A Granulite Facies Kalsilite-Leucite-Hibonite Association from Punalur, Southern India

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With 6 Figures

Summary

Kalsilite, leucite and hibonite occur together with spinel, corundum, sphene, perovskite, Ti-phlogopite and K-feldspar in a granulite facies gneiss in the Punalur district in Kerala, southern India. Kalsilite-leucite-perovskite-phlogopite and kalsilite-hibonite-spinel-corundum formed distinct, texturally equilibrated assemblages during the granulite facies metamorphism. Sphene occurs as coronas on perovskite suggesting the retrograde breakdown of the perovskite-leucite association; leucite is partially altered to symplectites of K-feldspar and kalsilite, while hibonite shows partial replacement by corundum and perovskite in spinel-rich domains. Unlike other terrestrial hibonites the majority of the Punalur hibonites contain no significant rare earths (ΣREE < 0.01 atoms per 19 O), with a composition approximated by $Ca_{0.85}Ti_{0.9}Mg_{0.58}Fe_{0.25}Al_{10.4}O_{19}$ although a few zoned hibonites have REE rich cores with ΣREE > 0.6 atoms per 19 O. Garnet-hypersthene granulites from Punalur and garnet-charnockites from elsewhere in Kerala suggest metamorphism at 700–800°C and 3.5–6.5 kbars; consistent with experimentally determined stability limit of leucite of low $a(H_2O)$. The metamorphic conditions recorded by the Punalur assemblages testify to relatively low pressure conditions for a granulite facies terrain but are by no means unique. The scarcity of potassium feldspathoid in the metamorphic record must therefore be attributed to the exceptional compositional requirements of extreme silica undersaturation combined with low Na/K ratios.

Zusammenfassung

Eine Kalsilit-Leucite-Hibonit Paragenese in Granulit Fazies von Punalur, Süd-Indien

Kalsilit, Leuzit, und Hibonit kommen zusammen mit Spinell, Korund, Titanit, Perovskit, Ti-Phlogopit und K-Feldspat in einem granulitfaziellen Gneiss des Punalur-Distriktes in Kerala, Süd-Indien vor. Kalsilit-Leuzit-Perovskit-Phlogopit und Kalsilit-Hibonit-Spinell-Korund bildeten während der Granulit-Fazies-Metamorphose deutliche Paragenesen, die texturell im Gleichgewicht sind. Titanit kommt als Koronas auf

Perovskit vor und dies weist auf den retrograden Zerfall der Perovskit-Leuzit Paragenese hin. Leuzit ist teilweise zu Symplektiten von K-Feldspat und Kalsilit umgewandelt, während Hibonit Verdrängung durch Korund und Perovskit in spinellreichen Domänen zeigt. Im Gegensatz zu anderen terrestrischen Hiboniten, führt die Mehrzahl der Hibonite von Punalur, mit einer ungefähren Zusammensetzung von $Ca_{0.85}Ti_{0.9}Mg_{0.58}Fe_{0.25}Al_{10.4}O_{19}$, keine wesentlichen Seltenen-Erd-Gehalte ($\Sigma SEE < 0.01$ Atome per 19 O). Trotzdem gibt es einige wenige zonierte Hibonite, deren Kerne reich an SEE sind mit $\Sigma SEE > 0.6$ Atome per 19 O. Granat-Hypersthen Granulite aus Punalur and Granat-Charnockite von anderen Teilen Kerala's weisen auf eine Metamorphose bei 700–800°C und 3.5–6.5 kbar hin; dies ist in guter Übereinstimmung mit der experimentell bestimmten Stabilitätsgrenze von Leuzit bei niederigen $a(H_2O)$. Die metamorphen Bedingungen, die die Punalur-Paragenesen dokumentieren, zeigen relativ niedrige Druckbedingungen für ein Granulit-Fazies Terrain an; das ist aber keineswegs einmalig. Die Seltenheit von Kali-Feldspathoiden während der metamorphen Entwicklung muß deshalb auf die ungewöhnlichen Erfordernisse extremer Silizium-Untersättigung, zusammen mit niedrigen Na/K-Verhältnissen, zurückgehen.

