

Stable isotope evidence for ca. 2.7-Ga-old Archean cap carbonates from the Dharwar Supergroup, southern India

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Carbon isotope compositions of carbonate rocks from ~2.7-Ga-old Neoproterozoic Vanivilas Formation of the Dharwar Supergroup presented earlier by us are re-evaluated in this study, besides oxygen isotope compositions of a few silica–dolomite pairs. The purpose of such a revisit assumes significance in view of recent field evidences that suggest a glaciomarine origin for the matrix-supported conglomerate member, the Talya conglomerate, which underlies the carbonate rocks of the Vanivilas Formation. An in-depth analysis of carbon isotope data reveals preservation of their pristine character despite the rocks having been subjected to metamorphism to different degrees (from lower greenschist to lower amphibolite facies). The dolomitic member of Vanivilas Formation of Marikanive area is characterized by highly depleted $\delta^{13}\text{C}$ value (up to -5% VPDB) and merits as the Indian example of ca. 2.7-Ga-old cap carbonate. This inference is further supported by estimated low temperature of equilibration documented by a few silica–dolomite pairs from the Vanivilas Formation collected near Kalche area. These pairs show evidence for oxygen isotopic equilibrium at low temperatures ($\sim 0\text{--}20^\circ\text{C}$) with depleted water ($\delta^{18}\text{O} = -21\%$ to -15% VSMOW) of glacial origin. We propose that the mineral pairs were deposited during the deglaciation period when the ocean temperature was in its gradual restoration phase. The dolomite of Marikanive area is the first record of cap carbonates from the Indian subcontinent with Neoproterozoic antiquity.

Keywords: Carbonate rocks, carbon and oxygen isotopes, Dharwar Craton, glaciomarine deposit, Neoproterozoic.

THE Earth has evolved through time during its 4.6 Ga history. This evolutionary account is faithfully documented in its rock record. Of particular interest are the glacial events, which took place throughout the Earth's history starting from the Neoproterozoic and Paleoproterozoic through Neoproterozoic to Cenozoic. These events naturally indicate that during such periods, the global temperatures were not much different from those of today. Logically, these events captured global attention and

many researchers are actively engaged during the past few decades to evaluate the interconnection between glacial cycles of the geological past and the associated biogeochemical changes, as well as, the atmospheric evolution. Of all the glacial records, our interest in the present study lies in the late Archean glaciogenic records from India¹. Globally there are several instances during the Neoproterozoic and Paleoproterozoic, when glaciations took place. For example, the oldest known mid-latitude glaciation happened at ~ 2.9 Ga and was documented in the Pongola Supergroup². The Stillwater Complex in Montana, USA records the ~ 2.7 -Ga-old second glaciogenic unit. Here the presence of both diamictites and dropstones that are typical glacial features, were noted^{3,4}. Subsequently the period between 2.45 Ga and 2.22 Ga was characterized by a series of glacial events, the complete record of which is now preserved within the Huronian Supergroup of Canada^{5–7}. The entire Huronian sequence is penetrated and capped by the Nipissing diabase, which is 2.22 Ga old⁸.

While the geologists around the globe are in search for new glaciogenic deposits of Archean and Proterozoic antiquity, it is refreshing that in a recent study from the western Dharwar Craton of India, a ~ 2.7 -Ga-old Neoproterozoic glaciomarine deposit (formation) has been documented¹. This matrix-supported conglomerate member, known as the Talya conglomerate, is interbedded with mudstone and sandstone units. Further, this new finding is significant in view of the already reported ~ 2.7 -Ga-old glaciogenic unit³ from the Stillwater complex in Montana, and adds another location in the inventory of ~ 2.7 -Ga-old glaciation event. Although at this stage it is not possible to envisage the extent of glaciation during 2.7 Ga, the two widely separated glaciogenic records in USA and India may point to the fact that this event perhaps could be more extensive on a global scale than previously thought.

