bona fide charnockitic pluton, but has been reinterpreted as an original hornblende-biotite granite having an orthopyroxene-producing metamorphic overprint (Rajesh et al., 2011). The “charnockite problem” is as actively debated currently

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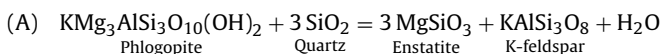


**Fig. 1.** Amphibolite- to granulite facies terrain of southern Karnataka, India and its relation to the Closepet Granite and the regional orthopyroxene-in isograd ("Fermor Line") of the Late Archean Dharwar Craton. The dominant country rock is hornblende-biotite felsic gneiss or its charnockitic equivalent with orthopyroxene. A mixed-facies transitional interval occurs in the region Kabbal–Satnur–Halagur, referred to in the text and references. From Hansen et al. (1984) with permission. Letters in squares refer to their sample localities.

as when Pichamuthu (1953) first defined the problem (Rajesh and Santosh, 2012).

"Incipient" or patchy charnockitic alteration of hornblende-biotite gneiss was first identified by Pichamuthu (1960) at the Kabbal locality in southern Karnataka (Fig. 1) and has since been described at many localities along the Fermor Line and in the Central Highlands of Sri Lanka (Hansen et al., 1987). These occurrences involve replacement of host rocks by veins and irregular patches of coarse-grained orthopyroxene-bearing rock. The transitional granulite facies terrane of Kabbal–Satnur–Halagur is a gradual coalescence of patchy charnockite southward into a dominantly charnockitic country rock (Devaraju and Sadashivaiah, 1969; Fig. 1). A curious circumstance of the transition in this area is that the Closepet Granite, a major N–S linear feature of Karnataka, phases out into migmatitic gneisses at approximately the latitude where orthopyroxene appears (Fig. 1).

The reaction conventionally assigned to a regional orthopyroxene isograd is the dehydration of biotite in the presence of quartz, modeled by:



Petrographic study indicated, however, that hornblende, along with biotite, was a precursor of orthopyroxene in the charnockite-forming reaction at Kabbal (Hansen et al., 1987; Stähle et al., 1987). The biotite at the orthopyroxene-in isograd is ferromagnesian, with additional Al as well as important TiO<sub>2</sub> and F contents; the orthopyroxene is hypersthene (Fe-bearing) with variable Al

content, and the K-feldspar is an intermediate (K, Na) solid solution. The H<sub>2</sub>O could not have been liberated as a pure fluid phase because the hydrous melting temperature of quartzofeldspathic rocks at 0.5 GPa and higher pressures (650–700 °C) is much lower than estimates based on thermometry of granulite minerals, 700–900 °C. Therefore, if dehydration takes place, the H<sub>2</sub>O must be absorbed into either a pore fluid which is dominated by anhydrous components, such as a CO<sub>2</sub>-rich fluid or a concentrated salt solution, or into a granitic melt. If the latter mechanism, termed "dehydration melting", is effective, a reaction analogous to Reaction A could be expressed as:



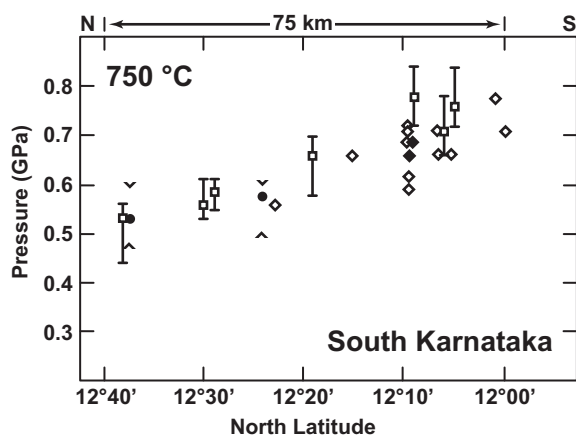
without the participation of a separate fluid phase.

Evidence for the presence of fluids during high grade metamorphism was brought forth by Touret (1971) with the discovery of common, if not ubiquitous, dense CO<sub>2</sub> fluid inclusions in minerals of granulites, and subsequently, by the identification of concentrated alkali chloride aqueous solutions as inclusions in minerals of some of these same rocks (Touret, 1985). The latter kind of fluid inclusion is more likely to be poorly preserved because of greater chemical reactivity and mobility than for the CO<sub>2</sub> inclusions, and also because early saline aqueous inclusions are likely to be later redistributed in the form of secondary inclusions (Nijland and Touret, 2001). Evidence in favor of partial melting as a desiccation mechanism is that gneisses at the regional orthopyroxene isograd are almost invariably migmatitic.

The mechanism of granulite facies dehydration and the significance of the trapped fluids in minerals of granulites have become central issues in petrogenesis discussions. In favor of the role of low-H<sub>2</sub>O fluids are the demonstration that the carbonic fluids and the brines could coexist as immiscible fluids even at the high temperatures and pressures of granulite facies metamorphism (Johnson, 1991; Gibert et al., 1998; Shmulovich and Graham, 2004) and that the densities of the CO<sub>2</sub> inclusions, as measured by microthermometry, are often found to be consistent with those expected from the high *P*–*T* equation of state of CO<sub>2</sub> (Touret and Bottinga, 1979). Indeed, the densities of CO<sub>2</sub> inclusions have been used as supporting evidence for paleopressures deduced from mineral stability calculations, as across the Fermor Line in the southern Karnataka area (Fig. 2; Hansen et al., 1984). In spite of the attempt of Lamb (1990) to discredit the latter CO<sub>2</sub> inclusions, it is clear from Fig. 2 that paleopressures calculated with the Touret and Bottinga (1979) equation of state of CO<sub>2</sub> are consistent with independently deduced paleopressures. The alteration veins of incipient charnockites like those of Kabbal are characteristically rich in one or both types of fluid, whereas those of the unaltered host rocks have neither (Hansen et al., 1984; Stähle et al., 1987; Perchuk et al., 2000; Safonov et al., 2012).