Introduction

The potassium feldspathoids kalsilite and leucite are virtually unknown in the metamorphic environment (e.g. *Deer* et al. 1964) while hibonite is exceedingly rare having been documented from only four terrestrial localities (*Curien* et al. 1956; *Kuzmin* 1960; *Yakovlevskaya* 1961; *Maaskant* et al. 1985). It is with some interest therefore that we report an association of these minerals, together with corundum, spinel, phlogopite, perovskite and sphene, from Punalur, Kerala, in the granulite facies khondalite belt of South India. As with all rare metamorphic parageneses it is important to establish whether scarcity is due to exceptional metamorphic conditions or due to bulk compositional constraints. The paragenesis of the potassium feldspathoids provides a case in point. The potassium feldspathoids require extreme silica undersaturation and low bulk Na/K. However, the general restriction of the potassium feldspathoids to volcanic parageneses raises the possibility that they are stable only at exceptionally high temperatures and low pressures, perhaps beyond the region of P-T-$a(H_2O)$ space, physically accessible to regional metamorphic terrains. For leucite, insights into its potential stability in the metamorphic environment have been provided by experimental work (e.g. *Scarfe* et al. 1965) that showed it should be stable in the P-T-$a(H_2O)$ environments of many low pressure granulite terrains. However, up to now this experimental prediction has remained unqualified by documentation from natural occurrences. In this paper we describe the occurrence and petrography of the Punalur feldspathoid-bearing gneiss and the granulites with which it is associated. The peculiar chemical characteristics of the hibonite in this rock will be described in detail elsewhere (*Santosh* et al., in press). The textural relationships exhibited by this unusual rock and relevant experimental data are used to reconstruct the petrogenesis of the potassium feldspathoid-hibonite association in the Punalur gneiss.

Background

The Punalur region forms part of an Archaean granulite terrain in the Kerala state of Southern India. This terrain consists predominantly of charnockites (pyroxene-

feldsparquartz ± garnet granulites), khondalites (garnet-sillimanite-biotite-feldspar-quartz ± cordierite granulites), leptynites (garnet-feldspar-quartz granulites) and migmatitic gneisses. The granulite facies metamorphism in this region is generally believed to be Archaean, ~2.6 Ga (Crawford 1969), although there is now some doubt about this age assignment as similar granulites from nearby Sri Lanka, which were also considered to have been Archaean by *Crawford* (1969), have recently been shown to have a Late Proterozoic metamorphic age (*Kroner* et al. 1987). The Punalur region occurs along a major northwest-trending shear zone of probable Proterozoic age termed the Achankovil Lineament. This structure separates an interlayered charnockite-khondalite-leptynite sequence to the south (the South India Khondalite belt) from a massive charnockite terrain to the north.

In the Punalur region garnet-cordierite (± hypersthene, sillimanite, spinel and biotite) rich gneisses occur interlayered with khondalites, leptynites and charnockites. The horizon containing the kalsilite-leucite-hibonite association forms a layer approximately 200 m wide which can be traced for approximately 3 km near the villages of Kakkopponu and Perunthol (Fig. 1), some 15 km north of Punalur. Exposure is restricted to isolated patches due to extensive lateritization, and we have not been able to observe directly the contacts with the adjacent rocks. However, our impression is that the horizon is concordant with the layering in the host khondalites. A small intrusive ultramafic composed of olivine, spinel, phlogopite and serpentine outcrops near the village of Kakkopponu close to the eastern extremity of the kalsilite-leucite-hibonite gneiss.

The feldspathoid-bearing gneiss is characterised by exceptionally high alumina contents (> 55% Al_2O_3 by weight) and low bulk Na/K (Table 1). The origin of the

Granite

Feldspathoid-hibonite gneiss

Meta-dunite

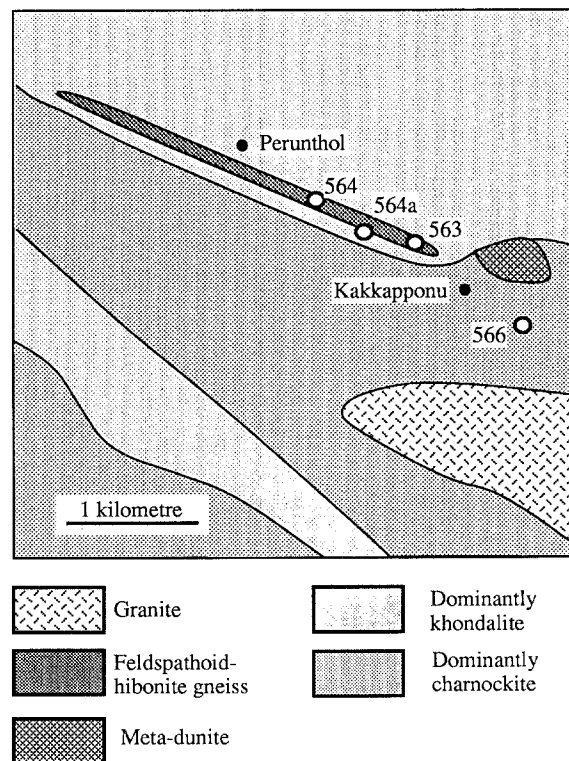Dominantly khondalite

Dominantly charnockite

Fig. 1. Geological map showing location and setting of the Punalur feldspathoid-hibonite gneiss