Following extensive glacial events, there are a number of other indirect proxies/evidences that point out Earth's intermittent glacial spells. For example, it has been observed that during the early Proterozoic and the Neoproterozoic, the climatic amelioration associated with postglacial, greenhouse-induced warming had led to the

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development of carbonate strata abruptly capping glacially laid sediments (also called cap carbonates) with highly negative $\delta^{13}\text{C}$ signatures^{9,10}, besides extensive deposition of banded iron and manganese formations particularly during the early Proterozoic as documented in the Hamersley and Transvaal Basins^{11,12} and iron formation of the late Proterozoic¹³. In view of the recent report of Talya glaciomarine formation¹ and occurrence of stratigraphically younger quartz arenite and carbonate sequences above this glaciomarine formation, it would be interesting to examine the carbon and oxygen isotope signatures of the chert-carbonate rock association. The purpose of the present paper is therefore to re-evaluate our earlier results^{14,15} on carbon and oxygen isotope compositions of chert-carbonate rocks of the Dharwar Craton and discuss their significance keeping in view the recent report of Talya glaciomarine formation¹. Such revisit assumes significance in view of our previously interpreted results, where we categorically stated that the carbon isotope compositions of carbonate rocks from the Archean Dharwar Supergroup have remained unaltered¹⁴. We therefore critically re-examine the carbon isotope records and attempt to build a first order carbon isotope chemostratigraphy based on the $\delta^{13}\text{C}$ compositions of carbonate rocks from the Archean Dharwar Supergroup. We also discuss the significance of these results in the light of behaviour of carbon cycle attendant with glacial events. This is followed by a brief discussion of the results obtained on the silica-dolomite pairs from the study area.

Geology and sample description

The >2.5-Ga-old Archean supracrustal rocks of the Dharwar Supergroup have been divided into the lower Bababudan and upper Chitradurga Groups¹⁶. 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 Hiriyyur formations. The basal part of Vanivilas Formation constituting the lowermost part of the Chitradurga Group is composed of polymictic conglomerate. The Talya and Kaldurga conglomerates of glaciogenic origin belong to this stratigraphic horizon¹. This is followed by a consanguineous association of quartz arenite and carbonate. The quartz arenites show trough- and herringbone-type cross-bedding as well as asymmetrical and symmetrical ripple marks. A bimodal, bipolar orientation of cross-bedding is characteristic, indicating accumulation of these sands in shallow shelf environments¹⁷. The quartz arenites are overlain by pelites and cherty dolomites. The latter display excellent development of discrete as well as colonial branched columnar and domical types of stromatolites^{18,19}. An intertidal to subtidal environment for the quartz arenite-carbonate association is inferred. Although

the lithological association indicates a very shallow water depositional environment, no evaporite minerals have been recognized in them. The stromatolitic cherty dolomites at places are manganese-rich and a facies gradation from cherty dolomite into manganese-rich iron formation is common. The manganese-rich cherts are composed of alternate layers of chert and manganese-rich iron bands. The cherty dolomites are followed by limestones, which are light grey in colour and carry micrite and sparry calcite. The carbonate sequence is capped by banded iron formation with minor mafic sills intruding the sequence. The quartz arenite-carbonate-BIF-BMF association overlying the polymictic conglomerate represents a change in sedimentary facies at different places. The Vanivilas Formation is overlain by pillow basalts, rhyolites, tuffs and sulphidic BIFs of the Ingaldhal Formation. The uppermost Hiriyyur Formation starts with greywacke and interbedded volcanic tuffs followed by deposition of BIFs. The 2600–2500 Ma granitoids invaded the Dharwar Supergroup²⁰. Table 1 presents the generalized stratigraphy of the western Dharwar Craton.

The carbonate rocks under study belong to the Vanivilas Formation and come from several locations (Figure 1). They are from metamorphosed Dharwar supracrustal belts that experienced lower greenschist to low-grade amphibolite facies metamorphism. Limestones are grey to greyish white in colour and they are microcrystalline to coarse-grained in the greenschist facies terrain. They are composed of calcite, dolomite, minor amounts of epidote, phlogopite, zoisite, quartz and rarely graphite. In the higher grade metamorphic regions representing the amphibolite facies, they are coarsely crystalline marbles, mostly 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 with alternate chert and dolomitic layers. Despite deformation and low grade metamorphism that has affected these carbonate rocks, at places they show well-preserved domical and columnar forms of stromatolites^{18,19}. At times small quartz veins of secondary origin are noted to traverse the cherty dolomites. Discrete metapelitic interlayers with minor graphite are also observed in some instances.