The most frequently uttered argument against the action of high grade fluids is the very low H<sub>2</sub>O activities that have been calculated based on the stability of orthopyroxene (Lamb and Valley, 1988) and local heterogeneity of the indicated H<sub>2</sub>O activity, as well as in calculated oxygen fugacity (*f*<sub>O<sub>2</sub></sub>) and oxygen isotope makeup of granulites, arguing for the absence of a pervasive fluid phase during metamorphism (Valley et al., 1990). The calculated low H<sub>2</sub>O activity is particularly significant because the lowest estimated values of this parameter would not be realizable by a chloride brine before salt saturation occurs, which limitation, if found to be generally true, would render the brine inclusions irrelevant.

The purpose of the present paper is to discuss the various estimates of H<sub>2</sub>O activity which could have prevailed during granulite facies metamorphism, particularly at the regional appearance of orthopyroxene, and to inquire whether the fluids observed as fluid



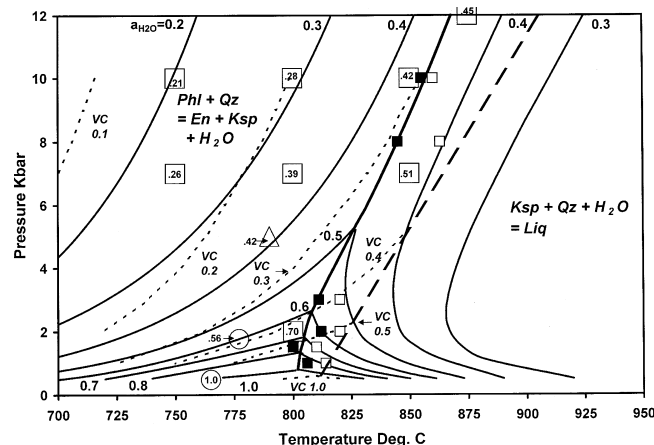
**Fig. 2.** North-south paleopressure gradient across the Feroor Line of Fig. 1. Pressures were calculated by Hansen et al. (1984) from pressure-sensitive but relatively temperature-independent mineral assemblages of charnockites and metapelites at a temperature of 750 °C, assumed to be representative of the transitional granulite facies metamorphism. Symbols: filled circles: garnet-sillimanite-plagioclase-quartz; open diamonds: garnet-orthopyroxene-plagioclase-quartz; filled diamonds: garnet-clinopyroxene-plagioclase-quartz; upward pointing arrows: garnet-cordierite-sillimanite-quartz ( $P_{\text{H}_2\text{O}} = 0$ ); downward-pointing arrows: garnet-cordierite-sillimanite-quartz ( $P_{\text{H}_2\text{O}} = P_{\text{total}}$ ). Shown also with uncertainty limits are the paleopressures calculated from measured densities of  $\text{CO}_2$ -rich fluid inclusions in the granulites, based on the high  $P$ - $T$  equation of state of  $\text{CO}_2$  (Touret and Bottinga, 1979).

inclusions in minerals of these rocks could qualify as effective dehydration agents.

## 2. Estimates of $\text{H}_2\text{O}$ activity

Table 1 lists  $\text{H}_2\text{O}$  activity estimates based on thermodynamic analysis of natural assemblages of the minerals participating in Reaction A. The occurrences are all very similar: incipient and transitional charnockites formed after granitic biotite gneisses. All have much the same kind of biotite, with about 2 wt.% of F, 4 wt.%  $\text{TiO}_2$  and Mg numbers about 0.5. Metamorphic temperatures and pressures are about the same for all occurrences: 650–750 °C and 0.5–0.7 GPa. All have dense  $\text{CO}_2$  fluid inclusions, and the Kurunegala, Sri Lanka and Halagur, Karnataka charnockites have concentrated brine inclusions as well. Brines have not been identified in the Kabbal or Satnur charnockites, but this may reflect the usually altered and disrupted condition of such inclusions, and therefore difficulty of identification. Some rocks in this zone (Fig. 1), including the Halagur charnockites and the Closepet Granite, are riddled with concentrated salty aqueous inclusions and disseminated salt crystals (Srikantappa and Zargar, 2009; Srikantappa and Malathi, 2008).

The large spread of estimated  $a_{\text{H}_2\text{O}}$ , ranging from 0.14 to 0.67 for very much the same parageneses, is unlikely to be the result of actual variation in metamorphic conditions, or because the inclusions are not interpretable as directly associated with the charnockitic metamorphism, but more likely stem from different thermodynamic formulations, especially in the standard free energy of formation of phlogopite, and the solid solution properties of biotite which define the activity of the phlogopite component. The standard free energy of formation of phlogopite can be derived from accurate experimental determination of Reaction A. This reaction is in equilibrium at very low  $\text{H}_2\text{O}$  pressures, below 0.1 GPa, where experimental reactions are very slow and equilibrium is hard to prove convincingly; thus, the several experimental studies are somewhat problematic (Wood, 1976; Wones and Dodge, 1977; Clemens, 1995). Small differences in the equilibrium pressure determined in the experiments make large differences in



