Absolute age dating of sedimentary rocks: A review of Rb-Sr, K-Ar and Ar-Ar dating techniques for clay minerals

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ABSTRACT

Dating of stratigraphic sequences encountered in sedimentary basins is of paramount importance in the context of petroleum exploration, as it provides basic parameters for integrated basin analysis and also establishes a quantitative link between the relative ages provided by fossil successions and the geological time scale. Improvements in analytical techniques during the past few decades have led to the development of geological subdisciplines, some of which, in turn, have potential in providing alternative means for dating and correlating sedimentary sequences. These techniques may prove particularly useful in the dating and correlation of those strata devoid of chronostratigraphically useful fossil remains. Authigenic clay minerals such as illites and glauconites formed within the sedimentary sequences are known to contain abundant K and Rb, and provide excellent avenues for application of the geochronological techniques like Rb-Sr, K-Ar and 40Ar/39Ar dating, especially for inferring the time of deposition/ subsequent diagenetic events.

The purpose of this paper is to bring together these diverse dating techniques, viz., Rb-Sr, K-Ar and 40Ar/39Ar, and to explore their potential to solve problems in stratigraphy. It is also the intention to introduce these techniques, each of which is familiar to specialist researchers, to a wider audience of petroleum geologists who may find them useful in the resolution of specific correlation problems. Therefore, we attempt to examine and review the Rb-Sr, K-Ar and 40Ar/39Ar methods for authigenic clay minerals illite and glauconite, with the aid of case histories of past work done from Indian sedimentary basins, i.e., Vindhyan, Jaisalmer, Kutch and Ganga basins, and Himalayan Foothills, by the Geochronology Laboratory, KDMIPE, ONGC, and evaluate their usability and limitations in determining the age of deposition and/or early diagenetic events.

INTRODUCTION

Absolute dating of the time of deposition of sedimentary rocks is of immense importance in various techniques of basin modelling and stratigraphic investigations. However, providing accurate and meaningful ages with least experimental error is a very difficult problem to solve, as accurate dates depend on thorough resetting of isotopic clocks. Hence dating of sediments through radiometric methods rests on a few assumptions, which govern the overall systematics and precision of various radiometric clocks.

In present scenario, biostratigraphy is not only the most readily available means of relative dating and correlation of sedimentary rocks, it is also the cheapest and the fastest. However, significant problems have arisen in dating and correlating those stratigraphic sequences which are impoverished in, or barren of, fossil remains. Popularity of magnetostratigraphy as a dating tool has also picked up lately, due to the fact that many sedimentary rocks are faithful recorders of the ancient magnetic field and that modern magnetometers are capable of measuring very weakly magnetized samples. On the other hand, the inadequacy of magnetostratigraphy to be applied to discontinuous or very short sedimentary records remains as the fundamental limitation.Popular radiometric dating methods are summarized in Table 1.

How does it work?

Out of the three main groups of sedimentary rocks, clastic (transported), carbonate (biological), and chemical, the minerals formed in chemical and carbonate sediments (e.g., evaporates, phosphates, shells and skeletons) are normally calcium rich (e.g., calcite, apatite) and show a limited range in

Table 1: Popular radiometric dating methods.

S. No.	Method	Principle	Half life	Errors (%)	Applicability
1	Potassium-Argon dating	Uses principle of natural radioactivity. Concentration of unstable parent (^{40}K) and stable daughter (^{40}Ar) isotopes present today in the rock is measured and the age is calculated with the help of half-life of the parent isotope.	1.3 billion	~ ±2-3%	Emplacement ages of igneous rocks, ages of deposition and diagenesis of sedimentary rocks using clays, glauconites etc., thermal/metamorphic events
2	Argon-Argon dating	Analytical conversion of conventional K-Ar dating method. In this method, isotopic ratio of ^{40}Ar, which is produced naturally by decay of ^{40}K over a period of time, and ^{39}Ar, which is artificially produced today in the nuclear reactor by neutron irradiation from ^{39}K, is measured. The measured ^{40}Ar/^{39}Ar ratio is related to age.	Not applicable	~± 1%	Emplacement ages of igneous rocks, thermal history of rocks, ages of deposition and diagenesis of sedimentary rocks using clays & glauconites etc.
3	Rubidium-Strontium dating	Uses principle of natural radioactivity. Concentration of unstable parent (^{87}Rb) and stable daughter (^{87}Sr) isotopes present today in set of comagmatic rocks is measured and age is calculated by isochron method.	47 billion	~1-2%	Emplacement ages of plutonic rocks, ages of deposition and diagenesis of sedimentary rocks using clays & glauconites etc., thermal/metamorphic events
4	Uranium-Series Dating	Uses principle of natural radioactivity. Concentration of unstable parent isotopes (238U, 237U &235U) which are converted to stable daughter isotopes (206Pb, 207Pb &208Pb) after a series of alpha and beta decay. The age is calculated using concordia diagrams.	4.5 billion 710 million	~1-2%	Crystallization/thermal ages of igneous rocks, detrital ages of sedimentary rocks
5	Rhenium-Osmium dating	Uses principle of natural radioactivity. Concentration of unstable parent (187Re) and stable daughter (187Os) isotope present today in the rocks is measured and age is calculated by isochron method.	43 billion years	~1-2%	Emplacement ages of igneous rocks, dating of organic-rich black shale, dating of hydrocarbon deposits

Rb-Sr/K-Ar, making the isotopic techniques unsuitable for their dating. However, siliciclastic sediments such as sandstone, siltstone and mudstone form at relatively lower temperatures at the Earth's surface as a consequence of erosion, transportation, and deposition of fragments and minerals from pre-existing rocks dominated by silicate minerals. Upon burial and diagenesis they become cemented into clastic sedimentary rocks and minerals that are unstable at surficial pressures and temperatures will tend to progressively break down to form new mineral phases, e.g., clays (illite, smectite, kaolinite), many of which are K-rich and thus theoretically provide potential for dating using Rb-Sr and K-Ar/ Ar-Ar methods.

According to the origin of Rb-or K-bearing phases present in the sedimentary rocks, they could be either allogenic or authigenic. Allogenic (detrital) minerals are moderately resistant to open-system behaviour during burial metamorphism, but problems arise from inherited isotopic signatures. Authigenic minerals are deposited directly from fluid phase such as seawater and hence display good initial Sr isotope homogeneity. However, they are highly susceptible to recrystallization after burial and may not remain closed system (Dickin, 1995).

A number of problems could be encountered in providing an accurate age for these minerals due to the process of sedimentation. One of the main difficulties is that the minerals dated from the siliciclastic rock may be of detrital origin and ages yielded would refer to the source rock. Most sandstones and clays consist of a mix of detrital phases and new authigenic minerals. In the case of detrital components that are derived from eroding the source region and have been transported unchanged or partially modified, the grains will retain a strontium ratio reflecting the amount of ingrowth of ^{87}Sr from the decay of ^{87}Rb since their source region cooled through the closure temperature of the mineral in question. To overcome this difficulty, one should look for a mineral which should be authigenic in nature i.e. generated therein the deposits itself. The radiometric ages obtained from such a mineral would directly correlate to the ages obtained by facies and palaeontological investigations.

Another very important assumption for the technique to work is that the Sr isotope systematics in the rock were homogenized during deposition or early diagenesis, and thereafter remained as a closed system until the present day. However, significant problems have arisen in dating and correlating those stratigraphic sequences which are impoverished in, or barren of, fossil remains.

In practice, two distinct dating approaches are associated with dating of the two types of sediments i.e. detrital and authigenic, through the isotopic techniques. Two clay mineral groups i.e. illite and glauconite, can be dated using isotopic methods. Analysis of detrital sediments has moved towards the analysis of fine-grained, almost authigenic, minerals such as illite, to escape the effects of the detrital component. Illite is a general term for a 10 angstrom (Å) potassium di-octahedral mica-like clay mineral common in sedimentary rocks such as shales and sandstones. On the other hand, analysis of authigenic minerals is mainly focussed on the sub-authigenic mineral glauconite, an iron potassium phyllosilicate mineral of characteristic green colour that occurs in sandstone and carbonate-rich sedimentary rocks (Meunier and Velde, 2004).

Rb-Sr Dating of Clays

The utility of the Rubidium-Strontium (Rb-Sr) isotope system results from the fact that ^{87}Rb (one of two naturally occurring isotopes of Rubidium) decays to ^{87}Sr with a half-life(λ) of 48.8 billion years. Different minerals in a given geologic setting can acquire distinctly different ratios of radiogenic strontium-87 to naturally occurring strontium-86 (^{87}Sr/^{86}Sr) through time; and their age can be calculated by measuring the ^{87}Sr/^{86}Sr in a mass spectrometer, knowing the amount of ^{87}Sr present when the rock or mineral formed, and calculating the amount of ^{87}Rb from measurement of the Rb present and knowledge of the ^{85}Rb/^{87}Rb weight ratio, with the help of following radioactive decay equations:

$$\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{\mathrm{P}} = \left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{\mathrm{I}} + \frac{^{87}\mathrm{Rb}}{^{86}\mathrm{Sr}}(e^{\lambda t} - 1)$$

Where, the present day Sr isotope ratio $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{P}}$ is measured by mass spectrometry, and the atomic ratio $^{87}\mathrm{Rb}/^{86}\mathrm{Sr}$ is calculated by weight ratio of Rb/Sr. If the initial ratio $(^{87}\mathrm{Sr}/^{86}\mathrm{Sr})_{\mathrm{I}}$ is known or can be determined, subject to assumption that the system has been closed to Rb and Sr mobility from time t until the present by the following expression:

$$t = \frac{1}{\lambda}\ln\left\{1 + \frac{^{86}\mathrm{Sr}}{^{87}\mathrm{Rb}}\left[\left(\frac{^{87}\mathrm{Sr}}{^{86}\mathrm{Sr}}\right)_{\mathrm{P}} - \left(\frac{^{86}\mathrm{Sr}}{^{87}\mathrm{Sr}}\right)_{\mathrm{I}}\right]\right\}$$

The age of a sample is determined by analysing several minerals/fractions within the sample. The $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ ratio for each fraction is plotted against its $^{87}\mathrm{Rb}/^{86}\mathrm{Sr}$ ratio on an isochron diagram (Fig.1). If these form a straight line then the samples are consistent, and the age will be reliable. The slope of the line dictates the age of the sample.

Detrital Rb-bearing minerals (mica, K-feldspar, clay minerals etc.) contain inherited old radiogenic Sr. Therefore, dating of such material should give an average of the provenance ages of the sedimentary constituents. However, if sufficiently fine-grained shales are sampled, it appears that the constituent minerals (mainly illite) often suffer substantial exchange of Sr during post-depositional diagenesis. In this case they may develop an almost homogeneous initial Sr isotope composition soon after deposition, thereafter remaining effectively closed systems until the present day.

During the analysis of whole rock Rb-Sr dating of shales, in some circumstances,the above conditions of homogeneity were closely approached (e.g. the State Circle shale from SE Australia; Compston and Pidgeon, 1962). However, in other cases (e.g. the Cardup shale of Western Australia; Compston and Pidgeon, 1962), gross inherited $^{87}\mathrm{Sr}/^{86}\mathrm{Sr}$ variations remained, preventing the calculation of a meaningful age. The reason for such disparity was attributed to be the presence of undecomposed detrital micas, probably sericite. As a result, subsequent work on the dating of shale sought to avoid problems of contamination with detrital micas and feldspars by analysing separated clay-mineral fractions e.g., illite, whose purity is checked by X-ray diffraction (XRD), thereby also providing information about the nature and origin of clay minerals in a shale that is to be dated,using the 'illite crystallinity index' (Kubler, 1966), which is defined as the width of the (001) XRD peak at half its height. A well-crystallised illite, characteristic of a relatively high-temperature history, has sharp peaks

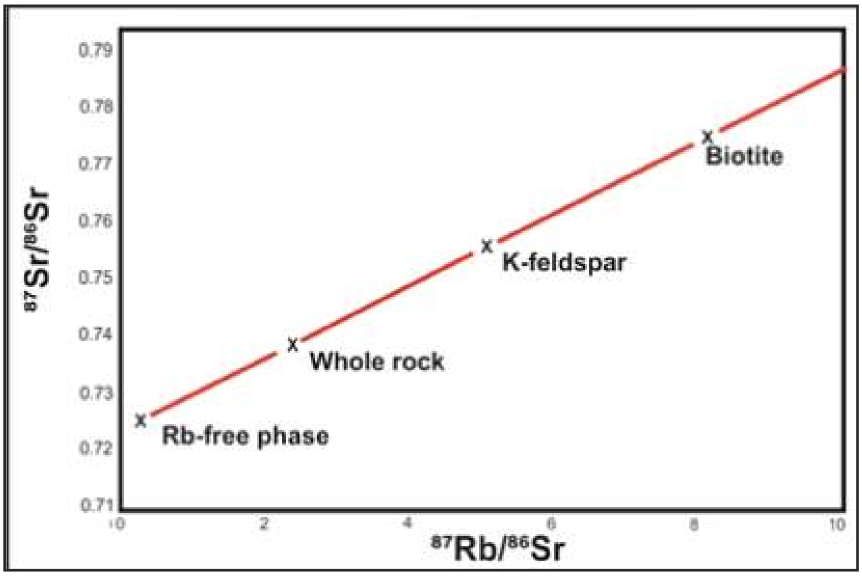

Fig. 1: Schematic Rb-Sr isochron diagram for a suite of co-magmatic igneous rocks

and therefore a low index, whereas low-temperature illites are more disordered and have irregular peaks with large indices. In addition to this discriminant, illite has high-temperature (2M) and low-temperature (1M) polymorphs, which can also be distinguished by XRD with the aid of illite crystallinity index (Dunoyer de Segonzac, 1969).