Results and inferences

Details pertaining to the methodologies adopted for treatment of carbonate and silicate (SiO_2 -fraction) samples for extraction of CO_2 and total O_2 respectively, were presented earlier by us^{14,15}. The isotope ratios of these samples were measured using a VG-903 stable isotope ratio mass spectrometer and the values are reported with reference to VPDB for $\delta^{13}\text{C}$ and VSMOW for $\delta^{18}\text{O}$. The carbon and oxygen isotope ratios of carbonate

Table 1. Generalized stratigraphy of the Western Dharwar Craton. Sources of geochronological data mentioned here are discussed in detail by Ojakangas *et al.*¹

2.6–2.5 Ga old gneisses and granitoids		
Dharwar Supergroup	Chitradurga Group	
	Hiriyur Fm.	BIF Greywacke, interbedded volcanic tuff Sulphidic BIF (predominantly)
	Ingaldhal Fm. (2.75–2.61 Ga)	Intermediate to felsic volcanic rocks and tuff Pillow basalt Stromatolitic cherty dolomite, limestone, shale
Bababudan Group	Vanivilas Fm.	BIF/BMF Polymictic conglomerate (e.g. the Talya and Kaldurga ¹)
	Disconformity	
	Mulaingiri Fm. (2.72 Ga)	BIF interbedded with felsic tuff near the base, graphitic schist
	Santaveri Fm.	Rhyodacite Basalt
	Allampur Fm.	Quartz arenite Gabbro, pyroxenite, basalt Quartz arenite interbedded with amygdaloidal basalt
Kalasapura Fm. (2.91 Ga)	Quartz arenite Quartz-pebble conglomerate	
Nonconformity		
Gneisses and granitoids with inclusions of older supra-crustal rocks (3.0–3.36 Ga, possibly > 3.5 Ga)		

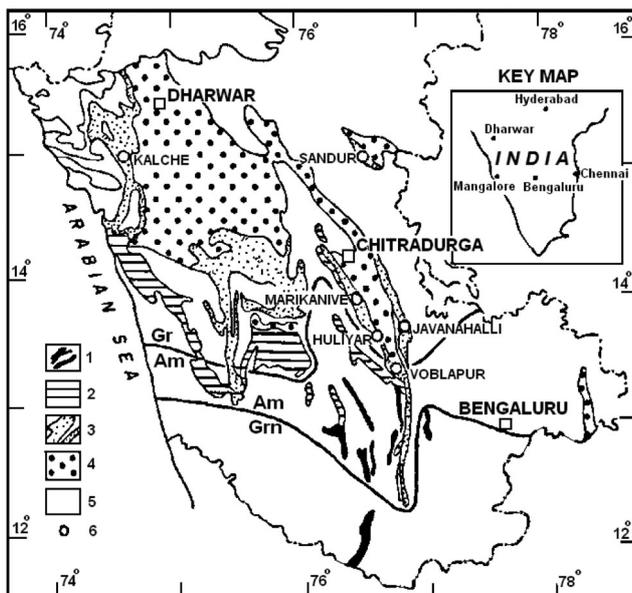


Figure 1. Geological map of the Archean Dharwar Craton showing sample locations. 1, High-grade Sargur metamorphic belts; 2, Bababudan Group platform volcano-sedimentary sequence; 3, Vanivilas Formation shelf sequence of Chitradurga Group; 4, Ingaldhal and Hiriyur formations deep water volcano-sedimentary sequence of Chitradurga Group; 5, Undifferentiated gneisses, granulites and granites; 6, Sample locations. Metamorphic isograds between greenschist–amphibolite (Gr/Am) and amphibolite–granulite (Am/Grn) transitions are also shown³⁵ by thick lines.

samples are presented in Figure 2. In order to get noteworthy insight, we also include in Figure 2 the carbon and oxygen isotope compositions from representative late Archean marine carbonate sequences that are available in the literature. All these carbonate sequences were deposited

during the late Archean to early Proterozoic period between ca. 2.7 and 2.5 Ga. Therefore in Figure 2 apart from our carbon and oxygen isotope data on carbonate rocks from the Dharwar Supergroup, the other data include: (i) carbonatic jaspilite of the Carajás Formation sampled by drill cores in the N4E iron deposit, state of Pará, Brazil²¹; (ii) late Archean carbonate rocks from the Transvaal Supergroup along the western margin of the Kaapvaal Craton, South Africa²² and other parts of Transvaal basin^{23,24}, and (iii) whole-rock limestone and dolomite from the Transvaal Supergroup, South Africa^{22–24}.

