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FTIR investigation on the fluid inclusions in quartz veins of the Penakacherla Schist Belt

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Penakacherla Schist Belt is a part of the eastern Dharwar craton lying along the Ramagiri–Hungund arc. Fluids entrapped in quartz veins of two mafic volcanic rocks of this area are characterized by FTIR spectroscopy in the wave number region 2000–8000 cm⁻¹. The quartz–carbonate vein from the central part of the schist belt contains H₂O, CO₂ and aliphatic hydrocarbon inclusions, with bicarbonate in the form of nahcolite (NaHCO₃) coexisting with quartz, whereas, that from the nearby Bhadrampalli mine area is depleted in CO₂ and hydrocarbons, and enriched in H₂O inclusions. Distinctly clear signatures of silanol (Si-OH) group and the coexistence of calcite with quartz have also been observed in the latter quartz. These observations indicate that re-crystallization of quartz in these two similar rocks occurred in vastly different hydrothermal environments.

QUARTZ–gold veins in metamorphic rocks usually contain low to moderate saline, mostly immiscible H₂O and CO₂ fluid inclusions. There has been some debate over the nature of these inclusions, whether dominantly metamorphic, meteoric or magmatic^{1–5}. The fluid inclusions, in general, are considered to preserve the conditions of mineral formation and are a measure of the genetic evolution¹. However, in the recent past there has been a host of experimental and theoretical evidence against the ‘closed’ system behaviour of fluid inclusions^{1,6–8}. Fluid inclusions are now considered to behave as an ‘open’ system and their contents may diffuse into or out of the host mineral or rock. Detailed characterization of interactions among fluid inclusions and the host mineral or rock, and formation of some daughter minerals are important to understand various metamorphic processes. Vibrational spectroscopy (IR and Raman) is a versatile and non-destructive analytical tool to characterize the physico-chemical conditions of fluid entrapment. Detailed structural variations due to environmental impact could be probed using this method^{9,10}. Infrared absorption of hydroxyl ions is generally strong, and combined FTIR study covering both IR and NIR regimes is preferred to resolve the nature of these ions in minerals, namely hydrogen in the form of hydroxyl or water of crystallization^{11,12}. On the contrary, Raman cross-sections for (OH) groups are less and, hence, IR spectroscopy is preferred

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in quantification of the hydroxyl contents in minerals¹³. In the present study, we report characterization of fluids and their behaviour in quartz veins in the mafic volcanic rocks of Penakacherla Schist Belt (PSB), using FTIR spectroscopy. The quartz veins from the mafic volcanic rocks selected for this study are one each from the central part of the schist belt (RM-5/33), and the nearby Bhadrampalli mine area (RM-4/2). The lateral distance between the two samples along the strike is about 3 km and these two samples are more or less equidistant from the centre of the shear zone (~300 m towards east; Figure 1)¹⁴⁻¹⁶. Hence, one normally expects similar matrix-fluid interactions in these two samples. However, our studies reveal that the nature of fluid inclusions in these two samples is distinctly different.

PSB is the northern continuation of the Ramagiri Schist Belt. It is one of the best-exposed parts of the NNW-SSE striking Ramagiri-Hungund shear zone system and adjoining granitoids. Both western and eastern contacts of the belt are well exposed and mostly show intrusive, in general, and tectonic contact, at a few places. The granites on both the sides are younger to the belt and contain enclaves of gneisses ranging in size from a few cm to tens of km. Width of the schist belt at the centre is about 2-3 km, and in north and south, it decreases to about 500 m. Truncation of the belt in the northeastern part has occurred due to an oblique fault, thereby bringing almost all rock types in contact with granites¹⁶.

Major rock types constituting PSB are amphibolites, intermediate and acid metavolcanic rocks (quartz-micaschist), Banded Iron Formation and minor carbonaceous schist (Figure 1)¹⁴⁻¹⁶. The contacts among the basic, intermediate and acid volcanic rocks are sharp. Carbonatized intermediate metavolcanic rocks are also an important part of the belt. Mafic rocks are strongly bleached and chloritized in the main shear zone.

The quartz veins vary in thickness and exhibit pinching and swelling nature. Quartz-carbonate veinlets, ranging in thickness from a few mm to a few cm, are along the phyllonite planes at close spacing. Formation of quartz and carbonates at a few mm to few cm lateral distances across the strike within phyllonites is more prominent near the Bhadrampalli mine area, whereas it is less prominent in the central part of PSB.

