Regional Carbonate Alteration of the Crust by Mantle-Derived Magmatic Fluids, Tamil Nadu, South India[1]

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ABSTRACT

Regional carbonate alteration of the crust associated with major shear zones provides direct evidence for CO_2-rich fluid mobility. A good example occurs within the Attur lineament, one of numerous Proterozoic shear zones which crosscut charnockitic gneisses and other lithologies of the southern Indian craton. At this locality, widespread carbonate alteration of silicate rocks has involved growth of ankerite and other carbonate minerals which replace preexisting silicates. Some of the ankerite was subsequently recrystallized to fine-grained calcite and iron oxide, accompanied by sericitization of feldspar. Carbon, oxygen, and strontium isotope analyses of samples of ankerite and calcite, together with some of the coexisting silicate minerals, have been used to constrain the conditions of formation of the carbonate alteration and the origin of the fluids involved. $\delta^{13}C$ values of ankerite are relatively homogeneous, ranging between -6.5 and $-3.9\permil$ with a mean of $-5.3\permil$. $\delta^{18}O$ is also fairly homogeneous, mostly ranging from $+7.4$ to $+9.3\permil$ with a mean of $+8.5\permil$. These values suggest that the ankerite was deposited from fluids with fairly uniform carbon and oxygen isotopic composition over a narrow temperature range. $\Delta_{quartz\text{-}plagioclase}$ and $\Delta_{quartz\text{-}ankerite}$ are uniform and low in all samples, and quartz-plagioclase fractionations are very similar to those observed in pristine, uncarbonated high-grade gneisses throughout southern India. The ankerite probably formed close to equilibrium with the silicate minerals, at temperatures at least as high as $\sim500°C$. The fine-grained calcite has a similar $\delta^{13}C$ to the ankerite (mean $= -4.5\permil$), but $\delta^{18}O$ ranges to much higher values (up to $+21.4\permil$), consistent with the calcite having formed at much lower temperatures by recrystallization of ankerite, possibly during late-stage infiltration of H_2O-rich fluids. The age-corrected $^{87}Sr/^{86}Sr$ ratios of bulk carbonate samples mostly fall between 0.704 to 0.710, extending to significantly higher values than the range of initial ratios of Late Proterozoic carbonatite, syenite, and alkali gabbro plutons that are found as small intrusions all along the Attur lineament. However, ankerite samples have almost identical carbon, oxygen, and strontium isotopic composition to these plutons. The igneous-like isotopic composition of the ankerite is consistent with its being deposited from magmatic fluids released from these alkalic, mantle-derived magmas. Carbonate alteration of this type, often localized along major shear zones, may represent a lower temperature mid-crustal manifestation of the deeper level CO_2 infiltration proposed as a mechanism for granulite formation in this and other areas.

Introduction

Regional carbonate alteration of the crust, usually associated with major shear zones or tectonic lineaments, is observed in many terranes, with little consensus on the origin of the fluids involved. Baratov et al. (1984) described a Hercynian shear zone in the Tien Shan region of Central Asia in which carbonate minerals replace metamorphosed sili-

cate metasediments by up to 20% along a 20 × 100 km zone. Stern and Gwinn (1990) reported similar regional carbonate alteration of Late Precambrian age in northeastern Sudan. Such large-scale carbonated zones have also been recorded by Chadwick et al. (1985) along the margins of the Archean Chitradurga schist belt in southern India, and by Faure and Harris (1991) in the shear zones separating the Kaap Valley tonalite pluton from the Barberton greenstone belt, southern Africa. Retrograde hydration and carbonation of granulites associated with major shear zones is observed in the Southern Marginal Zone of the Limpopo Belt in southern Africa

(van Schalkwyk and van Reenen 1992). Other notable examples of large-scale carbonate deposition or replacement in fault zones include hydrothermal dolomite within the Proterozoic Bamble shear belt, Norway (Dahlgren et al. 1993), calcite veins and pods within the Proterozoic Mary Kathleen Fold Belt, Australia (Oliver et al. 1993), quartz-carbonate veins cutting Archean greenstones and higher-grade rocks in Western Australia (Groves et al. 1989; Barnicoat et al. 1991), and found within greenstones of the Superior Province, Canada (Kerrich et al. 1987; Kerrich 1990; Cameron 1988; Veizer et al. 1989). Many of these occurrences are associated with significant gold mineralization.

Despite their widespread occurrence, there is little agreement as to the origin of the carbon in carbonated shear zones (magmatic, metamorphic, mantle-derived, or crust-derived) or even whether the various examples listed above share a common petrogenesis (see, for example, Cameron 1988; Burrows and Spooner 1987; Kerrich 1990). In this paper we describe the results of an isotopic study of regional carbonate alteration in southern India suggesting a possible link between this phenomenon, alkalic magmatism, and at deeper structural levels, granulite formation. The study area is a 20 km × 10 km tract of carbonate alteration of charnockitic ortho- and paragneiss within the prominent Attur shear zone in Tamil-Nadu, southern India (figure 1). The carbonates take the form of orange to pink ferroan dolomite and ankerite occurring as discrete rhombs or intergrown with silicate minerals, and diffuse patches of fine-grained calcite or discrete calcite veins. The carbonate alteration crosscuts the charnockites and gneisses along deformation-induced fractures but also forms widespread areas of more pervasive alteration (Khan 1989). Strontium, oxygen, and carbon isotope analyses of these rocks are used together with petrologic and field evidence to identify the nature and source of the fluids that caused the carbonate alteration within the Attur shear zone. The new data are combined with regional petrological and geochemical information to provide an integrated picture of the origin and magnitude of shear zone CO_2 fluxes in the continental crust of this and other regions. The widespread (though controversial) petrologic and geochemical evidence for involvement of CO_2 in granulite facies metamorphism in southern India (Hansen et al. 1987; Jackson et al. 1988) gives added relevance to this study.

Geological Occurrence

Regional Setting. Northern Tamil Nadu is part of a mobile belt (the Early Proterozoic mobile belt
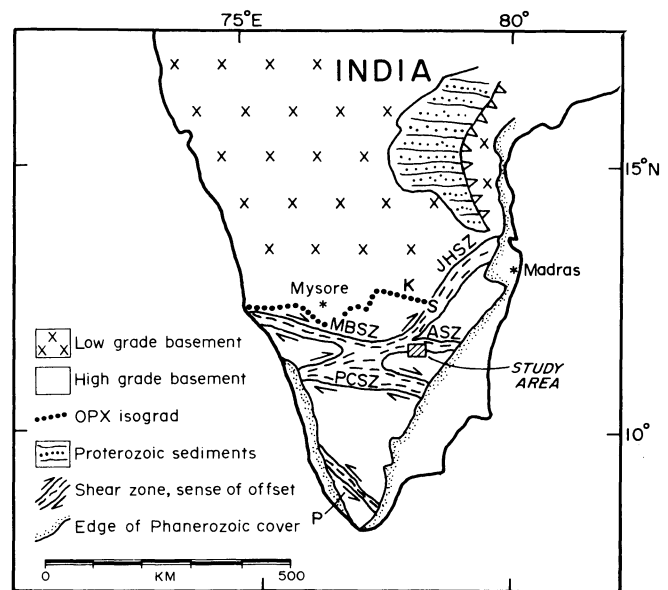

Figure 1. Simplified geological map of southern India, showing the location of the study area. PCSZ = Palghat-Cauvery shear zone; MBSZ = Moyar-Bhavani shear zone; ASZ = Attur shear zone; JHSZ = Jalapet-Hognekel shear zone; K = Krishnagiri; S = Sevathur carbonatite; P = Ponmudi. The hatchured line denotes the thrust fault bounding the east side of the Proterozoic Cuddapah Basin. Map modified after Drury and Holt (1980) and Choudhary et al. (1992). Note that the study area lies well to the south (high-grade side) of the regionally developed Archean orthopyroxene isograd.

of Radhakrishna and Naqvi 1986), comprising mostly granulite facies felsic charnockites and khondalites. Several prominent fault zone lineaments cut across this terrane and continue across most of southern India (figures 1 and 2). For example, the Palghat-Cauvery shear zone is a strike-slip system with a minimum of 70 km of dextral strike-slip offset and 10 km of vertical offset (Drury and Holt 1980). The Attur shear zone is the eastern extension of the Moyar-Bhavani shear zone. Drury and Holt (1980) consider this also to be a dextral strike-slip fault and an expression of regional transpression. The similarity of azimuth and offset between the Attur and the Palghat-Cauvery shear zones suggests that they may be components of an important Late Precambrian shear system in southern India.

Several carbonatite bodies (Deans and Powell 1968; Borodin et al. 1971) and corundum and melanite garnet-bearing syenites and olivine-nepheline-leucite-cpx-bearing gabbros (shonkinites) have been intruded along these lineaments (see figure 2). The NNE-trending Jalapet-Hognekal shear zone intersects the E-W—trending Moyar-Bhavani shear zone near the town of Salem, in the western part
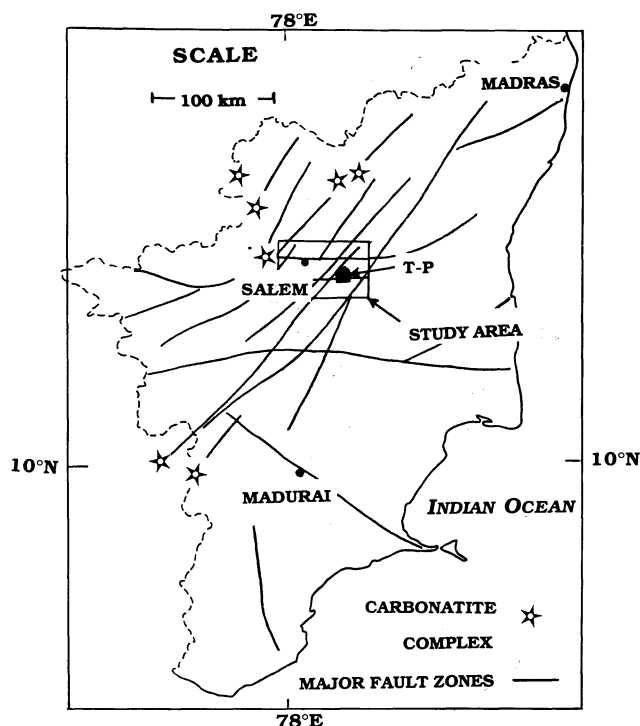
MAP OF TAMIL-NADU SHOWING THE MAJOR FAULT ZONES AND
CARBONATITE COMPLEXES

Figure. 2. A map of Tamil-Nadu (modified after Khan 1989) illustrates the locations of the major fault zone lineaments and the various carbonatite complexes in this part of southern India. Within the study area the Timmanayakanpatti block (location of the TP samples) is indicated.

giri area to the north of the area (figure 1; Peucat et al. 1989, 1993), while charnockite formation in southern India and Sri Lanka also occurred during the late Precambrian and early Paleozoic (Srikantappa et al. 1985; Hansen et al. 1985; Kröner et al. 1987; Burton and O'Nions 1990; Choudhary et al. 1992). The exact location and nature of the boundary between the older and younger granulite provinces awaits resolution; however, Choudhary et al. (1992) suggest that the Palghat-Cauvery shear zone approximates this boundary. Our study area lies just north of this shear zone, but in this paper we will present isotopic and petrological evidence suggesting that the processes of carbonate alteration and the formation of the younger granulites are related and may have been occurring contemporaneously at different levels in the crust. A similar relationship between massive hydrothermal dolomite emplacement and granulite facies metamorphism in the Bamble region of southern Norway was suggested by Dahlgren et al. (1993).

