Strontium Isotope Stratigraphy of Cochin Formation in Kerala Konkan Offshore: Implications on Mesozoic Hydrocarbon Exploration

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Summary

In this paper, we demonstrate the use of Strontium Isotope Stratigraphy (SIS) technique on the limestone sequence of Cochin Equivalent Formation encountered in between two basaltic horizons as an intertrappean, in the drilled well KKMZ-E-A in Kerala Konkan Offshore Basin, as a robust tool for absolute age dating of marine carbonates. The study establishes the high-resolution chronostratigraphy of studied limestone sequence of Cochin Equivalent Formation and attempts to resolve their age constraints in relation to the basaltic basement encountered in the studied well, as well in other wells of the Kerala Konkan Basin. The study constrains the total depositional age of the Cochin equivalent limestone sequence to be between 59.7 Ma and 61.7 Ma, which is agreeable and correlatable to reported ages of the basaltic basement in Kerala Konkan Basin. This model of depositional ages holds viable for the total timing of deposition for the Cochin Equivalent Formation vis a vis the emplacement history and petrogenetic similarity of upper and lower basalt units in the studied well, and in the other wells of Kerala Konkan Offshore Basin.

Introduction

The present-day configuration of Western Continental Margin of India (WCMI) is closely related to the tectonic history of the Indian subcontinent, its break up during continental rifting, magmatic and sedimentary history, northward movement of India and finally collision with the Eurasian plate. The margin is characterized by extensional tectonics resulted during early stage of passive margin formation. The WCMI evolved due to breakup of India from (i) Madagascar during mid-Cretaceous producing non-volcanic continental margin in the south, and (ii) Seychelles micro-continent during the early-Tertiary producing volcanic continental margin in the north (Courtillot et al., 1988; White and McKenzie, 1989; Storey et al., 1995; Bhattacharya and Chaubey, 2001 and references therein). The configuration of the WCMI was also dominated by two major geodynamic events: the onset of Reunion hotspot activity and Indo-Eurasian continental collisions.

The Kutch, Mumbai and Kerala-Konkan Offshore Basins are located in the northern, central and southern part of the western margin. These basins have been studied by earlier workers in detail vis-à-vis their structural styles and depositional history. However, information about the basaltic basement encountered in the Kerala Konkan Offshore Basin is sporadic and hence the delineation of emplacement histories of basement basaltic rocks was long warranted and overdue.

Geological Settings

The Kerala-Konkan Offshore Basin (KKOB) is situated along the west coast of India south of 16°N latitude. The KKOB is bounded on the eastern side by the Indian Peninsular shield; towards west and south, the basin opens up into the deep sea of the Indian Ocean. The tectonic limits for the KKOB are defined by the ENE-WSW trending Vengurla arch in the north and similar trending Trivandrum arch in the south. The Vengurla arch partially separates the KKOB from Mumbai Offshore Basin (DGH India).

In spite of more than three decades of exploration in Kerala Konkan basin (Fig.1) by different companies, it is yet to meet with any hydrocarbon discovery. Over the period several seismic campaigns have been undertaken and seventeen wells have been drilled so far in the basin. The wells mostly tested the Tertiary prospectivity except one well on Cochin High in

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Kerala basin which has penetrated Late Cretaceous sediments enhancing the hope of discovering Mesozoic petroleum system. Subsequently, few wells targeted for Mesozoic sediments have turned out to be volcanic raising the doubts on the understanding of Mesozoic sedimentation as well as basin configuration during this period (Das, 2013).

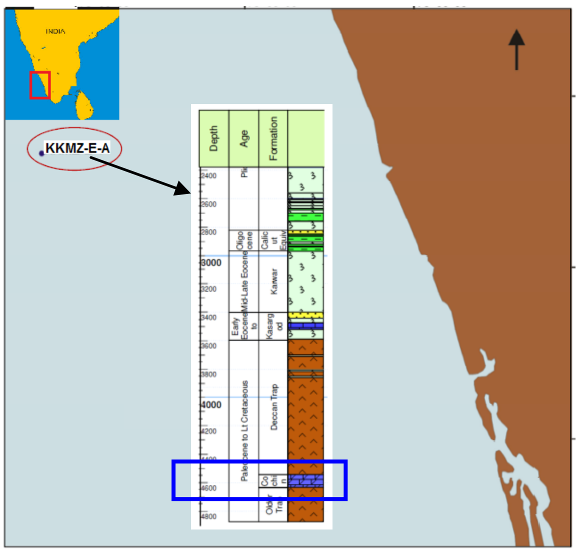

Fig. 1. Location map of the studied well and profile section showing the Cochin-equivalent Formation

In 2014, the well KKMZ-E-A was drilled as an exploratory location in Kerala Konkan Offshore with an objective to explore hydrocarbon potential of Mesozoic sequence. The well has penetrated through Trichur, Calicut equivalent, Karwar, Kasargod, Paleocene Trap, Cochin equivalent and terminated within the massive basaltic basement (lower basalt ?) at 4874.18 m.