Many examples have shown that that whole-rock Rb–Sr dating of shales is an unreliable geochronometer, but that analysis of separated illite fractions may give meaningful ages of diagenesis or low-grade metamorphism. In a series of representative sediment sample, <2 µm clay size fractions are separated and then further separated according to grain size. The samples are characterized by XRD to determine their illite crystallinity index to distinguish their authigenic nature as well as thermal history. The authigenic fractions are then leached in 10% acetic acid to facilitate slow removal of carbonate materials. Residual samples are washed repeatedly with Milli-Q water to remove completely the acid used for leaching. Clays from rock matrices are then disintegrated in Milli-Q using an ultrasonic bath. These samples are spiked and digested in pressure digestion bombs using mixture of ultrapure acids ($HF+HNO_3+HClO_4$) and then subjected to ion exchange column chromatography, which elutes the Rb and Sr from their matrices.

Measurement of Rb and Sr isotopic ratios is carried out in a thermal ionization mass spectrometer and the measured ratios of $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ are normalized against $^{86}Sr/^{88}Sr$ ratios of 0.1194 to correct for mass fractionation during analysis. These ratios are used to produce 3-point isochrons (leachate, residue and bulk) for each clay size fraction and age is determined from the slope of the isochron (Fig. 2).

The results from clay samples of different size fractions when plotted together yield a large scatter of ages but more importantly also reveal a trend of increasing age with increasing grain size (Gorokhov et al., 1994) (Fig. 3). In addition, the coarser-grained fractions, which are suggested to have crystallized at higher temperature through characterization by XRD, contain a significant detrital component and subsequently result in older ages. Most of the coarser grained clay fractions are considered to be mixtures between detrital and authigenic components and thus the isochrons do not represent geologically meaningful ages but are instead mixing arrays. Nevertheless, when the data are combined in terms of grain size and crystallinity, some potential meaningful age information can be obtained (Waight, 2015). For instance, the well-crystallized

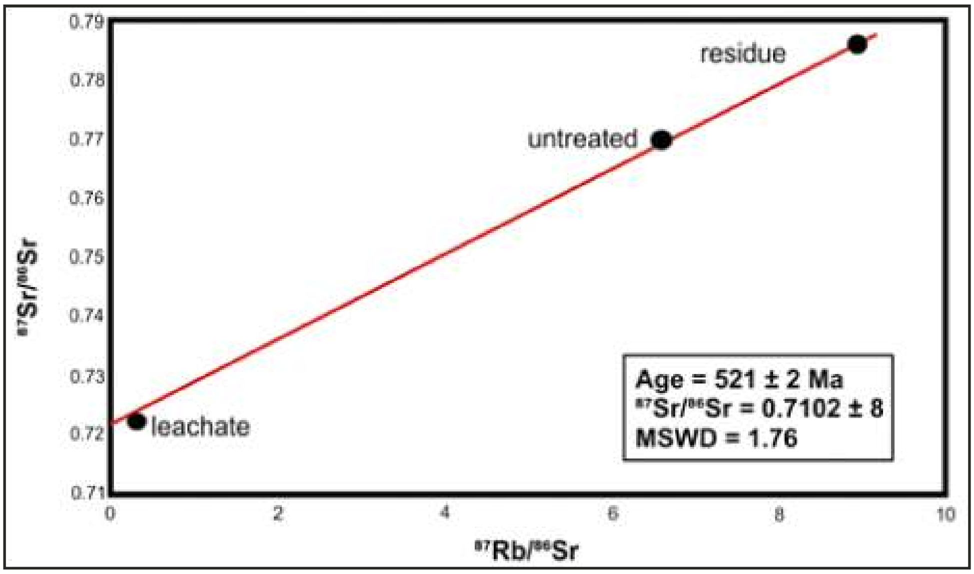

Fig. 2: Rb-Sr isochron for a representative clay sample from the Lontova claystones studied by Gorokhov et al., (1994).

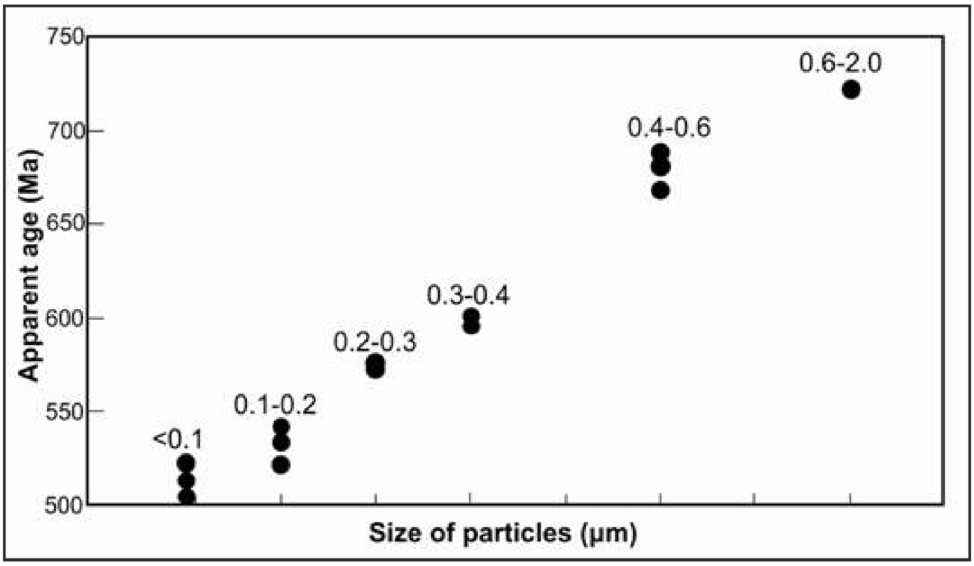

Fig. 3: Compilation of apparent Rb-Sr ages for clay fractions from Lontova claystones against size of the clay fractions analysed, showing a clear positive correlation between grain size and age (From Gorokhov et al., 1994).

fine grained (<0.2 µm) clays define an isochron with an age of 533±8 Ma which Gorokhov et al., (1994) interpret to be the best estimate of the age of sedimentation, whereas fine grained disordered clays yielded a younger age (430–480 Ma) that may be related to later disturbances and interactions with subsurface waters (Waight, 2015).

Rb-Sr Dating of Glauconite

The mineral glauconite offers an attractive possibility for dating sedimentary rocks directly, due to its high Rb content, easy identification and widespread stratigraphic distribution. Glauconite is a micaceous mineral similar to illite, which is best developed as macroscopic glauconitic pellets, as infillings within bioclast pores & as on-pallet stringers and blebs of glauconitic cement called 'glauconies'. Odin and Matter (1981) proposed the term glaucony as a facies name for authigenic pelleted material with no specific mineralogy, and either glauconitic mica or glauconitic smectite for end members of the specific mineral family. These are probably formed by the alteration of a very-fine-grained clay precursor intermixed with organic matter in a faecal pellet, near the sediment–water interface in the marine environment. During this process, the potassium and content of the galuconite increases, and this can therefore be used to monitor the maturation of the galuconites.

The Glauconite-rich portions from a representative sediment sample in question are crushed and sieved to the 50-70 mesh sizes and then washed and sonicated to clean the cracks developed during the growth of glauconite grains. Samples are then dried at low temperature (~60°C) and final purification is done under an optical microscope by hand picking the impurities. Scanning Electron Microscope (SEM) studies as well as XRD analysis is carried out on the glauconite samples in order to determine the authigenic nature of the grains.

For Rb-Sr analysis the digestion process for Glauconites is same as that for other clay minerals, which involves spiking the weighed sample with ^{84}Sr and ^{87}Sr and then digestion in bombs at 150°C with a mixture of ultrapure acids ($HF+HNO_3+HClO_4$), followed by ion exchange chromatography for separation of Rb and Sr, which are separately analysed on a thermal ionization mass spectrometer (TIMS) for their isotopic ratios. These corrected ratios (^{87}Sr/^{86}Sr and ^{87}Rb/^{86}Sr) are then plotted on an isochron diagram and the age is calculated from the slope of the best-fit line.

Cretaceous and younger glauconies often yield ages concordant with those obtained from other datingmethods, but Palaeozoic glauconies commonly give ages that are 10%–20% younger than expected (Dickin, 1995). This was attributed to post-depositional uptake of K and Rb during diagenesis by early workers, however later workers attributed the young ages to loss of ^{87}Sr from the expandable layers of the clay lattice, by some form of ion exchange with circulating brines.

K-Ar and Ar-Ar Dating of Clays

K-Ar (or potassium-argon) dating technique is an absolute dating method based on the natural radioactive decay of ^{40}K to ^{40}Ar used to determine the ages of rocks and minerals on geological time scales. On the other hand, Ar-Ar (or argon-argon) dating method is a variant of the K–Ar dating method fundamentally based on the natural radioactive decay of ^{40}K to ^{40}Ar, but which uses an artificially generated isotope of argon (^{39}Ar) (produced through the neutron irradiation of naturally occurring ^{39}K) as a proxy for ^{40}K (Lee, 2015).

Both conventional K-Ar and ^{40}Ar/^{39}Ar dating methods can be applied to clay minerals i.e., illite and glauconite. Detailed accounts of the conventional K-Ar and ^{40}Ar/^{39}Ar dating techniques have been described by Dalrymple and Lanphere (1969), Faure (1986), Dickin (1995), McDougall and Harrison (1999), and Kelly (2002). The ages of clay minerals can be determined by measuring the amount of the argon isotope ^{40}Ar relative to the potassium content. ^{40}Ar is produced by the radioactive decay of the potassium isotope ^{40}K. Minerals generally contain negligible amounts of argon when they are formed, although small amounts of atmospheric argon may adhere to samples, which can be corrected for by using the known atmospheric ^{40}Ar/^{39}Ar ratio of 295.5 (Steiger and Jäger, 1977).Thus, by measuring the ratio of ^{40}Ar to^{40}K, and knowing the decay rate of ^{40}K, it is possible to calculate the time since the clay mineral formed.

The K-Ar and ^{40}Ar-^{39}Ar methods allow dating of clay minerals formed since the formation of the solar system (Dalrymple, 1991) until a few thousand years before present (Renne et al., 1997), because of the relatively short half-life of about 1,250 Ma of the ^{40}K isotope. Special care is required in dating younger geological samples due to atmospheric ^{40}Ar/^{39}Ar contamination and error magnification (McDougall and Harrison, 1999).

The age of clay minerals determined by K-Ar or ^{40}Ar/^{39}Ar methods depend on following assumptions:

1. The clay mineral must behave as a closed system. There should be no loss of radiogenic ^{40}Ar produced by the decay of ^{40}K since the clay formation.
2. The radiogenic ^{40}Ar should only be produced by the decay of ^{40}K.
3. The atmospheric ^{40}Ar should be corrected to the present-day ^{40}Ar/^{39}Ar value of 295.5.

Apart from these assumptions, there are several factors that govern the dating of authigenic clay mineral, which include: (1) contamination effects, i.e., mixing with other K-bearing phases, (2) Ar closure, i.e., loss or capture of radiogenic ^{40}Ar during crystallization, (3) initial clay mineralogy (illite, illite-smectite). K-bearing clay minerals such as illite and glauconite can be dated by the conventional "spiked" K-Ar, the "unspiked" K-Ar, and ^{40}Ar/^{39}Ar methods.

Both dating methods have their limitations: (1) K–Ar dating requires relatively large samples (ca. 10–20 mg) incurring potential sample homogeneity problems, with two aliquots required for K and Ar analysis for an age determination, also inducing a higher analytical uncertainty; (2) an identified drawback of ^{40}Ar/^{39}Ar dating is Ar recoil and therefore potential loss that occurs during neutronic creation of ^{39}Ar from ^{39}K, mostly in the finer mineral particles.

In case of spiked K-Ar dating of K-bearing rocks or minerals, it is necessary to determine the concentrations of ^{40}K and of radiogenic ^{40}Ar on two aliquots of the same sample (Zwingmann, 2015). For Ar analysis by Noble Gas Mass Spectrometry, sample splits are loaded into clean Al, Cu, or Mo foil, weighed and preheated to 80°C for several hours to remove moisture, and reweighed using a high-precision balance. The measured dry weight is used in the K–Ar age calculation. For both K and Ar analytical procedures, international mineral standards and blank analyses are performed for quality control purposes.

The theory and analytical procedures of the unspiked K–Ar method have been summarized by Cassignol and Gillot (1982) and Sudo et al., (1996). The unspiked K–Ar method is able to date geologically very young basalt samples (several kyr) with high atmospheric ^{40}Ar contamination. With the use of this procedure on clay, the initial ^{40}Ar/^{36}Ar is calculated from the present atmospheric ^{38}Ar/^{36}Ar isotope ratio assuming mass-dependent isotopic fractionation during mineral formation.