Study Area. Carbonate alteration in the form of orange, brown, or pink ferroan dolomite and ankerite, occurring as veins and diffuse patches replacing charnockite and other lithologies, is seen all along the Attur shear zone, and further west of it in the Biligiri Rangan Hills (Khan, 1989). The region affected is over 100 km long and about 10 km wide. For this study, an area of 20 × 12 km, 15 km east of Salem was selected (figures 1 and 2). Within this area, zones of carbonation are extensive, and numerous fresh quarry surfaces expose centimeter- to meter-wide orange-pink carbonate veins which crosscut charnockite (figure 3A). This enables collection of both unaltered and carbonated material ranging from pervasively carbonated charnockite through bleached charnockite to fresh charnockite. Rock types found at this locality include charnockite of tonalitic-trondhjemitic composition that forms the dominant lithology (typically 50–70% of the outcrop area [Kahn 1989]), layers of highly folded two-pyroxene granulites (metabasalts), interbedded, banded magnetite quartzites, khondalites (quartzofeldspathic rocks with sillimanite and garnet), minor calc-silicate rocks, and late granites. Recrystallized ultramafic rocks (olivine-orthopyroxene-anthophyllite-Cr-rich hornblende-carbonate) also occur. Five discrete bodies of corundum syenite about 30 m thick, and a kilometer-long camptonitic lamprophyre dike are found within this region. A few meter-scale carbonatite dikes (sovites) occur west and north of the area, along with numerous shonkinite (alkali gabbro) dikes. These are probably related to the carbonatites and alkalic mafic and ultramafic rocks of the Sevathur area (figure 2).

of the study area (figure 2). Slightly to the east of the intersection, a mass of dunite hosting India's largest magnesite deposit occurs. Alkali gabbro dikes cutting the dunite have an Rb-Sr whole rock age of 808 ± 18 Ma with a $^{87}Sr/^{86}Sr_i$ of 0.703 (Reddy et al. 1994). This is similar to the age of 720 ± 30 Ma reported by Deans and Powell (1968) for biotite pyroxenite from the Sevathur-Korati carbonatite complex north of the study area (see figure 1 and 2). Based on the isotope data presented in this paper, it is probable that carbonate alteration of the older granulites (and perhaps also the dunite) took place at approximately the same time as the carbonatite and alkali basalt magmatism and that the two events are related. For this reason, an age of ~800 Ma is tentatively assigned to the carbonate alteration event studied here.

The alkalic-carbonatitic magmatism and carbonate alteration in this area may be related to a Late Pre-Cambrian generation of charnockitic alteration veins and larger masses of granulite facies rocks in southern India. Granulites of Late Archean age (ca. 2500 Ma) are found in the Krishna-
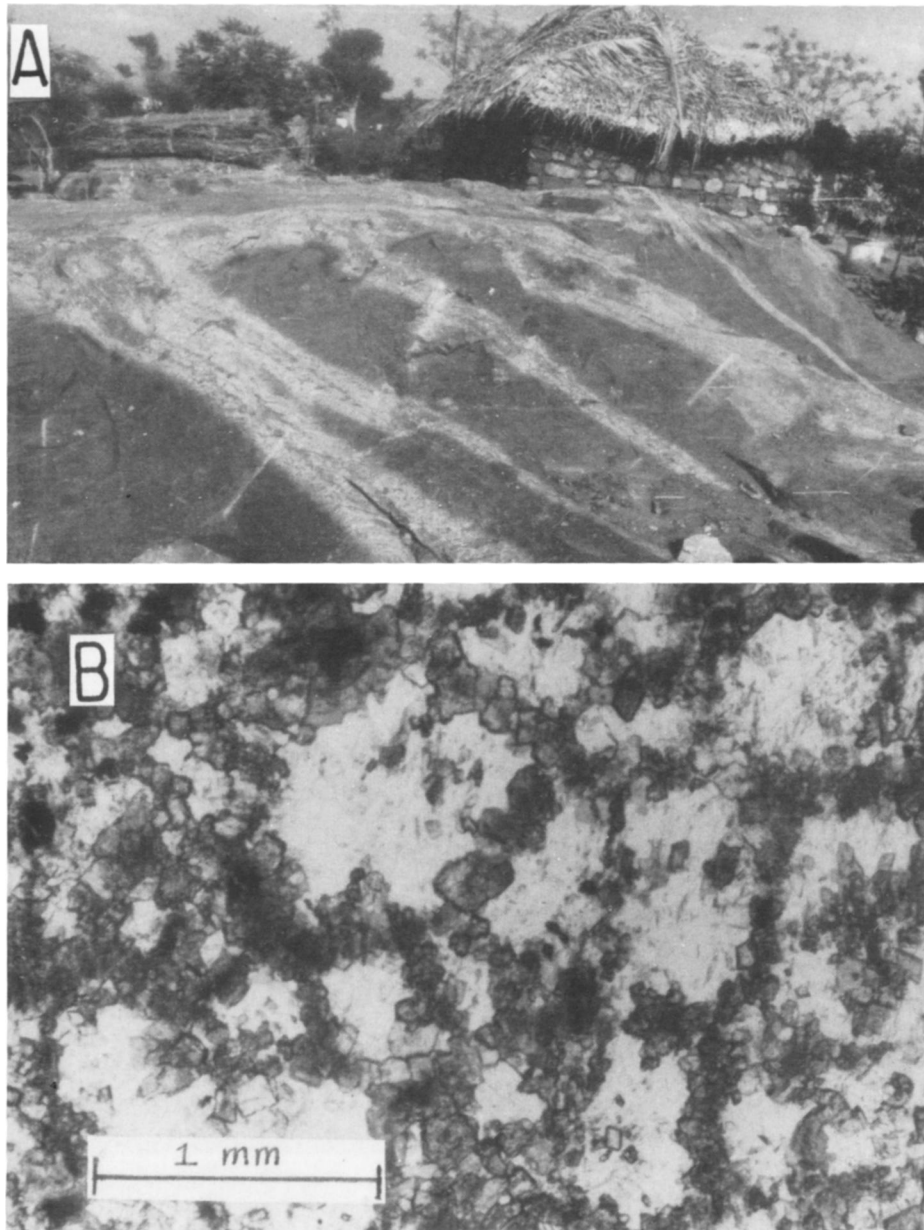
Figure 3. (*A*) Outcrop of partially carbonated charnockite at Kanipatti (location of the KP samples). Note that the light carbonated zones form a dense fracture network. (*B*) Photomicrograph of a carbonated gneiss. Note the pervasive growth of calcite and ankerite (euhedral crystals) along the grain boundaries of quartz and plagioclase crystals.

Other evidence for carbonate metasomatism in the study area includes the presence of abundant scapolite replacing plagioclase in the mafic two-pyroxene granulites and in enclaves of silicate rock within the carbonated zones. Carbonate also occurs within olivine + orthopyroxene + anthophyllite + spinel assemblages of the recrystallized ultramafic rocks. These occurrences support the argument that the vein carbonate and related alter-ation are not the products of a low-temperature (<250°C) hydrothermal alteration process involving shallow ground water, but instead may form part of a metamorphic process that commenced at quite high temperatures. The commonly observed association ankerite + calcite + muscovite + albite + epidote + chlorite and rare actinolite belongs to that of shallow-level greenschist to lower amphibolite facies alteration, although some or all
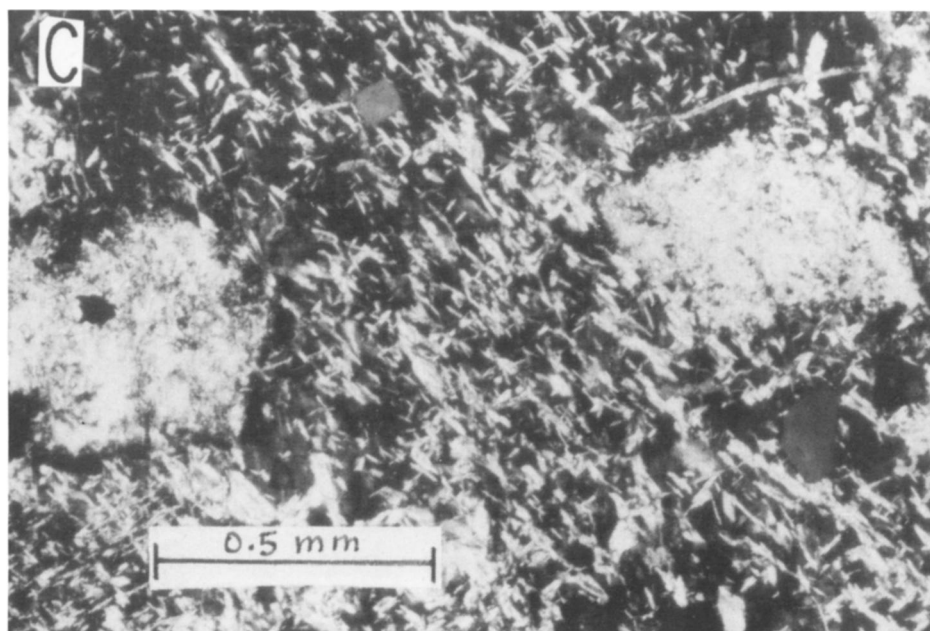
Figure 3. (Continued) (C) Euhedral crystals of ankerite within partially sericitized plagioclase. The ankerite is surrounded by a thin rim of iron oxide. All photographs reproduced after Khan (1989).

of the ankerite formed at higher grade (see below). The CO_2 content of the fluid responsible for this alteration should be high (>50 mole %), and under such conditions the assemblage quartz-dolomite (and by implication quartz-ankerite) may be stable up to temperatures well above 500°C at pressures of ~4 kbar (Harte and Graham 1975; Skippen 1974).