**Fig. 3.**  $\text{H}_2\text{O}$  isoactivity lines of the equilibrium: phlogopite + quartz = enstatite + K-feldspar +  $\text{H}_2\text{O}$  (Reaction A, text), as calculated by Aranovich and Newton (1998) from reversed determinations of the equilibrium in KCl- $\text{H}_2\text{O}$  solutions. Large open squares with  $a_{\text{H}_2\text{O}}$  values: Aranovich and Newton (1998) in KCl- $\text{H}_2\text{O}$  solutions. Triangle: Bohlen et al. (1983) in a  $\text{CO}_2$ - $\text{H}_2\text{O}$  solution. Circles: Berman et al. (1995) in pure  $\text{H}_2\text{O}$  ( $a_{\text{H}_2\text{O}} = 1.0$ ) and a  $\text{CO}_2$ - $\text{H}_2\text{O}$  solution ( $a_{\text{H}_2\text{O}} = 0.56$ ). Dashed curves are the  $\text{H}_2\text{O}$  isoactivity curves drawn by Vielzeuf and Clemens (1992) based on the phlogopite model of Clemens et al. (1987). Shown also are the  $\text{H}_2\text{O}$  isoactivity curves of the reaction: K-feldspar + quartz +  $\text{H}_2\text{O}$  = liquid from Vielzeuf and Clemens (1992), attributed to H. Nekvasil and C.W. Burnham. A dehydration melting curve (the equilibrium phlogopite + quartz = K-feldspar + liquid, Reaction B, text) is generated (bold solid curve) by the intersection of the melting curves with the Aranovich and Newton (1998)  $\text{H}_2\text{O}$  isoactivity curves of Reaction A. The dashed bold line is the dehydration melting curve generated by the intersection of the melting curves with the  $\text{H}_2\text{O}$  isoactivity lines (dashed) of Vielzeuf and Clemens (1992). It is seen that the Aranovich and Newton (1998) dehydration melting curve satisfies most of the Vielzeuf and Clemens (1992) experimental melting brackets (smaller squares).

derived  $\text{H}_2\text{O}$  activities at higher pressures. The dehydration melting reaction B was the subject of two thorough studies (Bohlen et al., 1983; Vielzeuf and Clemens, 1992). The latter study produced several experimental brackets in the range 800–900 °C and 15 kbar (Fig. 3) and has influenced most current thinking about the proper range of  $\text{H}_2\text{O}$  activity during granulite facies metamorphism.

Aranovich and Newton (1998) produced several reversals of Reaction A at low  $\text{H}_2\text{O}$  activity, hence higher pressure, in KCl solutions of known  $\text{H}_2\text{O}$  activity (Aranovich and Newton, 1997). These data greatly extend the conditions under which  $a_{\text{H}_2\text{O}}$  may be defined from Reaction A. Fig. 3 shows all definitive reversals which have been performed, including a few of very long experimental duration at low pressure (Berman et al., 1995). Based on these reversed brackets, Aranovich and Newton (1998) revised the standard free energy of formation of phlogopite to a value about 6 kJ less negative than the value given by Clemens et al. (1987), which was used by Vielzeuf and Clemens (1992) to construct their preferred dehydration melting curve in Fig. 3. The consequence of the Aranovich and Newton (1998) revision for phlogopite is that the activity of  $\text{H}_2\text{O}$  based on Vielzeuf and Clemens (1992) should be revised upward by a factor of nearly  $\exp(6000/RT)$ , or about 2. Fig. 3 shows the revised  $\text{H}_2\text{O}$  isoactivity  $P$ - $T$  lines of Reaction A of Aranovich and Newton (1998).

Vielzeuf and Clemens (1992) introduced an ingenious independent method of determining the dehydration melting curve of phlogopite + quartz. Isoactivity lines of  $\text{H}_2\text{O}$  calculated from the preferred Clemens et al. (1987) thermodynamic data for phlogopite form, by intersection with hydrous melting curves of sanidine + quartz at constant  $\text{H}_2\text{O}$  activity, an alternative dehydration melting curve shown by the dashed bold line in Fig. 3, which line is apparently their preferred model, though, as is seen, it departs from their experimental brackets by as much as 30 °C. If, on the other hand, the revised  $\text{H}_2\text{O}$  isoactivity lines are used with the same sanidine-quartz melting curves, a dehydration melting

**Table 1**  
Estimates of temperature, pressure and H<sub>2</sub>O activity at the opx-in isograd.

Author	Locality	Description	T (°C)	P (GPa)	H <sub>2</sub> O activity
Hansen et al. (1984)	Kabbal, Karnataka	Incipient charnockite	700–750	0.55–0.65	X <sub>H<sub>2</sub>O</sub> < 0.3
Raith et al. (1989)	Kabbal, Karnataka	Incipient charnockite	650–720	0.5–0.7	X <sub>H<sub>2</sub>O</sub> < 0.3
Santosh et al. (1990)	Kabbal, Karnataka	Incipient charnockite	700–750	0.55 ± 0.19	X <sub>H<sub>2</sub>O</sub> = 0.2–0.3
Burton and O’Nions (1990)	Kurunegala, Sri Lanka	Incipient charnockite	738 ± 60	0.69 ± 0.12	0.18 ± 1.2
Sen and Bhattacharya (1990)	Satnur, Karnataka	Transitional charnockite	670–730	0.5–0.64	0.14–0.20
Perchuk and Gerya (1993)	S. Lake, Baikal	Incipient charnockite	700–730	0.3–0.6	0.37–0.42
Perchuk et al.	SW Finland	Transitional granulite	685–759	0.53–0.66	0.32–0.46
Perchuk et al.	S. India, Sri Lanka	Incipient charnockite	670–760	0.5–0.7	0.36–0.46
Perchuk et al. (1994)	Quetico, Ontario	Orthopyroxene isograd	680–770	0.4–0.6	0.15–0.25
Perchuk et al. (2000)	Kurunegala, Sri Lanka	Incipient charnockite	650–750	0.5–0.7	0.53–0.67

curve, shown by the bold solid curve in Fig. 3, passes through nearly all of the Vielzeuf and Clemens (1992) experimental brackets of Reaction B. This may be taken to be an indication of the internal consistency of the revised thermodynamic data for phlogopite, which generally lead to higher H<sub>2</sub>O activities defined by the assemblage phlogopite–quartz–enstatite–sanidine at a given P and T.