The ^{40}Ar/^{39}Ar dating system is based on the decay scheme of the isotope ^{40}K. The ^{40}Ar/^{39}Ar method is modification of K-Ar technique, which obviates this requirement of two separate measurements by converting the parent isotope to the same element as the daughter. The sample is irradiated by fast neutrons in a nuclear reactor to convert some of ^{39}K into ^{39}Ar. The fixed natural ratio ^{39}K/^{40}K provides an estimate for the parent ^{40}K by the measurement of ^{39}Ar. In order to know the conversion factor of ^{39}K to ^{39}Ar and to take care of other interfering nuclear reactions a sample of known K-Ar age and pure salts of K and Ca are irradiated along with the sample. The unknown age of the sample is then derived by comparison with the monitor sample.

As it is clear that the ^{40}Ar/^{39}Ar method relies upon a known age sample, which is used to monitor the neutron fluence, this monitor sample is very critical. Usually the following criteria are followed for choosing a monitor sample: 1) It should have uniform ^{40}Ar to ^{40}K ratio distributed homogeneously in order to calculate the accurate and precise K-Ar age of this sample, 2) It should be sufficiently coarse grained to minimize the health hazards due to the radioactivity after the irradiation, 3) It should be available in sufficient quantity. A major advancement was achieved when it was realized that after irradiation the sample need not be fused in a single step, instead it can be degassed incrementally in various steps and the gas released at each step can be analysed for isotopic ratio for obtaining 't' and thus an age spectrum of many apparent ages can be obtained instead of a single total fusion age or K-Ar age. This technique known as 'step heating' or 'incremental heating' technique (Merrihue and Turner, 1966) has additional advantage of providing the inner distribution of ^{40}Ar relative to ^{39}K which in turn is related to ^{40}K.

Numerous studies have documented the ^{39}Ar recoil phenomenon, resulting from irradiation of the samples by fast neutrons, needed to transmute ^{39}K into ^{39}Ar. This recoil effect, which can cause problems of isotopic loss at the surface of small clay crystals, represents a major disadvantage for clay ^{40}Ar/^{39}Ar dating, as a precise ^{39}Ar measurement is required to calculate indirectly the amount of K present in the mineral phases. However, Smith et al., (1993) showed that this problem might be overcome by encapsulating clay mineral grains in small glass ampoules prior to irradiation. The recoil products can then be collected for analysis, in order to correct the Ar release from the rest of the grain.

Applications of Clay dating

Clay minerals occur in different geological settings and are associated with soil formation, erosion and sedimentation processes, and diagenetic processes that occur during burial from surface locations (Velde, 1992; Meunier and Velde, 2004). Following applications of clay dating can be summarized:

1. Deep burial authigenesis of clay mineral in sandstones: Dating of illite offers the prospect of establishing the absolute timing of diagenetic events such as heating or fluid flow events

within a sedimentary basin.

2. Glauconite dating for stratigraphic age: Glauconite formation takes place during deposition of sediment at the water-sediment interface. Maximum galuconite abundance & maturity are characteristics of condensed sections, which occur at events of marine flooding intervals. Hence, it is a reliable indicator of low sedimentation rate. Dating of K-bearing clay minerals using the isotopic systems offers the prospect of establishing the absolute timing of sedimentation.
3. Deformation events: brittle fault and gouge zone dating: Displacement on discrete fault planes often results in the development of fault gouge composed of crushed rock fragments and authigenic illite clay minerals. The understanding of fault processes and specifically the timing and extent of fault gouge formation through dating of authigenic clay minerals is important for regional correlation of shallow faults in neotectonic studies, hydrocarbon exploration, CO_2 sequestration and diffusion, identification of earthquake hazards etc.

In order to examine and review the usability and applications of above techniques, we revisit a few case studies of the K-Ar and Rb-Sr dating of clays and glauconites from Indian sedimentary basins, carried out by the Geochronology Laboratory in the past.

Case Study 1: K-Ar Dating of Glauconites from Sirbu Shales of Vindhyan Supergroup, India

In this study, Rathore et al., (1999a) report K-Ar ages of glauconites separated from outcrop samples of the Sirbu Shale Formation of Bhander Group of Upper Vindhyans, which is the first quantitative age assigned to Sirbu Shales and is consistent with the other age data based on biostratigraphic studies.

The Vindhyan sediments have been least metamorphosed and are considered one of the best-preserved Proterozoic sedimentary sequences of India. The age of these poorly fossiliferous sediments has been difficult to establish because of the scarcity of dateable material (e.g. interfringed volcanics). The rare fossil records that have been reported are of doubtful affinity, and are thus incapable of defining a particular age range (Venkatachala et al., 1996).

The Vindhyan Supergroup of sediments us built up on two megasequences, i.e., Lower Vindhyans (Semri Group) and Upper Vindhyans (Kaimur, Rewa and Bhander Groups), which are separate by a basin-wide unconformity (Sastry and Moitra, 1984). These Groups are further divided into various Sub-Groups/Formations based on lithology. The Vindhyan sediments were deposited by and large in shallow marine environment and are characterized by a lithological assemblage comprising predominantly quartz-arenite, shale-siltstone, limestone and porcellanite with subordinate feldspathic and lithic arenite (Padhy, 1995). Various horizons within the Vindhyan Supergroup are enriched in glauconites, and therefore provide a good opportunity to date the time of deposition of the sequences embodying the glauconite material.

In the study, glauconite rich samples were collected from the south bank of Sonar River near village Narsinghgarh on Damoh-Narsinghgarh Road in Damoh district of Madhya Pradesh. At the sampling site, the Nagod Limestone was exposed on river bed followed by the exposures of Sirbu Shale which are about 30 ft thick with thin beds of sandstone containing glauconite and trace fossils (Fig. 4).

The glauconites from Sirbu Shale member of Bhander Group were found to be quite evolved, having K_2O content more than 6.6% and good for isotopic dating. The K-Ar data of the studied glauconites are presented in Table 2.

Samples Sirbu-1, Sirbu-2 and Sirbu-2D (duplicate) yielded K-Ar ages of 738±19 Ma, 746±15 Ma and 740±15 Ma, respectively. One glauconite standard (GL-O), analysed to check the accuracy of the

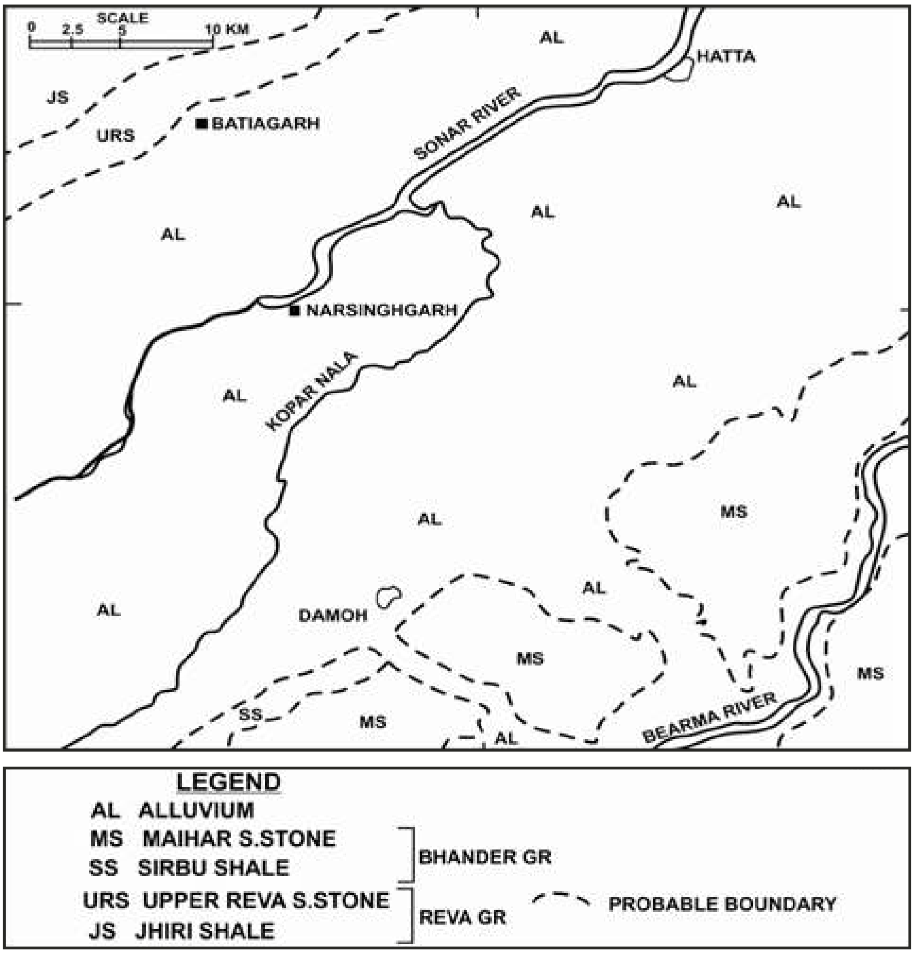

Fig. 4: Simplified geological map of Upper Vindhyans from Damoh Area (M.P.) (after Rathore et al., 1999a

Table 2: Analytical data and obtained ages from Sirbu Shales of Bhander Group.

S.No.	Sample no.	K %	Total ^{40}Ar	Rad ^{40}Ar	Age $^{(\pm 2\sigma)}$ (Ma)
1	Sirbu-1 (80 mesh)	5.64	213.83	199.94	738±19
2	Sirbu-2 (120 mesh)	5.50	213.67	197.61	746±15
3	Sirbu-2 D (120 mesh)	5.50	221.67	195.68	740±15
4	GLO*	6.46	281.844	250.171	95.69±1.9

*Standard with reported age of 95.03±1.11 Ma (Odin et al., 1982)

measurement, has yielded a K-Ar age of 95.69±1.91 Ma against its reported age of 95.03±1.11 Ma (Odin et al., 1982). The ages obtained for these glauconites were in agreement within the experimental error and provide a mean age of 741±9 Ma, which can be interpreted as the depositional age of the Sirbu Shales.

Tugarinov et al., (1965) reported the ages of 1400 Ma, 1140 Ma, 940 Ma and 910 Ma for the glauconites separate from Lower Semri, Upper Semri, Lower Kaimur and Upper Kaimur Groups, respectively, which were also supported by Crawford and Compston (1970). Fission Track ages ranging from 675 Ma to 710 Ma have also been reported from Govindgarh Sandstone Formation of Upper Vindhyans by Srivastava and Rajagopalan (1988). However, these ages are associated with high errors varying from 110 Ma to 125 Ma.

The Jodhpur sandstone of western Rajasthan which is commonly correlated with the uppermost part of the Vindhyans overlie the Malani rhyolites with an erosional disconformity, which have been dated to be 779±10 Ma (Rathore et al., 1996). Therefore the overlying sandstones and hence the equated uppermost Vindhyans ought to be younger than ~780 Ma. The mean age of 741±9 Ma obtained from the glauconites from Sirbu Shale of Bhander Group in the present study, which have been interpreted as the depositional age of the Sirbu Shales, is the first quantitative age for this member of Upper Vindhyans and is consistent with the suggested stratigraphic correlation.

Case Study 2: K-Ar and Rb-Sr ages of Cretaceous Glauconites from Jaisalmer Basin, Rajasthan

In this case study Vijan et al., (2000) report the first quantitative age estimation of glauconite samples separated from subsurface cores of Goru and Pariwar Formations of Jaisalmer Basin, Rajasthan, using both K-Ar and Rb-Sr techniques. Glauconite normally contains abundant K and Rb which makes it chemically favourable for both K-Ar and Rb-Sr dating (Morton and Long, 1980), as well as its green colour and pelletal shape makes it easily identifiable in the field. Moreover, a high iron content and correspondingly high magnetic susceptibility aid in concentrating and purifying glauconite pellets as well.

The western Rajasthan shelf located to the west of Aravalli mountain range, comprises three important basins, namely Jaisalmer, Bikaner-Nagaur and Barmer, stretching over an area of about 1,20,000 sq. km. The Precambrian Malani Group of igneous rocks constitutesthe basement of these basins. Each basin had different geological and sedimentary histories, albeit at some point of time there were some common elements. The Bikaner-Nagaur and Barmer basins are essentially Palaeozoic and Cenozoic, respectively, however, the Jaisalmer Basin has both well-documented Mesozoic and Cenozoic histories (Misra et al., 1993).

The pericratonic Jaisalmer Basin mainly represents the west-dipping eastern flank of the Indus shelf and occupies an area of about 30,000 sq. km. The basin is divided into four geotectonic units: (1) the Jaisalmer-Mari High extending through the central part of the basin with a NW-SE trend, (2) the monoclinal Kishangarh sub-basin towards N and NE, (3) the synclinal Shahgarh sub-basin towards S and SE, and (4) the Miajlar sub-basin towards S and SE (Fig. 5). Pariwar, Goru and Parh Formations represent the subsurface Cretaceous sediments of the Jaisalmer Basin. The Pariwar Formation is mostly arenaceous and overlain by the Goru Formation, which is informally subdivided into two units: the lower Goru, dominated by clastics and the mainly argillaceous Upper Goru. The upper Goru Formation is conformably overlain by the Parh Formation.