Although metasedimentary carbonate rocks are extremely rare in the study area, about 60 km to the south of here, around Shankari, extensive marble layers of Archean age are present. Two samples of these marbles, from near Jogipatti, were also analyzed. In the study area itself, only two minor occurrences of calc-silicate rocks of meter size are exposed.

Petrographic Description.   Charnockites are well foliated dark greenish-grey rocks with alternating layers rich in mafic and quartzofeldspathic minerals. The foliation generally trends ENE-WSW, parallel to the Attur shear zone. These rocks are granoblastic and contain quartz (40%), plagioclase (An_{18-22}, 20–40%), orthopyroxene (En_{55}, 4–15%), and reddish-brown biotite (1–4%). Small quantities of perthite and brownish hornblende are also present.

Biotite gneiss is the next most abundant rock type after charnockite. These rocks form leucocratic "bleached" zones within charnockite, especially along shear zones, and appear to be products of shear-induced retrogression of charnockite. Blue-green actinolitic hornblende replaces orthopyroxene and the only other mafic phase is biotite, which occurs as both brown (~2% TiO_2) and green varieties. Plagioclase is partially epidotized and sericitized with a decrease in An content from ~An_{25} to An_{0-3} (Khan 1989). Muscovite is common.

Carbonated gneiss: Orange-brown or pink ankerite-dolomite-bearing carbonated gneiss forms extensive outcrops particularly well developed around the village of Timmanayakanpatti (TP sample series), enveloping almost all older lithologies. They have ribbed brownish limonitized weathered surfaces. Fresh specimens are medium- to coarse-grained (0.5 to 2.0 mm grain size), massive leucocratic rocks showing pinkish, iron-rich carbonate layers alternating with dirty-white feldspathic layers. Carbonates form up to 30–40% of the rock. In the northern part of the study area, the carbonated gneisses are found mostly as centimeter- to meter-wide veins, almost always within the center of "bleached" zones of biotite gneiss in charnockites (see figure 3A) and follow through-going fractures. Phyllonites and mylonites are abundant at these localities. The veins usually form along sets of parallel NNW-SSE vertical fractures or joints, cutting across the charnockite foliation at high or low angles. The fabric of the biotite gneiss and charnockite continues uninterrupted through the carbonated zones. Only late quartz veins, which are

sometimes abundant at the carbonated localities, have not suffered carbonation.

In thin section, the original high-grade gneiss is strongly altered and devoid of all original mafic mineral constituents. Quartz occurs as two textural generations, an earlier, more abundant type showing undulose extinction, and a later, finer-grained, polygonal, and relatively unstrained type. Plagioclase is sometimes extensively converted to a mass of very fine-grained (40–20 μm) sericite, saussurite, and calcite, such that the original lamellar twinning can barely be distinguished. The relict feldspar may approach pure albite in composition. Muscovite is common, along with chlorite. The carbonates often occur as small intergranular crystals betwen quartz and plagioclase (figure 3B). However, large individual rhombs of carbonate growing within plagioclase laths are also common (figure 3C) and are almost always outlined by a rim of reddish iron oxide or hydroxide. Laths of sericite sometimes overgrow these oxide rims and are

rarely observed overgrowing the rhombs themselves, suggesting that sericitization probably postdated their formation. The large carbonate rhombs, together with carbonates within veins, have high MgO and FeO contents and are best classified as ferroan dolomite or ankerite. The other variety of carbonate—calcite—is fine-grained and occurs mostly within plagioclase. It also forms as a low-temperature breakdown product of the ankerite rhombs with the released iron forming rims of opaque oxide. Carbonate alteration of two isolated dark mafic dikes (SP2, IMC 1) reaches up to 50%, with the mafic minerals completely altered to a fine-grained mixture of talc-chlorite-actinolite with rhombs of ankerite. Representative microprobe analyses of the main silicate and carbonate phases from charnockites, biotite gneisses, and carbonated gneisses are given in table 1.

Sample Collection and Analytical Techniques. Care was taken to collect specimens mostly from fresh quarry surfaces where discrete carbonated

Table 1. Average Electron Microprobe Analyses of Representative Samples from Zones of Carbonation and Retrogression

	Charnockite			Biotite Gneiss			Carbonated Gneiss			
	Opx	Bio	Plg	Br Bio	Gr Bio	Musc	Plg	Musc	Ank-erite	Calc
No. analyses	(6)	(6)	(4)	(5)	(3)	(3)	(9)	(6)	(5)	(1)
SiO_2	51.56	36.40	61.45	35.80	37.89	46.01	67.36	45.62	.65	...
TiO_2	...	4.97	...	2.41	.14	...	...	...	...	...
Al_2O_3	1.72	15.40	24.48	17.63	18.68	33.01	20.95	33.50	.35	...
FeO	30.58	18.43	...	23.31	21.90	3.36	...	2.90	16.78	1.37
MgO	16.65	11.41	.20	7.33	7.74	1.46	.30	.96	10.01	...
K_2O	...	9.83	.41	8.89	9.03	10.44	.56	10.44	...	...
Na_2O	...	...	7.83	...	...	...	10.65	...	...	...
CaO	.40	...	5.24	...	...	...	.42	...	26.60	51.40
Total	100.90	96.64	99.61	95.43	95.38	94.28	100.24	93.42	54.39	52.77
No. oxygens	6	24	8	24	24	24	8	24	24	24
Si	1.97	6.01	2.73	6.04	6.28	6.80	2.97	6.76	.25	...
Ti	...	.63	...	.31	.02	...	...	...	...	...
Al	.08	2.97	1.28	3.51	3.60	5.87	1.07	5.92	.17	...
Fe	.98	2.54	...	3.30	2.90	4.21	...	.39	5.61	.49
Mg	.95	2.73	.02	1.80	1.84	.32	.07	.24	6.03	...
K	...	2.05	.02	1.95	1.90	1.84	.03	1.94	...	...
Na	...	...	.68	...	...	...	.91	...	...	...
Ca	.016	...	.26	...	...	...	.02	...	11.52	23.51

	Ankerites, Carbonated Gneiss			
	SP-1 (Carbonate rhomb)		KP-1	
	core	rim	core	rim
FeO	11.14	19.35	13.26	14.92	17.62
MgO	13.40	8.19	12.66	12.94	9.10
CaO	29.42	27.03	27.92	30.24	29.26

zones are well exposed on vertical surfaces. The KP, SP, and most of the IMC sample series belong in this category. Samples cover all gradations from central carbonated zones through adjacent biotite gneisses to surrounding charnockite. Samples of the TP series come from areas of more diffuse carbonate alteration. Carbonated specimens of two mafic dikes (SP2, IMC 2) are also included. A thin section of the same rock shows almost complete alteration to carbonate, chlorite, and talc, with carbonate forming up to 50% modal. The carbonate component within the carbonated gneiss samples (which normally contain 20–30% carbonate) was concentrated by hand-picking composite grains of orangeish carbonate with quartz and/or feldspar. It was established by X-ray diffraction that the carbonate in these grains was mostly ankerite. Very fine-grained calcite (<50 μm) contained within plagioclase and ankerite rhombs could not be further separated by hand picking.

Carbon and oxygen isotope determinations on aliquots of the same carbonate concentrates were carried out at the University of Chicago. The samples had previously been finely ground in a pestle and mortar to ~2 μm for better reaction. Since it was impossible to separate physically the calcite and ankerite components because they were intergrown on such a fine scale, the samples were treated with 100% phosphoric acid for different periods of time and at different temperatures, in order to liberate CO_2 from the calcite and ankerite separately. First the samples were reacted at 25°C for about 24 hrs, which liberated CO_2 from the calcite component in the sample (McCrea 1950). This was extracted, purified, and the carbon and oxygen isotopic composition was measured on a Delta E mass spectrometer. The remaining residue was then reacted at 50°C for another 24–48 hrs, which liberated all remaining CO_2 in the sample, presumed to be mostly derived from the ankerite (Becker and Clayton 1972). The isotopic composition of the CO_2 released at 50°C was also determined. A technique using ethylene diamine tetra-acetic acid (EDTA) was subsequently used for some samples, whereby the calcite was first dissolved in EDTA, and the ankerite residue was then treated with phosphoric acid at 50°C. This technique resulted in a more effective separation of calcite from ankerite.

The oxygen isotopic composition of plagioclase and quartz, separated by hand picking from several carbonated charnockites, was also determined. Oxygen was liberated from these samples using a fluorination technique similar to that described by Taylor and Epstein (1962). Since field evidence points to a possible connection between the car-

bonatites and alkaline syenite on one hand and gabbro plutons and the carbonate alteration on the other, the isotopic composition of three carbonatites from the Sevathur body were also analyzed, together with two whole-rock samples of alkali gabbro dikes cutting the Salem dunite body. Two samples of marble from Jogipatti were analyzed and also four magnesite samples from the Salem deposit. All $\delta^{18}O$ values are reported relative to SMOW with a value for NBS 28 of +9.2. $\delta^{13}C$ values are reported relative to PDB.

Strontium isotope determinations were carried out at the University of Texas at Dallas. The carbonate-rich portions of 20 of the carbonated gneiss samples were leached with 0.5N HCl for about an hour to release the carbonate. For three samples (SP-1, TP-1.3 and KP-3.2), ankerite was purified by dissolving the calcite in the sample in H_3PO_4 at room temperature in exactly the same way as described above for the stable isotope determinations. The remaining mixture of ankerite and silicate was leached with 0.5N HCl to isolate ankerite, and the silicate residue dissolved in HF; thus for these three samples, Rb-Sr data are reported for the mixed carbonate, ankerite and silicate residue. For all other samples, Rb-Sr data are reported for the mixed carbonate leachate.