Based on analysis of global data²⁵, it has been argued in general that the ~2.9 to 2.5-Ga-old Archean carbonate rocks are characterized by ‘best preserved’ $\delta^{13}\text{C}$ values close to 0‰ (VPDB) and $\delta^{18}\text{O}$ values of ~25‰ (VSMOW). Notwithstanding the above, it has been further documented that for majority of Archean shelf dolostones, the carbon isotope compositions do not show much scatter compared to the pristine value of 0‰, whereas their oxygen isotopic compositions may be characterized by wide variations ranging from best preserved value of ~25‰ to values as low as 8‰ (VSMOW). The lower values of $\delta^{18}\text{O}$ are in accordance with the geological criteria of post-depositional alteration processes, during which dissolution and reprecipitation process makes the successor carbonate phase depleted in ^{18}O owing to moderately high temperature (150–300°C) isotopic exchange and/or large-scale interaction with isotopically light meteoric water²⁵. Figure 2 therefore brings out the fact that the global general scenario observed for the carbon and oxygen isotope compositions of carbonate rocks is valid for the intertidal to subtidal carbonate rocks of the Dharwar Supergroup as well. However, there are some

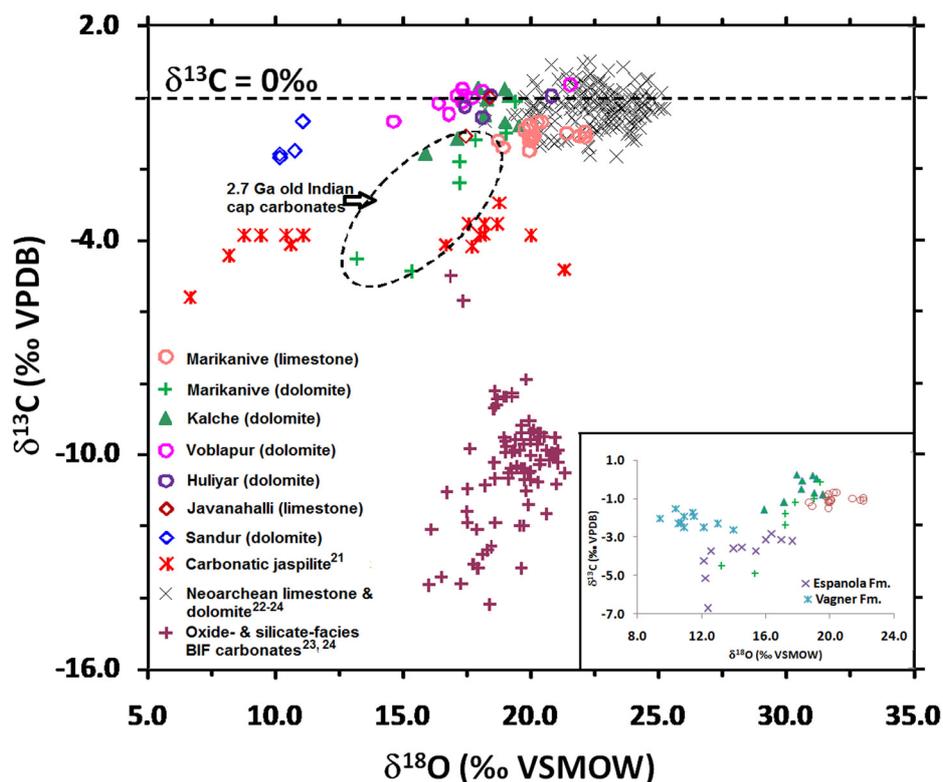


Figure 2. $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ plot of Archean carbonate rocks. Stable isotope data from different locations of the Vanivilas Formation of Chitradurga Group are shown. For better understanding of the cause and effect relationship, representative global data from specific depositional makeup (e.g. carbonatic jaspilite, Carajás Formation, Brazil²¹, Neoproterozoic limestones and dolomites from the Transvaal basin^{22–24}, as well as oxide- and silicate-facies BIF carbonates^{23,24}) are also plotted. The broken horizontal line corresponding to $\delta^{13}\text{C} = 0\text{‰}$ represents the best-preserved average Neoproterozoic seawater isotopic composition²⁵. The carbonate rocks of the Vanivilas Formation sampled from Marikanive and Kalche areas of the Dharwar craton (shown within ellipse) are moderate-to-highly depleted in ^{13}C . Inset shows comparison of stable isotope values of carbonate rocks from these two locations with those of ca. 2.4-Ga-old cap carbonates²⁷ from the Espanola Formation (Huronian Supergroup, Ontario, Canada) and Vagner Formation (Snowy Pass Supergroup, Wyoming, USA). Based on such excellent agreement, the carbonate samples from Marikanive and Kalche areas are inferred to represent ~2.7-Ga-old cap carbonates from India (see text for discussion).

exceptions from the above-mentioned general global scenario. Therefore, these unusual circumstances are discussed below.