Glauconite rich samples, belonging to the Goru and Pariwar Formations were selected from the conventional cores of the wells GT-F, GT-J and SD-A (Fig. 5), for separation of the glauconites.

SEM studies of samples indicated a good degree of evolution of the glauconites in Goru and Pariwar Formations exhibiting 'caterpillar' structure with well-developed lamellae, up to 4-5 µm long. XRD studies indicated the potassium content of the Goru and Pariwar glauconites to be ranging between 6.8 to 7.4% and meet the criteria provided by Clauer et al. (1992) for obtaining reliable stratigraphic ages (>4%).

K-Ar data for glauconites from Goru and Pariwar Formations of Jaisalmer Basin have been presented in Table 3 and Rb-Sr analytical data for glauconites from Goru Formation have been summarized in Table 4.

Three samples from Goru Formation, Goru-1, 2 and 4, yield K-Ar ages of 103±5 Ma, 105±6 Ma and 102±5 Ma respectively (Table 3). Five samples belonging to Goru Formation were attempted for Rb-Sr dating (Table 4), out of which four samples define an isochron (Fig. 6) corresponding to an age

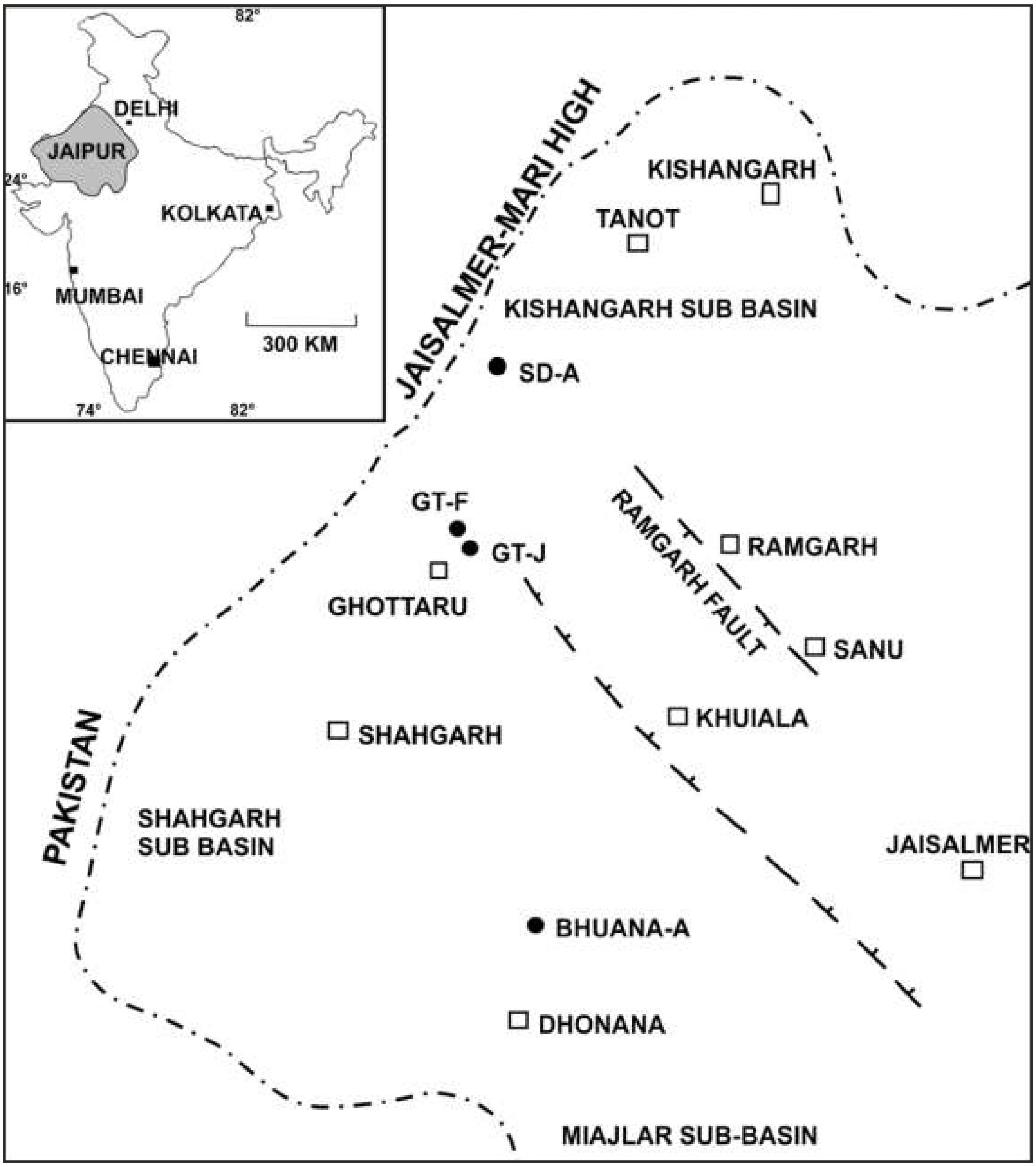

Fig. 5: Map of the study area showing locations of studied wells

Table 3: K-Ar Analytical data and obtained ages from Goru and Pariwar Formations of Jaisalmer Basin

S.No.	Sample No.	K (Wt%)	Total ^{40}Ar	Rad ^{40}Ar	Age$^{(\pm2\sigma)}$ (Ma)
1	Goru-1	5.94	28.20	24.37	103±5
2	Goru-2	5.62	25.32	23.66	105±6
3	Goru-4	5.99	25.51	24.52	102±5
4	Pariwar-1	5.97	24.41	24.41	102±4
5	Pariwar-2	6.08	35.15	25.86	106±5
6	Pariwar-3	5.99	25.39	25.39	106±5
7	Pariwar-5	5.81	27.41	25.68	109±6
8	GLO*	6.46	29.84	24.31	94.3±1.9

*Standard with reported age of 95.03±1.11 Ma (Odin et al., 1982)

Table 4: Rb-Sr analytical data from Goru Formation of Jaisalmer Basin.

S.No.	Sample No.	Rb (ppm)	Sr (ppm)	^{87}Rb/^{86}Sr (atomic)	^{87}Sr/^{86}Sr atomic)±σn
1	Goru-2	273.4	106.0	7.47±0.15	0.71942±0.00007
2	Goru-3	279.8	119.4	6.79±0.14	0.71822±0.00010
3	Goru-4	282.5	173.2	4.72±0.09	0.71555±0.00258
4	Goru-5	308.2	86.9	10.28±0.21	0.72398±0.00043
5	Goru-6	393.2	113.1	10.07±0.20	0.71982±0.00007

*Standard with reported age of 95.03±1.11 Ma (Odin et al., 1982)

of 108±5 Ma with an MSWD of 1.09.

The Rb-Sr age of 108±5 Ma obtained from Goru glauconite can be interpreted as the depositional/early diagenesis age. K-Ar system is generally more susceptible than Rb-Sr system to post depositional changes (Clauer and Choudhari, 1995).

The average K-Ar age of 103±3 Ma and Rb-Sr age of 108±5 Ma obtained from these glauconites from Goru Formation are in good mutual agreement and consistent with an Albian age assigned to these sediments on the basis of palaeontological evidences (Chidambaram, 1991; Misra et al., 1993; Narayanan and Krishna, 1983) The upper part of Goru Formation was conclusively dated as Albian to basal Cenomanian (Sigal and Singh, 1980) based on planktonic zone-*Hedbergella washitensis* – *Planomalina buxtorfi*. Lucrose (1972) assigned an Albian or older age to the lower Goru Member on the basis of spore genus *Callialasporitis*.

The samples belonging to the uppermost Pariwar Formation (Pariwar-1, 2, 3 and 5) yield K-Ar ages of 102±4 Ma, 106±5 Ma, 106±5 Ma and 109±6 Ma, respectively (Table 3). The average K-Ar age of 106±3 Ma can be interpreted as the time of diagenesis. The upper and lower parts of Pariwar Formation are devoid of any micro-fauna, while the middle part shows their poor to moderate presence. The lower Goru/Pariwar boundary has tentatively been marked as the Albian/Aptian boundary on the basis of first downhole occurrence of *Globigerinelloides ferrolensis* (Chidambaram, 1991) in the middle part of Pariwar Formation. Upper Jurassic to Lower Cretaceous age based on Palynological studies (Maheshwari and Singh, 1974) and Lower Cretaceous age based on

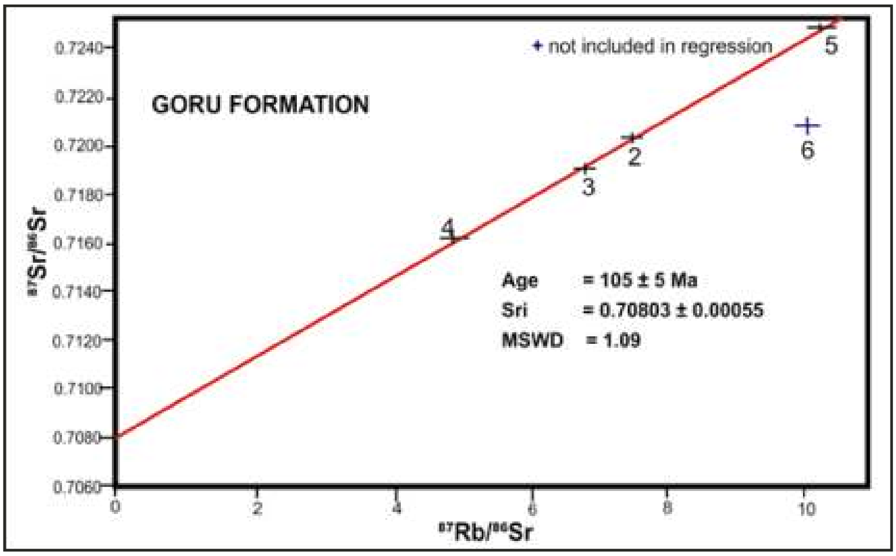

Fig. 6: Rb-Sr isochron age obtained from Goru glauconites, Jaisalmer Basin.

arenaceous foraminiferal assemblages (Mehrotra and Singh, 1968) have also been assigned to these sediments. The present K-Ar ages correspond to an Early Albian time for the deposition of sediments of upper Pariwar Formation.

Case Study 3: K-Ar ages of Ukra glauconites from the Kutch Basin, India

In this study Rathore et al., (1999b) report the K-Ar ages determined on glauconites samples collected from the Ukra Member of the Mesozoic Bhuj Formation in two different sections, one located on the Ghuneri-Ghaduli road near Katesar Mahadeo temple and the other at the base of the Ukra Hill in the northwestern part of the Kutch Mainland area.

The Kutch sedimentary basin, extending from the Great Rann of Kutch in the north to the Kathiawar (Saurashtra) peninsula in the south, in typically a peri-continental embayed basin occupying a rifted graben (Biswas, 1991). The Mesozoic rocks are exposed in six highland areas of Kutch (Mainland, Wagad, Pachham, Khadir, Bela and Chorar) whereas the Tertiary strata are exposed only in the bordering plainland (Fig. 7). In the Kutch Mainland area, a complete and thicker succession ranging from Middle Jurassic to Early Cretaceous is

