An Isotopic Study in Petroliferous Basin to understand Palaeotemperature Fluctuation & Distinguished of Geological Boundaries in the Study Areas. (A case study in Karewa Basin, North India)

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ABSTRACT

The study area is a petroliferous basin in Kashmir Valley adjacent to commercial oil fields in Pakistan. The pattern of isotopic fractionation and their positive $(+)\delta^{13}C$ values indicate an oceanic event, corres-ponding with relatively high sea level stand plus relatively high palaeotemperature which may also corresponding to increased carbon content in marine sediment of the basin. Increase in negative $\delta^{18}O$ with that of positive $\delta^{13}C$ may reflect either increasing temperature or the influx of meteoric water and $\delta 18O$ maybe related to palaeohydrology of the basin and evolution of digenetic Solution.

Interpretation of the progressive negative trend of δ^{18} O in the area has led the author to consider this as evidence for increasing temperatures of precipitation of new calcite or dolomite, change in δ^{18} O values have been related to palaeotemperature & palaeo-salinity fluctuation in ocean surface water. After uplift other possibility for further recrystallisation occur in presence of isotopic ally light water may cause appreciable shift in δ^{18} O values in the system such a shift observed in the present data may be related to the depositional history, basinal condition, sea level changes etc. On regional scale in the broader context of Permian-Triassic geological setting.

Keywords: Isotope $\delta 13C$ & $\delta 18O$, Palaeotemperatue, discriminate geological boundaries, Petroliferous Basin, Karewa Basin, India

Introduction

The Karewa basin is one of petroliferous basin in India (Bhandari, 1983) Fig.1 based on their analogy with other world petroliferous, productive basins which is situated in Kashmir valley and adjacent to the commercial oil fields in Pakistan at Balks field (Paleozoic), Surijan & Dhulian fields (Jurassic) and Pirkoh & Dhoduk fields in the Cretaceous sediments.Carbon, Oxygen, Magnesium &Calcium primarily constitute the pure end member of carbonates. Initially starting with the distribution pattern of carbon isotopes in nature (Craig, 1953), valuable information have been obtained at least 13C and 18O, stable isotopes of carbon and oxygen which occur in relatively high concentration in carbonates. Such studies including abundance data, pattern of isotopic fractionation and their significance in understanding genetic factors, palaeotemperature, palaeo-geographic situation of the studied rocks etc. have

been carried out by a number of researchers (Urey, 1947;Craig,1953,1963;Epstein et al.,1953;Epstein,1950;Clayston & Epstein, 1958; Degens, 1969 and others), hardly any study of this type has been carried out on stratigraphically- controlled samples of rocks in India and the data base of this character does not exist. it is in this context that the author has a tempted to obtain some valuable data on 13C and 18O contents in the analyzed samples, primarily of carbonates, of the studied area. These isotopes are determined by N-s, primarily of carbonates, of the stu O out on stratigraphically- controlled samples of rocks i eir type Mass spectrometer for ratio estimation (Ratio Mass Spectrometry). The ratio measured is that of heavier (less abundance) isotope to the lighter (more abundance) isotope e.g. 13 C / 12C , 18 O / 16O etc.A compromise between the large mass difference and relative abundance dictates the choice of the heavier isotope for elements which consist of more than two isotopes. Differences in the estimated ratios between the sample and standard are a function of differencing isotopic abundances. The differences are conventionally denoted as delta (δ) deviation.

METHODOLOGY

The whole-rock samples selected for the analysis represent different litologies (carbonates, calcareous shale's, calc- arenite) from the study area and they were homogeneous, which have been investigated in detail using diverse methods during the present study. The 14 whole rock samples consisting of carbonates, calcareous shale and shale belonging to carboniferous and Triassic sequence of the study area were analyzed due to their predominantly fine grained / micritic nature for $\delta 13C \& \delta 180$ values at isotope laboratory KDMIPE (ONGC), Dehra dun, India using the ratio mass spectrometer (VG) 903E and following the procedure standardized in the laboratory with analytical precision, PDB I0. 2‰.

In order to facilitate inter- laboratory comparisons of similar isotopes data the comparative analysis is done against standards. The standards used are Standard Mean Ocean Water (SMOW) for hydrogen & oxygen and the Chicago PDBI standard (Cretaceous belemnite from the peedee Formation, South Carolina) for carbon (Craig, 1953, 1957). Delta values for these standards are zero per mil by definition δ 13.C and δ 18O are defined In terms of 13C / 12C and 18O / 16O ratios respectively. Differences in the estimated ratios between the sample and standard are a function of differing isotopic abundances. The differences are conventionally denoted as delta (δ) deviations of the heavier isotope. 13C & 18O in the sample relative to the standard expressed in the unit per mil (parts per thousand, %) values. SMOW has a δ 180 value of -30.8 on the PDB scale and PDB standard is normally used for determination of carbon and oxygen isotopes in case of carbonate rocks & minerals. Isotope of ratio of C and O in the carbonates are determined by the method described by (Magaritz and Kafri 1981) and the measurements are done relative to PDB with reproducibility on replicated samples being more than 0.10 % for δ 13C. If for example, δ 13C of substance is + 1.5 % it is enriched in 13C by 13C relative to the standard. The equation for measurement of stable carbon and oxygen isotopes are:

13C / 12C (sample) - 13C / 12C (standard)

* 10

- *10

 $\delta 13C$ (sample) (‰) =

13C / 12C (standard)

and

180 / 160 (sample) - 180 / 160 (standard)

 $\delta 180$ (sample) (‰) =

180 / 160 (standard)

RESULTS

The analyzed data of ¹³C and ¹⁸O obtained for the study area content as δ values (vs. PDB), show that all the analyzed samples of carboniferous carbonates (12, 13, 15, 25, 26, 29, 30, 35), calc. arenite (14) and calcareous shale (23) exhibits a range in δ^{18} O values from -7.71 ‰ to -19.82 ‰. The observed variation in δ^{18} O values is of the order of about 12‰ in the carboniferous rocks while in the Triassic carbonates (1,2,4) and calcareous shale (8) it is about 4 ‰. The range in values of δ^{13} C in carboniferous rocks is between + 0.6 ‰ and -6.93 ‰ where as in Triassic carbonates and calcareous shale it varies from - 0.10 ‰ to + 2.25 ‰.

The analyzed data have been plotted on the diagrams (Fig.2) & (Fig. 3) after Bathurst (1983). In this diagram carboniferous samples (25, 26, 29, 30) fall in the field of carboniferous cement, sample No. 15 in the field of late Devonian Spar, while the Triassic carbonate samples occupy the field for average marine limestone. The values ave been determined with respect to PDB standard and all correction factors (Craig, 1957) have been applied to all carbon and oxygen isotopes in carbonate minerals and rocks. The natural variation of oxygen and carbon isotopes is reported as ${}^{18}\text{O}/{}^{16}\text{O}$ and ${}^{13}\text{C}/{}^{12}\text{C}$ ratios or $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ which is the par mil (%) deviation in the radio relative to standards like SMOW or PDB the delta values are reported as positive (+) indicating enrichment in heavy isotope like ¹⁸O or ¹³C or negative (-) signifying depletion of these heavy isotopes or enrichment of lighter isotope ¹⁶O or ¹²C in the analyzed samples, relative increases in ${}^{13}C/{}^{12}C$ or ${}^{18}O/{}^{16}O$ (higher values of $\delta^{13}C$ or δ^{18} O) are conventionally referred in these ratios (decreased values of δ^{13} C or δ^{18} O) are termed on " more negative "or" light event" particularly comparative studies of sequence of rocks. The analyzed data (range) are +2.13 % to $-0.10\% \delta^{13}$ C (Triassic carbonates), +2.25 % δ¹³C (Triassic Calc. shale), +0.61 % to +2.87 % δ¹³C (Carboniferous carbonates), -6.93 ‰ δ^{13} C (Carboniferous Calc. arenite), and -6.49 ‰ δ^{13} C in Calc. shale, indicating their marine nature . This is further confirmed by the δ^{18} O data , from the study area, which are -9.99 ‰ to 13.53 ‰ δ^{18} O (Triassic carbonates), -14.18 ‰ δ^{18} O (Triassic calc. shale), -7.71 ‰ to - 17.12 ‰ δ^{18} O (Carboniferous carbonates), -9.76 ‰ $\delta^{18}O$ (Carboniferous calc. arenite) and -19.82 δ^{18} O in Carboniferous calc. shale samples are presented in table.2.

CONCLUSION

The oxygen isotope data show more variation than 13C indicating the relatively more alteration of former during diagenesis. The ratio oxygen Baud et al., (1989) are of the view that samples exhibiting low value of $\delta 13C$ may be dedolomitised in pore water / oxygen in rock, in extremely porous carbonate ooze (initially), is high while an inverse relationship may be envisaged for carbon. In addition to this, temperature fractionation can play an important role during burial –digenetic cementation Friedman and O Neil (1977), Keith and Weber (1964) have reported $\delta 18O$ values of -4 % to >-10‰ in Triassic and between -7 % to 4.5 % in carboniferous marine carbonates as against the value of -3 % to -5.8 % in non marine carbonates of Triassic and from -2 % to -8 % in carboniferous carbonates. The analyzed data detailed in the present study fall within the above-mentioned range of $\delta 18O$ and may be considered to support the preceding observations Sabetamiri (1995).