Table 1. *Major element analyses of the Punalur feldspathoid gneiss as determined by conventional wet chemical techniques*

	563	564	564a
SiO_2	15.89	14.78	16.19
TiO_2	0.45	0.42	0.38
Al_2O_3	56.59	57.61	59.65
FeO^*	6.52	7.52	7.09
MnO	0.01	0.01	0.01
MgO	9.92	7.36	6.08
CaO	2.24	2.46	3.14
Na_2O	0.42	0.39	0.42
K_2O	4.90	6.38	4.90
$H2O$	0.14	0.19	0.16
LOI	1.34	1.37	0.94
Total	98.4	98.5	99.0

Oxides are given as weight %.
*All Fe calculated as Fe^{2+}.

gneiss is obscure, in as much as it is difficult to assess the degree to which its composition has been modified during the metamorphic process. Certainly, it is far too aluminous for any primary ultrapotassic magma with which the potassic feld-spathoids are usually associated. If the present alumina content reflects the metamorphic precursor, then the precursor is likely to be derived from a surficial weathering processes, eg. bauxite. It is however unusual for a bauxite to contain significant potassium, and in particular high K/Na ratios. It is indeed this combination of high K/Na and extreme silica undersaturation, together with the high temperature, low pressure, low a (H_2O) metamorphism (see below) that has allowed the development of the unique mineral association. The high potassium contents may reflect the stability of kaolinite in the primary bauxite or, alternatively, a metasomatic origin. Indeed metasomatic rocks consisting largely of muscovite and corundum of similar bulk composition have recently been recorded from other Precambrian metamorphic terrains (*Kerrich* et al. 1988).

Petrography and Mineral Chemistry

Electron microprobe analyses of the Punalur feldspathoid gneiss are presented in Table 2 and of a Punalur khondalite in Tables 3. Table 5 shows analyses of co-existing garnet, hypersthene and plagioclase in quartz bearing charnockites from various localities elsewhere in Kerala. Analyses were performed on the Cambridge University, Department of Earth Sciences, energy dispersive microprobe operating at 20 kV accelerating potential, and on the JEOL-JX5A wavelength dispersive microprobe in the Department of Geology, University of Melbourne, operating at 15 kV accelerating potential.

In addition to kalsilite, leucite and hibonite, the Punalur gneiss contains significant proportions of spinel and corundum, and subordinate apatite, perovskite, sphene, K-feldspar and phlogopite. The modal proportions of these minerals vary considerably on the thin section scale with spinel, hibonite and corundum forming

Table 2. *Electron microprobe analyses of minerals from the Punalur feldspathoid gneiss*

	1	2	3	4	5	6	7	8
SiO_2	37.87	55.10	0.31	29.40	0.20	35.00	0.15	0.24
TiO_2			58.69	38.99		9.40	2.15	9.89
Al_2O_3	32.07	23.97	0.81	0.91	67.59	16.88	77.32	74.43
Fe_2O_3	0.08		0.27	0.70				
FeO					12.57	5.51	1.98	2.72
MnO					0.20			
MgO					19.71	16.73	3.34	2.72
CaO			38.77	28.96			2.53	6.53
Na_2O	0.04			0.08		0.02	0.08	0.32
K_2O	30.21	21.13		0.03		9.83		
ΣREE_2O_3							12.09	<0.01
Total	100.27	100.2	98.85	99.07	100.27	93.37	99.54	98.07
Oxygens	4	6	3	5	4	22	19	19
Si	0.998	1.991	0.007	0.974	0.005	5.139	0.018	0.029
Ti			1.002	0.971		1.038	1.188	0.871
Al	0.996	1.021	0.022	0.036	1.992	2.922	11.088	10.312
Fe^{3+}	0.002		0.005	0.017				
Fe^{2+}					0.263	0.677	0.202	0.266
Mn					0.004			0.003
Mg					0.734	3.661	0.606	0.644
Ca			0.943	1.028			0.330	0.890
Na	0.002			0.005		0.006	0.020	0.055
K	1.015	0.974		0.001		1.842		
ΣREE							0.539	<0.001
Total	3.012	3.986	1.978	3.032	2.999	15.285	12.990	13.002