Hornblende, plagioclase, chlorite, epidote, sulphides and iron oxides are the main constituents of amphibolites. Intermediate and acid volcanic rocks are primarily made up of quartz, plagioclase, K-feldspar, chlorite, sericite, sulphides and iron oxides. Hydrothermal alteration and deformation within the shear zone of PSB resulted in an alteration assemblage of chloritized amphiboles, recrystallized plagioclase and other minerals like carbonates, quartz, sulphides and gold. Quartz, ankerite, calcite, pyrite, arsenopyrite, chalcopyrite, chlorite and sericite are essential minerals of the alteration zone. The mineral

assemblage indicates that the rocks of PSB have undergone upper greenschist to lower amphibolite facies metamorphism. Chloritization, silicification and carbonatization are more abundant in the shear zone¹⁶.

FTIR study was carried out on NEXUS FTIR spectrometer of the Thermo-Nicolet, using thermo-electrically cooled DTGS detector and XT-KBr beam splitter, and having working wave number range 375-12,500 cm⁻¹, with an ultimate resolution of 0.5 cm⁻¹. Spectra obtained in this study are in the range 1500-10000 cm⁻¹, with each spectrum being the resultant of 480 scans, with an aperture of 13 and resolution 1 cm⁻¹. Doubly-polished, thin sections (about 60 µm) were used to record the spectra. The spectra were corrected for the background absorption, collected before and after, the sample. Hence, the contributions due to the environmental H₂O and CO₂ with the sample are negligibly small.

FTIR spectra of the samples in the wave number range 2000-8000 cm⁻¹, with an inset showing NIR spectra, are shown in Figure 2. Sample RM-5/33 contains mostly H₂O, CO₂ and hydrocarbon inclusions, with characteristic infrared absorption bands for H₂O around 3424 and 5200 cm⁻¹. The mode at 3424 cm⁻¹ is due to stretching of OH group, and the mode at 5200 cm⁻¹ is due to a combination of stretching and bending modes of H₂O (ref. 12). The presence of CO₂ is confirmed by weaker absorption band around 2350 cm⁻¹. Other weaker modes around 2956, 2924, 2869 and 2852 cm⁻¹ indicate the presence of aliphatic hydrocarbons¹⁷. The bands around 2670, 2595 and 2493 cm⁻¹ could be due to (OH) stretching modes observed in nahcolite (NaHCO₃)¹⁸. Two other weaker modes around 2130 and 2240 cm⁻¹, which could be due to combinations of Si-O bond, clearly indicate the matrix under study as quartz¹⁹. Absence of infrared bands around 3600 and 4500 cm⁻¹ indicates non-existence of Si-OH groups in this quartz sample. In sample RM-4/2, a sharper band around 3598 cm⁻¹ that is typical of Si-OH stretching is recorded. Occurrence of silanol group is further confirmed by near infrared absorption bands around 4500 and 7060 cm⁻¹ (refs 11 and 12). The characteristic band of CO₂ (around 2350 cm⁻¹) is almost absent, indicating its depletion. Additionally, there exist two other stronger absorption bands at around 2514 and 2578 cm⁻¹, which could be due to a daughter mineral, calcite (CaCO₃)¹⁸.

Non-leakage behaviour of the entrapped fluid inclusions may be expected, if the post-metamorphic cooling path approximately follows the isochore path of the fluid mixture. However, the inclusions may diffuse into the matrix if any deviations occur in the cooling conditions^{1,6,7,20}. The leakage behaviour and the daughter mineral formation, etc. are the typical signatures of post-entrapment effects^{1,21}. It is clear from Figure 2 that the fluids in rock sample RM-5/33 are different from those in the sample RM-4/2, though they are from the same rock type and are entrapped in quartz matrix. The inclusions in

