Carbon and oxygen isotopic compositions of the regionally metamorphosed Archaean carbonate rocks of the Dharwar craton: A preliminary appraisal

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Carbon and oxygen isotopic data of the carbonate rocks from the greenschist to upper amphibolite facies metamorphosed Archaean Dharwar Supergroup show that, while the carbon isotopic compositions have remained unaltered, there is a 5‰ depletion in $\delta^{18}O$ ratios in response to increase in the grade of metamorphism. Exchange with metamorphic pore water at temperatures in excess of 400°C is considered to have caused this shift.

The primary carbon and oxygen isotope ratios are prone to alteration by post-depositional diagenetic and metamorphic processes. It is therefore necessary to screen the data for secondary alteration that may have affected the primary signatures before using isotopic ratios to infer biogeochemical processes and environments prevalent at the time of deposition. With this aim we have undertaken a study of the carbon and oxygen isotopic compositions in the carbonate rocks of different metamorphic grades of the Archaean supracrustal belts of the Dharwar craton.

The > 2.5 Ga Archaean supracrustal rocks of the Dharwar Supergroup[1] have been divided into the lower Bababudan and upper Chitradurga Groups. The Bababudan Group comprises metamorphosed quartz arenite–basalt–rhyolite–BIF association. This is unconformably overlain by the Chitradurga Group which has been subdivided into Vanivilas, Ingaldhal and Hiriyur formations. The Vanivilas Formation constituting the lower part of the Chitradurga Group is composed of quartz arenite–carbonate association with minor mafic sills intruding the sequence. These are overlain by pillow basalts, rhyolites and tuffs of the Ingaldhal Formation and greywackes of the Hiriyur Formation.

Approximately E–W trending isograds transect the NNW–SSE trending Dharwar supracrustal belts, such that greenschist facies rocks are exposed in the north, amphibolite in the middle and granulite facies rocks in the south[2,3] (Figure 1). In the amphibolite/granulite grade terrain, the supracrustal rocks have been considered by some workers[4,5] to belong to a sequence older than the Dharwar Supergroup—namely the Sargur Group. However, Srinivasan[6] and Naha *et al.*[7] have provided evidence to show that the supracrustal rocks of the Sargur Group

