Geochemical Characteristics of Quartzite in Parts of Paleoproterozoic Dhanjori Group, Singhbhum Craton, Eastern India: Implications for Provenance and Paleoweathering

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ABSTRACT

Singhbhum craton preserves the records of sedimentation, magmatism, and tectono-thermal events from Mesoarchaean to Neoproterozoic. The Dhanjori Group (DG), located on the northeast margin of the Singhbhum craton, comprises of a variety of rocks including quartz pebble conglomerate, quartzite, schist, interlayered with mafic to intermediate and rarely acidic lava flows, tuff and agglomerate. Petrography and geochemical characteristics of the Dhanjori quartzite have been undertaken to interpret paleoweathering and provenance characteristics. Studied quartzites are made up of abundant quartz, feldspar, mica, and lithic fragments. With the help of geochemical data, the studied quartzites are classified as quartz-arenites and sub-arkoses. In addition to the A-CN-K plot, various chemical indices such as the chemical index of weathering (CIW), chemical index of alteration (CIA), and plagioclase index of alteration (PIA) indicate moderate to intense chemical weathering of the provenance under semi-humid climatic conditions. Rare earth element (REE) chondrite normalized patterns of the studied samples illustrate enriched $\text{light rare earth elements (LREEs)} \left(\text{La}_{\text{N}}\text{/Sm}_{\text{N}}\text{=}3.11\text{--}6.19\right), \text{depleted}$ **heavy rare earth elements (HREEs) (Gd^N /Yb^N = 0.35 – 3.12) and negative Eu anomaly (Eu/Eu* = 0.55 - 0.87, ~ 0.68). Such patterns are similar to that of the upper continental crust (UCC). In the discrimination function diagram, studied samples of the Dhanjori Group fall in quartzose sedimentary field. In addition, La/Sc vs. Th/Co and La-Th-Sc diagrams, various ratios like Th/Sc (~0.61), La/Sc (~4.42), Th/Co (~0.03), La/Co (~0.11), and Cr/Th (~141.62) imply a mixed provenance for the studied samples. Hence, it has been inferred that the meta-sediments and orthoamphibolites of the older metamorphic group, Singhbhum granitoid complex, as well as associated Archaean metavolcanic suites, would have acted as the probable source rocks for the studied Dhanjori quartzites.**

INTRODUCTION

Singhbhum craton (SC) (Fig.1) is one of the world's few Precambrian terrains that exhibit volcanism and sedimentation ranging in age from the Paleoarchaean to Neoproterozoic (Prabhakar and Bhattacharya, 2013; Nelson et al., 2014, De et al., 2015; Olierook et al., 2019). The SC reveals a large tract of Precambrian rocks covering about 50,000 km² areas. In the SC, from south to north, three different petrotectonic zones have been recognized: (1) southern Archaean nucleus composed of iron formations, granitoids, Neoarchaean sedimentary formations (Mazumder et al., 2012) and newer dolerite dykes (Saha, 1994; Mir et al., 2011a, b; Mir and Alvi, 2015), (2) North Singhbhum mobile belt, made up of Chandil, Dhalbhum, Dalma, Chaibasa formations, and Dhanjori Group (Gupta and Basu, 2000; Alvi et al., 2019), (3) Chotanagpur granite gneissic complex (CGGC) made up of migmatites, granites, gneisses, etc. The DG is considered as younger to the Singhbhum Group (SG), by Dunn and Dey (1942) and in the revised stratigraphic succession of Saha (1994). However, many other workers believe that the DG is older to the SG (Mukhopadhyay, 1976; Basu, 1985; Gupta et al. 1985). The SC, an Archaean craton of the Indian shield, conserves sedimentary records of Mesoarchaean to Neoproterozoic period; however, geochemical studies on sedimentary formations and relating to Archaean upper crust composition are scarce. The earlier research works have been carried out to assess sedimentological and stratigraphic studies of the DG (e.g. Mazumder and Sarkar, 2004; Mazumder, 2005; Bhattacharya and Mahapatra, 2008; Mazumder et al., 2012; De et al., 2015). Hence, the objective of the current work is to determine the provenance and source area weathering characteristics of the quartzites of the Paleoproterozoic Dhanjori Group. Such geochemical studies of the Dhanjori Group of rocks may play a vital role in understanding the early post-Archaean evolution of the Dhanjori Group and the evolution of the Singhbhum craton.