It can be observed from Figure 2 that the $\delta^{13}\text{C}$ values pertaining to many carbonate horizons across the globe are characterized by negative values that range up to -15‰ . There are several models that have been discussed in the literature to account for such depletion in the $\delta^{13}\text{C}$ values. First, based on deeper, intermediate and shallower carbonates of the Transvaal Supergroup with characteristic $\delta^{13}\text{C}$ signatures, it has been argued that the basinal waters might have been stratified with respect to carbon isotopic composition in response to hydrothermal fluid input²³. Under such condition, the deeper basinal waters would be characterized by lighter carbon isotope composition close to the mantle $\delta^{13}\text{C}$ value of -5‰ compared to the surface waters where normal $\delta^{13}\text{C}$ value of 0‰ is retained²³. The second model²⁶ based on combined Si, Fe and C isotope signatures of carbonates from the Trans-

vaal and the Hamersley successions argue that the negative $\delta^{13}\text{C}$ value is a reflection of incorporation of carbon within carbonate phases that is predominately released from degradation of organic matter during diagenesis. This process is also accompanied by Fe(III) reduction and is documented in Fe isotope signature as well²⁶. Therefore either ocean stratification in terms low $\delta^{13}\text{C}$ or derivation of some dissolved inorganic carbon from remineralized organic debris or both can give rise to ^{13}C depleted carbonates. In addition to the above two models, there is a third model, which can account for highly ^{13}C depleted character of carbonates. Such carbonate horizons (also called cap carbonates) have been documented globally and are characteristic of both Neoproterozoic snowball earth event¹⁰ as well as Palaeoproterozoic glacial event²⁷. According to this third model, the observed negative shift in $\delta^{13}\text{C}$ compositions associated with cap carbonates of glacial origin is attributed to abrupt decrease in biological productivity during the glacial events. With

the onset of deglaciation, biological productivity gradually increases so that the carbon isotope ratios of seawater is restored slowly and carbonates precipitated in the oceans ultimately return to normal values¹⁰. The carbonate rocks plotted in Figure 2 that are characterized by depleted $\delta^{13}\text{C}$ compositions, are therefore discussed in the light of the above three models.

The drill core samples from Carajás Formation²¹ exhibiting negative $\delta^{13}\text{C}$ values of around -3% to -6% and the ~ 2.5 -Ga-old carbonates from the Transvaal Supergroup of South Africa^{22–24} do not document any evidence of glaciations. Therefore out of the three models discussed above, the carbonate horizons from the Carajás Formation and the Transvaal Supergroup might have resulted in accordance with either of the first two models or a combination of both. Similar negative $\delta^{13}\text{C}$ values were also recorded in the ~ 2.7 -Ga-old carbonate facies associated with the Temagami banded iron formation in Canada²⁸.