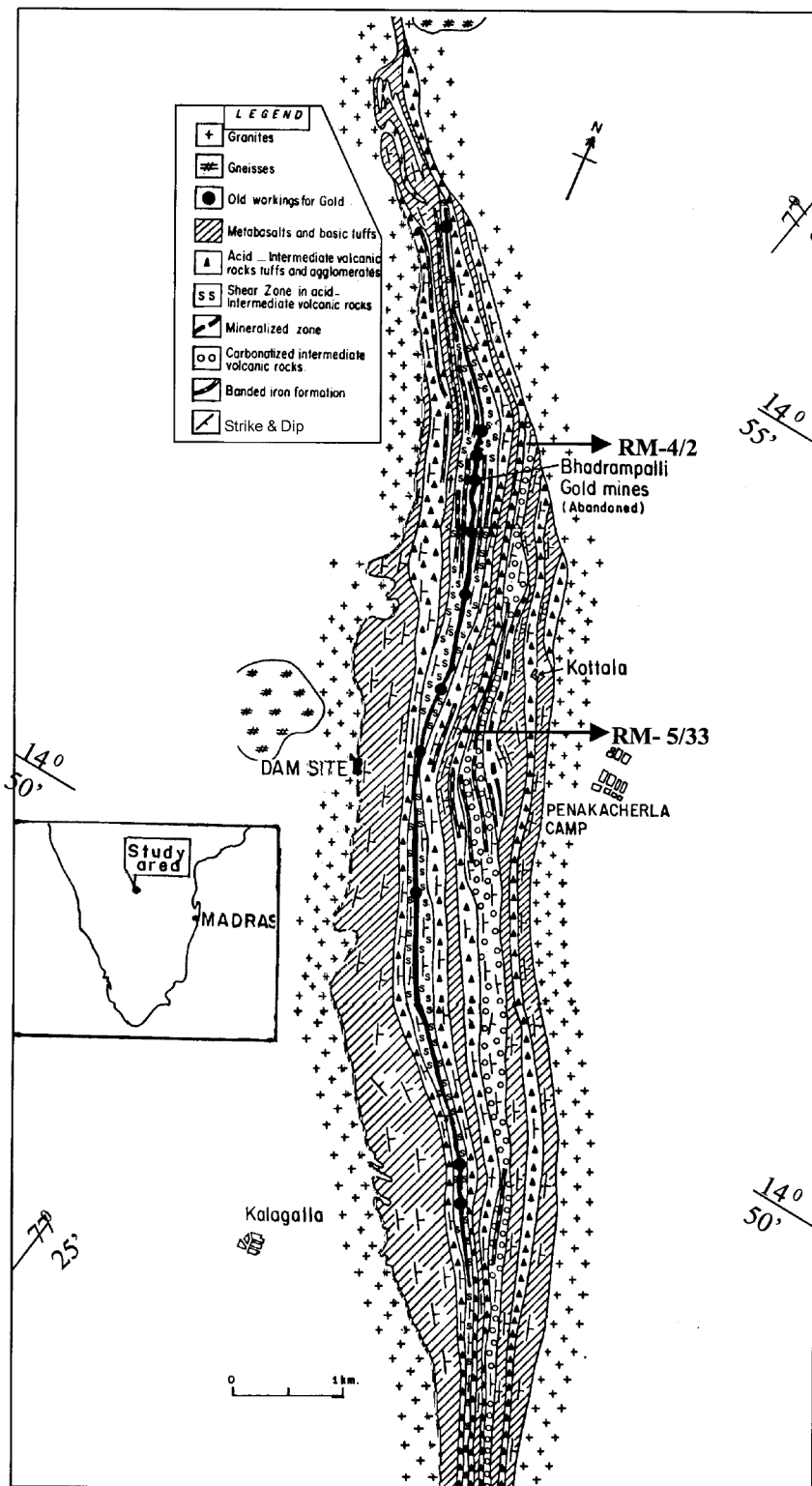


Figure 1. Geological map of the part of Penakacherla Schist Belt (after Manikyamba *et al.*¹⁴).

sample RM-5/33 are typical of a 'closed' system, whereas those in sample RM-4/2 are like in an 'open' system'. FTIR spectra of fluids in the sample RM-5/33 at higher temperatures, by heating to the desired tempera-

ture in a muffle furnace for about 15 min and quenching to the ambient temperature, are shown in Figure 3. It is evident that the peak absorbance at around 3424 cm^{-1} , decreased from about 0.4 to 0.1 when the temperature is