There is thus evidence that the higher range of H<sub>2</sub>O activity estimates for transitional granulite facies metamorphism should be given consideration. The highest range, that of 0.53–0.67 of Perchuk et al. (2000) incorporates the revised standard properties of phlogopite of Aranovich and Newton (1998). According to Perchuk et al. (2000), incipient charnockitic metamorphism of hornblende–biotite gneiss at Udadigana, Sri Lanka, involved partial melting of the gneiss in the “charnockitic core” regions of charnockite patches, based on textural and mineralogic evidence. Burton and O’Nions (1990) also found evidence of melting in their isotopic analysis of the very similar paragenesis at nearby Waraddana. Perchuk et al. (2000) derived the high a<sub>H<sub>2</sub>O</sub> range of 0.59–0.67 for these core charnockites, inferred to have been partially melted during formation of the orthopyroxene.

The thermodynamic data and equations used by Perchuk et al. (2000) to calculate a<sub>H<sub>2</sub>O</sub> can be tested by the Vielzeuf and Clemens (1992) method of intersection of H<sub>2</sub>O isoactivity lines of granite melting with H<sub>2</sub>O isoactivity lines of Reaction A predicted by Perchuk et al. (2000). To evaluate the latter, the condition of equilibrium for Reaction A is used:

$$0 = \Delta G_A^0 + RT \ln(f_{\text{H}_2\text{O}}) + RT \ln(K) + RT \ln(a_{\text{H}_2\text{O}})$$

where K is the ratio  $a_{\text{En}}^3 \cdot a_{\text{Ksp}} / a_{\text{Pl}}$ , assumed to be nearly constant over the temperature range ±50 °C and pressure range ±2 kbar, and En, Ksp, and Pl denote, respectively, the activities of MgSiO<sub>3</sub> in orthopyroxene, KAlSi<sub>3</sub>O<sub>8</sub> in alkali feldspar, and KAlMg<sub>3</sub>Si<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub> in biotite. Using Perchuk et al.’s (2000) Eq. (r5) in their Appendix for  $\Delta G_A^0$ , and their mean value of incipient melting at 720 °C and 6 kbar of  $a_{\text{H}_2\text{O}} = 0.64$ , K comes out to be 0.607. The resulting H<sub>2</sub>O isoactivity lines for Reaction A are shown in Fig. 4. The corresponding H<sub>2</sub>O isoactivity lines of simple granite melting, derived from the experimental melting data of Ebadi and Johannes (1991) in CO<sub>2</sub>–H<sub>2</sub>O mixtures and the H<sub>2</sub>O activities of these mixtures given by the experimental work of Aranovich and Newton (1999), determine, by intersection with the isoactivity lines of Reaction A, the dehydration melting curve shown by the bold line in Fig. 4.

The consistency of the Perchuk et al. (2000) a<sub>H<sub>2</sub>O</sub> activity scale can be seen by the fact that the dehydration melting point shown by the filled square in Fig. 4 lies at a H<sub>2</sub>O activity almost identical with the experimental determination of the H<sub>2</sub>O activity at melting of a simple granite at 720 °C and 6 kbar by Aranovich et al. (2013) in NaCl–KCl solutions of known activity (Aranovich and Newton, 1997). Fig. 4 indicates that the a<sub>H<sub>2</sub>O</sub> values consistent with Perchuk et al.’s (2000) geothermometry/barometry of Udadigana assemblages (660–700 °C and 0.5–0.6 GPa) would fall in the range 0.4–0.6.

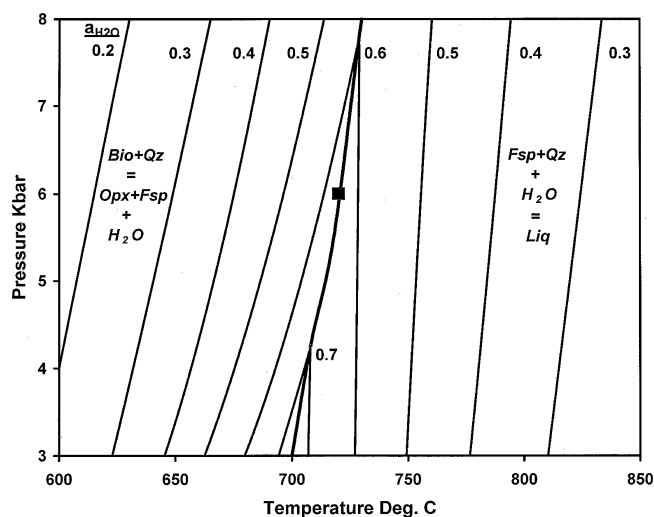
The bold line in Fig. 4 can be considered a fluid-present dehydration melting curve. It lies about 60 °C lower than the first melting of a fluid-absent model tonalite assemblage where the biotite contains 3.6 wt.% TiO<sub>2</sub> and 0.22 wt.% F (Singh and Johannes, 1996), and about 70 °C higher than the H<sub>2</sub>O-saturated melting point of granite (Luth et al., 1964) at the same pressure.

The concept of fluid-present dehydration melting that of fluid-absent dehydration melting and provides a mechanism for the metasomatic features commonly observed in high-grade migmatite complexes, as discussed later in this paper.