Rb and Sr were isolated using conventional cation exchange chromatography. Rb concentration data were determined by isotope dilution and using the UTD 12″ radius Shields-type single collector thermal ionization mass spectrometer. Sr concentrations and isotopic compositions were determined simultaneously using very pure ^{84}Sr spike and the MAT-261 multi-collector thermal ionization mass spectrometer at UTD. Fractionation corrections were made using $^{86}Sr/^{88}Sr = 0.1194$, and $^{87}Sr/^{86}Sr$ for each sample was adjusted so that $^{87}Sr/^{86}Sr$ for the E&A $SrCO_3$ standard = 0.70800. Accuracy for $^{87}Sr/^{86}Sr$, which is fundamentally the long-term reproducibility of the E & A standard, under normal operating conditions is ±0.00004 or better. Analytical precision for the data reported here, in all cases, was an order of magnitude better than this. Total processing blanks for Rb and Sr are less than 0.2 and 2 ng, respectively. For a few samples, corrections for Rb blank were necessary.

Results

Stable Isotope Data. The carbon and oxygen isotopic compositions of CO_2 extracted from the carbonate concentrates at 25°C and 50°C are listed in table 2. $\delta^{18}O$ values for each carbonate sample were calculated by assuming that the 25°C fraction was liberated entirely from calcite and the 50°C

Table 2. Carbon and Oxygen Isotope Composition of Calcite and Ankerite, Oxygen Isotope Composition of Silicate Minerals, and Strontium Isotope Composition of Carbonates

Sample	$\delta^{18}O$ CO_2 (25°C)	$\delta^{18}O$ calcite	$\delta^{18}O$ CO_2 (50°C)	$\delta^{18}O$ ankerite	$\delta^{13}C$ calcite	$\delta^{13}C$ ankerite	$(^{87}Sr/^{86}Sr)_{800}$[b]
Carbonated gneiss samples							
SP1	+25.9	+15.7	+19.1	+8.6	−4.6	−5.9	.70537
SP2	+21.7	+11.5	+19.5	+8.9	−3.8	−3.8	.70697
SS208	+22.1	+11.9	+18.6	+8.1	−5.7	−6.3	.70840
M2	+31.6	+21.4	+20.0	+9.5	−4.1	−5.5	.70575
IMC1			+19.8	+9.3		−4.2	.71056
IMC2	+30.6	+20.4	+22.2	+11.7	−4.3	−5.4	.70535
IMC3	+28.1	+17.9	+20.5	+10.0	−4.8	−6.3	.70533
TP1.3	+28.1	+17.9	+19.2	+8.7	−3.9	−5.3	.70949
TP2	+26.9	+16.7	+19.0	+8.5	−4.0	−3.9	.70893
TP3			+18.6	+8.1		−5.1	.70908
KP1	+34.3	+24.1	+28.6	[+18.1][a]	−4.2	−5.1	.70678
KP3.1	+27.0	+16.8	+19.6	+9.1	−4.8	−5.4	.70670
KP3.2	+25.2	+15.0	+17.9	+7.4	−5.2	−6.0	.70735
Mean		+17.2		+9.0	−4.5	−5.2	
Carbonatite							
CB1	+17.5	+7.3			−5.0		.70489
CB2	+18.1	+7.9			−4.7		.70535
CB3	+18.7	+8.5			−5.0		.70515
Magnesite							
MAG1	+38.8	+28.6			−2.9		.71094
MAG3	+37.2	+27.0			−4.0		.70847
MAG4	+38.5	+28.3			−2.8		.70626
MAG5	+38.6	+28.4			−4.0		.70795
Marble							
J1	+32.1	+21.9			+2.8		.70703
J2	+32.0	+21.8			+2.7		.70870
Silicate analyses							

	quartz	plagioclase	whole rock	$\Delta_{quartz-plagioclase}$	$\Delta_{quartz-ankerite}$
SP1	+9.1	+7.9		+1.2	+.5
SS208	+8.9	+7.3		+1.6	+.8
IMC3	+9.1	+7.7		+1.4	+1.0
TP2	+8.2	+6.6		+1.6	−.3
TP3	+8.3	+6.3		+1.9	+.2
KP3.1	+8.7	+6.1		+2.6	−.5
KP3.2	+7.9	+6.6		+1.3	+.5
KP4	+8.2	+5.9			
Alkali gabbro (shonkinite)					
R405			+6.2		
R258			+6.4		

[a] [ ] omitted from mean.

[b] $\frac{^{87}Sr}{^{86}Sr}$ of sample at 800 Ma.

fraction entirely from ankerite, and by using published values for $\Delta_{CO2\text{-}calcite}$ and $\Delta_{CO2\text{-}ankerite}$ at the appropriate temperatures (Friedman and O'Neil 1978; Rosenbaum and Sheppard 1986). Because the fractionations are very similar for ankerite and calcite, the calculated values will be similar regardless of which fractionation factor is used. Magnesite samples were corrected using the oxygen isotope fractionation factors of Perry and Tan (1972).

The carbon and oxygen isotope data for the carbonates from each temperature fraction are plotted in figure 4. Where samples were treated with EDTA in order to isolate ankerite more effectively, the EDTA value is plotted. The 25°C and 50°C (calcite-rich and ankerite-rich) fractions form two distinct groups. $\delta^{18}O$ values for calcite display a wide range of values from +11.5 to +21.4‰ (mean = +17.2‰) while $\delta^{13}C$ varies much less, between

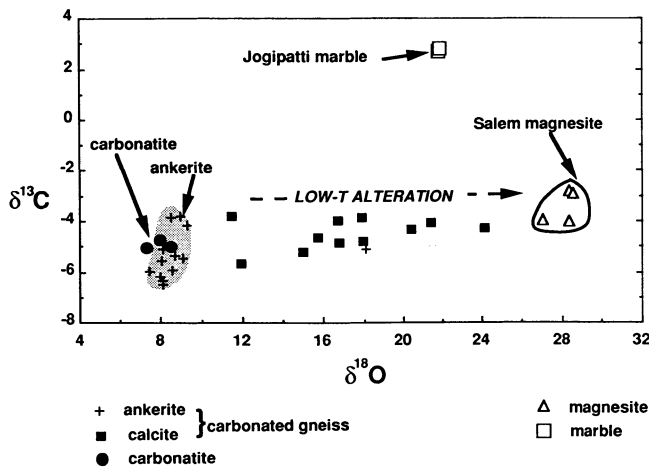**Figure 4.** $\delta^{13}C$ and $\delta^{18}O$ in calcite and ankerite from the carbonated gneisses, and also in calcite from carbonatite and marble samples from elsewhere in Tamil-Nadu, and in magnesite from the Salem magnesite deposit (see figure 2). The ankerite samples form a tight cluster of points having very similar isotopic composition to the carbonatites, while the values for calcite extend to much higher $\delta^{18}O$, trending toward the field of magnesite samples. The Jogipatti marble samples have distinctly different $\delta^{13}C$ from any of the other carbonates and appear unrelated to carbonate metasomatism in the Attur shear zone.

-5.7 and -3.8% (mean $= -4.5\%$). The ankerite samples, on the other hand, show much less variation in $\delta^{18}O$ and, with the exception of sample KP1 ($+18.1\%$), range from $+7.4\%$ to $+11.7\%$ (mean $= +9.0\%$, not including KP1). This anomalous sample contained an unusually large fraction of calcite compared to ankerite, which may have contributed a significant fraction of CO_2 to the 50°C sample and contaminated the ankerite-derived CO_2. The EDTA procedure could not be used on this sample because all of the material was exhausted in making the first analysis. The ankerite $\delta^{13}C$ values range from -6.5 to -3.9% (mean $= -5.3\%$), similar to the range of the calcite samples but ranging to slightly lower $\delta^{13}C$. Interestingly, the relatively well-defined cluster of ankerite data points lie at the low $\delta^{18}O$ end of the trend shown by the calcite samples.

The isotopic compositions of the ankerite and calcite samples imply a complex exchange history, consistent with the complex textures observed in these carbonated rocks. The cluster of 50°C (ankerite) $\delta^{18}O$ and $\delta^{13}C$ values in many samples from several localities within the study area suggests that they were deposited from fluids with fairly uniform isotopic composition at relatively uniform temperature. This is supported by the observation

that quartz and plagioclase $\delta^{18}O$ values are also fairly uniform in seven carbonated gneiss samples, quartz ranging between $+9.1$ and $+7.3$ and plagioclase between $+7.9$ and $+5.9$. Most important, quartz-plagioclase and quartz-ankerite fractionations are strikingly uniform and low in all of these samples ($\Delta_{quartz\text{-}plagioclase} = 2.6$ to 1.2; $\Delta_{quartz\text{-}ankerite} = 1.0$ to -0.5).

This feature is well illustrated in figures 5 and 6. Figure 5 plots the $\delta^{18}O$ value of quartz against that of plagioclase and ankerite in the same samples. The data do not form steep disequilibrium arrays cutting across the slope-one, equilibrium fractionation line, as is commonly observed in quartz-feldspar pairs from hydrothermally altered rocks. Instead, they show a weak positive correlation and cluster around the $\Delta = 2$ line in the case of quartz-plagioclase and $\Delta = 0.5$ in the case of quartz-ankerite. The distribution is thus more typical of slowly cooled high-grade mineral assemblages than those subjected to low-temperature, retrograde alteration.