The limestone section encountered in the Cochin equivalent formation in between the two basalt units as an intertrappean appears to be very hard and compact with negligible development of porosity and thus has poor reservoir characteristics (Rajguru et al., 2014). However, the occurrence of this limestone horizon has generated more questions related to the genetic affiliation of basalts occurring below, and by analogy, above the limestone horizon. This paper attempts to resolve the depositional history of the encountered Cochin equivalent formation in the well KKMZ-E-A by determining their absolute ages through Strontium Isotope Stratigraphy techniques, and hence, integrating this age data with that of isotopic and geochemical parameters of basalts occurring above and below to firm up the Paleocene history of basement rocks in KK Basin.

Theory and Methodology

Strontium isotope stratigraphy (SIS) is finding widespread use for the dating and correlation of sediments. The SIS technique is now an established chronostratigraphic tool for dating of marine carbonates and can be a crucial correlation tool in the absence of adequate chronostratigraphic control. The technique is based on the assumption that the seawater strontium isotopic ratio ($^{87}Sr/^{86}Sr$) has always been homogeneous on a global scale and has remained constant at a given point of time but has varied with time. This is because the residence time of Sr in the oceans (~ 10^6 years) is far longer (1000 times) than the mixing time of Sr in the oceans (~ 10^3 years), so the Strontium is homogeneously mixed throughout the oceans. Accordingly, a standard seawater curve, showing variation in Sr isotopic ratio with time from Cambrian to Recent has been prepared. For this purpose more than 4000 data used (Veizer et al., 1997; McArthur et al., 2012). Present-day strontium isotopic ratio of seawater is points whose ages are precisely known have been 0.7092. This method works only for marine minerals.

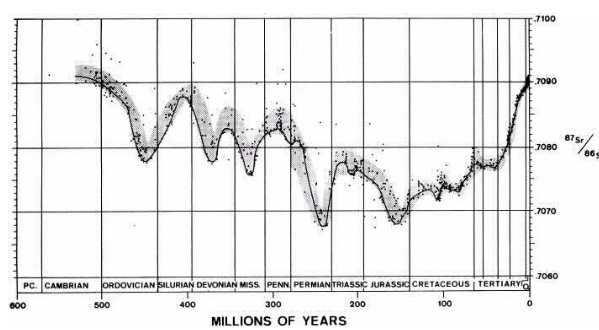

Fig. 2. Standard seawater strontium isotope curve (after Veizer et al., 1997; McArthur et al., 2012)

Materials for Strontium Isotope Dating:

Most of the Neogene Sr-calibration curve is based on analysis of foraminiferal calcite, largely from DSDP/ODP sites (e.g., works by Farrell1995; Hodell et al., 1991, Hodell and Woodruff, 1994), which makes them most suitable for SIS studies. For

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Mesozoic and Palaeozoic sedimentary rocks, most useful samples have been Belemnite guards (Jones et al.,1994a,b) and Brachiopod shells (Veizer et al., 1999), because both materials resist diagenesis well. Acid-leached nannofossil ooze (McArthur et al., 1993), ammonoid aragonite (McArthur et al.,1994), atoll carbonates (Jenkyns et al., 1995) and inoceramid prisms (Bralower et al., 1997) have all yielded good data in the middle to late Mesozoic, and hence can successfully be employed to this technique.

Determination of Sr ages:

Sr ages are calculated by plotting isotopic data on Standard Seawater curve and also using the lookup table (McArthur et al., 2001) and also by LOWESS-fitted standard sea-water curve developed by McArthur et al. (2012). The LOWESS Isotopic Database is based on statistical non-parametric regression method (Locally Weighted Scatterplot Smoother of Cleveland, 1979; Chambers et al., 1983; Thisted, 1988; Cleveland et al., 1992) to obtain a best-fit curve for the $^{87}Sr/^{86}Sr$ data as a function of time. The database is updated from McArthur and Howarth (2004) and uses >4100 data points whose ages are precisely known based on Biostratigraphy, Magnetostratigraphy and Radiometric dating.