1. Kalsilite, 2. leucite, 3. perovskite, 4. sphene, 5. spinel, 6. phlogopite, 7. REE-hibonite core, 8. hibonite rim.

Table 3. *Electron microprobe analyses of minerals in the Punalur pelitic gneiss (sample 566). Assemblage also includes K-feldspar, biotite and quartz. All Fe calculated as FeO*

	1	2	3	4
SiO_2	48.94	38.98	59.39	51.00
TiO_2	0.18			
Al_2O_3	7.01	22.06	25.31	33.60
FeO^*	21.17	23.05	0.47	4.02
MnO	1.68	6.44		0.29
MgO	20.11	8.88		10.62
CaO		0.98	6.81	
Na_2O			7.05	
K_2O		0.18		
Total	99.09	100.39	99.21	99.53

1. Hypersthene, 2. garnet, 3. plagioclase, 4. cordierite.

discrete aggregates up to 3 cm across (Fig. 2) surrounded by leucocratic moats consisting predominantly of feldspathoids (Fig. 3), but also including phlogopite,
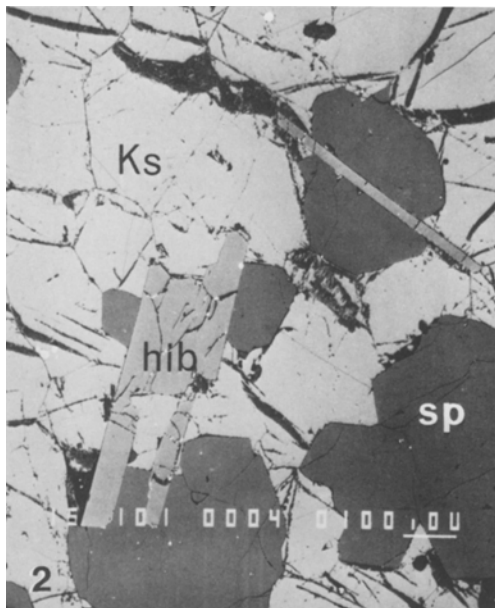
Fig. 2. SEM image (backscattered electron mode) showing hibonite (*hib*) prisms clumped in aggregates with spinel (*sp*) and kalsilite (*Ks*). Bar scale is 100 μm
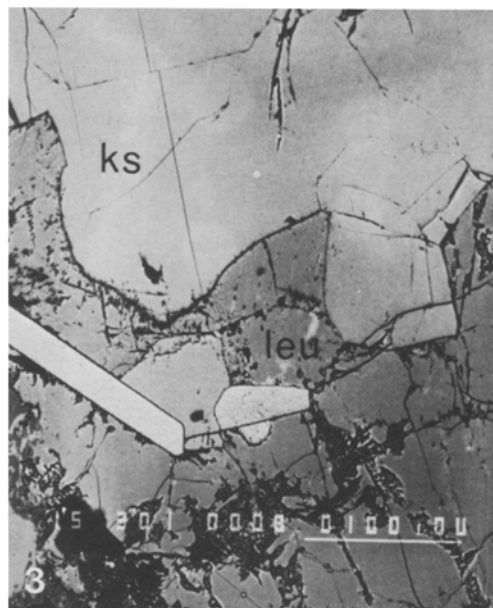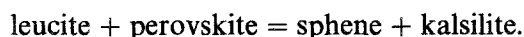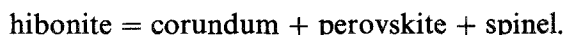
Fig. 3. SEM image (backscattered electron mode) showing leucite (*leu*) kalsilite (*ks*) phlogopite (phl) association. Bar scale is 100 μm

sphene, and perovskite. Spinel, kalsilite and leucite occur as equant grains ~2 mm in diameter while hibonite occurs as prisms up to 10 mm long. Corundum occurs both as equant, inclusion free grains as well as as prisms characterised by abundant perovskite inclusions which appear to partially replace hibonite. Leucite is restricted to the interior of the leucocratic moats and does not occur in contact with spinel, corundum or hibonite. Leucite is partially altered to a very fine grained symplectite consisting of K-feldspar and kalsilite (Fig. 4) with symplectitic kalsilite mostly altered to an unidentified secondary Ca-K bearing aluminosilicate. Perovskite occurs as aggregates of tiny blebs within leucite grains, and less commonly kalsilite, and is frequently but not always surrounded by coronas of sphene. Hibonite occasionally shows optical zoning corresponding to an abrupt change in composition (Fig. 5, see below).