The absence of marked disequilibrium is also apparent in figure 6, where the quartz-plagioclase and quartz-ankerite fractionations are plotted against each other for those samples where oxygen isotope analysis of all three coexisting minerals were obtained. The data form a fairly tight cluster of points corresponding to a close approach to iso-
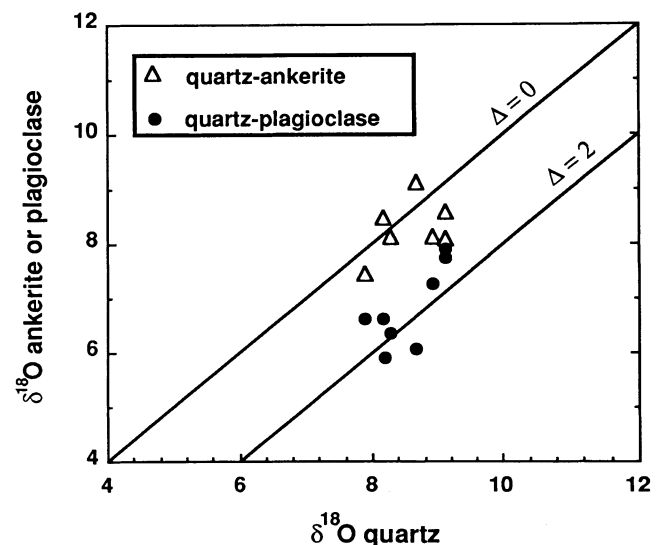

Figure 5. $\delta^{18}O$ of coexisting quartz, plagioclase, and ankerite from the carbonated gneiss samples. Quartz-plagioclase pairs cluster near the $\Delta = 2$ fractionation line while quartz-ankerite pairs fall closer to the $\Delta = 0$ fractionation line. Both sets of data show a weak positive correlation and are unlike the steeply oriented arrays that are typical of isotopic disequilibrium.
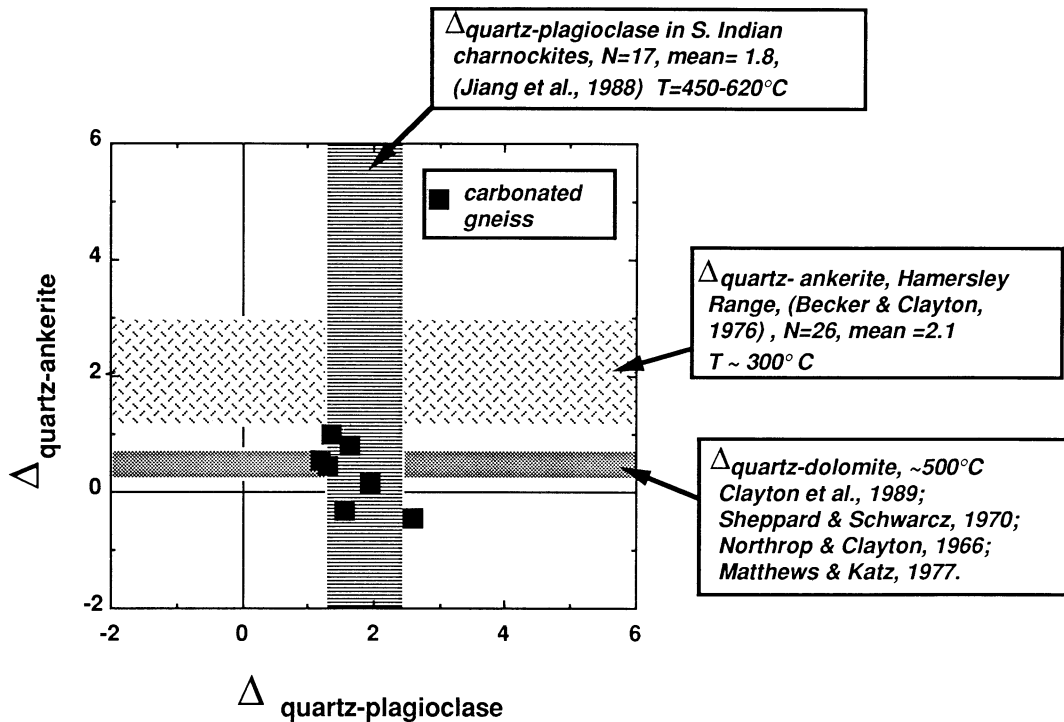
Figure 6. $\Delta_{\text{quartz-ankerite}}$ plotted against $\Delta_{\text{quartz-plagioclase}}$ for carbonated gneiss samples in which $\delta^{18}O$ was measured in all three phases. The quartz-plagioclase fractionations have a very similar range to the data of Jiang et al. (1988) who analyzed a group of pristine, uncarbonated charnockite samples from various localities in southern India. Quartz-ankerite fractionations are similar to those predicted for quartz-dolomite at a temperature of $\sim500°C$ (Northrop and Clayton 1966; Sheppard and Schwarcz 1970; Matthews and Katz 1977; Clayton et al. 1989) and indicate significantly higher temperatures than the quartz-ankerite pairs from the Hamersley Range iron formation (Becker and Clayton 1976) for which a temperature of $\sim300°C$ has been suggested.

topic equilibrium in these samples. $\Delta_{\text{quartz-plagioclase}}$ ranges from 1.2 to 2.6‰, with an average of 1.7‰, almost identical to the range and the average of quartz-plagioclase fractionations in pristine high-grade charnockites from a number of different localities across southern India (Jiang et al. 1988; see figure 6). The quartz-plagioclase fractionations correspond to temperatures of 450–620°C (Chiba et al. 1989). $\Delta_{\text{quartz-ankerite}}$ ranges from -0.5 to 1.0‰, with a mean of 0.3‰. The two negative values may be due to the ankerite analyses being slightly contaminated by CO_2 from high-$\delta^{18}O$ calcite. Even so, the narrow range of quartz-ankerite fractionations suggest that they represent near-equilibrium values.

The carbon isotopic compositions of the ankerites are relatively homogeneous. The mean $\delta^{13}C$ for the entire ankerite group is -5.2‰, close to the accepted mantle carbon $\delta^{13}C$ value of -5.5 (Des Marais and Moore 1984) and to the local carbonatite mean of -4.9. The range to slightly higher $\delta^{13}C$ in a few ankerite samples might represent source heterogeneity, fractionation of $^{13}C/^{12}C$ during decarbonation or magma degassing, or partial

exchange or contamination of fluids or magmas with crustal carbonate material. For example, although it is not from the immediate vicinity, the high-grade Jogipatti marble samples have $\delta^{13}C$ of $+2.8$. The similarity of $\delta^{13}C$ values of the retrogressed calcite samples to the range in the ankerites reflects the fact that retrogression did not introduce any external carbon and was effectively a closed system process for this element.

The regional occurrence of mantle-derived intrusive rocks (including carbonatites) in southern India supports the hypothesis that these magmas introduced the CO_2-rich magmatic volatiles that caused widespread high-temperature carbonation of the local country rock. In order to test this hypothesis, we measured $^{13}C/^{12}C$ and $^{18}O/^{16}O$ in three samples of calcite from the Sevathur carbonatite complex (figure 2). The $\delta^{13}C$ and $\delta^{18}O$ values are plotted in figure 4 and are almost identical to the field of ankerite data points. Although these samples are from a locality ~100 km from the area of carbonate metasomatism we have studied in the Attur shear zone, the close correspondence in isotopic composition provides clear evidence that

similar CO$_2$-rich magmas could very plausibly have caused carbonate alteration of basement rock-types throughout the region. Such rock-types (carbonatites, syenites, and alkali gabbros) are in fact found as small dikes throughout the study area, although their total abundance in the area of maximum carbonate alteration is fairly low (Khan 1989).

Strontium Isotope Data. Rb and Sr concentrations and $^{87}Sr/^{86}Sr$ data for 19 mixed carbonates, three ankerites, and three silicate residue fractions are reported in table 3. Based on our stable isotope data, we suggest that the carbonate alteration was

contemporaneous with alkalic magmatism at about 800 Ma; therefore the data have been corrected for 800 Ma of in situ growth of radiogenic ^{87}Sr, and $^{87}Sr/^{86}Sr$ at that time is plotted as a histogram in figure 7. It is important to note that for most samples, the Rb/Sr ratio is so low that the corrected $^{87}Sr/^{86}Sr$ is relatively insensitive to age. The data vary widely from 0.7044 to 0.7106. This range is much larger than that observed by Stern and Gwinn (1990) in similar carbonated gneiss samples from a much larger region in northeastern Africa, which yielded (with two exceptions) an initial $^{87}Sr/^{86}Sr$ range of 0.7029 to 0.7048. There are

Table 3. Rb and Sr concentrations and $^{87}Sr/^{86}Sr$ Data

Sample	Rb (ppm)	Sr (ppm)	$^{87}Rb/^{86}Sr$	$^{87}Sr/^{86}Sr^a$	$(^{87}Sr/^{86}Sr)_{800\ Ma}{}^b$
SP-1	.43	245	.00508	.70543	.70537
Ankerite	.67	182	.011	.70589	.70576
Silicate	12.3	783	.045	.70491	.70440
SP-2	.073	406	.00519	.70703	.70697
SS-208	.48	269	.00514	.70846	.70840
M-2	.13	329	.00115	.70576	.70575
IMC-1	1.28	451	.00819	.71062	.71056
IMC-2	.72	324	.00638	.70542	.70535
IMC-3	.40	278	.00415	.70538	.70533
IMC-3.1	.52	264	.00570	.70545	.70538
TP-1.2	1.02	301	.00982	.70916	.70905
TP-1.3	.59	360	.00477	.70954	.70949
Ankerite	6.3	33.0	.551	.71301	.70671
Silicate	44.4	234	.550	.71292	.70664
TP-2	.31	362	.00248	.70896	.70893
TP-3	.41	353	.00339	.70912	.70908
TP-4.3	1.2	483	.00724	.70808	.70800
KP-1	.80	787	.00296	.70681	.70678
KP-1.2	.65	613	.00307	.70668	.70664
KP-1.3	1.33	734	.00523	.70684	.70678
KP-2	.66	736	.00259	.70696	.70693
KP-3.1	1.11	492	.00652	.70677	.70670
KP-3.2	.59	586	.00293	.70738	.70735
Ankerite	2.0	12.5	.464	.71070	.70540
Silicate	41.9	167	.725	.71245	.70417
Jogipatti Marbles					
J-1	3.66	239	.0442	.70753	.70703
J-2	.47	430	.00316	.70874	.70870
Alkali gabbro dykes					
R258	209	1,082	.558	.71129	.70491
R405	95	736	.374	.70963	.70536
Salem magnesite					
MAG1	.097	2.37	.118	.71229	.71094
MAG3	.17	14.9	.033	.70885	.70847
MAG4	.24	10.0	.071	.70707	.70626
MAG5	.22	2.25	.278	.71113	.70795
Carbonatites					
CB1	.96	4,863	5.7×10^{-4}	.70490	.70489
CB2	.07	8,355	2.4×10^{-5}	.70535	.70535
CB3	.31	5,200	1.7×10^{-4}	.70515	.70515

Note.   Analyses carried out on leachates produced by 0.5N HCl, except for ankerites, dissolved in 6N HCl.
[a] Relative to E&A SrCO$_3$ $^{87}Sr/^{86}Sr$ = 0.70800. Accurate to ±0.00004
[b] Corrected for radiogenic growth over 800 Ma, using analyzed $^{87}Rb/^{86}Sr$.