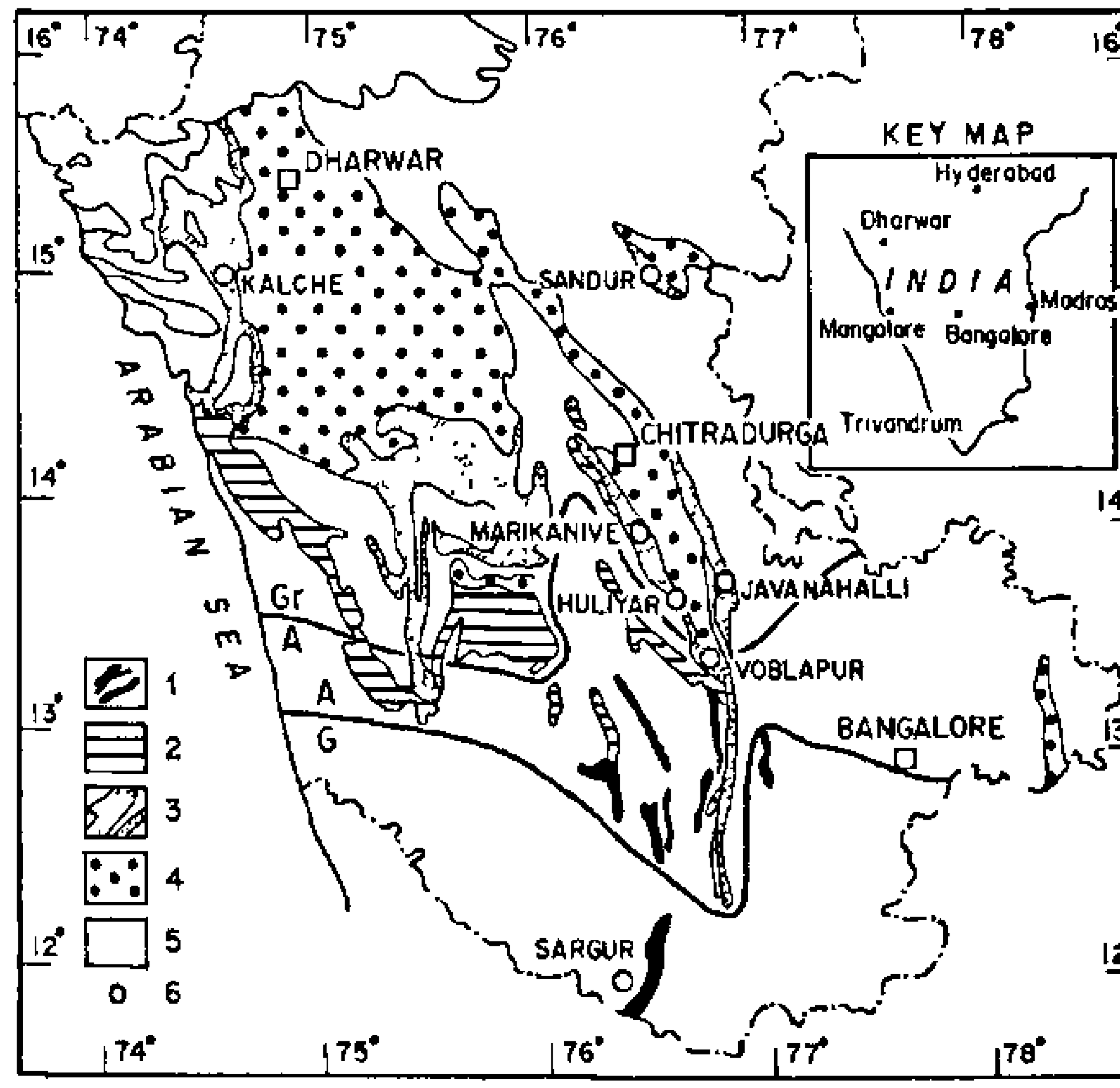

Figure 1. Geological map of the Dharwar craton showing sample locations **1**, Sargur supracrustal belts; **2**, Bababudan Group of Dharwar Supergroup, **3**, Vanivilas Formation of Chitradurga Group of Dharwar Supergroup, **4**, Ingaldhal volcanic and Hiriyur Formations of Dharwar Supergroup; **5**, Undifferentiated gneisses, granites and granulites; **6**, Sample locations. Heavy lines Gr/A and A/G are metamorphic isograds between greenschist-amphibolite and amphibolite-granulite respectively (after Raase *et al.*[3])

represent higher grade metamorphic equivalents of those of the Dharwar Supergroup, which view has been adopted in this paper. The classification of the supracrustals is summarized in Table 1. The carbonate rocks under study belong to the Vanivilas Formation in the greenschist to low grade amphibolite facies metamorphosed Dharwar supracrustal belts (low grade metamorphic terrain) and also by their stratigraphic equivalents in the high grade Sargur supracrustal belts (high grade metamorphic terrain).

Limestones are generally cement grey to greyish white in colour in the greenschist facies terrain. They are microcrystalline to coarse grained and are composed of calcite, dolomite, minor amounts of epidote, phlogopite, zoisite, quartz and rarely graphite. By contrast, in the amphibolite and granulite facies these are coarsely crystalline marbles usually greyish white to white in colour. They are composed of calcite, dolomite, ankerite, tremolitic amphibole, garnet, phlogopite and rarely forsterite. Dolomites of low grade metamorphic terrain are usually cherty in which beds or laminae of chert alternate with dolomitic layers. Dolomite as well as chert layers are usually microcrystalline. Despite deformation and low grade metamorphism that has affected these carbonate rocks, at places they show well-preserved domical as well as columnar forms of stromatolites[8]. Small quartz veins are seen traversing the cherty dolomite. Discrete metapelitic interlayers with minor graphite are sometimes

Table 1. Classification of Archaean supracrustal rocks of Dharwar Supergroup

	Low grade metamorphic terrain		High grade metamorphic terrain
Dharwar Supergroup >2.5 Ga[1]	Chitradurga Group	Hiriyur Formation	= Sargur Group[6,7]
		Ingaldhal Formation	
		Vanivilas Formation	
	Bababudan Group		

observed. The graphites are usually disseminated and 'amorphous'. Dolomite in the high grade metamorphic terrain also has interbands or layers of coarsely crystalline quartz which represent recrystallized cherts. The dolomite, however, is generally microcrystalline.

The carbonate rocks were digested in 100% orthophosphoric acid at 25°C for about 24 h in the case of limestones and about 72 h for dolomites following the method of McCrea[9]. The CO_2 evolved was analysed at the National Geophysical Research Institute, Hyderabad using a VG–903 mass spectrometer under computer control. NBS–18 and NBS–19 analysed during the course of this study gave $\delta^{13}C$ and $\delta^{18}O$ within ± 0.1‰ of the reported values of –5.08‰ (PDB), 7.2‰ (SMOW) and 1.93‰ (PDB), 28.65‰ (SMOW) respectively[10].