The textures in the Punalur emery suggest that two distinct associations developed during its high temperature metamorphic history. One association consisted of kalsilite, leucite, perovskite and possible phlogopite, while the second consisted of spinel, kalsilite, corundum and hibonite. Coronas of sphene on perovskite suggest the breakdown of the leucite-perovskite association according to the reaction:

$$\text{leucite} + \text{perovskite} = \text{sphene} + \text{kalsilite}.$$

The partial replacement of hibonite by corundum crystals with numerous perovskite inclusions suggests a late stage reaction:

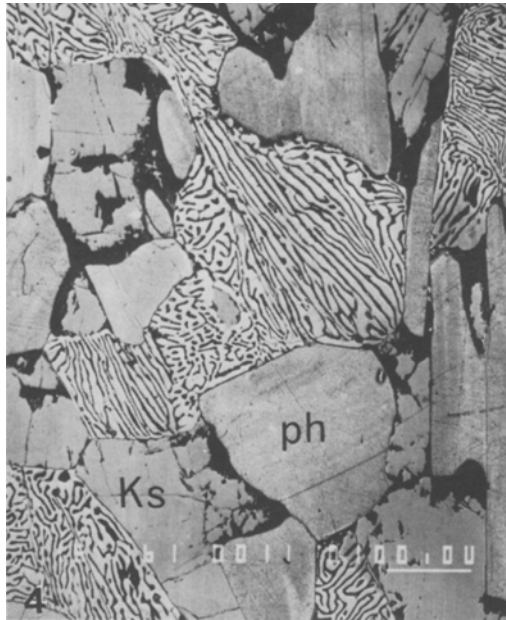$$\text{hibonite} = \text{corundum} + \text{perovskite} + \text{spinel}.$$

Fig. 4. SEM image (backscattered electron mode) showing fine grained symplectite of potassic phases, possibly sanadine and kalsilite, replacing leucite. Bar scale is 100 μm
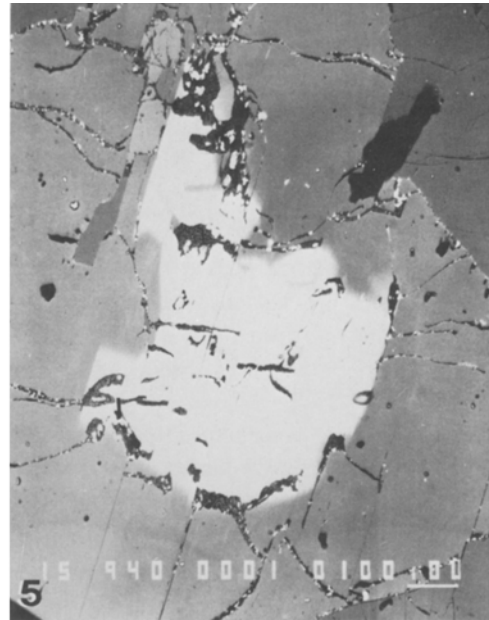
Fig. 5. SEM image (backscattered electron mode) showing abrupt zonation in hibonite between REE-free rim and REE-rich core. Bar scale is 100 μm

It is possible, though by no means demonstrable, that early in the metamorphic history leucite formed a stable association with hibonite (or spinel), prior to the development of the kalsilite moats. The fine grained kalsilite-K-feldspar symplectites point to the late stage reaction:

$$\text{leucite} = \text{K-feldspar} + \text{kalsilite}.$$

The unusual crystal chemical features of the Punalur hibonites are described in detail elsewhere (*Santosh* et al. in press) and are only briefly summarised here. In common with all previously recorded terrestrial hibonites (*Curien* et al. 1856; *Kuzmin* 1960; *Yakovlevskaya* 1961; *Maaskant* et al. 1985), the Punalur hibonites contain significant Ti, Mg and Fe. However, in contrast with previous terrestrial records total REE are typically very low (ΣREE < 0.01 atoms per 19 O), although the cores of the (rare) zoned grains are strongly enriched in REE (ΣREE > 0.6 atoms per 19 O). The Punalur hibonites are unusual in having a deficiency in 12-fold co-ordinated site occupancy, with minor substitution of Na for Ca in REE-free grains. The possibility of non-stoichiometry means that it is not possible to determine the ferric/ferrous ratio from the microprobe data. The compositions of the REE-free hibonites can be related to theoretical hibonite $CaAl_{12}O_{19}$ by the Ti-tschermak exchange $Ti(Fe, Mg)Al_{-2}$ (e.g. *Burns* and *Burns* 1984), while the compositions of the REE-rich cores are related by the additional exchange $REE(Fe, Mg)Ca_{-1}Al_{-1}$. The X_{Fe} (where $X_{Fe} = Fe/Fe + Mg$) of REE-free hibonites ($X_{Fe} = 0.25$) is slightly lower than the REE-rich hibonites ($X_{Fe} = 0.29$), with these values spanning the composition of the coexisting spinel ($X_{Fe,sp} = 0.27$).