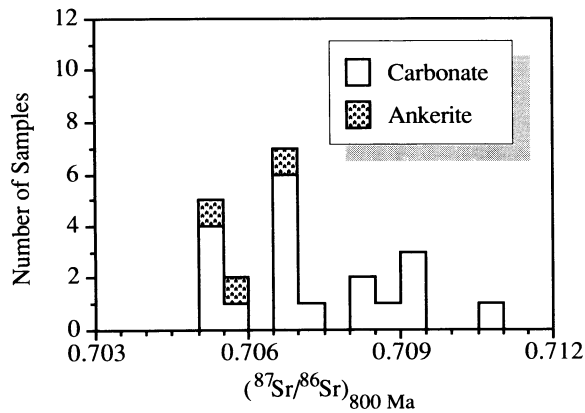**Figure 7.** Initial ^{87}Sr/^{86}Sr ratio for ankerites and mixed carbonates at 800 Ma.

probably two reasons for the range to elevated ^{87}Sr/^{86}Sr in the Indian carbonated gneisses. First, the source of the CO_2 probably contained relatively radiogenic strontium. The existence of such a source is demonstrated by the relatively high initial ^{87}Sr/^{86}Sr measured in the late Precambrian Sevathur carbonatite complex about 100 km to the north (0.705–0.706; Deans and Powell 1968; this study). We infer from these data that the mantle source of the carbonatite and other alkalic magmas was old and isotopically heterogeneous, most likely located within the lithospheric keel of the Archean Darwar craton. The initial ^{87}Sr/^{86}Sr at 800 Ma for the three ankerite samples cluster between 0.7054 and 0.7067. Unfortunately, because two of the three ankerites are relatively high ^{87}Rb/^{86}Sr (>0.46), for these the calculated initial ^{87}Sr/^{86}Sr is sensitive to the age chosen. Only for ankerite SP-1 is the ^{87}Rb/^{86}Sr low enough that the calculated initial (0.7058) is insensitive to the age chosen. Nevertheless, this value falls within the range of mantle-derived carbonatites in this region, providing further support for the hypothesis, based on stable isotope data, that the carbonate alteration was caused by CO_2-rich fluids released from mantle-derived magmas.

The range in initial ^{87}Sr/^{86}Sr of the mixed carbonates has a different explanation. Even though all of our carbonates have relatively low Sr contents compared with Sevathur carbonatites (<800 ppm vs. 0.75% Sr; Deans and Powell 1968), Sr contents of the mixed carbonates are invariably higher than in the coexisting ankerites (table 3). For example, KP 3.2 mixed carbonate has 586 ppm Sr, whereas KP 3.2 ankerite contains 12.5 ppm Sr. This indicates that the ankerite breakdown reaction to form calcite and iron oxides did not occur

in a closed system. We presume that Sr was scavenged from ankerite as well as from silicates during retrogression, most likely from feldspars, but possibly also in small quantities from biotite. Some of the silicate Sr could have been considerably more ^{87}Sr-rich than the ankerite Sr.

Rb-Sr systematics of two of the samples for which we have data for mixed carbonate, ankerite, and silicate yield isochrons (figure 8) with ages of 439 to 494 Ma. The third sample (SP-1) does not yield an isochron, most likely because the ankerite contained more radiogenic Sr than the gneiss it metasomatized (table 1), and isotopic equilibrium was not developed. The ages of the two samples yielding isochrons are similar to biotite-plagioclase cooling ages of 440–460 Ma for Ponmudi incipient charnockites (figure 1; Choudhary et al. 1992) and 486 Ma for Sri Lanka charnockites (Burton and O'Nions 1990), and quite different from the 2.3–2.4 Ga cooling ages obtained north of the Palghat-Cauvery shear zone (Buhl 1987, quoted in Choudhary et al. 1992; see also Peucat et al. 1993). We interpret the Rb-Sr ages we have obtained as
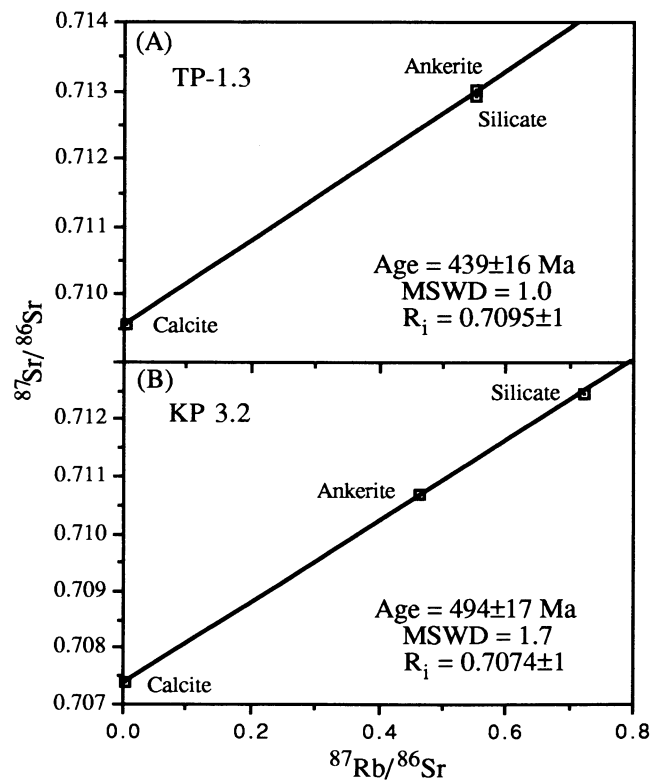

Figure 8. Rb-Sr isochron diagrams for samples TP-1.3 (A) and KP 3.2 (B). In each case the age presented by the isochron is similar to the biotite-plagioclase ages obtained by Choudhary et al. (1992) from the Ponmudi locality and interpreted by them to represent the age of uplift of the south Indian terrane.

approximating the time of breakdown of the anker-
ite and plagioclase, probably accompanying infil-
tration of water. These ages are interpreted as dat-
ing hydration and retrogression rather than simple
post-granulite facies cooling, although the two
events may have been almost simultaneous. Alter-
natively, it is equally possible that breakdown of
ankerite and formation of low-temperature alter-
ation minerals occurred during post-metamorphic
uplift, long after both granulite facies metamor-
phism and the regional carbonate metasomatic
process that is the subject of this study.

Figure 9 presents a $^{87}Sr/^{86}Sr$ vs. $\delta^{18}O$ diagram of
all the samples from this study for which we have
Sr and O isotope data. The strontium data have
been corrected to 800 Ma but, as noted above, most
of the samples are quite insensitive to age correc-
tions because they have extremely low Rb/Sr ra-
tios. The only exceptions are two of the ankerite
samples, the silicate fractions and the alkali gabbro
samples. This diagram illustrates the scatter in the
bulk carbonate samples to higher $^{87}Sr/^{86}Sr$ but also
emphasizes the close correspondence between the
ankerites and the carbonatites.

Discussion

The regional alteration of silicate crustal rocks to
carbonated assemblages within the Attur shear
zone, and similar occurrences elsewhere, represent
an important geochemical process of considerable
relevance to deep crustal CO_2 fluxes and to crustal

and mantle outgassing (e.g., Kerrich et al. 1987;
Veizer et al. 1989). Such occurrences provide com-
pelling evidence for intermittent, localized high-
CO_2 fluxes associated with major shear zones (e.g.,
Baratov et al. 1984; Newton 1990b; van Schalk-
wyk and van Reenen 1992; Dahlgren et al. 1993).

Our new stable and radiogenic isotope data
allow us to constrain the processes involved and
to identify the fluid source more accurately than
has previously been possible. The oxygen and car-
bon isotope systematics are consistent with two
stages of alteration. The relatively tight cluster of
$\delta^{13}C$ and $\delta^{18}O$ ankerite values is consistent with
fairly isothermal deposition from an isotopically
uniform CO_2-rich fluid (figures 4 and 6). The high
$\delta^{18}O$ values of some calcite samples (figure 4) sug-
gest deposition at lower temperatures when
calcite-fluid fractionation factors were higher. The
spread in the calcite values indicates that equilib-
rium was not attained during this later process,
which may have occurred during cooling after the
main higher temperature alteration event, during a
later minor heating event (see below) or even have
resulted simply from groundwater alteration in the
shallow sub-surface. The lack of a significant shift
in $\delta^{13}C$ in the calcite samples suggests that this
calcite-forming event occurred in the presence of
C-poor (presumably water-rich) fluids.