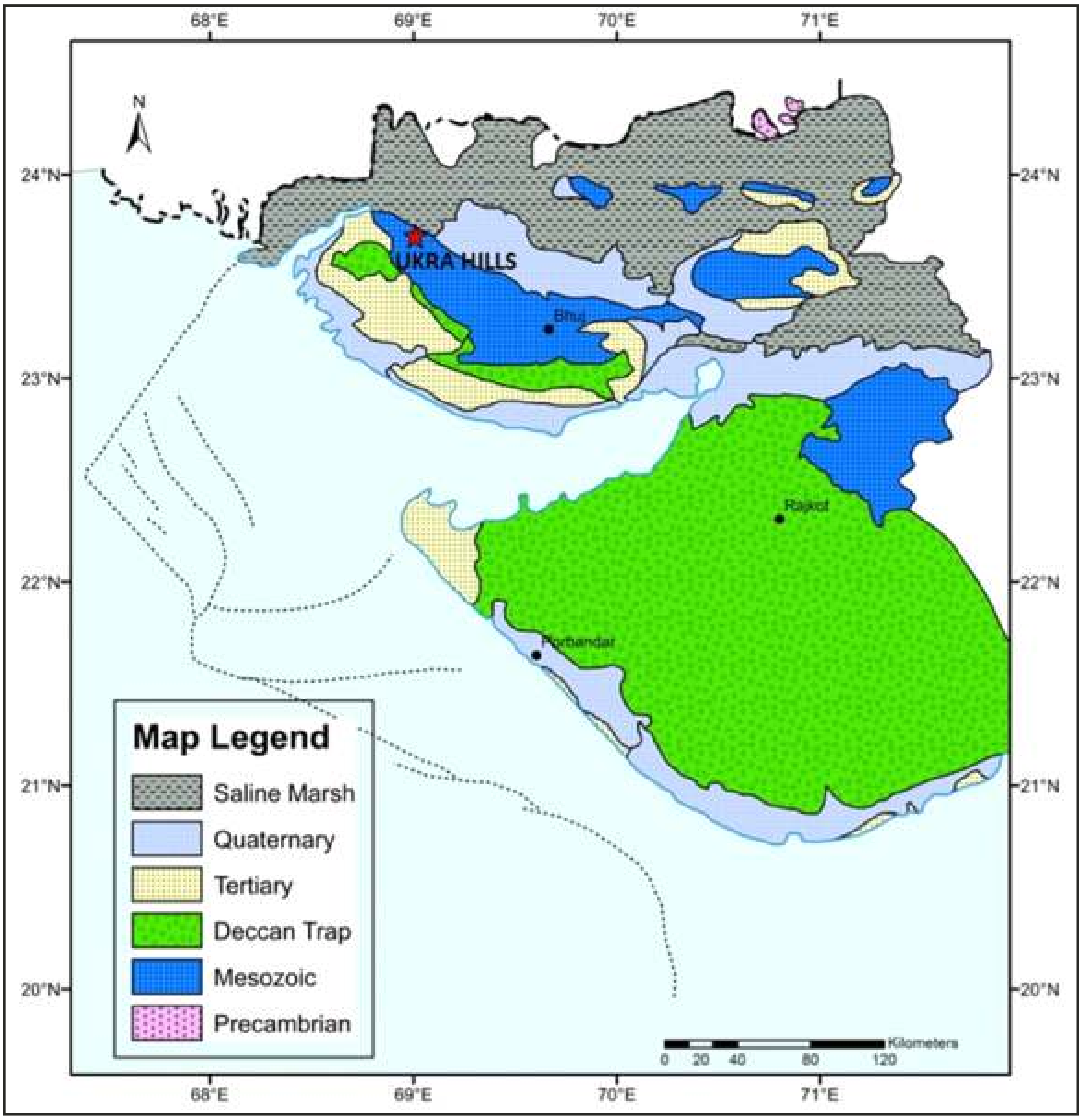

Fig. 7: Simplified geological map of Kutch (after Biswas, 1977) showing locations of studied samples.

exposed. The Mesozoic sediments in this area are divided into four lithostratigraphic units, viz. Jhurio, Jumara, Jhuran and Bhuj Formations ranging in age from Bathonian to Albian (Biswas, 1977).

The Bhuj rocks are exposed extensively in the mainland, occupying about three-fourth of the total area of the Mesozoic outcrops, and are divided into Ghuneri, Ukra and Upper Member in western Kutch. The Ukra Member of the Bhuj Formation, consisting mainly of fossiliferous glauconitic shale and sandstone, is a marine lithosome developed locally within the formation (Biswas, 1977).

The occurrence of the Ukra Member, which forms the middle part of the Bhuj Formation, is restricted and is best exposed at two places, one along the roadside near the Katesar Mahadeo temple on the Ghuneri-Katesar road and the other at the base of the Ukra hill near village Ghuneri, east of Lakhpat (Fig. 7). Glauconite samples used in the present study were collected from both the localities. Four samples (Ukra-KT-1-4) were collected from the bottom to the top of the Katesar temple section, consisting of about 90 cm thick friable glauconitic sandstone, which are underlain by a red ferruginous band. Additionally, four samples were also collected from and around the main Ukra hill (Ukra-UH-1-4). Analytical K-Ar data and calculated K-Ar ages of studied glauconite samples have been summarized in Table 5.

Three untreated samples, viz., Ukra-KT-1N, Ukra-KT-4N and Ukra-UH-3N, have yielded K-Ar ages of 107.9±3.4 Ma, 105.5±3.3 Ma and 103.5±3.4 Ma, respectively. Some of the samples were also treated with 0.5N HCl and 0.1N HCl to see the effect, if any, of the acid treatment on K-Ar ages. Those treated with 0.5N HCl and analysed in duplicate (Ukra-KT-1A and Ukra-KT-1AD), have yielded a relatively lower but concordant ages of 104.4±3.2 Ma and 103.6±3.2 Ma, respectively, which are in distinguishable from that of the untreated samples within the experimental error (Table 5). The sample treated with 0.1N HCl (Ukra-KT-4B) yielded an age of 106.5±3.3 Ma, which is also in concordance with the age of untreated samples. These results indicate that mild acid treatment (up to 0.5N HCl) does not lead to any argon loss and can safely be used for purification of glauconites, especially for dissolution of carbonate impurities.

Based on the mean age obtained for the glauconites, Rathore et al., (1999b) assigned an average stratigraphic age of 105.2±1.3 Ma to the Ukra Member, which had earlier been assigned biostratigraphic age of Lower Albian to Aptian (Pascoe, 1959; Krishnan, 1968; Biswas, 1971; 1977). The Ukra Member has also been suggested to be Late Aptian (Australiceras) to Early Middle Albian (Lemuroceras) based on ammonoid studies (Krishna, 1994). The K-Ar ages obtained in the present study from two different sections of the Ukra Member are indistinguishable and hence provide the first quantitative radiometric age estimation to this member to be 105.2±1.3 Ma as the

Table 5: K-Ar analytical data and obtained ages from Ukra Glauconite samples from Kutch.

S.No.	Sample No.	K (Wt%)	Total ^{40}Ar	Rad ^{40}Ar	Age$^{(\pm 2\sigma)}$ (Ma)
1	Ukra-KT-1N	5.42	304.56	234.08	107.9±3.4
2	Ukra-KT-1A	5.42	291.42	226.36	104.4±3.2
3	Ukra-KT-1AD	5.42	301.84	224.39	103.6±3.2
4	Ukra-KT-4N	5.64	281.16	238.11	105.5±3.3
5	Ukra-KT-4B	5.64	284.93	240.43	106.5±3.3
6	Ukra-UH-3N	5.19	259.63	244.51	103.5±3.4
7	GLO*	6.46	298.408	243.086	94.3±2.8

N-Untreated sample, A-Sample treated with 0.5N HCl, B-Sample treated with 0.1N HCl, D-Duplicate Analysis, *-Glauconite standard with reported age of 95.03±1.11 (Odin et al., 1982) formation/deposition age of the glauconites of the Ukra Member.

Case Study 4: Rb-Sr dating of illites from Pre-Tertiaries of Ganga and Vindhyan basins and Himalayan Foothills

Several core samples of pre-Tertiary sediments and metasediments have been dated for illite dating using Rb-Sr technique during 1994-95 by Vijan et al. (1995). Three subsurface cores from wells Jabera-A (Rohtas Limestone, Vindhyan Basin), Puranpur-B (Bahraich Formation, Ganga Basin) and Jwalamukhi-B (Basal Dharmshala/ Subathu Formation, Himalayan foothills) were taken up for Rb-Sr dating as a part of NRBC sponsored project.

Well Jabera-A was drilled in Jabera dome located in the Son valley part of the Vindhyan Basin. Rb-Sr studies in this well were confined to CC-3 (529.5 m–538.5 m). The sediments belong to the Rohtas Limestone Formation, which forms the topmost part of the Semri Group (Lower Vindhyans) as shown in Fig 8. The sediments of CC-3 are dominantly alternations of shale and siltstone, the shales dark grey to black, poorly fossiliferous, moderately hard and feebly calcareous with distinct partings at places. The siltstones are light grey to dirty white, moderately hard and occur as bands and intercalations in shale (Sen et al., 1993).

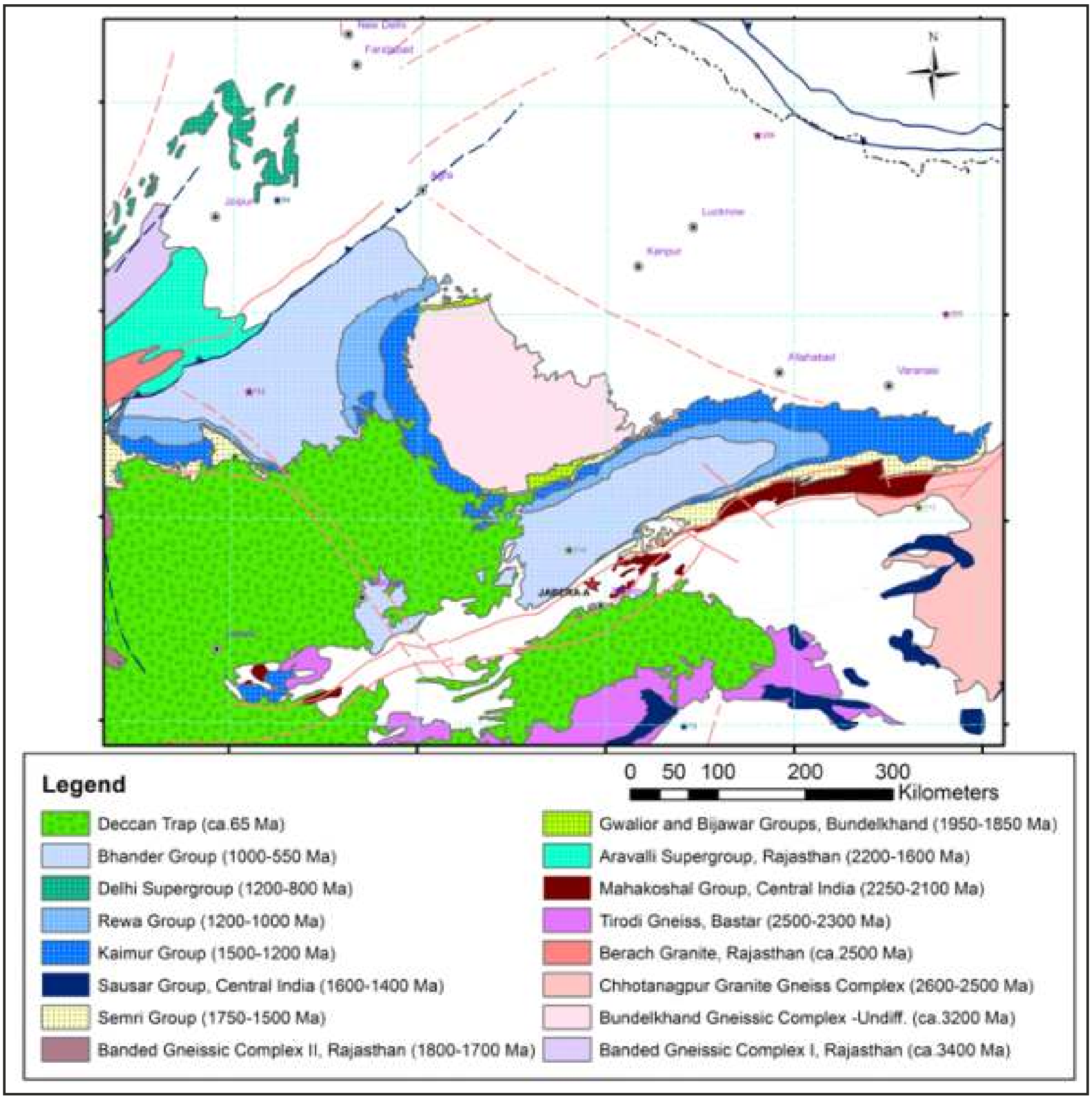

Fig. 8: Map of Son Valley part of Vindhyan Basin showing location of the studied well Jabera-A.

The Ganga Basin is divided into several depressions/lows in which Tertiary Siwalik sediments overlie Vindhyan/Baraich sediments. The lower Vindhyan sediments are confined to Madhubani depression while the Upper Vindhyans have considerable thickness in the Puranpur and Gandak depressions (Shukla et al., 1993). The well Puranpur-B is located in the Puranpur depression (Fig. 9). Conventional core CC-17 (4232.5 m–4234.0 m) from this well was selected for Rb-Sr studies. Petrographic studies of this core, belonging to Baraich Formation, indicate that the rock has suffered incipient metamorphism due to load effect (Tikku et al., 1979) with secondary growth as well as suturing as in the case of metaquartzite.

The Himalayan Foothill belt, which mainly exposes Tertiaries, ranges in age from late Riphean to Quaternary underlain by igneous and metamorphic rocks of the basement. The well Jwalamukhi-B, drilled in Jwalamukhi structure of the basin, was terminated in the Tertiary Basal Dharmshala/ Subathu Formation, from which conventional core CC-13 (6647 m–6652 m) was selected for the study (Fig. 10).

The sediments of CC-13 representing Basal Dharmashala/ Subathu Formation, are dominantly argillaceous, consisting of silty sand and shales in alterations. Owing to the presence of greenish grey argillofacies, their highly calcitic veined nature and occurrence of carbonaceous matter, the Basal Dharmshala sediments occurring in this well have been considered to be the depositional product of the remnant Subathu Sea (Tyagi et al., 1990). However, there are different opinions by other workers (Shukla et al., 1993) that the Subathus are not encountered in these wells, and the sediments in question encountered in Jwalamukhi-B belong to Lower Dharmshala Formation.