Thirty-two samples of carbonate rocks from sub-greenschist to greenschist facies terrain were analysed in this study. In addition to these new data, 26 analyses of carbonate rocks of upper greenschist to lower amphibolite transition zone from Huliyar to Dodguni area[11] and 10 amphibolite grade carbonates from Sargur region[12] have been used for understanding the relationship between C and O isotopic compositions with the grade of metamorphism. Samples collected near the contact with other schistose material and those with calcite-quartz veins were excluded from this study in order to avoid the local effects on isotopic abundances. Distribution of samples with reference to the metamorphic isograds is shown in Figure 1.

Mean and range of isotopic compositions of carbonates from greenschist to upper amphibolite facies are given in Table 2 and the isotopic ratios are plotted in Figure 2. For comparison, we have also included in Table 2 the data of carbonate rocks from Archaean greenstone belts of other parts of the world given in Veizer *et al.*[13].

Except in the case of ^{13}C compositions of a few dolomites of Marikanive and ^{18}O compositions of dolomites of Kalche and Sandur (which will be discussed separately), the mean $\delta^{13}C$ compositions for the carbonates from rest of the areas range between –1.4 and –0.1‰ PDB and are similar to those of the unmetamorphosed marine carbonate rocks reported from other parts of the world[13,14]. However, the $\delta^{18}O$ depletion in the carbonates on an average is about 5‰ from the greenschist to the upper amphibolite/granulite facies. It has been observed that in impure siliceous carbonates the effect of increasing metamorphism is progressive depletetion of ^{13}C and ^{18}O (refs. 15, 16). This is because impure siliceous carbonates start decomposing even at the greenschist facies, releasing CO_2. The isotopic equilibria between CO_3^{2-} and gaseous CO_2 favour the release of ^{13}C and ^{18}O along with the volatile CO_2 phase in the range of metamorphic temperatures[17,18]. Thus progressive devolatilization with increasing grade of metamorphism would result in a linear correlation between carbon and oxygen isotope compositions. However, it is known that nearly pure carbonate rocks free from siliceous components do not show depletion in ^{13}C and ^{18}O compositions under metamorphic conditions. Although the average wt% of carbonates in the rocks analysed by us is ~ 88% and that by Srikantappa and Valley[12] is ~ 76%, the plot between $\delta^{18}O$ and $\delta^{13}C$ shown in Figure 2, of these impure carbonate rocks does not show any evidence of decarbonation. In order to explain 5‰ depletion in $\delta^{18}O$, three processess have to be discussed: (i) differences in pre-metamorphic sedimentary compositions, (ii) freshwater interaction during diagenesis, and (iii) external fluid infiltration. Premetamorphic $\delta^{18}O$ heterogeneity is reflected if one finds a positive correlation between $\delta^{18}O$ versus wt% of carbonate. Such positive correlation results due to isotopic equilibration between variable proportions of high $\delta^{18}O$ marine carbonate and low $\delta^{18}O$ clastic material during metamorphism. Absence of correlation between $\delta^{18}O$ and wt% of carbonate observed by us and by Srikantappa and Valley[12] rules out the possibility of

Table 2. Carbon and oxygen isotopic data in per mil for the Archaean carbonate rocks of the Vamvilas Formation and its high grade metamorphic equivalents along with calculated $\delta^{18}O_{H_2O}$ of metamorphic water

Area, rock and number of samples	$\delta^{13}C$ (PDB) Range	Mean	$\delta^{18}O$ (SMOW) Range	Mean	Temp.* (°C)	$\delta^{18}O_{H_2O}$ (SMOW)
Kalche						
dolomite (n = 9)	−1.6 to 0.2	−0.5 ± 0.6	15.9 to 19.5	18.2 ± 1 06	68	−7.5 to −5
Marikanive						
limestone (n = 16)	−1.5 to −0 7	−1 1 ± 0.2	18.7 to 22 1	20 3 ± 1 0	450	17.9
dolomite (n = 7)	−4.9 to −0 1	−2 3 ± 1.7	13.2 to 19.4	17 0 ± 1.9	550	15.5
Huliyar†						
dolomite (n = 4)	−0.6 to 0	−0.2 ± 0.3	17.4 to 20.8	18.7 ± 1.3	500	16 6
Voblapur†						
dolomite (n = 10)	−0.7 to 0.3	−0 1 ± 0.3	14.6 to 21.5	17.4 ± 1.6	500	15.3
Javanahalli†						
limestone (n = 2)	−1.1 to 0	−0.55 ± 0.6	17.4 to 18.4	17.9 ± 0 5	550	16.7
Sargur†‡						
limestone (n = 14)	−1.6 to −0.2	−0.8 ± 0 4	11.4 to 17.6	15.3 ± 1 8	750	15.5
dolomite (n = 2)	−1.0 to −0.7	−0 85 ± 0.2	17.4 to 18.1	17.75 ± 0 4	750	15.5
Sandur†						
dolomite (n = 4)	−1.7 to −0.7	−1.4 ± 0.4	10.2 to 11.1	10.6 ± 0.4	–	–
Archaean greenstone belt[12]						
limestone (n = 103)	−2.0 to 2.5		6.1 to 23 6			
dolomite (n = 11)	−5 0 to 2.0		25.0 to 28.8			