The Punalur phlogopite is unusually titaniferous, with the 1.04 Ti atoms per unit formula (20 O, 4 OH, F) near the maximum recorded for metamorphic micas (cf. *Whitney* and *McClelland* 1983). Titanium appears to be accommodated principally by the Ti-tschermaks substitution $Ti^{vi}Al^{iv}_2Si^{iv}_{-2}(Fe, Mg)^{vi}_{-1}$ and the Ti-vacancy substitution $Ti^{vi}v^{vi}(Fe, Mg)^v_{-2}$.

Metamorphic Conditions

The P-T conditions prevailing during granulite facies metamorphism of the Punalur feldspathoid gneiss have been estimated using a garnet-hypersthene-cordierite paragenesis (sample 566) in surrounding pelitic gneisses. Analyses of coexisting minerals are shown in Tables 3 and 4 and the results of average pressure calculations

Table 4. *Summary of compositional data for Punalur pelitic gneiss* (566) *and core* (c) *and rim* (r) *assemblages in Kerala garnet charnockites (519, 521, 530) used in average pressure calculations* (see Table 5)

	566	519c	519r	521c	521r	530c	530r
a(an)	0.344	0.405	0.416	0.365	0.389	0.415	0.411
a(en)	0.316	0.0673	0.0681	0.0606	0.0671	0.0820	0.905
a(fs)	0.110	0.476	0.502	0.496	0.487	0.439	0.405
a(gr)	$1.9\ 10^{-5}$	0.00126	0.00182	$9.33\ 10^{-4}$	0.00115	0.00102	0.00113
a(py)	0.0390	$5.94\ 10^{-4}$	$2.31\ 10^{-4}$	$7.5\ 10^{-4}$	$4.32\ 10^{-4}$	0.00125	$7.52\ 10^{-4}$
a(alm)	0.121	0.427	0.462	0.479	0.475	0.465	0.458
a(crd)	0.620	-	-	-	-	-	-
a(fcrd)	0.028	-	-	-	-	-	-
ln K(1)	-10.676	-10.795	-12.364	-9.934	-11.325	-10.116	-11.296
ln K(2)	-5.246	-	-	-	-	-	-
ln K(3)	3.706	-	-	-	-	-	-
ln K(4)	-3.776	-	-	-	-	-	-

$$\ln K(1) = \left(\frac{a(gr)\ a(py)^2}{a(an)^3\ a(en)^3}\right)$$

$$\ln K(2) = \left(\frac{a(gr)\ a(alm)^2}{a(an)^3\ a(fs)^3}\right)$$

$$\ln K(3) = \left(\frac{a(crd)\ a(en)^2}{a(py)^2}\right)$$

$$\ln K(4) = \left(\frac{a(fcrd)\ a(fs)^2}{a(alm)^2}\right)$$

an = anorthite, en = enstatite, fs = ferrosilite, gr = grossular, py = pyrope, alm = almandine, crd = Mg-cordierite, fcrd = Fe-cordierite. Activity expressions have been calculated assuming ideal mixing.

(after *Powell* and *Holland* 1988) are shown in Table 5. The independent reaction set used in the average pressure calculations includes:

(1)   3 anorthite + 3 enstatite = grossular + 2 pyrope + 3 quartz

(2)   3 anorthite + 3 ferrosilite = grossular + 2 almandine + 3 quartz

(3)   2 pyrope + 3 quartz = cordierite + 2 enstatite

(4)   2 almandine + 3 quartz = Fe-cordierite + 2 ferrosilite

Average pressure calculations were performed assuming ideal mixing of all species, largely because of the prevailing uncertainty concerning which if any of the alternative activity models is appropriate (moreover, for most models the activity coefficients will, to a large extent, cancel). Because of the dependence of cordierite stability on $X(CO_2)$ and $X(H_2O)$ average pressure calculations are presented for a range of values appropriate to essentially anhydrous granulite facies assemblages (viz. $X(CO_2) = 0-1.0, X(H_2O) = 0-0.5$). Harley's (1984) Fe–Mg exchange thermometer yields equilibration temperatures for coexisting garnet and orthopyroxene of ~700–800°C; approximately coincident with the range of temperatures for which average pressure calculations yield the best statistics. In this temperature range the average pressure estimates range from 4.3 ± 0.74 kbars at 700°C, $X(CO_2) = 0.0$ and $X(H_2O) = 0.0$ to 5.7 ± 0.84 kbars at 800°C, $X(CO_2) = 0.5$ and $X(H_2O) = 0.5$.