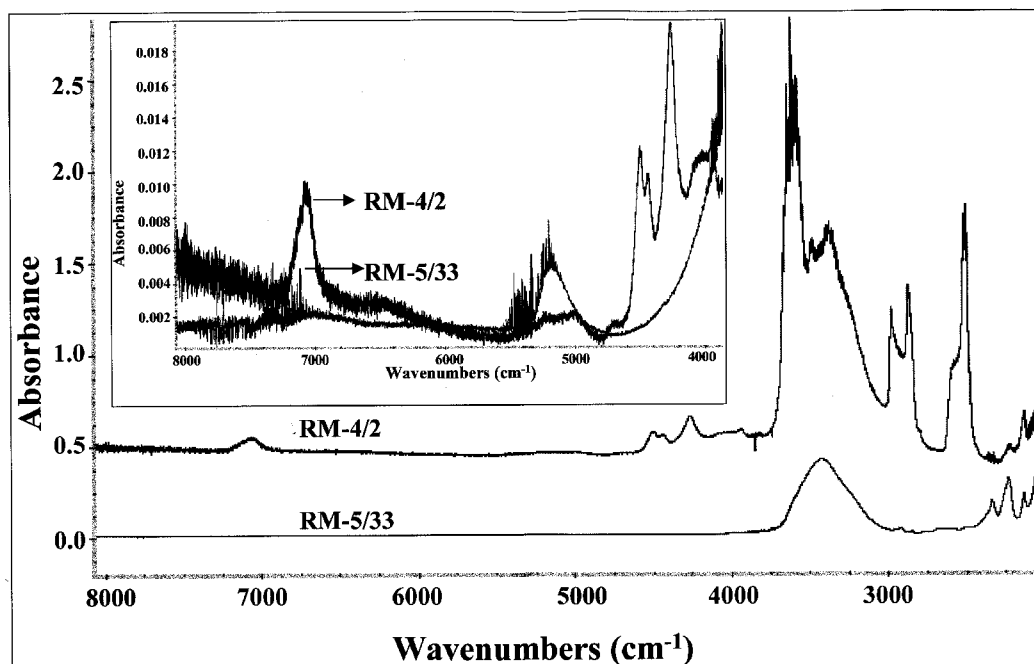


Figure 2. Background corrected IR spectra of two quartz-carbonate vein samples in the wave number range 2000–8000 cm^{-1} . (Inset) Same spectra in the wave number range 4000–8000 cm^{-1} .

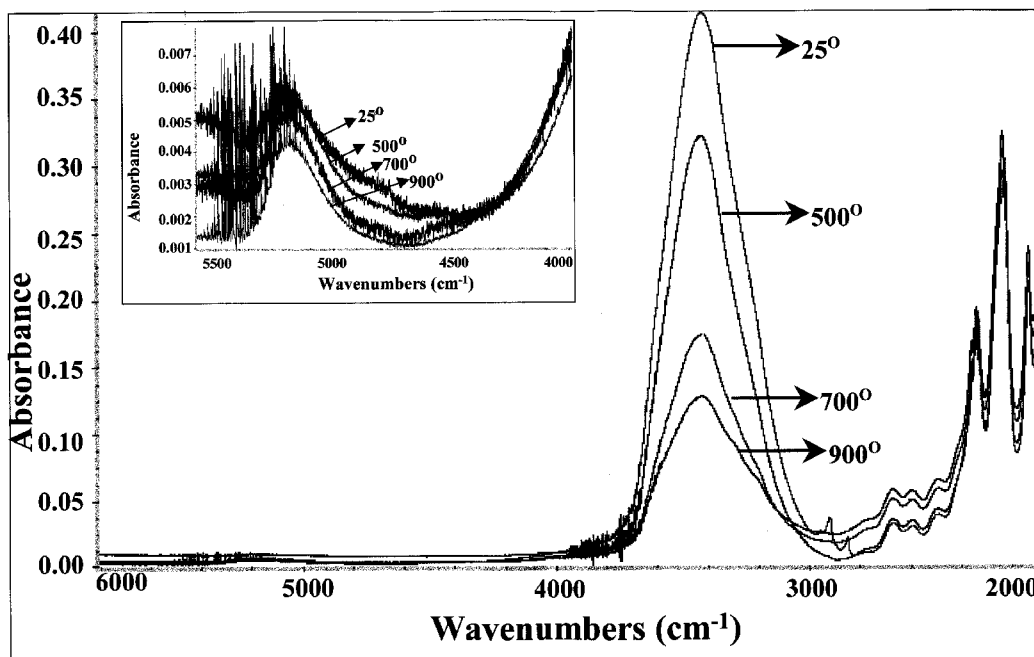


Figure 3. IR spectra of RM-5/33 in the wave number range 2000–6000 cm^{-1} at various temperatures as indicated along with the traces. (Inset) Same spectra for the combinational mode around 5200 cm^{-1} .