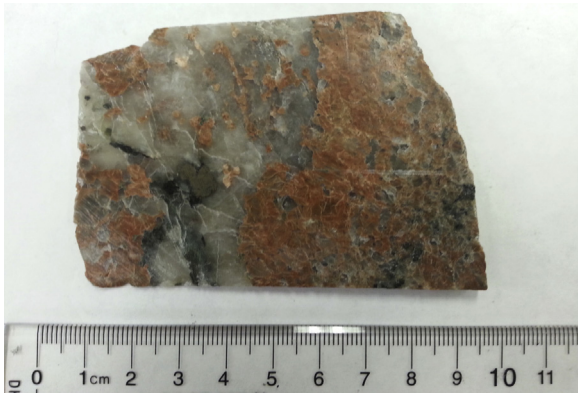
### 3. Fluid inclusion evidence

Fluid action at transitional granulite facies metamorphism in the Archean Craton of southern India is implicated by a number of observations:

- (1) The area marks the southern termination of the Closepet Granite, a 400-km-long north–south linear feature of the Craton. Metasomatism-induced anatexis has been implicated for the



**Fig. 4.** Dehydration melting curve (Vielzeuf–Clemens-type plot, bold line) of granitic biotite gneiss as determined by the intersection of the H<sub>2</sub>O isoactivity lines of the assemblage biotite–quartz–orthopyroxene–feldspar, from Perchuk et al. (2000) based on their mineral analyses and calculations of this assemblage at Udadigana, Sri Lanka, and the H<sub>2</sub>O isoactivity lines of simple granite (albite–K-feldspar–quartz) hydrous melting as determined from the CO<sub>2</sub>–H<sub>2</sub>O granite melting experiments of Ebadi and Johannes (1991) with the H<sub>2</sub>O activity values in CO<sub>2</sub>–H<sub>2</sub>O solutions at high T and P of Aranovich and Newton (1999). The filled square is the melting point of simple granite measured by Aranovich et al. (2013) in NaCl–KCl–H<sub>2</sub>O solutions. Their melting-point H<sub>2</sub>O activity of 0.64 at 720 °C and 0.6 GPa is in nearly perfect agreement with the estimate of a<sub>H<sub>2</sub>O</sub> of Perchuk et al. (2000) at these conditions for the fluid-present orthopyroxene-producing anatexis at their locality, which lends credence to their estimates of a<sub>H<sub>2</sub>O</sub> at the orthopyroxene-in isograd in biotite gneiss, considerably higher than the estimates of previous workers (Table 1).



**Fig. 5.** Quartz–K-feldspar vein in Closepet Granite from near Satnur, Karnataka (locality SG, Fig. 1). Vein contains a large orthopyroxene crystal in central quartz-rich portion. Normal granite portion of sample in lower right-hand corner.

southern portion of this body (Jayananda et al., 1995). K-feldspar megacrysts of the dominant phase of this granite at the type area of Ramanagaram at the northern edge of Fig. 1 show trace element zonation that is best explained by alteration by saline fluids (Slaby et al., 2012). Quartz in the granite from this locality contains abundant hypersaline fluid inclusions (up to 43 wt.% NaCl equivalent) as well as CO<sub>2</sub>-rich inclusions (Srikantappa and Malathi, 2008).

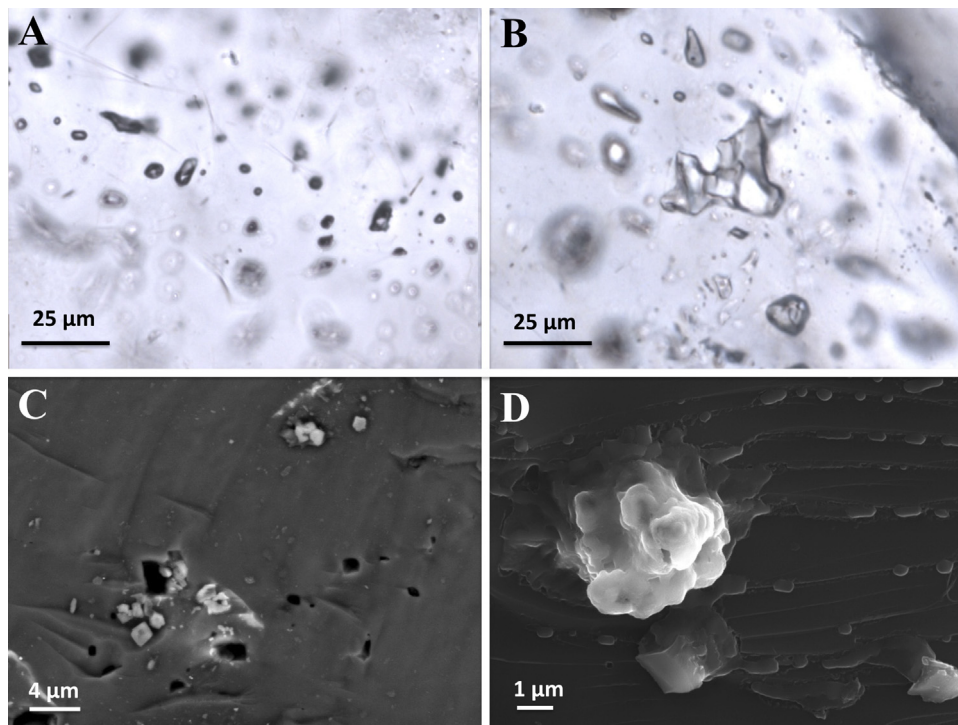
- (2) Many occurrences of incipient charnockite have been reported from the hornblende-biotite gneisses of this area. The map of Jayananda et al. (1995, their Fig. 1) shows a few such localities. These include the type Kabbal locality

(Pichamuthu, 1960). This kind of patchy orthopyroxene-producing alteration always displays dense CO<sub>2</sub>-rich fluid inclusions and/or hypersaline fluid inclusions in minerals of the charnockite but not in the host rock (Hansen et al., 1987; Perchuk et al., 2000).