GEOLOGICAL SETTING

The DG covers an area of around 800 km^2 , contains sedimentary, volcanic, and volcaniclastic rocks and show low grade green-schist facies metamorphism (Gupta et al., 1985; Basu, 1985; Singh and Nim, 1998). The DG extends from Singpura to Narwapahar in the eastwest direction and dips towards the north (Fig.2). The DG lies unconformably over the Archaean nucleus and is conformably overlain by the Chaibasa Formation (Mukhopadhyay, 1976; Mazumder et al., 2015; De et al., 2015). It comprises of siliciclastic, mafic to minor felsic volcanic, and volcanoclastic rocks (De et al., 2015). Researchers like Dunn and Dey (1942), Sarkar and Saha (1983) believed that the DG is younger to the Chaibasa Formation, whereas Sarkar and Deb (1971) and Mukhopadhyay (1976) stated that the normal stratigraphic order is shown by the Dhanjori and Chaibasa successions. However, occurrences of 3.04-3.09 Ga old (Acharyya et al., 2010) U bearing quartz-pebble-Cconglomerate at the bottom of the Dhanjori metasediments (Sunil Kumar et al., 1998), Pb-Pb WR isochron ages of 2858 ± 17 ; 2749 \pm 210 Ma obtained for the Dhanjori metavolcanic rocks (Mishra and Johnson, 2005) and Sm-Nd T_{DM} model ages of 2460, 2498, 2517, 2519 Ma obtained for soda granitoids (Pandey et al., 1986) perhaps points towards the older age of the Dhanjori Group, which corroborates the observation of Mukhopadhyay (1976, 1988). The Dhanjori Group is made of the lower formation (contains quartzites, phyllites, schist, and conglomerate) and upper formation (contains volcanic rocks, volcanoclastic rocks, quartzites, and phyllites) (Gupta et al., 1985).

METHODOLOGY

Studied samples of the Dhanjori Group were collected randomly

Fig.2. Simplified geological map of the Dhanjori Group showing studied locations around Rakha, Rukmini Temple and Surda (after P.K. Banerjee, 1982).

from the scattered outcrops near Rukmini temple, Surda and Rakha localities, Singhbhum craton, Jharkhand, eastern India. Out of 25 quartzite samples, 10 least altered or fresh samples were selected for thin-sections and whole-rock geochemical analysis. The bulk samples were broken and pulverized to -200 mesh dimensions using a ball mill at the Department of Geology, Aligarh Muslim University (AMU), Aligarh. A whole-rock major elemental and trace elemental (including rare earth elements) analysis was performed by X-ray fluorescence (XRF) spectrometer and inductively coupled plasma mass spectrometer (ICP-MS) techniques respectively at the National Geophysical Research Institute (NGRI), Hyderabad, India. The analytical protocols for data precision and accuracy are given by Krishna et al. (2007) and Satyanarayanan et al. (2018) for XRF and ICP-MS, respectively. The solution was prepared by following the closed digestion method. 50 mg rock sample powder was dissolved in savillex vessels (closed digestion vessel) containing 10 ml acid mixture of HF: $HNO₃$ in a 7:3 ratio and these vessels were kept on a hot plate at 150°C for 48 hours in closed condition. After complete digestion, 2–3 drops of perchloric acid $(HClO₄)$ was added and the entire mixture was evaporated to complete dryness until a crystalline paste was obtained. 10 ml of 1:1 $HNO₃$ was added to each vessel and these vessels were put on hot plates at ~80°C for 10–15 minutes. After addition of 5 ml of 1 ppm rhodium solution as an internal standard, the volume was diluted to 250 ml with double distilled water. 5 ml of this solution was further diluted to 50 ml for the preparation of the final solution. This solution was used for the estimation of trace (including REEs) elements using ICP-MS techniques. All the available data was standardized against the international reference rock standard GSR4 and JG2. The recovery values of the analytes are listed in Table 5. The analytical precision for major oxides is (<4%) RSD and for trace elements and REEs, it is <5%.