Two sets (one unspiked and the other spiked with ^{84}Sr and ^{87}Rb) from each of the separated clay fractions of Jwalamukhi-B and Jabera-A as well as

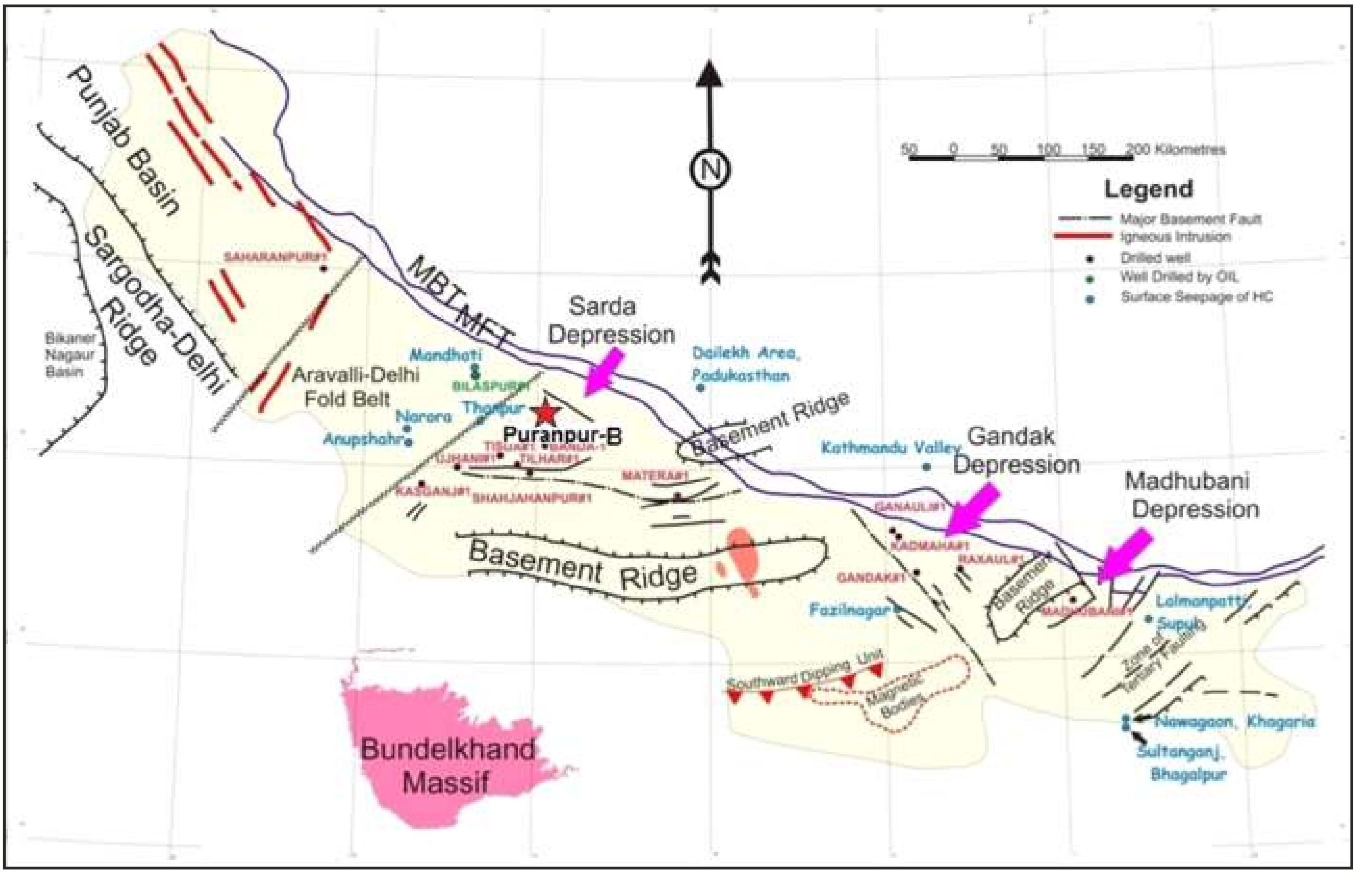

Fig. 9: Map of Ganga Basin showing location of the studied well Puranpur-B.

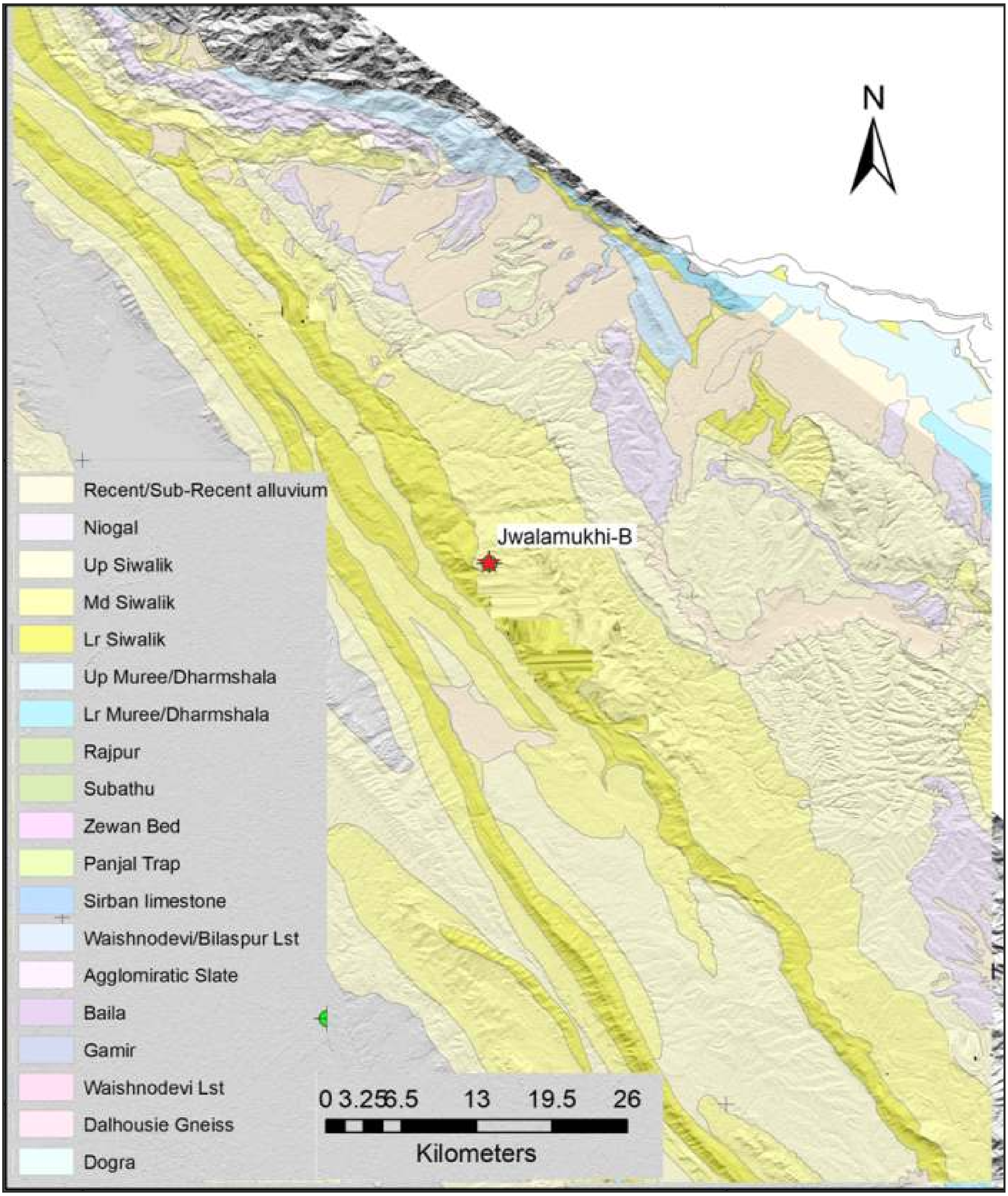

Fig. 10: Map of Himalayan Foothills belt showing location of studied well Jwalamukhi-B (After Mazumder et al., 2016)

from whole rock samples of CC-17 of Puranpur-B were digested, and Rb and Sr were separated using ion-exchange chromatography following standard procedure, after which Rb and Sr isotopic measurements were carried out on a VG-354 thermal ionization mass spectrometer. Rb-Sr analytical data for three cores have been summarized in Table 6.

Five whole rock samples of metasediments were analysed from CC-17 of well Puranpur-B. The best fit line obtained from the data points comprising the measured $^{87}Sr/^{86}Sr$ and $^{87}Rb/^{86}Sr$ ratios on the isochron gives a slope corresponding to an age of 924±44 Ma and an initial $^{87}Sr/^{86}Sr$ ratio of 0.7271±0.0023 (Fig.11).

The Bahraich Group of sediments in the Ganga Basin, comprising of epigrade metamorphic rocks viz., phyllite, quartzite, sericite schist and marble, have been correlated to those forming the Gwalior series exposed in the southern part of the basin (Shukla et al., 1993). These sediments have been assigned depositional ages in the range 1600-2000 Ma (Krishna and Tandon, 1994) based on classification of Precambrian rocks of peninsular India (Crawford and Compston, 1970; Sarkar, 1983). Also, an absolute Rb-Sr age of 1600±15 Ma was obtained by Singh et al., (1992) for orthoquartzitic sediments of Bahraich Group. It is obvious, therefore, that the isochron age of 924±44 Ma, obtained for metaquartzite and phyllitic sediments in CC-17 of well Puranpur-B, does not indicate the time elapsed since its deposition, rather it reflects the time elapsed since a post-depositional thermal event which led to isotopic re-equilibrium of Sr in these sediments. This event could be one of the reported number of metamorphic and plutonic events which took place at depth in the Aravalli-Delhi, Satpura and Eastern Ghat orogenic belts during 900-1000 Ma (Sarkar, 1980; 1983).

For the CC-3 of well Jabera-A, $^{87}Rb/^{86}Sr$ and $^{87}Sr/^{86}Sr$ ratios obtained from <2μm illite rich clay fractions define an isochron which gives a slope corresponding to an age of 939±44 Ma and an initial

Table 6: Rb-Sr analytical data from studied samples of Puranpur-B, Jabera-A and Jwalamukhi-B from Ganga, Vindhyan and Himalayan Foothills, respectively.

S.No.	Sample No.	Rb (ppm)	Sr (ppm)	$^{87}Rb\ ^{86}Sr$	$^{87}Sr/^{86}Sr$
(a) Puranpur-B; CC17 (4232.5-4334.0)					
1	1/2T	19.68	27.39	2.0887	0.754292±0.000060
2	1/2M	73.03	28.47	7.5053	0.824337±0.000066
3	1/2B	21.70	14.07	4.4968	0.788489±0.000252
4	2/2T	35.19	18.71	5.4888	0.796890±0.000176
5	2/2B	17.12	12.56	3.9730	0.782967±0.000046
(b) Jabera-A; CC-3 (529.5-538.5 m)					
1	2/10-S4	288.18	18.89	47.1341	1.400613±0.000140
2	2/10-S7	366.47	17.05	68.0583	1.682368±0.000168
3	4/10-S12	305.92	19.02	50.3240	1.537788±0.000092
4	5/10-S18	304.38	20.77	45.1384	1.369568±0.000082
5	7/10-S25	318.84	13.72	74.1644	1.758541±0.000140
(c) Jwalamukhi-B; CC-13 (6647-6652 m)					
1	1/5-S2	265.35	77.83	9.9059	0.750676±0.000090
2	1/5-S6	250.91	89.35	8.1583	0.749580±0.000045
3	3/5-S15	205.14	71.72	8.3107	0.750453±0.000060
4	4/5-S20	227.52	73.85	8.9508	0.750046±0.000060
5	5/5-S25	296.23	72.00	11.9577	0.754030±0.000100