Other Databases for Sr age determination have also been developed, e.g. the Bochum-Ottawa Database (Veizer et al., 1999; Shields and Veizer, 2002; Prokoph et al., 2008) details over 5000 $^{87}Sr/^{86}Sr$ results for Phanerozoic and Precambrian time, which can either be used as stand-alone reference or with the combination of LOWESS database. Calibration curve incorporates all uncertainties on original ages of the data used, including boundary recognition (both Bio- and Magnetostratigraphic), diachroneity, sedimentation rate etc.

To calculate the ages for the Sr isotope ratio obtained from Mass-Spectrometric analysis, the values of $^{87}Sr/^{86}Sr$ are plotted on the Y-axis of a scatterplot against numerical age on the X-axis.

Inter-Laboratory Bias:

Measurement of $^{87}Sr/^{86}Sr$ ratios is affected by inter-laboratory bias. To correct for this, standards, whose Strontium isotopic ratios i.e. $^{87}Sr/^{86}Sr$ are known and accepted globally, are run along with samples. Measured values of $^{87}Sr/^{86}Sr$ of the standard are brought to the reported value by applying a correction factor and the same correction factor is applied to actual samples. During our study, NIST 987 (formerly known as SRM-987), a strontium carbonate standard was analysed in every turret (set of 21 samples) and correction for inter-laboratory bias was applied based on the $^{87}Sr/^{86}Sr$ ratios obtained from the NIST standard accordingly. During the course of this study, 23 analysis of NIST 987 standard gave a mean value of 0.710238 as against the reported value of 0.710248.

Experimental

For Strontium Isotope Stratigraphy (SIS) studies, pure limestone pieces handpicked under the microscope from cuttings/cores were ultrasonically cleaned and dried. It was very important to set an appropriate protocol for dissolution of marine carbonates for meaningful Sr isotopic studies. Among other available methods, the one detailed by Li et al. (2011) was adopted for leaching of carbonates from limestone samples for SIS studies.

Table 1. Summary of studied samples and ages obtained from Sr Isotope Stratigraphy method:

Sl. No.	Sample No	Depth	Corrected $^{87}Sr/^{86}Sr$ ratio	Age assigned (Ma)
1	C-1-A	4550-55	0.707802	59.7
2	C-1-B	4550-55	0.707808	60.75
3	C-2	4560-65	0.707809	61.0
4	C-12	4565-70	0.707808	60.8
5	C-3	4570-75	0.707803	59.85
6	C-4-A	4580-85	0.707810	61.25
7	C-4-B	4580-85	0.707812	61.65

Around 100 mg of carbonate sample was weighed and treated with 3 mL 0.3% acetic acid (freshly prepared from glacial acetic acid) for 24 hours. After 24 hours the aliquot was filtered using Whatmann 42 filter paper. The filtrate was dried and dissolved in 2(N) HCl.

The Sr was separated from the leachate by conventional cation exchange column chromatography and loaded onto tantalum filament for mass spectrometric analysis as per the procedure set in-house by Rathore et al. (2010) on TRITON

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thermal ionization mass spectrometer (TIMS) from Thermo Fischer Scientific, Germany. The measured ratios are normalized to $^{86}Sr/^{88}Sr$ = 0.1194. To remove inter-laboratory bias, NIST 987 strontium standard was analysed along with every set of samples (21 nos) and the measured $^{87}Sr/^{86}Sr$ ratios of the standard were adjusted to published value of 0.710248. The same correction was applied to the measured $^{87}Sr/^{86}Sr$ ratio of the samples. The calculated ratios were plotted on the standard seawater Sr Growth curve of McArthur et al. (2012).

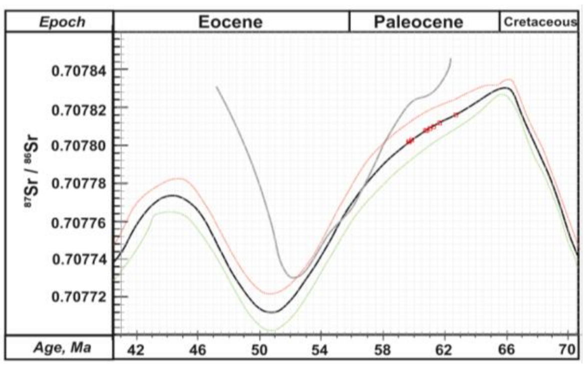

Fig. 3: $^{87}Sr/^{86}Sr$ ratios plotted against their ages on a standard seawater curve for carbonate samples from studied well

Results

14 samples from well KKMZE-A, from interval 4560-4620 m, were collected and processed for Sr isotopic studies. However, only 07 samples were found suitable for the studies and yielded meaningful Sr ages. The analytical details are summarized in Table 2. The obtained Sr ratios are plotted on a LOWESS curve (Fig. 3) and ages are calculated from the best fit curve.