This proposed two-stage isotopic alteration his-
tory is also consistent with textural evidence sug-
gesting both low- and high-temperature carbonate
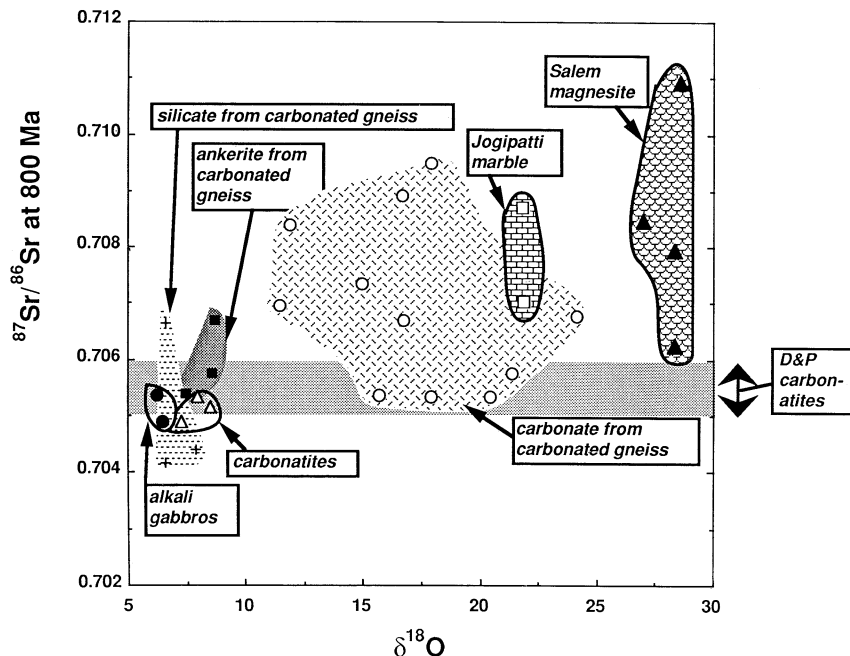mineral growth. High-temperature alteration is

Figure 9. $^{87}Sr/^{86}Sr$ at 800 Ma plot-
ted against the $\delta^{18}O$ value of various
samples analyzed in this study.
Note the close correspondence be-
tween the field of ankerite values
and carbonatites from other Tamil-
Nadu localities. The spread of
mixed carbonate values to higher
$\delta^{18}O$ and $^{87}Sr/^{86}Sr$ reflects mixing
with more radiogenic strontium and
partial re-equilibration of oxygen
isotopes during retrogression of the
ankerite. The fine-grained calcite
formed at this time probably incor-
porated more radiogenic Sr from
some of the silicate minerals (e.g.,
biotite).

represented by the euhedral ankerite rhombs observed in many samples (figure 3). The assemblage ankerite + quartz will be stabilized to higher temperatures by high X_{CO_2} in the fluid phase and by higher pressures (Harte and Graham 1975) and if the ankerite formed at ~4 kbar, the observed assemblages are consistent with this process commencing above 500°C and perhaps as high as 600°C. The second stage of alteration occurred at much lower temperatures and is represented by the fine-grained masses of carbonate, sericite, and epidote within plagioclase, and by the breakdown of ankerite rhombs, which have recrystallized to iron oxide and hydroxide rims and fine-grained calcite and are partly overgrown by tiny sericite laths. The Salem magnesite body, which has a $\delta^{18}O$ value only slightly higher than the most ^{18}O-rich fine-grained calcite and a $\delta^{13}C$ similar to the rest of the carbonate alteration within the Attur shear zone (figure 4), may have formed at the same time, during secondary low-temperature alteration.

If the CO_2 was originally introduced into these rocks during the higher temperature, ankerite-forming event, what was its original isotopic composition and how high was the temperature? Quartz and feldspar from the partially carbonated silicate rocks have oxygen isotope fractionations suggesting equilibration at 450–600°C, and the remarkably narrow range of $\delta^{18}O_{ankerite}$ and $\Delta_{quartz-ankerite}$ values could represent a close approach to equilibrium with the silicate minerals within this temperature range.

The variation of $\Delta_{quartz-ankerite}$ with temperature is not well known, as there are few natural datasets and no experimental or theoretical studies. Of the various studies (mostly of quartz-carbonate veins) reporting $\delta^{18}O$ values of coexisting quartz and ferroan dolomite (see Kerrich, 1987 for a summary), many report quartz-dolomite fractionations that are too large or too scattered to represent isotopic equilibrium, and few yield temperatures concordant with independent silicate pair fractionations. However, Becker and Clayton (1976) reported an extensive oxygen isotope data set for ankerite and coexisting quartz from the Hamersley Range banded iron-formation in Western Australia in which systematic fractionations were observed. These samples had $\Delta_{quartz-ankerite}$ clustering near 2, and equilibration temperatures for these assemblages were estimated to have been 180–280°C (based on quartz-magnetite pairs) or 270–370°C (based on quartz-siderite pairs). The $\Delta_{quartz-ankerite}$ values measured in this study (mean = 0.3) imply a considerably higher equilibration temperature than the Hamersley rocks.

An alternative approach is to assume that the oxygen isotope partitioning in ankerite is similar to that in the structurally similar mineral dolomite (see Golding and Wilson 1983, for discussion). The variation of $\Delta_{quartz-dolomite}$ with temperature may be estimated from experimental and empirical determinations of the fractionation between the mineral pairs quartz-calcite and dolomite-calcite (Northrop and Clayton 1966; Sheppard and Schwarcz 1970; Matthews and Katz 1977; Clayton et al. 1989). If ankerite partitions oxygen isotopes similarly to dolomite, then the measured quartz-ankerite fractionations would correspond to a temperature of about 500°C (consistent with the temperature range suggested by the quartz-feldspar data; see figure 6). Such a temperature is consistent with the observed mineral assemblages, provided that X_{CO_2} in the fluid was high and $P \gtrsim 4$ kbars.

Although there is probably no way to constrain the temperature of ankerite formation very precisely, the combined isotopic and textural evidence suggests that it formed at (or above) a temperature of approximately 500°C and closely approached oxygen isotope equilibrium with the silicate minerals. Such a high temperature for carbonate alteration suggests that in southern India there may be a connection between carbonate metasomatism and ankerite formation, and at deeper crustal levels and higher temperatures, granulite formation. There is widespread mineralogical evidence in southern India for the formation of granulite facies, orthopyroxene-bearing charnockite from pre-existing amphibolite facies gneiss, accompanied by a change from H_2O-dominated to CO_2-dominated fluid inclusions (e.g., Newton 1985, 1990a). This transition has been interpreted to result from infiltration of CO_2-rich fluids into amphibolite-facies gneisses at temperatures of ~750°C (Newton 1985; Hansen et al. 1987).

The carbonated gneisses we have studied may represent a slightly lower temperature and lower pressure consequence of the same phenomenon. In addition to the abundant alkaline igneous rocks along the length of the Attur lineament (including carbonatites, alkali gabbros, and syenites), it is possible that some of the massif charnockites that dominate large parts of the southern India high-grade terrane may themselves also represent CO_2-rich intrusive magma bodies (Howie 1955; Subramanian 1959; Wickham 1988; see also Vry and Brown 1992 for a North American example). These intrusive magmas were all potentially rich in CO_2 and have ages in the range 700–900 Ma (Deans and

Powell 1968; Reddy et al. 1994). We believe that there is probably a genetic link between these Late Precambrian intrusions, the widespread charnockitization of similar age to the south, and the carbonate alteration. The carbonate alteration mostly has $^{87}Sr/^{86}Sr$ at 800 Ma lying between 0.704 and 0.708, which spans the range of initial ratios of the Late Proterozoic intrusive igneous suite. In particular, there is a very close match between the O, C, and Sr isotopic composition of the ankerite and carbonatite samples that we have studied. The isotopic composition of the ankerites is thus consistent with them having formed from reaction between charnockite and magmatic fluids released during crystallization of these and the other types of alkaline magma. These results would presumably have been ultimately derived from enriched mantle lithosphere beneath the southern Indian craton.

This model of granulite formation and carbonate alteration is illustrated in figure 10, which shows a schematic cross-section through the southern Indian crust in the vicinity of a major, steeply dipping shear zone. Successive bodies of CO_2-rich magma rise along near vertical fractures, releasing CO_2-rich fluids as they move to lower pressure. At deep crustal levels (6 to 8 kbar, 20–25 km depth, 650–800°C), the infiltration of these magmas and associated fluids promotes dehydration of hydrous silicates and local precipitation of graphite where oxygen fugacity is sufficiently low (cf. Frost et al. 1989). At shallower levels (3–5 kbar, 10–15 km depth) temperatures are low enough (400–600°C) to allow dolomite and ankerite to be stable in the presence of quartz and as a result, infiltration of the country rock causes extensive carbonation of mafic silicates and feldspars and growth of ankerite. Some alteration may continue down to lower temperatures, although the close-to-equilibrium oxygen isotope fractionations suggest that low-temperature fluid infiltration was limited. The growth of fine-grained calcite and the partial breakdown of the ankerite may have occurred during the final low-temperature stages of the same intrusive event, or it may have formed much later, perhaps during uplift of the region at ~450 Ma (see figure 8 and Choudhary et al. 1992).

This model of combined carbonate metasomatism and granulite formation occurring simultaneously at different crustal levels is consistent with the model of Farquhar and Chacko (1991), who studied the partially charnockitized locality at Ponmudi in Kerala (see figure 1). Based on $^{13}C/^{12}C$ and carbon abundance data, they suggested that at Ponmudi, biotite dehydration had been driven by release of CO_2 from intrusive charnock-

ite dikes. The same magmas, intruding at higher crustal levels, could have caused the carbonation within the Attur shear zone. The similar, Late Proterozoic age of igneous rocks and charnockite from both areas further supports this correlation.

In figure 11 we address the question of how much magma would have been required to cause the observed carbonation in the Attur shear zone and other terranes. The average weight fraction of CO_2 within the rocks of a carbonated gneiss terrane is hard to estimate precisely, but approximate ranges for the Attur shear zone (2.5 to 5 wt %) and northeast Africa (5 to 10 wt %) are indicated based on field mapping (Khan 1989; Stern and Gwinn 1990). If this CO_2 is derived from magmas, then we can calculate the mass of magma required, assuming that all the CO_2 originally dissolved in the magma is added to the crust of these regions. Four curves are plotted corresponding to magmatic CO_2 contents ranging from 30% (carbonatite) to 2% (alkali basalt). It is evident that for the Attur shear zone, even if the CO_2 was derived exclusively from basalt, a magma/crust ratio of only 2:1 would be required. For carbonatite the ratio would be as little as 1:5. These are still much larger quantities of carbonatite or alkali gabbro than are actually observed within the Attur shear zone, but much of the magma may have passed through this region and intruded at higher crustal levels or been erupted at the surface (see figure 10). A similar argument was made by Farquhar and Chacko (1991) at Ponmudi, although the quantity of CO_2 (and hence magma) required for granulite formation is considerably smaller. For northeast Africa the volume of magma required is larger but not unreasonable. Even the maximum level of regional alteration observed in the Tien Shan region of central Asia (20%—see Baratov et al. 1984) could be achieved with a carbonatite to rock ratio of <1:1.