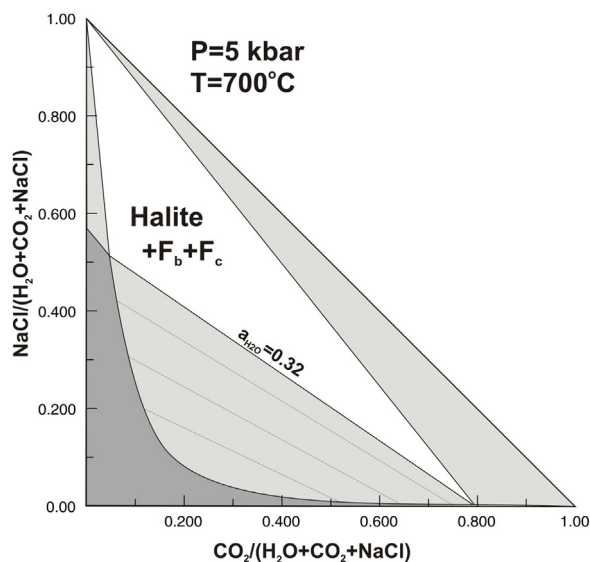
- (3) Banded charnockitic gneisses from near Halagur (Fig. 1) contain abundant hypersaline inclusions in the quartz, as well as CO<sub>2</sub>-rich inclusions (Srikantappa and Zargar, 2009). U–Th–Pb isotope measurements on zircons from this locality give ages clustering around 2.52 Ga, identical to zircons from incipient charnockite and Closepet Granite at Kabbal (Mojzsis et al., 2003; Friend and Nutman, 1992). There is thus a close temporal link among Closepet Granite, incipient charnockite and regional granulite facies metamorphism in this area.

We investigated fluid inclusions in quartz from an orthopyroxene-bearing granite from a fresh road cut near Satnur (Locality SG, Fig. 1). This granite has very coarse-grained veins of quartz and K-feldspar, some showing discrete monomineralic zoning of the minerals. One specimen contains a large orthopyroxene crystal embedded in the quartz-rich portion of the vein (Fig. 5). Standard 100- $\mu$ m-thick doubly polished sections were made on quartz from the vein and the finer-grained granite shown in the lower right-hand portion of the sample (Fig. 5). The granite portion proved to be more tractable in that smaller individual quartz crystals could be studied in their entirety for fluid inclusion populations.

The quartz contains myriads of small fluid inclusions (<10  $\mu$ m) aligned along healed microfractures (“trails” in the fluid inclusion literature). CO<sub>2</sub>-rich inclusions and somewhat larger aqueous inclusions, most of them halite-bearing, coexist within a single trail, indicating immiscible fluids (Fig. 6A). Isolated large CO<sub>2</sub>-rich



**Fig. 6.** Saline fluid inclusions and disseminated halite crystals observed in quartz of granite, Fig. 5. (A) Transmitted light photo of portion of fluid inclusion trail containing gaseous (CO<sub>2</sub>-rich) inclusions (small, dark) and saline inclusions (somewhat larger, with halite cubes). Both types are strikingly separated, indicating coexisting immiscible fluids. (B) Large irregular aqueous inclusion in same trail as (A) containing two isotropic crystals, one smaller, perfectly cubic, the other more irregular. Smaller inclusions around the larger central one are also aqueous, many of them with a small vapor bubble, most of them without a halite cube, indicating apparent salinity increase by expulsion of some liquid. (C) Scanning electron microscope (backscatter) image of broken quartz grain from granite of Fig. 5. Broken surfaces show ubiquitous small rectangular halite crystals, some seemingly dislodged from cavities of the same shape, which may be evidence of co-precipitation of quartz and halite (halite saturation of quartz-crystallizing fluid). (D) Backscatter image of interior of empty cavity in quartz crystal with aggregates of small platy halite crystals, possibly deposited by ultrasaline fluids during late cooling period.



**Fig. 7.** Ternary system H<sub>2</sub>O–CO<sub>2</sub>–NaCl at 700 °C and 0.5 GPa (5 kbar), from Aranovich et al. (2010). F<sub>b</sub> denotes brine fluid; F<sub>c</sub> denotes CO<sub>2</sub>-rich fluid. The diagram shows that an incipient charnockite isograd in biotite gneiss could take place in the presence of a concentrated NaCl solution of H<sub>2</sub>O activity 0.4–0.6, as calculated by Perchuk et al. (2000), but that the solution would be halite saturated at H<sub>2</sub>O activities lower than 0.32 at the estimated metamorphic *P*–*T* conditions.

inclusions of the sort reported by Srikantappa and Malathi (2008) were not found in our sample. In trail-bound inclusions, the halite relative volume corresponds to a salinity of 20–40 wt.%. Larger irregular saline aqueous inclusions may contain several daughter crystals, all optically isotropic (Fig. 6B). They are surrounded by a swarm of smaller discrete saline inclusions, many of them containing a small vapor bubble, which may have been derived from bursting of the large disrupted (imploded?) hypersaline inclusions (Nijland and Touret, 2001). It is not possible to estimate with any confidence the salinity of original (primary) aqueous fluid inclusions except to state that they were of very high salinity.

The large amount of crystalline salt in the quartz of the orthopyroxene-bearing granite suggested that scanning electron microscope images of crushed quartz grains might yield further information. Individual grains of about one mm size were plucked from the granite, crushed with pliers, and quickly carbon-coated so that any soluble intracrystalline material might be preserved. The fragments were imaged with the scanning electron microscope at the Laboratory of Geology, Ecole Normal Supérieure, Paris, D. Deldicque, analyst. SEM images showed myriad small crystals of halite, apparently displaced from discrete rectangular cavities in the quartz (Fig. 6C). There were in addition irregular mostly empty cavities occasionally with small clusters of halite of diverse habit, some as clusters of platy crystals on the cavity walls (Fig. 6D).