The relatively high Mn-content of the assemblage, reflected principally in the high spessartine content of the garnet (X(spessartine, garnet) = 0.0027) used in the average pressure calculations introduces considerable uncertainty. However, these estimates are in considerable agreement with the estimates from mineral core compositions of three Mn-poor, garnet-bearing charnockitic gneisses from neighbouring regions of Kerala (samples 519, 521, 530, see Table 4 for summary of compositional data) derived using reaction (1) which is essentially temperature independent for the range of $\ln K_{(1)} = -9.934$ to -10.795 (Table 5). Note, that mineral rim compositions from these charnockitic gneisses yield significantly lower $\ln K_{(1)} = -11.296$ to -12.364 which, in view of the essentially temperature independence of $\ln K$ in this range e.g., *Powell* and *Holland* 1988), suggests partial reequilibration of assemblages at somewhat lower pressures. Finally, the estimated P-T conditions from the Punalur pelitic gneiss are comparable with the estimates from elsewhere in the Kerala khondalite belt suggested by *Chacko* et al. (1987).

Discussion: Feldspathoid and Hibonite Petrogenesis in the Metamorphic Environment

The average pressure calculations performed on rocks for the Kerala region imply granulite facies metamorphism proceeded, most probably, at conditions in the realm of 3.5–6.5 kbars at temperatures of 700–800°C (Table 5). These conditions certainly reflect relatively low pressure metamorphism for the granulite facies environment, but are by no means unique (see review of estimates of conditions of granulite formation in *Harley* 1989, Table 1). The occurrence of the exceptional association of kalsilite and leucite together with hibonite in the Punalur granulites cannot, therefore, be regarded as a consequence of the exceptional metamorphic environment. Rather the extreme rarity of these minerals in the metamorphic environment

Table 5. *Summary of average pressure calculations* (after *Powell* and *Holland* 1988) *for Punalur pelitic gneiss (566) and core (c) and rim (r) assemblages in Kerala garnet charnockites (519, 521, 530)*. Results of average pressure calculation and statistics (*Powell* and *Holland* 1988) are presented for 700°C and 800°C

	$X(CO_2)$	$X(H_2O)$	$P_{av}(700°)\pm sd$	fit (700°)	$P_{av}(800°)\pm sd$	fit (800°)
566	0.0	0.0	4.3 ± 0.74	0.6	4.7 ± 0.82	0.7
-	0.5	0.0	4.6 ± 0.74	0.6	5.0 ± 0.82	0.8
-	0.1	0.0	4.8 ± 0.74	0.9	5.3 ± 0.82	0.9
-	0.0	0.5	5.1± 0.74	0.8	5.4 ± 0.82	0.9
-	0.5	0.5	5.4 ± 0.74	0.9	5.7± 0.84	1.0
519c	-	-	*3.4± 2.09	-	*3.4± 2.09	-
519r	-	-	*1.6± 2.26	-	*1.5± 2.26	-
521c	-	-	*4.4± 2.21	-	*4.6± 2.21	-
521r	-	-	*2.8± 2.24	-	*2.8± 2.24	-
530c	-	-	*4.2± 2.13	-	*4.3± 2.13	-
530r	-	-	*2.8± 2.17	-	*2.8± 2.17	-

Pressures estimates marked by * are not averages; rather they represent the pressure bracket for reaction (1) only.
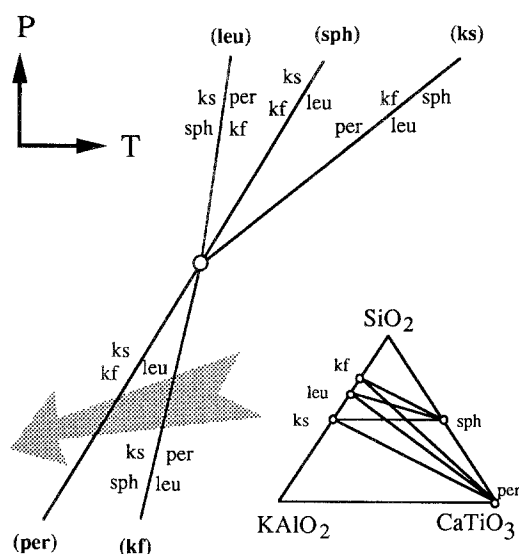

Fig. 6. Schematic P-T grid for the system $CaTiO_3$-$KAlO_2$-SiO_2 involving the phases sphene (*sph*), perovskite (*per*), leucite (*leu*), kalsilite (*ks*) and k-feldspar (*kf*). See text for discussion

must be considered a consequence of the exceptional bulk composition requirements, namely extreme silica undersaturation and low Na/K. Indeed, the occurrence of coexisting kalsilte-leucite assemblage at Punalur provides support for the experimental stability field of leucite determined by *Scarfe* et al. (1966) (see Fig. 6). In the following discussion we briefly consider some of the curious petrogenetic problems raised by the Punalur feldspathoid gneiss.