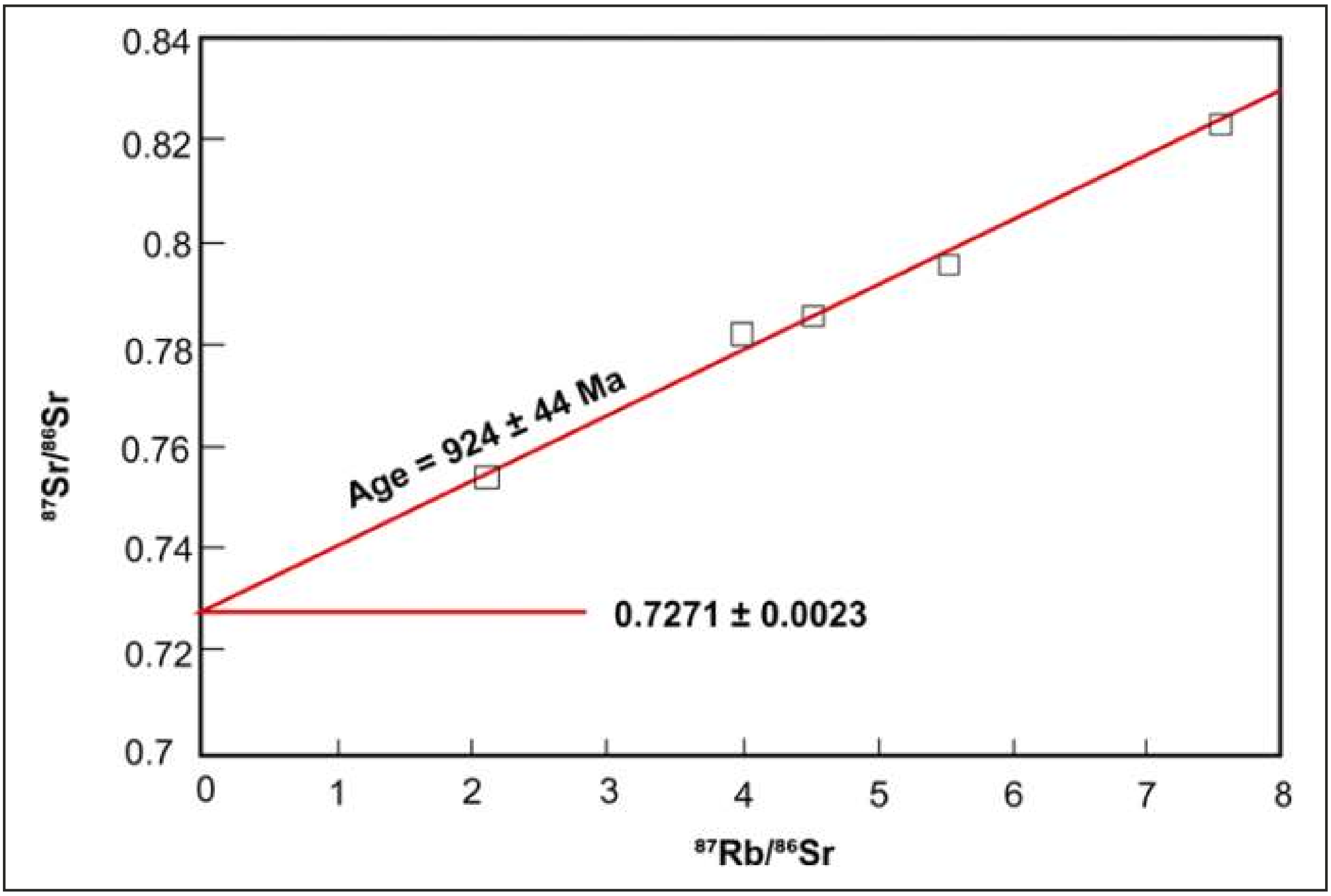

Fig. 11: Rb-Sr isochron age obtained from studied well Puranpur-B.

$^{87}Sr/^{86}Sr$ ratio of 0.765±0.035. The very high initial ratio probably indicates secondary alteration of the sediments or post depositional diagenesis.

Based on an apparent Rb-Sr age of 1140±12 Ma for phlogopites from Majhgawan Kimberlites which intrude Upper Vindhyan Kaimur Sandstone near Panna in M.P., Crawford and Compston (1970) have placed the base of Upper Vindhyans at about 1150 Ma. Tugarinov et al., (1965), on the other hand, based on K-Ar analysis of glauconites from several horizons in Mirzapur (Son valley) and Chittorgarh, have assigned ages of 910 Ma and 940 Ma for Upper and Lower Kaimur series, and 1140 Ma and 1400 Ma for Upper and Lower Semri series, respectively, which indicates that the boundary between upper and lower Vindhyans could be between 940 Ma and 1140 Ma (Tugarinov et al., 1965). The Upper Vindhyan sediments (Ujhani and Karnapur Formations) deposited in the Puranpur depression are also believed to be younger than 950 Ma (Shukla et al., 1993). An age of 939±44 Ma obtained CC-3 of Jabera-A (Fig. 12) from Rohtas Limestone which is broadly consistent with the ages reported by Tugarinov et al., (1965) and also with the tectonic regime suggested by Shukla et al., (1993).

For the CC-13 from well Jwalamukhi-B, five <2µm size illite dominant clay samples yield a mutually concordant Rb-Sr isochron age of 94±10 Ma (Fig. 13) with an initial $^{87}Sr/^{86}Sr$ ratio of 0.7378±0.0014. The date obtained from the isochron plot is much older than the generally accepted age of deposition for Basal Dharmshala/Subathu sediments. Based on palynofossil assemblages recorded in this well, Palaeocene to Lower Eocene ages have been inferred for Basal Dharmshala/Subathu Formations encountered in this well (Mishra and Kapoor, 1994). In the Rb-Sr dating technique for clay rich sedimentary rocks, the success of obtaining meaningful dates depends on a thorough mineralogical study, which in the case of present

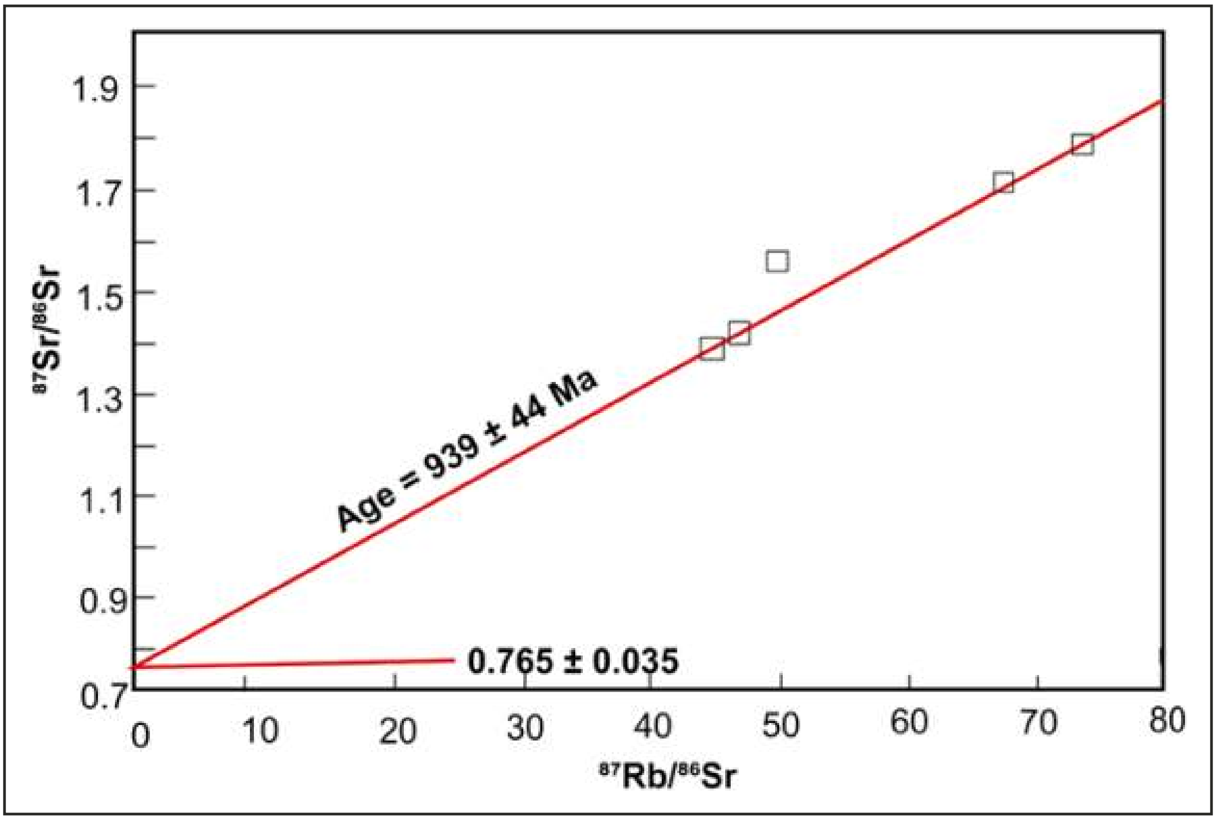

Fig. 12: Rb-Sr isochron age obtained from studied well Jabera-A.

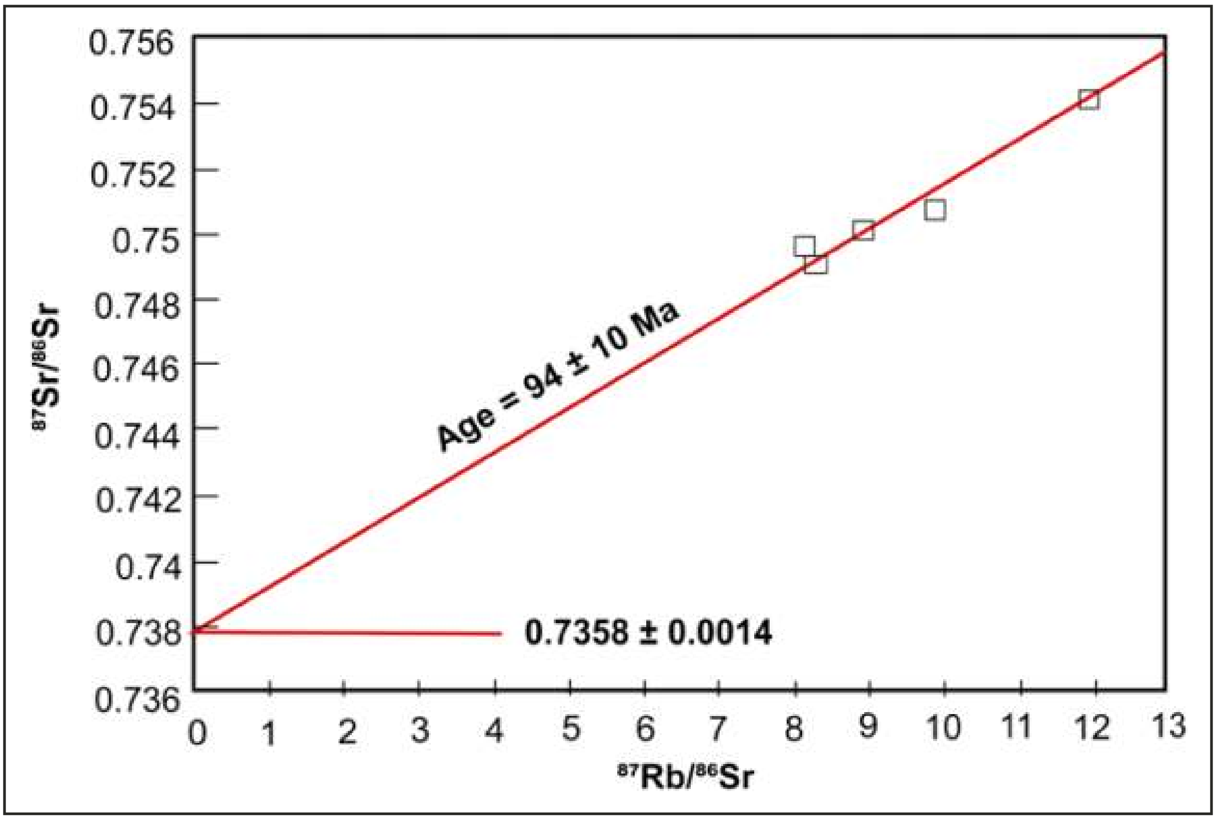

Fig. 13: Rb-Sr isochron age obtained from studied well Jawalamukhi-B

study, were not carried out. It has been recognized that <2μm illite rich clay fractions may contain clays that are either authigenic or that were transformed during deposition and diagenesis, whereas coarser size fractions may be composed predominantly of detrital clays whose presence leads to overestimation of the time of deposition. In addition, illite can occur in several polymorphic forms (1M, 1Md and 2M), out of which 1M and 1Md polymorphs form at low temperatures and are authigenic/diagenic in nature, whereas 2M polymorphs form at higher temperatures and mostly represent detrital illites.

Although, the clays (<2μm) separated from CC-13 of Jwalamukhi-B were found to be illite rich, it was not determined quantitatively the various illite polymorphs due to the lack of standardized in-house procedures, and might have resulted to overestimation of the time of deposition. The age of 94±10 Ma therefore probably corresponds to an age between the time of deposition of these sediments and the age of the source.

DISCUSSIONS

1. Despite recent developments in $^{40}Ar/^{39}Ar$ dating, the conventional K–Ar method is still a valuable tool for clay dating due to a convenient and straightforward use supported by a standardized and well-controlled technical approach. K-Ar technique has always been able to provide good and reliable ages for glauconite dating which are consistent with biostratigraphic ages. This has been well demonstrated in the presented case studies where K-Ar analysis of glauconites of various grain sizes from different formations and members of prominent sedimentary basins like Vindhyans, Jaisalmer and Kutch, yielded reliable quantitative glauconite ages with very little 1σ errors.
2. Rb-Sr technique has also been successfully utilized in providing mutually concordant depositional ages for glauconites which are indistinguishable and agreeable to the obtained K-Ar ages within the error range, as demonstrated in case of Goru Formation of Jaisalmer Basin.
3. The studies also indicated that mild acid treatment (up to 0.5N HCl) on the glauconites does not cause any loss in radiogenic argon and may be helpful in purification of samples.
4. Clay minerals from metaquartzitic and phyllitic sediments of Bahraich Formation from well Puranpur-2 of Ganga Basin, illite rich clay fractions from well Jabera-A of Vindhyan Basin as well as those from well Jwalamukhi-B of Himalayan Foothills were attempted for Rb-Sr dating. However, only those from well Jabera-A were able to provide biostratigraphically consistent early diagenetic age of Lower-Upper Vindhyan transition for Rohtas Limestone. Rest of the studied samples from Ganga Basin and Himalayan Foothills sediments appear to have been affected by isotopic re-equilibrium and/or an artefact of detrital fractions/polymorphs and hence yielded much younger, or older ages by using Rb-Sr dating technique.