PETROGRAPHY

The studied Dhanjori quartzites possess quartz as the predominant phase, which occurs as common quartz (monocrystalline quartz) with undulose extinction and polycrystalline quartz (recrystallized and stretched quartz, Fig.3a). In addition to quartz, some thin.-sections also contain K-feldspar (microcline, Fig.3c) and plagioclase grains. Plagioclases are often altered to micaceous minerals (sericite, Fig.3b). Mica occurs as muscovite and biotite (Fig.3d). The rock fragment and heavy mineral (zircon) are also present. Monocrystalline quartz has the inclusion of zircon (Fig.3e). The primary cementing material is found to be iron and silica. The modal mineralogy of the studied quartzite samples have been determined by the point-counting method. It is observed that monocrystalline quartz (Qm) ranges from 77.8 to 94.56% (average 87.6%) and polycrystalline quartz (Qp) ranges from 1.3 to 17.9% (average 8.4%), feldspar is around 1 %, and lithic fragment ranges from 1 to 2%. Mica "occurs as lath shaped or a tiny to large elongated flakes" with its abundance ranging from 1.0 to 5.0%. On the ternary diagrams of Dickinson (1985) like Qt-F-L and Qm-F-Lt, the studied samples plot in the craton interior and quartzose field (Figs. 4a and b).

RESULTS

Major Element Geochemistry

Geochemical data (including major and trace elements) of the Dhanjori quartzites are given in Table 1 and 2. Major oxide variations are as SiO_2 (90.60 – 97.84%; average 94.99 %), Al_2O_3 (0.12 – 4.56%; average 1.67 %), $Fe₂O₃$ (0.13 – 2.74%; average 0.76%), K₂O (0.08–

Fig.3. Microphotograph (under crossed-polarized light) of Dhanjori Quartzite showing; **(a)** domination of monocrystalline quartz (Qm) and polycrystalline quartz(Qp); **(b)** Plagioclase altered into sericite and coated iron cement; **(c)** K-feldspar (microcline) coated by iron and surrounded by monocrystalline quartz (Qm); **(d)** Oriented mica (muscovite) embedded in monocrystalline quartz (Qm); **(e)** Monocrystalline quartz exhibiting inclusion of zircon (Zr).

Fig.4. (a) Qt–F–L diagram (Dickinson, 1985); **(b)** Qm-F-Lt diagram (Dickinson, 1985) for the , where, $Qt=$ Total Quartz ($Qm+Qp$), Qm= monocrystalline Quartz, Qp= Polycrystalline quartz, F= Total Feldspar, L=Total Lithic Fragments, Lt= (L+Qp).

1.28%; average 0.45%), MgO (0.01–0.34%; average 0.15%) and Na2O (0.02–0.12%; average 0.05%); CaO, MnO, TiO₂ and P_2O_5 are in minor amounts. In the Herron's geochemical plot (1988), the studied samples fall in quartz-arenite and sub-arkose fields (Fig.5a). Whereas in the Na₂O vs. K₂O diagram (Crook, 1974) most of the samples plot in quartz-rich field (Fig.5b). The high value of Al_2O_3 in a few samples is due to the presence of clay minerals and feldspars. $K₂O$ is mainly derived from the weathering of potash feldspar and mica. A low $\text{Al}_2\text{O}_3/$ $SiO₂$ (0.001-0.050) ratio indicates quartz enrichment in the sediments whereas, low Na₂O/ K₂O (0.05-0.66) ratio indicates the dominance of K-feldspars over plagioclase in the samples or presence of the micaceous minerals. The K_2O/Al_2O_3 values are applied to point out the primary compositions of sediments (Cox et. al., 1995). For example, K_2O/Al_2O_3 values in feldspars and clay minerals from $(0.3 - 0.9)$ and $(0.0 - 0.3)$ respectively. In the case of studied Dhanjori quartzites, K_2O/Al_2O_3 values vary from 0.13 to 0.82 (average 0.34), which indicates a prevalence of K-feldspars and micas over clay minerals in the provenance. Pearson correlation coefficient (r) values are given in

Table 1. Major oxides compositions (wt. %) of Dhanjori quartzite.