Perovskite (per), sphere (sph), kalsilite (ks), leucite (leu) and K-feldspar (df) define an univariant association in the system $KAlO_2$-$CaTiO_3$-SiO_2 (KACTS). The reactions in this system together with the approximate slopes calculated from volume and entropy data from *Robie* et al. (1978) are:
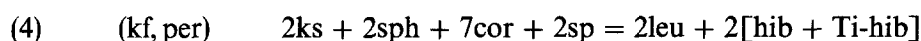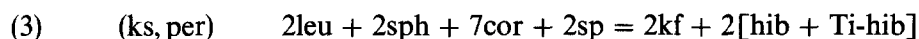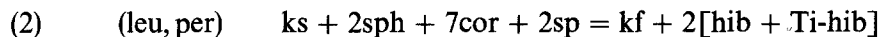
(per, sph)	ks + kf = 2leu	~30°C/kbar
(kf)	ks + 2sph = leu + 2per	~20°C/kbar
(ks)	kf + per = leu + sph	~45°C/kbar
(leu)	ks + sph = kf + per	~15°C/kbar,

A schematic petrogenetic grid for this system is shown in Fig 6. *Scarfe* et al. (1966) directly investigated the degenerate (sph, per) reaction at low $a(H_2O)$ (following the standard convention, univariant reactions are marked by absent phases enclosed in round brackets, while invariant points are marked by absent phases enclosed in square brackets). This reaction was intersected at ~500°C at atmosphere and ~800°C at 8 kbars. The location of the invariant point is not constrained by direct experimental observation and given the uncertainties in the enthalpy data (e.g., *Holland* and *Powell* 1985) the position of the intersection is poorly constrained. However, the evidence for the high temperature stability of the kalsilite-leucite-perovskite association in the Punalur gneiss indicates that this invariant point occurs at higher pressures and lower temperatures than the peak metamorphic conditions recorded by the Punalur gneisses.

Since previously documented terrestrial hibonites contain significant REE, it has appeared that within the terrestrial environment hibonite is stable only in unusual, REE-rich bulk compositions (e.g. *Maaskant* et al. 1980). However, much of the Punalur hibonite is REE-free, indicating the possibility of a terrestrial stability field for REE-free hibonites, and it is therefore interesting to consider the reactions limiting the stability of REE-free hibonite with respect to the other minerals in the Punalur gneiss. In the Mg end-member system containing the phases Ti-Mg-bearing hibonite, sphene, perovskite, spinel (sp), kalsilite, leucite, corundum (cor) and K-feldspar. The composition of the Ti-hibonite in this model system (K_2O-CaO-MgO-Al_2O_3-TiO_2-SiO_2) is given by hibonite ($CaAl_{12}O_{19}$) (hib) plus the Ti-tschermak substitution ($TiMgAl_{-2}$) (Ti-hib). In this system, the reactions limiting hibonite stability (and Ti-tschermak content) with respect to perovskite bearing assemblages are:

(1)	(leu, kf, ks, sph)	2per + 7cor + 2sp = 2[hib + Ti-hib]

and with respect to sphene bearing assemblages:

(2)	(leu, per)	ks + 2sph + 7cor + 2sp = kf + 2[hib + Ti-hib]
(3)	(ks, per)	2leu + 2sph + 7cor + 2sp = 2kf + 2[hib + Ti-hib]
(4)	(kf, per)	2ks + 2sph + 7cor + 2sp = 2leu + 2[hib + Ti-hib]

The textures indicating retrograde breakdown of hibonite to perovskite and corundum imply that REE-free hibonite is limited to the high T side of (1). With the addition of REE to the system the stability field of hibonite will be greatly extended. In the Fe-bearing system these reactions are necessarily divariant. The order of

Fe-Mg partitioning in the Punalur gneiss ($X_{Fe,REE-free\,hib} < X_{Fe,sp}$) suggests that the hibonite-limiting, spinel-bearing assemblages will expand to (?marginally) higher temperatures with increasing bulk rock X_{Fe}.

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