It is important to stress at this point that in contrast to Fe carbonates associated with BIF, the isotopic composition of other sedimentary carbonates such as limestone and dolomite mostly constitute a record of seawater isotopic composition close to $\delta^{13}\text{C}$ value of 0% (ref. 25). In this context it may be noted that the carbonate rocks of the Dharwar Supergroup presented in this study correspond to compositions that are either calcitic or dolomitic in nature. Hence they are expected to yield a $\delta^{13}\text{C}$ composition corresponding to the global average value close to 0% . While majority of samples from the Dharwar Supergroup plotted in Figure 2 do adhere to such a general scenario, there are a few dolomitic carbonate samples from Marikanive and Kalche areas that are characterized by moderate-to-high negative $\delta^{13}\text{C}$ values (see inset of Figure 2) which needs explanation.

Of all the carbonate samples of the Vanivilas Formation, the Marikanive dolomites (Figures 1 and 2) represent the lowermost carbonate horizon that stratigraphically overlies the Talya conglomerates and hence perhaps could merit as cap carbonate with depleted $\delta^{13}\text{C}$ signatures. This inference is further strengthened when their $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values are compared with the corresponding values of cap carbonates from ca. 2.4-Ga-old Espanola Formation constituting the Huronian Supergroup, Ontario, Canada²⁷ and Vagner Formation of the Snowy Pass Supergroup, Wyoming, USA²⁷ (see inset of Figure 2). Besides this, it is worthwhile to point out that the dolomites near Kalche area come from the least metamorphosed region. Therefore if these carbonate rocks behaved as a closed system (i.e. no isotopic exchange) since their deposition, one would expect the highest $\delta^{18}\text{O}$ values for these rocks. However, this is not the case as evident from Figure 2. On the other hand, if their $\delta^{18}\text{O}$ values shown in the inset of Figure 2 are compared with the cap carbonates of the Espanola and Vagner formations²⁷, they are enriched in ^{18}O compositions. In the following, we therefore try to extract additional information,

although we are aware that their validity may be questioned by some researchers. This is because the general robustness documented for the carbon isotopic composition of carbonate rocks of the Archean and subsequent younger periods is not always reflected in the oxygen isotope compositions. The main reason for this has been attributed to various secondary alteration processes, where the pristine oxygen isotopic records are obliterated owing to fluid–rock interactions. Therefore strict criteria are laid down and they need to be satisfied. For example, identification of different Marine Isotope Stages (MIS) that are primarily based on oxygen isotope records of the pristine carbonate phases, are dependent on fulfilling the criteria of absence of any secondary alterations²⁹.

Notwithstanding the above, the oxygen isotope compositions of coexisting mineral phases can yield the temperature of equilibration. If there are N number of minerals that equilibrated oxygen in a reservoir, then there will be $N - 1$ pairs that can be used to obtain the temperature of equilibration. More importantly, the knowledge of oxygen isotopic composition of exchanging fluid is not essential. The $\delta^{18}\text{O}$ values of coexisting silica–dolomite pairs representing two samples from Kalche area of the Vanivilas Formation are used to estimate the corresponding temperature of equilibration (Figure 3). Assuming that each pair of silica and dolomite in these samples corresponds to an equilibrium assemblage, their $\delta^{18}\text{O}$ values can be used to calculate the equilibration temperature from the equation $\Delta = 0.74 \times 10^6 T^{-2} - 4.24$. The formulation of this temperature-dependent silica–dolomite fractionation equation is based on experimentally derived $\text{SiO}_2\text{--H}_2\text{O}$ (ref. 30) and protodolomite– H_2O (ref. 31) fractionation equations at low temperatures. The estimated