*Based on references 3 and 20; †From reference 11; ‡From reference 12.

pre-metamorphic $\delta^{18}O$ heterogeneity due to differences in compositions of sedimentary protolith. ^{18}O depletion in some localized zone could result due to exchange with fresh water. However, such isotopic exchanges cannot be visualized for the regionally observed systematic depletion of $\delta^{18}O$ in the present case. It is therefore possible that the observed progressive depletion in ^{18}O is the result of exchange with fluids at metamorphic temperatures. However, the amount of aqueous fluids required to bring about isotopic equilibration at the time of metamorphism should be large. It has been observed in the granulite facies marble-schist contact at Naxos, Greece, that the fluids derived from pelitic rocks infiltrate not more than a meter of the carbonate body[19]. Hence carbonate rocks are impervious to extraneous fluids compared to pelites or other detrital sedimentary rocks, and the extraneous fluids tend to get channelized through the associated pelitic rocks in preference to carbonates. It is therefore difficult to assess whether the large amount of metamorphic fluids involved in isotopic exchange were intrinsic to the protoliths or there was some process operative to produce enhanced permeability for the extraneous fluids into the carbonate body under study. Calculation of $\delta^{18}O_{H_2O}$ of metamorphic fluids using average $\delta^{18}O$ values of carbonates, mineral equilibria temperatures[3,20] and temperature dependence of fractionation factors[21,22] show a range from 15.3 to 17.9‰ SMOW for the metamorphic waters. This agrees with the range of metamorphic $\delta^{18}O_{H_2O}$ given by Taylor[23].