Discussions

The limestone samples from Cochin equivalent formation encountered in the studied well yielded ages ranging from 59.7 Ma to 61.7 Ma with an average age of 60.7 Ma. The upper part of the sequence (4550-55 m) shows the minimum age i.e. 59.7 Ma, whereas oldest age has been measured from the interval 4580-85 m, i.e. 61.7 Ma. The ages obtained show a more-or-less increasing trend with increasing depth, which shows the deposition of limestone throughout the sequence has been fairly consistent. Therefore, the age of Cochin Formation encountered in the well KKMZE-A can be constrained between ~60-62 Ma based on absolute Sr isotopic ages of limestones obtained.

Rajguru et al. (2014) reported a late-Paleocene age based on larger benthic foraminifera Miscellana miscella from the depth 4564 m in a single side-wall core from the lower packstone unit, which was not observed at any other studied interval (4560-4620 m) in the sequence. However, assigning a Late-Paleocene age for the intertrappean will have anomalous emplacement ages for the basalt unit overlying the limestone formation, as no such event in Late Paleocene or later has been reported to have taken place in the western continental margin of India, with Deccan volcanism culminating at ~62 Ma (Early Paleocene). Further, the occurrence of the reported fossil appears to be sporadic in the sequence, as they haven't been reported from any other interval in the sequence.

Rathore et al. (2016), on the basis of extensive Sr-Nd isotopic work and major/trace/rare-earth elements geochemistry, suggested that the basaltic horizons occurring above and below the limestone sequence have similar isotopic and geochemical characteristics and therefore are petrogenetically similar in nature and belong to same emplacement event in the Kerala Konkan Offshore. They further suggested that the emplacement of Kerala Konkan Offshore basalts are a direct consequence of a hotspot-mid-oceanic ridge interaction and therefore are Enriched-type Mid Oceanic Ridge basalts (E-MORB). This holds true for the basalts and volcanics reported from Chagos-Laccadive Ridge and South Mascarene Plateau as well, which were in close proximity to Western Continental Margin of India during Late Cretaceous/Early Paleocene.

Furthermore, Rathore et al. (2007) reported Ar-Ar ages 62.1±0.6 Ma and 61.0±0.6 Ma from the basaltic basement of two wells from Kerala Konkan Offshore. Therefore, available evidences in terms of isotopic and geochemical parameters and reported ages (Rathore et al., 2007; 2016) effectively sets the new age constraints of ~62 Ma for the upper and lower basalts encountered in the well KKMZ-E-A as well. On this analogy, the Late Paleocene biostratigraphic ages reported by Rajguru et al. (2014) cannot be considered to hold viable for the Cochin equivalent limestone sequence in the well KKMZ-E-A.

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However, the Strontium Isotope reported in this paper (60-62 Ma) satisfies the age relationship criteria for Kerala Konkan Basin and therefore holds true for the studied limestone sequence as well.

Conclusions

1. High-resolution Strontium Isotope Stratigraphy (SIS) of carbonate samples of Cochin-equivalent Formation from well KKMZ-E-A in Kerala Konkan Offshore Basin was attempted to establish chronostratigraphic age constraints of the limestone sequence encountered as intertrappean within two basaltic horizons.
2. The study constrains the total depositional age of the Cochin equivalent limestone sequence to be between 59.7 Ma and 61.7 Ma, which is correlatable to reported ages of the basaltic basement in Kerala Konkan Basin.
3. These ages have provided new geochronological constraints for the first time, for the intertrappean limestone sequence encountered in the well KKMZE-A, and also demonstrates that the SIS technique can be used very effectively for providing absolute ages of marine carbonates and resolving biostratigraphic limitations.
4. This also has implications in Mesozoic exploration strategy in KK Basin as the ages of both lower and upper basalt unit appears to be same (Early Paleocene, ~62 Ma), and therefore eliminating the possibility of encountering Mesozoic sequences in the Kerala Basin.

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