Identification of hypersaline fluid inclusions and halite monocrystals embedded in quartz and seemingly without associated fluid, provides further evidence of the action of hypersaline fluids in the charnockitic metamorphism and suggests that, in some cases, the fluids (or granite magmas) were actually salt-saturated, as postulated by Touret (1985) for some saline inclusions in the Bamble region of southern Norway. Another possibly comparable example of the action of salt-saturated aqueous fluids is the Sybille Monzodiorite from the Laramie Anorthosite Complex, Wyoming, USA, a charnockite-related rock (Frost and Touret, 1989).

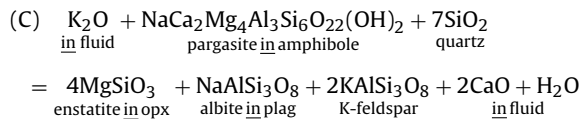
The phase relations of a metamorphic fluid may be portrayed in the simple system H<sub>2</sub>O–CO<sub>2</sub>–NaCl (Fig. 7). According to the ternary relations depicted by Duan et al. (1995) and Aranovich et al. (2010), the brine-rich fluid in equilibrium with a CO<sub>2</sub>-rich fluid would have only about 5 mol% of CO<sub>2</sub>, almost independently

of temperature and pressure, and the CO<sub>2</sub>-rich fluid would have about 2 mol% NaCl, according to Duan et al. (1995) and less than half a mol% NaCl according to Aranovich et al. (2010) at 700 °C and 5 kbar (0.5 GPa). These small departures from binary behavior allow a H<sub>2</sub>O isoactivity line to be drawn from salt saturation at these conditions in the H<sub>2</sub>O–NaCl binary (Aranovich and Newton, 1996) to the H<sub>2</sub>O–CO<sub>2</sub> binary (Aranovich and Newton, 1999) with small uncertainty. This line, which is the field boundary of the invariant 3-phase triangle halite–brine–CO<sub>2</sub>-rich fluid, has a H<sub>2</sub>O activity of 0.32. Its intercept on the CO<sub>2</sub>–H<sub>2</sub>O axis is 79 mol% CO<sub>2</sub>. The ternary phase-equilibrium diagram according to Aranovich et al. (2010) is shown in Fig. 7.

Fig. 7 indicates that, at the *P*–*T* conditions of incipient charnockite formation, the NaCl concentration of a brine phase may be close to halite saturation. Other salt components in the brine phase, such as KCl and carbonates, would lower the H<sub>2</sub>O activity for salt saturation somewhat further, but probably not to the level of 0.2, which is the H<sub>2</sub>O activity associated with charnockitic metamorphism advocated by some authors (Table 1). Fig. 7 suggests that the CO<sub>2</sub>-rich fluid in equilibrium with a saturated brine at 700 °C and 5 kbar is not nearly pure CO<sub>2</sub>, but has a substantial H<sub>2</sub>O content. Some fluid inclusion evidence also points in the same direction. Srikantappa and Zargar (2009) state that some larger CO<sub>2</sub>-rich inclusions from their Halagur charnockites have an observable H<sub>2</sub>O-rich layer lining the cavities, estimated to be 5–15 volume%, similar to CO<sub>2</sub>-rich inclusions from Bamble, described by Touret (1971). Because of the large molar volume difference between H<sub>2</sub>O and CO<sub>2</sub> (27.4 cm<sup>3</sup> versus 46.0 cm<sup>3</sup> at the assumed conditions), the molar H<sub>2</sub>O content of a CO<sub>2</sub>-rich fluid coexisting with a nearly salt-saturated brine would be consistent with Srikantappa and Zargar's (2009) estimate (roughly twice the observed volume proportion).

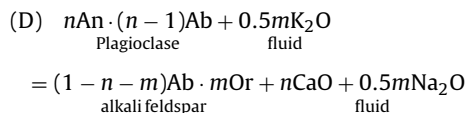
#### 4. Role of metasomatism

Variation in the activities of fluid components, notably alkalis and Ca species, may be important factors, along with decrease in H<sub>2</sub>O activity, in the generation of orthopyroxene. Most of the studies of incipient charnockite formation in amphibole-biotite gneiss, as at Kabbal, S. India (Stähle et al., 1987) and Udadigana, Sri Lanka (Perchuk et al., 2000), report decrease of hornblende and loss of CaO and gain of K<sub>2</sub>O in the whole-rock compositions. This alteration can be modeled by an open-system reaction similar to:



It is seen from this reaction that the critical H<sub>2</sub>O activity for the formation of orthopyroxene may depend to some degree on the concentration ratio K/Ca in an infiltrating fluid. This is probably the main reason why hornblende-bearing biotite gneisses can undergo incipient charnockitic metamorphism at a higher H<sub>2</sub>O activity than such rocks without hornblende (see Newton and Tsunogae, in this volume).

Incipient charnockite formation is often accompanied by the emplacement of microscopic networks of alkali feldspar veins replacing plagioclase along grain boundaries (e.g. Perchuk et al., 2000). Korzhinskii (1946) suggested that replacement of plagioclase by K-feldspar, often observed in high-grade gneisses of the Aldan Shield, Eastern Siberia, corresponds to the reaction:



It is likely that alkalis and lime are highly mobile in Cl-bearing fluids (Newton and Manning, 2010). Therefore, the presence of K-feldspar alteration of plagioclase (replacement antiperthite: Griffin, 1969) may be an indication of the former presence of highly saline, hence low-H<sub>2</sub>O-activity, infiltrating fluids.