The common presence of intrusive alkalic rocks in other regions of major carbonate alteration (e.g., within shear zones of the Abitibi greenstone belt, Canada; Wyman and Kerrich 1987) suggests that our model may also be relevant to these other settings. In some of these occurrences, however, there is disagreement as to the origin of the carbon, with interpretations favoring magmatic sources (Burrows and Spooner 1987; Oliver et al. 1993), crustal sources (Kerrich 1990), or mixed metamorphic and magmatic sources (Kerrich et al. 1987). The range in $\delta^{13}C$ of the carbonate in the Superior Province occurrences indicates that, notwithstanding fractionation effects during transport and deposition, the source of the carbon was isotopically more heterogeneous than has so far been demonstrated in
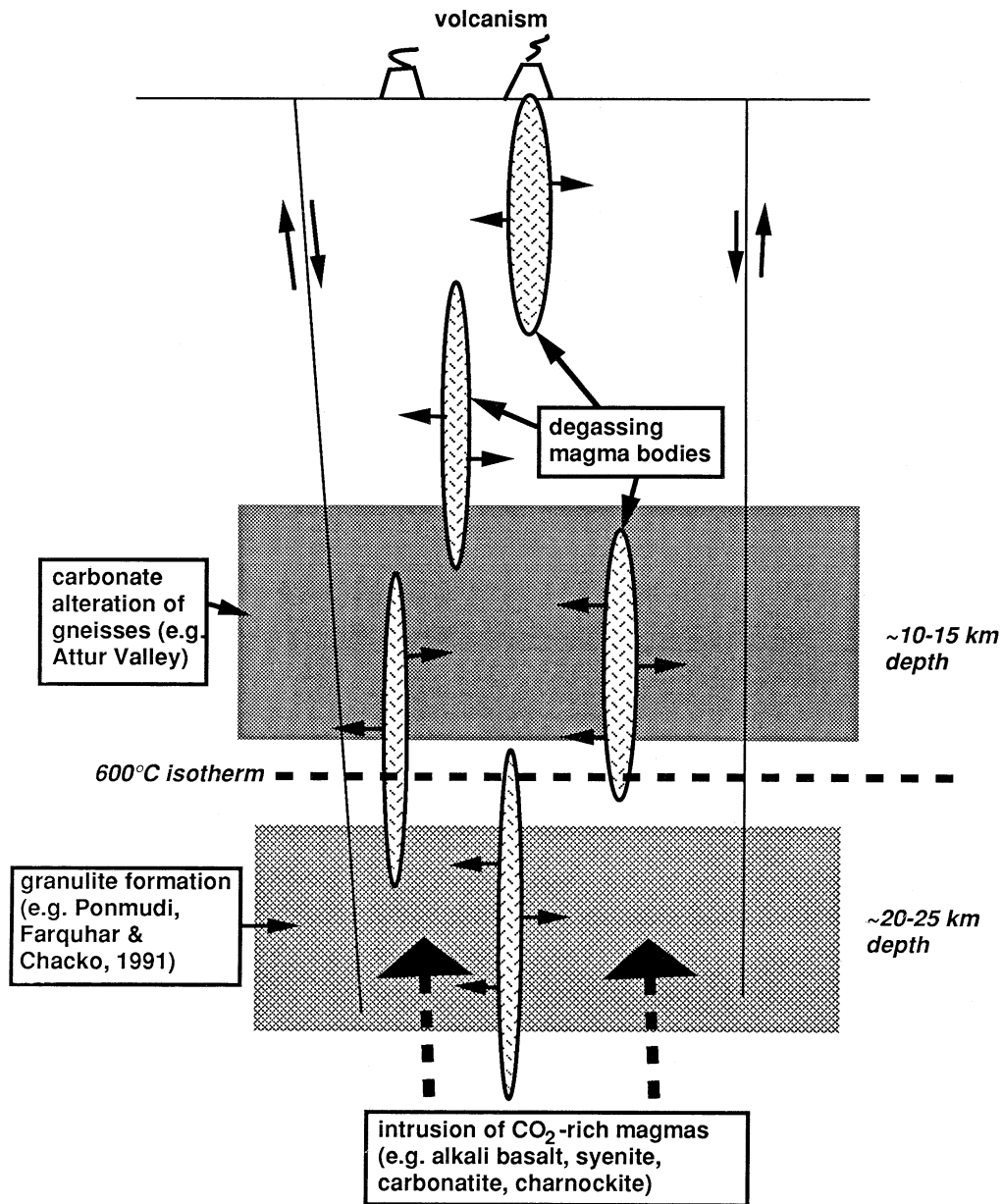
Figure 10. Schematic diagram showing the consequences of passage of CO_2-rich magmas through the southern Indian crust. At deep crustal levels (20–25 km) release of CO_2 and its transport into adjacent lithologies causes biotite dehydration and growth of orthopyroxene as observed at partially charnockitized localities such as Ponmudi (Farquhar and Chacko 1991). At shallower depth (~10–15 km) and lower temperatures (<600°C) the CO_2 influx causes extensive carbonation of pre-existing lithologies. The intruding magma bodies may rise to much shallower crustal levels or even to the surface, and need not be preserved at the level at which carbonate metasomatism occurs.

Tamil-Nadu and may require a significant crustal input (Kerrich 1990).

Conclusions

The Attur shear zone is a classic example of regional carbonate alteration of the crust, occurring over hundreds of square kilometers and representing a significant addition of CO_2 to the crust of this region. Similar phenomena of varying age are recognized in many other continental regions, usually associated with major shear zones and sometimes associated with significant gold concentrations. These occurrences span a range of crustal depths and temperatures of alteration.
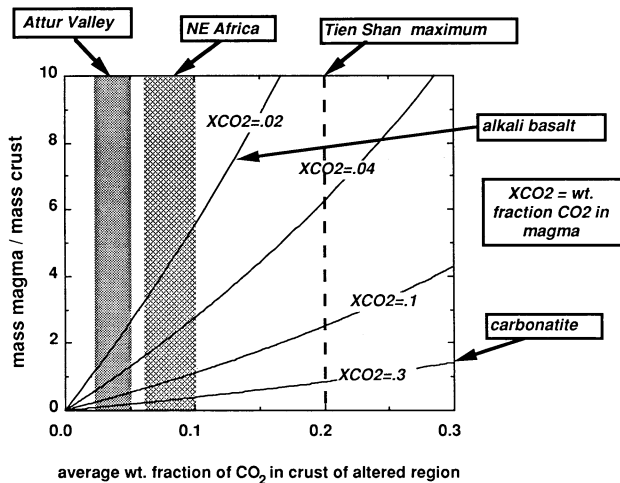
Our combined C, O, and Sr isotope study of

Figure 11. A simple mass balance calculation gives the ratio of magma to altered crust required to cause various amounts of carbonate alteration (measured as the final average weight fraction of CO_2 in the crust of an altered region). For very CO_2-rich magmas such as carbonatite, less than a $1:1$ ratio is required to cause even extreme alteration ($\leq 20\%$), as observed in the Tien Shan region (Baratov et al. 1984). The calculation assumes that all of the magmatic CO_2 is used to carbonate the crustal rocks of the altered region. The CO_2 could either be degassed from ascending magma (e.g., alkali basalt) or there could be direct reaction between magma and wall rock (e.g., carbonatite). See text for discussion.

these rocks suggests that carbonation occurred by growth of ankerite replacing mafic silicates and feldspar at moderately high temperatures of ~500°C with ankerite, quartz, and plagioclase closely approaching oxygen isotopic equilibrium. Subsequently, much lower temperature retrogression—possibly caused by limited influx of H_2O-rich fluids—caused alteration of ankerite to fine-grained calcite plus iron oxides. The C, O, and Sr isotopic composition of the ankerite is similar to that of carbonatites and alkali gabbros from elsewhere in Tamil-Nadu and is very different from the isotopic composition of metasedimentary marble or magnesite from the same region. We conclude that the ankerite and regional carbonate metasomatism are directly linked to CO_2-rich alkalic magmatism in the same area.

Such magmas could have introduced CO_2 at various crustal levels with differing results. At deep crustal levels and high temperatures (600–800°C) where carbonate minerals were not stable in the presence of quartz, the main consequences were destabilization of hydrous minerals (i.e., granulite formation—see also Frost et al. 1989). At mid-

crustal levels and intermediate temperatures (350–600°C) extensive, possibly pervasive carbonate alteration occurred, such as in the Attur shear zone. At shallower levels still, the main effects are likely to have been extensive carbonate veining, possibly coupled with ore deposition.

Magmatism in Tamil Nadu and granulite formation in southern India and Sri Lanka appear to have occurred during the Late Proterozoic (see Choudhary 1992, and references therein) and it is likely that the carbonate metasomatism in the Attur shear zone has a similar age. However, a similar style of regional carbonate alteration has been described by Chadwick et al. (1985) from the Chitradurga region further to the north, where the country rock and associated intrusions are Late Archean in age. This suggests that the Chitradurga occurrence is considerably older than the Attur shear zone locality, and that there may have been at least two distinct episodes of carbon alteration (just as we now know that there were two episodes of granulite formation—see Choudhary et al. [1992]) in southern India. This observation requires a substantial and long-lived source for CO_2-rich magmas beneath the southern Indian craton. An obvious source is carbonate-rich peridotite of the mantle lithosphere of this region. Such enriched lithosphere could have formed during much earlier (Early Archean?) subduction or large-scale underthrusting events and thereafter remained a potent source of CO_2-rich magma during subsequent melting events. The elevated ${}^{87}Sr/{}^{86}Sr$ ratios of Tamil Nadu carbonatites (0.705–0.706) attest to the long-term existence of enriched mantle material beneath this region.

Hypotheses invoking the influx of CO_2-rich fluids as a leading cause of granulite formation have been criticized in part due to the absence of a significant regional carbonate enrichment in granulite terranes. Carbonated shear zones provide direct evidence for such an influx, although at shallower levels than those of granulite formation. In India, our isotopic study has implicated CO_2-rich mantle-derived magmas as the primary source of the carbonate. Any continental region where CO_2-rich magmatism is prevalent (most notably intracratonic regions) has the potential to experience carbonate metasomatism of this type, the mineralogical consequences dependent upon the level within the crust (and hence the temperature) at which this occurs. Carbonated gneiss terranes provide evidence for major CO_2 outgassing events, with potentially important relevance to the geochemical cycle of carbon (Veizer et al. 1989).

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