The decreasing δ 18O value with age in marine carbonates Keith and Weber (1964) was firstly interpreted as due to digenetic alteration of older material but presently this is not considered to be entirely correct Popp et al., 1986; Lehmann and Walker, 1989; Railsback and Bruce., 1990). Two formulations have been advanced (Railback and Bruce., 1990) to explain this trend viz, 1) ancient oceans were depleted in 180 relative to Modern Ocean and 2) ancient oceans were warmer than modern oceans, resulting in reduced fractionation between sedimentary minerals and sea water. Increase in negative 180 with that of positive $\delta 13C$ may reflect either increasing temperature or the influx of meteoric water and $\delta 18O$ may be related to palaeo-hydrology of the basin and evolution of diagenetic solution. 18O is more susceptible to diagenetic alteration than 13C. This is because of the fact that the oxygen system is dominated by the oxygen of the altering water; while the carbon system is dominated by the carbon of the carbonate rock as has been shown in numerous case studies (e.g. Magaritz, 1975). Based on model calculation assuming typical isotope parameter, it has been observed that even though oxygen isotope ratios, carbon isotope ratios were not appreciable decreased until the water /rock ratio was raised to 1000 or more. Magaritz (1989) did not observe over all correlation shifts of $\delta 13C$ with $\delta 18O$, suggesting that even if $\delta 18O$ was altered by diagenesis, $\delta 13C$ was not similarly effected. In the analyzed rocks of the study area, no appreciable shift in $\delta 13C$ values in carbonates vs. $\delta 18O$ has been witnessed (Fig. 2) and a reverse relationship i.e. more +ve $\delta 13C$ with -ve $\delta 18O$ in carboniferous carbonates is noticed . In the case of calcareous shale and calc. arenite both $\delta 13C$ and $\delta 18O$ are negative. The role of isotopic composition of sea water related to differing sea level stand may be of significance in this context. The isotopic trend observed in the data of the study area is comparable to that obtained from the equivalent components in the Phanerozoic limestone (Walls et al ., 1979). These researchers observed that dolomite spar with more negative 18O value indicates precipitation at higher temperature during burial. The decrease in $\delta 13C$ as has been observed in some Triassic and Carboniferous carbonates of the area under investigation (Fig .2, Table.2) indicates a contribution of 12C from diagenetic decomposition of organic matter. Interpretation of the progressive negative trend of 18O (e.g. in fig. 3) has led researcher to consider this evidence for increasing temperature of precipitation of the new calcite (or dolomite). Change in $\delta 180$ value has been related to palaeo-temperature and paleosalinity fluctuation in ocean surface water (Savin, 1977). The carbon isotope composition of marine carbonate rocks shows large variation through the

geological record (veizer et al., 1990). One such significant variation has been the enrichment in $\delta 13C$ during Late palaeozoic time (Holser et al., 1986; Popp et al., 1986) which marks an outstanding unusual event matched only in the Late Precambrian (Knoll et al ., 1986; Magaritz et al ., 1986). Very detailed investigations have shown that the carbon isotope composition of marine carbonates during the Pennsylvanian and Permian fluctuated between low and high values of $\delta 13C$. This may be related to the low and high stands of sea level .Holser et al ., (1986) observed that the last of these " high" was detected in the Western U.S.A., North western Europe and Alps .The end of this " high " was evidently a major geochemical event and a fall of more than -6 % $\delta 13C$ has been noted , which is much more than -3 ‰ observed at the Cretaceous – Tertiary boundary (Perch –Nielsen et al., 1982; Zachos and Arthur, 1986). In the studied samples from Kashmir valley, a wide fluctuation in $\delta 13C$ data is observed in Carboniferous and Triassic samples. In the Carboniferous, the high value is +2.81 ‰ while the fall is of the order of -6.93 ‰ $\delta 13C$. As against this, the fall is quite low i.e. -.94 % and the high +2.25 % δ 13C. The data obtained during the present investigation support the above mentioned observations by Holser et al., (1986) and others. On a tentative basis, it was considered to be associated, firstly with the Permian / Triassic boundary itself (Holser and Magaritz, 1985; Holser et al., 1986). However, lately the data has been found to reveal that final drop was gradual across the statigraphic Permian /Triassic (P /Tr) boundary, reaching a minimum in earliest Triassic(Magaritz et al., 1988) The data presented in this work reveal such a phenomenon (Sabetamiri 1995).

On a global scale, one of the significant transformations in Earth, s history took place during the Permian –Triassic time, i.e., a major tectonic cycle ended with the creation of Pangaea (Smith et al., (1981), a major period of glaciation's ended in mid-Permian (Hambery and Harland, 1981; Caputo and Crowell., 1985); and fauna changed from Palaeozoic fauna to Modern fauna (Sepkoski, 1981). All these phenomena should have enough relationship with the above mentioned fluctuations in $\delta 13C$ values. The data accruing from the investigations by the author could be correlated and explained by the observations made by Baud et al., (1989) based on study of a number of Late Permian and early Triassic sections of the Tethyan region.(including Zanskar, Ladakh) on the Gondwana margin.

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