CONCLUSIONS

- Absolute dating of the age of deposition or early diagenesis of sedimentary rocks is highly problematic, but by maintaining good analytical control, meaningful depositional ages can be obtained.
- In order to avoid problems of detrital components present in the clastic rocks, it is mandatory that authigenic minerals such as glauconites, illites are to be selected for Rb-Sr, K-Ar and $^{40}Ar/^{39}Ar$ dating.
- For clay analysis, detailed mineralogical analyses are required to identify different generations and polymorphs of clays developed during various diagenetic and post-diagenetic processes and to avoid detrital minerals that may still be present in fine grained clay fraction.
- Studies of glauconites have shown that the well evolved mature glauconites with high K_2O contents appear to fulfil the requirement of having a homogeneous isotopic source and

produce meaningful ages of deposition and early diagenetic events.

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REFERENCES

Biswas S.K. (1971) Note on the Geology of Kutch. *Qtly. Jour. Geol. Min. Met. Met. Soc. India,* 43 (4), 220-235.

Biswas S.K. (1977) Mesozoic rock stratigraphy of Kutch, Gujarat. *Qtly. Jour. Geol. Min. Met. Met. Soc. India,* 49 (3-4), 1-52.

Biswas S. K. (1991) Stratigraphy and sedimentary evolution of the Mesozoic basin of Kutch, western India. *In: Sedimentary Basins of India: Tectonic Context (Editted by S. K. Tondon and S. M. Cashyap),* 74-103.

Cassignol C. and Gillot P. Y. (1982) Range and effectiveness of unspiked potassium-argon dating: experimental ground-work and applications. *In Odin, G. S. (ed.), Numerical Dating in Stratigraphy. Chichester, Part 1: Wiley*, 159–179.

Chidambaram L. (1991) Mesozoic biostratigraphy, paleobathymetry and paleogeography of subsurface sediments in western Rajasthan. *In: Conf. on Integrated Expl. Research: Achievements and Perspectives, J. Pandey and V. Banerjee, (Eds.), KDMIPE, Dehradun,* 179-187.

Clauer N. and Choudhari S. (1995) Clay in crustal environments: Isotope dating and tracing, *Springer, Berlin.*

Clauer N., Keppens E. and Stille P. (1992) Sr isotopic constraints on the process of glauconitization. *Geology,* 20, 133-136.

Compston W. and Pidgeon R.T. (1962) Rubidium–strontium dating of shales by the total-rock method.*J. Geophys. Res*., 67, 3493–502.

Crawford A. R. and Crompston W. (1970) The age of Vindhyan system of Peninsular India. *Quart. J. Geol. Soc. London,* 125, 351-371.

Dalrymple G.B. (1991) The Age of the Earth. *Stanford: Stanford University Press*.

Dalrymple G.B. and Lanphere M. A. (1969) Potassium-Argon dating. *San Francisco: W.H. Freeman.*

Dickin A.P. (1995) Radiogenic Isotope Geology. *Cambridge: Cambridge University Press*.

Dunoyer de Segonzac G. (1969) Les min´eraux argileux dans la diagen`ese. *Passage au m´etamorphisme. M´em. Serv. Carte G´eol. Alsace Lorraine,* 29, 320 pp.

Faure G. (1986) Principles of Isotope Geology. *New York: Wiley.* 589 pp.

Gororkhov I.M., Clauer N., Turenko T. L., Melnikov N. N., Kutyavin E. P., Pirrus E., and Basakov A. V. (1994) Rb-Sr systematics of Vendian-Cambrian claystones from the East European platform: implications for a multi-stage illite evolution. *Chemical Geology*, 112, 71–89.

Kelley S. (2002) K-Ar and Ar-Ar dating. *Reviews in Mineralogy and Geochemistry*, 47 (1), 785–818.

Krishna A.M. and Tandon A.N. (1994) Study of regional seismic lines in Puranpur-Baraich area and identification of major structural/stratigraphic features.,*Unpub. Rep. EGB, NRBC, ONGC, Dehradun.*

Krishna J. (1994) Environmental reconstruction studies of Mesozoic sedimentary sequences in western Kachchh. *Unpub. Project rept. Submitted to KDMIPE, ONGC, Dehradun*

Krishnan M.S. (1968) Geology of India and Burma. *Madras, Higginbothom.*

Kubler B. (1966) La cristallinit´e d'illite et les zones tout `a fait sup´erieures du m´etamorphisme. Colloque sur les ´etages tectoniques. *Universit´e de Neuch^atel `a la Baconni`ere Neuch^atel*, 105–22.

Lee J. K. W. (2015) Ar-Ar and K-Ar dating. *In: Encyclopedia of Scientific Dating Methods, Springer Pub.,* pp. 58-72.

Lucrose N.G. (1972) Palynological evidence of the age of Lathi formation, western Rajasthan, India. *Seminar on Paleopalynology and Indian Stratigraphy, Calcutta Univ.,* 155-159.

Maheshwari H.K. and Singh N.P. (1974) On some plant fossils from Pariwar formation, Jaisalmer Basin, Rajasthan. *The Palaeobotanist,* 23, 116-123.

Mazumder S., Mishra B.K., Blecy Tep, Pangtey K.K.S. (2016) Morphotectonic Analysis of Himalayan Foothill and adjoining foreland areas from Punch to Tanakpur. *Unpub. ONGC Report.*

McDougall I. and Harrison T.M. (1999) Geochronology and Thermochronology by the ^{40}Ar/^{39}Ar Method, *2nd edn. Oxford: Oxford University Press.*

Mehrotra R.B. and Singh N.P. (1968) Micropalaeontological report on the wells drilled in Jaisalmer area. *Unpub. Report, KDMIPE, ONGC, Dehradun.*

Merrihue C. and Turner G. (1966) Potassium–argon dating by activation with fast neutrons. *J. Geophys. Res.* 71, 2852–7.

Meunier A. and Velde B. (2004) Illite: Origins, Evolution and Metamorphism. *Berlin: Springer*. 286 pp.

Mishra C.M. and Kapoor P.N. (1994) Palaeocene to Middle Miocene palynoflora, age and palaeoenvironment in Jwalamukhi well-B, Himalayan Foothills. *In: Proc. 2nd Sem. Petroliferous basins of India, 1991. (Ed.) Biswas S. K. et al., Indian Petroleum Publishers, Dehradun, India,* 147-160.

Misra P.C., Singh N.P., Sharma D.C., Kakroo A.K., Upadhyay J. and Saini M.L. (1993) Lithostratigraphy of Indian petroliferous basins, document II: Western Rajasthan Basin. *Unpubl. Report, KDMIPE, ONGC, Dehradun.*

Morton J.P. and Long L.E. (1980) Rb-Sr dating of Palaeozoic glauconite from the Llano region, central Texas. *Geochim. Cosmochim. Acta,* 44, 663-672.

Narayanan V. and Krishna A. (1983) Biostratigraphy of Ghotaru-A well, Rajasthan. *Unpubl. Report, KDMIPE, ONGC, Dehradun.*

Odin G.S. and 35 Collaborators (1982) Interlaboratory standards for dating purposes. *In Odin G. S. (ed.), Numerical dating in Stratigarphy, John Wiley, Chichester,* 123-150.

Odin G.S. and Matter A. (1981) De glauconiarum originae. *Sedimentology*, 28, 611 - 641.

Padhy P.K. (1995) Proterozoic hydrocarbon prospects – an Indian scenario. *Proc. Petrotech-95, New Delhi, India.* 1-20.

Pascoe E.H. (1959) A manual of geology of India and Burma. *Geol. Surv. India.,*2, 484-1343.

Rathore S.S., Venkatesan T.R. and Srivastava R.K. (1996) Rb-Sr and Ar-Ar systematics of Malani volcanic rocks of southwest Rajasthan: Evidences for a younger post-crystallization thermal event. *Proc. Indian Acad. Sci. (Earth Planet. Sci.),* 105 (2), 131-141.

Rathore S.S., Vijan A.R., Krishna, Prabhu B.N. and Misra K.N. (1999a) Dating of glauconites from Sirbu Shales of Vindhyan Supergroup, India. *Proceedings Third Int. Pet. Conf. & Exbn, Petrotech-99*, 191-196.

Rathore S.S., Prabhu B.N., Vijan A.R., Vig K.C. and Misra K. N. (1999b) K-Ar age of Ukra glauconites from the Kutch Basin, India. *Proc. Indian Acad. Sci. (Earth Planet. Sci.)*, 108 (1), 49-55.

Renne P.R., Sharp W.D., Deino A.L., Orsi G., and Civetta L. (1997) ^{40}Ar/^{39}Ar dating into the historical realm: calibration against Pliny the Younger. *Science*, 277, 1279–1280.

Sarkar S.N. (1980) Precambrian stratigraphy and geochronology of Peninsular India: A review. *Ind. Jour. Earth Sci.,* 7 (1), 12-26.

Sarkar S.N. (1983) Present status of Precambrian stratigraphy and Geochronology of Peninsular India: A synopsis. *Ind. Jour. Earth Sci.,* 10 (1), 104-106.

Sastry M.V. A. and Moitra A.K. (1984) Vindhayn Supergroup – A review. *Geol. Surv. India Mem.,* 116 (II), 109-148.

Sen A.K., Gawli S.C. and Ramdev C.M. (1993) Well completion report of Jabera-1.

Shukla S.N., Katiyar G.C., Mudiar B., Krishna A.M. and Misra M.M. (1993) Lithostratigraphy of Indian petroliferous basins. *Document I: Ganga, Punjab and Purnea basins, Unpub. Rep., KDMIPE, ONGC, Dehradun.*

Sigal J. and Singh N.P. (1980) Cretaceous biostratigraphy of Jaisalmer subsurface, Rajasthan, India. *VIII Colloq. Indian Micropal. Strat.* 22-23.

Singh R.R., Pal M., Rathi P. and Arora S.R. (1992) Rb-Sr geochronological report of core-8 from Matera-A (NRBC), Bahraich depression of Ganga basin. *Unpub. Report, KDMIPE. ONGC, Dehradun.*

Smith P.E., Evensen N.M. and York D. (1993) First successful ^{40}Ar/^{39}Ar dating of glauconies: argon recoil in single grains of cryptocrystalline material. *Geology,* 21, 41–4.

Srivastava A.P. and Rajagopalan G. (1988) F-T ages of Vindhyan glauconitic sandstone beds exposed around Rawatbhata area, Rajasthan. *J. Geol. Soc. India,* 32, 527-529.

Steiger R.H., and Jäger E. (1977) Subcommission on geochronology: convention on the use of decay constants in geo-and cosmochronology. *Earth and Planetary Science Letters*, 36, 359–362.

Sudo M., Tagami T., Sato K., Hasebe N. and Nishimura S. (1996) Calibration of a new Ar analytical system for the K-Ar dating method and analytical results of K-Ar age known samples. *Memoirs of the Faculty of Science, Kyoto University, Series of Geology and Mineralogy*, 58, 21–40.

Tikku C.L., Gupta V.K., Sharma S.M., Abbasi N.A., Kararia A.D. and Gupta J. P. (1979) Well completion report of Puranpur-2.

Tugarinov A.I., Shanin L.L., Kazakov G.A. and Arakeyants M.M. (1965) On the glauconite ages of the Vindhyan system (India). *Geochemica,* 6, 652-660.

Tyagi A.K., Rana G.S., Bhatnagar A.K., Nayal A.K. and Prasad K.N. (1990) Sedimentological studies of recently drilled exploratory wells in northern region i.e. Jwalamukhi-B, Nurpur-A and Surinsar-B., *Unpub. Report, KDMIPE, ONGC, Dehradun.*

Velde, B. (1992). Introduction to Clay Minerals: Chemistry, Origins, Uses, and Environmental Significance. *New York: Chapman & Hall,* pp. 198.

Venkatachala B.S., Sharma M. and Shukla M. (1996) Age and life of the Vindhyans–Facts and conjectures. *Mem. Geol. Soc. India,* 36, 137-165.

Vijan A.R., Ghosh N., Krishna, Prasad S. and Prabhu B.N. (1995) Geochronological studies on surface samples and cores of different wells of NRBC. *Unpub. Report. KDMIPE, ONGC. Dehradun.*

Vijan A.R., Rathore S.S., Vig K.C., Bansal M., Singh M.P. and Prabhu B.N. (2000) K-Ar and Rb-Sr ages of Cretceous glauconites from Jaisalmer Basin, Rajasthan. *Jour. Geol. Soc. India,* 56, 15-25.

Waight, T. (2015) Sedimentary Rocks (Rb-Sr Geochronology) *In: Encyclopedia of Scientific Dating Methods, Springer Dordrecht, Heidelberg*

Zwingmann H. (2015) Clays and Glauconites (K-Ar/Ar-Ar). *In: Encyclopedia of Scientific Dating Methods, Springer Dordrecht, Heidelberg.*