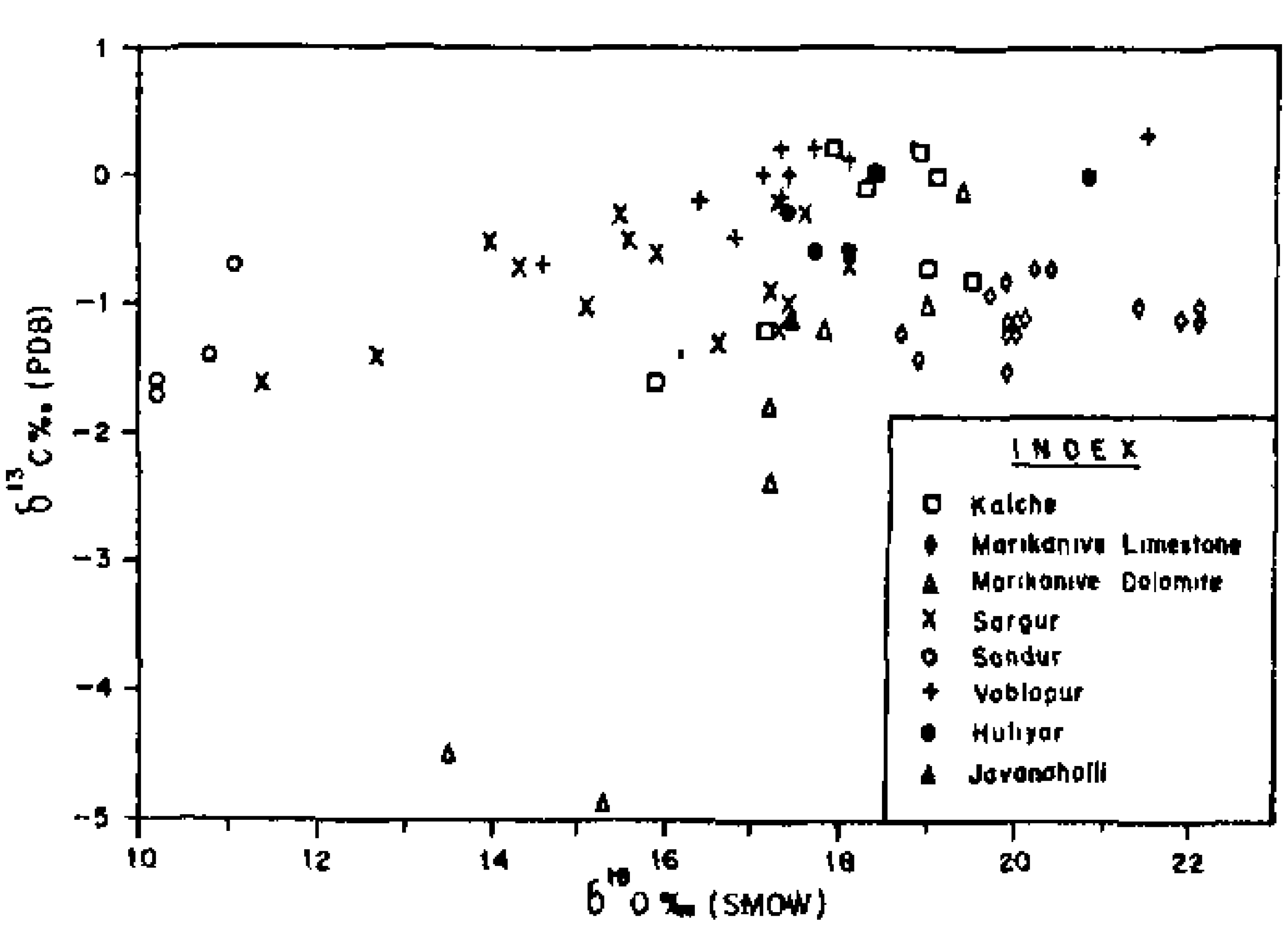

Figure 2. $\delta^{13}C$ [PDB] versus $\delta^{18}O$ [SMOW] for Archaean carbonate rocks of the Vamvilas Formation and its high grade metamorphic equivalents in the Dharwar craton.

The general relationship between the grade of metamorphism and C and O isotope compositions in the low to high grade supracrustal belts of the Dharwar craton discussed in the foregoing has some exceptions: (i) ^{13}C compositions of a few dolomites of Marikanive, (ii) ^{18}O compositions of dolomites from Sandur and Kalche. We explain these anomalous situations below.

The depleted ^{13}C ratios of a few dolomites from

Marikanive (see Figure 1) are from samples near the contact of dolomite with a mantled gneiss dome (Seeranakatte gneiss)[24]. Since cherty dolomites of this area are stromatolitic and contain minor amounts of disseminated graphite at places, it is possible that the low $\delta^{13}C$ values for these dolomites are due to exchange of light graphitic carbon with the carbonate carbon during metamorphism.

The Sandur carbonates are highly depleted in ^{18}O. Although these carbonates occur in the same Vanivilas Formation, they are in a terrain affected by higher grade of metamorphism associated with remobilization of Peninsular gneiss and emplacement of late to post-tectonic Closepet Granite[25,26]. The high temperature metamorphism characteristic of this belt may be responsible for the observed isotopic depletion.

Of all the carbonates, the dolomite near Kalche comes from the least metamorphosed area. If these carbonate rocks behaved as a closed system (no isotopic exchange) since their deposition, one would expect highest $\delta^{18}O$ values for these rocks. As these dolomites show lighter oxygen enrichment, we have analysed the $\delta^{18}O$ of 5 co-existing cherts. The average values of $\delta^{18}O$ of these 5 coexisting chert-dolomite pairs are 20.9‰ SMOW and 18.7‰ SMOW respectively. Calculation of temperature based on silica-dolomite fractionation[27,28] gives 68°C, which in our opinion represents diagenetic temperature (detailed results have been communicated elsewhere). The isotopic composition of water in which these carbonate rocks equilibrated has been estimated to be between –7.5 and –5‰ SMOW. Thus the dolomites of Kalche, although unmetamorphosed, got depleted in ^{18}O due to exchange with fresh water during diagenesis.

Carbon isotopic compositions of the carbonate protoliths have largely remained undisturbed during regional metamorphism in the Dharwar craton. This is consistent with the findings of Veizer *et al.*[13] for the carbonates of the Archaean greenstone belts in general. The oxygen isotopic ratios, however, have been modified to varying degrees due to pore water–rock interaction during metamorphism. Therefore the oxygen isotopic data should be used with caution in inferring the depositional environmental conditions in Archaean oceans of the Dharwar craton.

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