increased to about 900°C. Similar decrease was also observed for the combination mode occurring around 5200 cm^{-1} . An important point to be noticed is that there

are no IR bands around 3600 and 4500 cm^{-1} , even at higher temperatures, indicating the absence of Si-OH groups. On the other hand, weaker modes observed

around 3000 cm^{-1} due to hydrocarbons, completely disappeared in the samples heated over 300°C . The loss of water due to temperature rise is plotted in Figure 4.

Interaction and chemical exchange between H_2O and SiO_2 is an important aspect in fluid inclusion study and this may be facilitated by pipe diffusion along dislocations¹². The two samples of the present investigation were more or less equidistant from the shear zone, and thus, it is assumed that the behaviour of fluids is governed by the regional metamorphic events. It is known that total available fluids are more during retrograde metamorphism than during prograde^{22,23}. The prograde and retrograde metamorphic processes are known to be active in gold mineralization. Significant alterations in mineral assemblages are often reported in such a mineralization process triggering greater wall-rock interactions^{11,24}. Quartz, in general, cannot accommodate significant amount of H_2O . However, a small amount of hydrous component may coexist with silica in quartz form¹². The greater adsorbing nature of silica originates from the formation of silanol groups that are normally seen in any form of silica and are known to be stable up to 940°C in vacuum²⁵. Using the infrared absorbance around 3400 cm^{-1} , H_2O contents in both the samples were estimated as 820 and 2200 ppm respectively, following the procedure described in Kronenberg and George²⁶. The lower H_2O content in the former sample is comparable to typical shear-zone quartz²⁶⁻²⁸. The spectral behaviour at high temperatures is worth noticing. Intensity of the main band as well as that of combination mode decreased with temperature. Concentration of trapped water molecules decreased exponentially (as shown in Figure 4) with temperature. On the other hand, absorbance around 2350 cm^{-1} due to CO_2 is almost constant. Similar features are observed for IR modes around

2500 cm^{-1} . From these observations it is concluded that the silanol groups may not have formed in this quartz. Two fluids, namely H_2O and CO_2 , entrapped in this sample, remain non-interactive even at higher temperature. The signatures of daughter carbonate mineral are significantly weaker in this sample. These results indicate that the quartz veins of this rock could have crystallized during the prograde metamorphic process or along isochoric paths during retrograde cooling.

As already noticed, the FTIR spectrum of quartz in the sample RM-4/2, is rich in H_2O (about 2.7 times higher than the sample RM-5/33) and is depleted considerably in CO_2 . Further, a sharper IR band around 3598 cm^{-1} and other bands around 4500 cm^{-1} and 7060 cm^{-1} indicate the presence of hydrogen-bonded silanol groups¹². Higher water content in this sample cannot be attributed to other forms of silica like chalcedony, as the weaker combination modes characteristic of quartz around 2130 and 2240 cm^{-1} are prominently observed¹². The other second-order FTIR modes around 2972 , 2926 , 2879 , 2578 and 2514 cm^{-1} indicate the presence of a daughter mineral, calcite^{18,21}. Two distinctly different locations that are spatially separated by about 2–3 cm, with one dominated by quartz-carbonate and another by calcite²¹, are found. The presence of calcite is further confirmed by the presence of skeleton carbonate modes around 1443 , 880 and 715 cm^{-1} (ref. 18). Precise reasons for more silanol groups in sample RM-4/2 are not clear at this juncture. The mineralization process could trigger the interactions between fluids and the matrix leading to carbonization¹⁶, or the emplacement of granites near this place (Figure 1)¹⁴⁻¹⁶ might have remobilized the fluids more intensely, which resulted in the emplacement of quartz veins into the amphibolite. However, the results suggest that they can form by the interaction of H_2O and SiO_2 during hydrothermal conditions. The present high-temperature experiments show that silanol groups cannot be formed at higher temperatures alone. Silanol groups are known to adsorb more water molecules by forming hydrogen bonds with them^{12,29}. Thus, the quartz with structural hydroxyls (silanol) can attract more water molecules, which can interact with the matrix. Dominance of the calcite also indicates that the recrystallization of quartz in sample RM-4/2 may have occurred during retrograde metamorphic conditions.