Table 1. Major oxides compositions (wt. 70) or Dilamorf quartzite.										
Sample No	$U-1/RT$	$U-2/RT$	$U-4/RT$	$U-7/RT$	$U-8/RT$	$U-9/RT$	$SU-6$	$SU-7$	$U-16/R$	$U-19/R$
SiO ₂	94.37	95.83	96.63	95.78	96.41	93.33	95.76	97.84	93.38	90.60
Al_2O_3	2.35	1.95	1.17	0.91	1.18	3.12	0.97	0.12	0.35	4.56
Fe_2O_3	0.35	0.16	0.35	1.09	0.13	0.43	0.82	0.43	2.74	1.14
MnO	0.00	0.00	0.00	0.02	0.00	0.01	0.00	0.00	0.00	0.01
MgO	0.11	0.03	0.01	0.32	0.08	0.28	0.19	0.06	0.04	0.34
CaO	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
Na, O	0.04	0.04	0.03	0.02	0.06	0.07	0.07	0.05	0.04	0.12
K_2O	0.78	0.25	0.19	0.22	0.40	0.85	0.19	0.08	0.28	1.28
TiO ₂	0.09	0.03	0.03	0.07	0.06	0.13	0.03	0.02	1.25	0.23
P_2O_5	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.02
Total	98.11	98.31	98.41	98.45	98.32	98.24	98.05	98.61	98.10	98.31
CIA	71.73	84.78	81.78	76.00	68.29	74.41	74.34	41.44	47.47	73.86
CIW	96.67	96.09	95.23	94.36	91.09	95.54	88.35	57.38	81.90	95.28
PIA	94.90	95.49	94.29	92.57	86.62	93.77	85.64	30.73	34.12	93.35
Al_2O_2/SiO_2	0.02	0.02	0.01	0.01	0.01	0.03	0.01	0.00	0.00	0.05
K_2O/Na_2O	20.47	6.92	6.20	9.77	6.51	11.53	2.64	1.52	7.28	10.49
Na_2O/K_2O	0.05	0.14	0.16	0.10	0.15	0.09	0.38	0.66	0.14	0.10
K_2O/Al_2O_2	0.33	0.13	0.16	0.24	0.34	0.27	0.20	0.62	0.82	0.28
$\text{Al}_2\text{O}_2/\text{TiO}_2$	25.51	64.90	38.93	13.60	18.95	23.96	31.19	6.47	0.28	20.28

Fig.5. (a) $\log (SiO_2/Al_2O_3)$ vs. $\log (Fe_2O_3/K_2O)$ diagram by Herron (1988) and **(b)** Na₂O vs. K₂O diagram by Crook (1974) for the classification of studied Dhanjori quartzites.

Table 4. The Al_2O_3 exhibits a negative correlation against SiO_2 [r = –0.785, significance level (P) = 0.007)] as expected because of $SiO₂$ and AI_2O_2 contents in sedimentary rocks are controlled by quartz and aluminous clay phases respectively. Whereas, positive correlations between Al₂O₃ and K₂O (r = 0.937, P = 0.0001) and Al₂O₃ and Na₂O ($r = 0.709$, $P = 0.022$) is due to K-bearing minerals. The low concentrations of CaO (0.01%), Na₂O (0.02 – 0.12%), Al₂O₃ $(0.12 - 4.56%)$ are compatible with the low plagioclase content. The SiO_2/Al_2O_3 is > 10, which suggests highly mature nature of sediments.