## 5. Conclusions and interpretations

The coexistence of concentrated brine inclusions and dense CO<sub>2</sub>-rich inclusions in minerals of transitional granulites such as in southern Karnataka, India, and the Kurunegala District of Sri Lanka, and their nearly total absence in non-charnockitic rocks of the same zones, make it appear highly likely that these fluid inclusions indeed represent mineralizing fluids attending, and probably, responsible for, charnockitic metamorphism of biotite gneiss. The trapped fluids have undoubtedly been modified by post-entrapment processes of contamination, leakage, and, in some cases, observable decrepitation, but these effects do not totally obscure the systematics consistent with their role as granulite facies metamorphic fluids. The attempts of some authors (Lamb and Valley, 1988; Lamb, 1990) to amass evidence that the observed fluids in granulite minerals are irrelevant do not take into account some of the most pertinent fluid inclusion and petrographic observations and associated physical chemistry.

Some authors of recent comprehensive studies of incipient charnockitic metamorphism, which studies have included detailed descriptions of the fluid inclusions, conclude that previous estimates of H<sub>2</sub>O activity for the formation of orthopyroxene in felsic hornblende-biotite are considerably too low. Evidence has been presented here from experimental petrology to support such an upward revision of  $a_{\text{H}_2\text{O}}$  at the beginning of granulite facies metamorphism. Earlier estimates of  $a_{\text{H}_2\text{O}}$  of about 0.2 may need to be revised upward by a factor of two or more. This revision would bring H<sub>2</sub>O activity into a range that would be consonant with a concentrated chloride brine at the commonly inferred transitional granulite facies conditions of 700–750 °C and 5–7 kbar, and which would allow a significant H<sub>2</sub>O component in associated immiscible CO<sub>2</sub>-rich fluids.

Some assessment of the solute load of an aqueous NaCl solution in equilibrium with quartzofeldspathic rocks at incipient granulite facies conditions, 700 °C and 0.5 Pa, can be made from measured solubility data. Newton and Manning (2000) report a solubility of quartz of about 0.25 molal, or about 0.62 wt.%, in a 30 mol% solution of NaCl at 700 °C and 0.5 GPa. At 650 °C and the same pressure, Shmulovich et al. (2001) report a solubility of albite of 0.29 wt.% in a NaCl solution of 31 mol%. Other components including FeO and CaO are also significantly soluble in concentrated NaCl solutions at elevated pressures and temperatures (Chou and Eugster, 1977; Newton and Manning, 2006).

Solubilities of quartz and feldspar in a CO<sub>2</sub>-H<sub>2</sub>O solution of the same H<sub>2</sub>O activity as a co-existing concentrated NaCl solution are smaller by factors of 6–8 at the same *P*-*T* conditions (Newton and Manning, 2000; Shmulovich et al., 2001), indicating that the small but measurable metasomatism characteristic of incipient charnockitic alteration of biotite-hornblende gneiss is more likely to result from the passage of the saline, rather than the carbonic, solutions (for a review of metasomatism in incipient charnockite formation, see Newton and Tsunogae, in this volume).

The very small shifts in oxygen isotope ratios between incipient charnockites and their host rocks (Jiang et al., 1988; Jackson et al., 1988) suggest that fluid/rock ratios of infiltrating fluids were small. However, only quite small amounts of concentrated brines are needed to break down biotite in a felsic gneiss to produce orthopyroxene. If a NaCl solution interacting with a biotite gneiss at 700 °C and 0.5 GPa is near salt saturation ( $a_{\text{H}_2\text{O}} = 0.32$ ), and if

the solution comes into biotite-orthopyroxene equilibrium with  $a_{\text{H}_2\text{O}} = 0.4$  before exiting, it can be shown that the fluid/rock ratio need have been only 5–6 wt.%. These small amounts of fluid would not be sufficient to produce significant isotopic change in the overwhelming amount of oxygen of the rocks, even if the infiltrating oxygen were isotopically considerably different from that of the country rocks.

There is evidence that some of the occurrences of incipient charnockitic alteration involved partial melting. This kind of fluid-induced anatexis takes place at lower H<sub>2</sub>O activity and higher temperature in the presence of a concentrated salt solution than for a nearly pure H<sub>2</sub>O pore fluid. Fluid-present dehydration melting should be considered as an alternative to the commonly-discussed fluid-absent dehydration melting.

Though the saline and associated CO<sub>2</sub>-rich fluids may have had a common origin, either as exhalations from deep-seated magmatic intrusions or liberated from metasediments in high-grade metamorphic reactions, it should not be concluded that the disparate fluids were infiltrated simultaneously. The much greater grain-boundary-wetting ability, hence ability to penetrate rocks under low-porosity conditions, of saline as opposed to carbonic, fluids (Johnson, 1991; Gibert et al., 1998) suggests that their association in some incipient charnockites may indicate only that they used the same deformational pathways. Their compositions, as observed in fluid inclusions, indicate, however, that at some time during the metamorphism they could have coexisted as immiscible fluids.

The origin of such low-H<sub>2</sub>O-activity fluids is unknown. Raith et al. (1989) suggested that the CO<sub>2</sub> portion of charnockitizing fluids at Kabbal, S. India, was derived from a “fossil reservoir” of fluid inclusions in an underlying, older charnockitic crust. The fluids were thought to be ultimately of primary mantle origin based on their carbon isotope measurements of CO<sub>2</sub>-rich fluid inclusions. However, Mojzsis et al. (2003) found no radiometric evidence in zircons of the nearby Halagur charnockites of an older granulite facies metamorphism. Instead, the zircons showed an emphatic metamorphic signature of about 2.52 Ga, the same as for the Kabbal incipient charnockites and the Closepet Granite (Friend and Nutman, 1992). These data appear to link the Closepet Granite, the incipient charnockites, and the massif granulites underlying them as members of a single late-Archean process involving fluids of probable deep-crustal or upper mantle origin.

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