In summary, fluids in two quartz veins, collected from the PSB and laterally separated by about 3 km along the strike, are characterized using FTIR spectroscopy. The quartz vein from the central part of the schist belt, RM-5/33, contains H_2O and CO_2 inclusions. Temperature evolution of spectral features of these inclusions suggests that the behaviour is typical of non-interactive, 'closed' system inclusions. On the other hand, the quartz vein from nearby Bhadrampalli mine area, RM-4/2, is depleted in CO_2 and enriched (by about 2.7 times) in H_2O inclusions. Distinct signatures of silanol (Si-OH) group

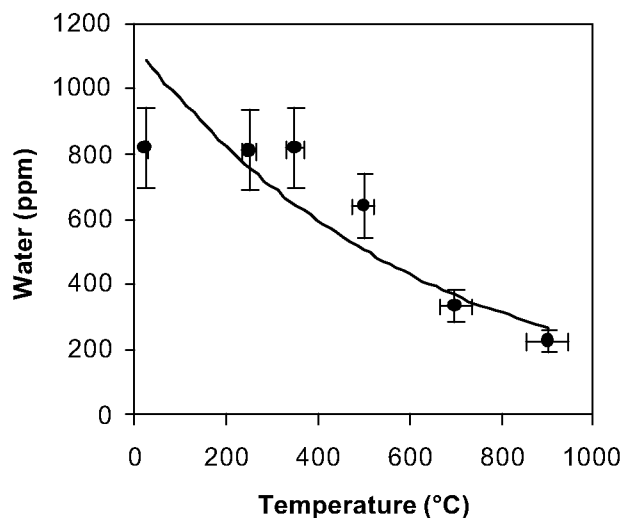


Figure 4. Variation of water content with temperature in RM-5/33 estimated from absorbance of IR band around 3420 cm^{-1} .

and the coexistence as a mineral, calcite (CaCO_3), have been observed in this, indicating that the recrystallization of this quartz may have occurred during retrograde metamorphic processes.

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On the correlation of seismicity with geophysical lineaments over the Indian subcontinent

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A large number of earthquakes of different magnitudes are recorded over the years in the Indian subcontinent, including Southern Peninsular shield. Geophysical images enable one to understand the tectonic and structural fabric of the region. The spatial distribution of earthquakes and their correlation with geophysical mega lineaments are demonstrated.

EARTHQUAKES of magnitude 7 and above are generally confined to the Himalayan region, the northeast and parts of western India. However, historical data suggest that the subcontinent has witnessed several hundreds of earthquakes of varied magnitude^{1–5}. Several workers have prepared catalogues and maps giving epicentre, magnitude and other relevant parameters of these earthquakes. The National Seismic Information Centre, World Data Centre for Seismology of the United States Geological Survey (USGS) Denver, USA also maintains a popular site (www.usgs.gov), which includes information on earthquakes over the Indian subcontinent.

The long recurrence interval of moderate earthquakes in the amplitude range of 4 to 6 in peninsular India gives an impression that this region is relatively stable. The 1967 Koyana and 1993 Latur earthquakes have demonstrated that earthquakes can occur in parts of peninsular India but due to their scarcity, there have been fewer opportunities to study them. Clearly, there are many gaps in our knowledge about the earthquake sources and processes in the southern peninsular shield. As is well known, distribution of the seismic stations over the country is not uniform and different stations have varying recording sensitivities. Although there are difficulties due to these inherent problems, the preponderance of seismic activity over the subcontinent calls for a relook into the spatial distribution of earthquakes and their correlation with tectonics and structural fabric of the subcontinent in general and the southern shield in particular. Geophysical data, particularly the gravity and magnetics, provide a window to understand the tectonic and structural fabric of the region. The spatial distribution of earthquakes and their correlation with geophysical mega lineaments form the subject of this communication.

The recent development of an ‘Auto trace and Digitize Methodology’⁶ provided an opportunity to transform large volume of available gravity and magnetic data from

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