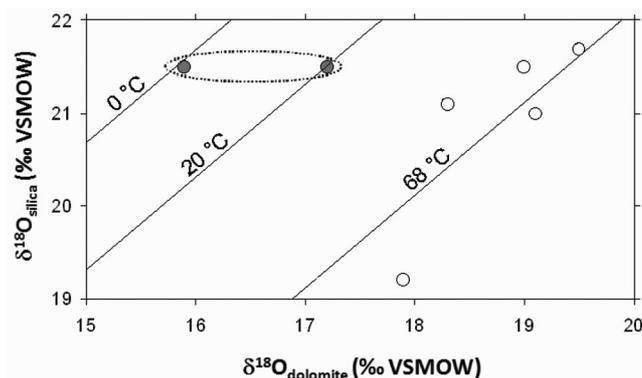


Figure 3. $\delta^{18}\text{O}$ (dolomite) versus $\delta^{18}\text{O}$ (silica) plot for chert–dolomite pairs. These samples are representative of the Vanivilas Formation sampled from Kalche area (see also Figure 1). Isotherms corresponding to $T = 0, 20$ and 68°C are shown. Majority of sample pairs (five) plot close to the 68°C isotherm, indicating that oxygen isotopic equilibrium was attained during low temperature diagenesis¹⁵. However, two sample pairs (filled symbol) that were collected ~ 0.5 km away from the rest five (shown within ellipse) are characterized by low temperature oxygen isotope equilibration in the temperature range of about $0\text{--}20^\circ\text{C}$. These sample pairs are inferred to have been deposited in ice-melt seawater during the deglaciation period (see text).

equilibration temperatures for the two samples from Kalche area are low and range from 1°C to 21°C, indicating that the carbonate rocks of the Kalche area were perhaps deposited during deglaciation event during which slow and gradual restoration to normal seawater temperature with attendant enrichment of ^{13}C composition towards 0‰ had occurred (Figure 3). It may be worthwhile to mention that based on the maximum $\delta^{18}\text{O}$ value documented within the texturally preserved (oolitic) cryptocrystalline silica from the Nagargali area within the Dharwar–Shimoga supracrustal belt, the ocean temperature during the Neoproterozoic period was estimated to be ~40°C (ref. 15). Therefore the inference drawn above for the dolomites of Kalche area that they were deposited during the deglaciation period seems to be valid.

Furthermore, although the estimated temperature for silica–dolomite association from Kalche area calculated above is independent of $\delta^{18}\text{O}$ of water from which these minerals precipitated, it may be insightful to use these temperatures to evaluate the $\delta^{18}\text{O}$ values of water in which the minerals under study equilibrated oxygen employing the $\text{SiO}_2\text{--H}_2\text{O}$ (ref. 30) and protodolomite– H_2O (ref. 31) fractionation equations. The significance of such an exercise can be appreciated as it yields the range of isotopic compositions of water with which the silica–dolomite pairs of Kalche area equilibrated oxygen to be highly negative in $\delta^{18}\text{O}$ (ranging from –21‰ to –15‰ VSMOW) and are comparable to modern high-latitude precipitation and Holocene snows on Huascarán³². Therefore the oxygen isotope data of Precambrian carbonates might perhaps yield additional insight into the depositional environment if they are evaluated taking into consideration the geological makeup of the area of study (e.g. glaciomarine deposit in this particular case). It is also pertinent to mention that five other samples that were collected from another location within the Kalche area yielded a different mean value of temperature close to ~68°C, indicating that the oxygen isotope records were preserved only at specific sites (Figure 3). Using fluid-buffered open system exchange model³³, it is inferred that post-depositional diagenetic recrystallization took place at about 68°C for these samples (Figure 3).

Based on the isotopic data presented in this study together with similar data elsewhere in the globe along with geological makeup of glaciogenic origin of the Talya and Kaldurga conglomerates¹, and documented presence of manganese-rich iron bands in the study area, we conclude the following:

- (i) the Marikanive dolomites with negative $\delta^{13}\text{C}$ compositions might represent the first Indian example of 2.7-Ga-old cap carbonates;
- (ii) the silica–dolomite pairs from Kalche area yielding low temperature of equilibration (1°C to 21°C) indicate that these chemical precipitates equilibrated oxygen with glacial waters and seem to have been deposited during the deglaciation period;
- (iii) the carbonate rocks of the Vanivilas Formation therefore represent the oldest record of glaciogenic carbonates from the Dharwar Supergroup with late Archean antiquity;
- (iv) manganese-rich iron bands observed within the Vanivilas Formation are perhaps one of the oldest records when anaerobic ecosystems prevailed globally in general;
- (v) the 2.7-Ga-old glacial event recorded in the Dharwar Supergroup might have restrained biological productivity drastically at the initial stage, but subsequent melting of the oceanic ice perhaps led to a cyanobacterial bloom, thereby creating a local oxygen-rich euphotic zone, ultimately leading to the oxidative precipitation of iron and manganese in the area, and finally
- (vi) the above inference is in conformity with the conclusion that oxygenic photosynthesis, originating at ca. 2.72 Ga, eventually triggered the rise of aerobic ecosystems³⁴.

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