Trace and Rare Earth Element Geochemistry

The ranges of some transitional elements in the studied samples are Sc (0.58-10.62, average 2.39), Cr (8.75-181.63, average 63.94), Ni (9.58-52.36, average 23.31), and V (3.66-34.32, average 12.65). In addition to these trace elements, REEs show negative correlation against $SiO₂$ (Table 4) which indicates a decrease in elemental abundance with quartz dilution. Al_2O_3 is positively correlated with K₂O (r = 0.937, P = 0.0001), Rb (r = 0.864, P = 0.001), Ba (r = 0.875, $P = 0.001$), and Cs (r = 0.719, P = 0.019) suggesting that these elements are fixed in K-rich clays. Rb and Ba show a strong correlation against K₂O (r = 0.919, P = 0.0002 and r = 0.905, P = 0.0003 respectively), indicating that K-feldspars and clay minerals (i.e. kaolinite or illite) host these elements (Újvári et al., 2008). The positive relationship of Al₂O₂ with Cr (r = 0.893, P = 0.001) and V (r = 0.499, P = 0.142) suggests that these elements are controlled by alumina-silicate phases.

Table 3. Range of elemental ratios of Dhanjori quartzite compared with the ratios derived from felsic rocks, mafic rocks and upper continental crust.

Elemental ratio	Dhanjori quartzite	Ranges in sediments from felsic sources 1	Ranges in sediments from mafic sources 1	Upper Continental Crust ²
$Eu/Eu*$	$0.55 - 0.87$	$0.40 - 0.94$	$0.71 - 0.95$	0.63
La/Sc	$0.40 - 10.79$	$2.50 - 16.3$	$0.43 - 0.86$	2.21
Th/Sc	$0.11 - 1.40$	$0.84 - 20.5$	$0.05 - 0.22$	0.79
La/Co	$0.02 - 0.38$	1.80-13.8	$0.14 - 0.38$	1.76
Th/Co	$0.0006 - 0.09$	$0.67 - 19.4$	$0.04 - 1.40$	0.63
Cr/Th	1.37-666.25	$4.00 - 15.0$	25-500	7.76

¹Cullers et al (1988); Cullers (2000); Cullers and Podkovyrov (2000). ²McLennan (2001); Taylor and McLennan (1985).

A few large ion lithophile elements (LILEs) such as Rb (3.93–43.65, average 14.38), Sr (3.25–8.66, average 5.22), Ba (18.15–123.90, average 55.48), Th (0.09–17.38, average 2.44), and U (0.36– 4.38, average 1.32) show variations. Such a high Rb contents in the studied samples reflect the presence of high proportion of K-feldspar in the rocks of provenance. Upper continental crust (UCC) normalized multielement spider diagram of trace elements (Fig.6) shows enhancement of Zr, Rb, U, Y, and Hf and reduction of K, Th, Nb, and Sr. The depletion of Sr suggests a minor enrichment of plagioclase, this is further verified by negative Eu-anomaly of studied samples. Zr enrichment is attributed to the abundance of zircon mineral, which implies the dominance of silicic rocks in the source terrain. The chondrite normalized REE diagram (Fig.7) show slight enrichment of light-REE (LREE) with negative Ce anomaly, which indicates oxidizing environment $(La_N/Sm_N = 3.11$ to 6.19; average 4.17) and flat heavy-REE (HREE) ($Gd_N/Yb_N = 0.35$ to 3.12; average 1.34) pattern with negative Eu anomaly (0.55 to 0.87; average 0.68). A high LREE and a low HREE may be attributed to the quartz dilution. The effect is further accompanied by low ΣREE ranging from 11.71 – 78.12 ppm (average 27.29) and is lower than the average UCC (Taylor and McLennan, 1985).

Fig.6. Upper continental crust trace element normalized plot for the studied Dhanjori quartzites (Taylor and McLennan, 1985).

Fig.7. Chondrite normalized (Taylor and McLennan, 1985) rare earth element (REE) pattern for the studied Dhanjori quartzites.

SiO ₂ 1.000 -0.785 1.000 Al_2O_3 0.007 -0.459 -0.177 1.000 Fe_2O_3 0.625 0.182 1.000 MnO -0.102 0.057 0.133 0.779 0.876 0.713 -0.572 0.592 0.093 1.000 MgO 0.711	
0.021 0.083 0.071 0.798	
-0.730 0.855 -0.055 0.376 1.000 CaO 0.640	
0.016 0.284 0.001 0.881 0.046	
-0.164 1.000 -0.655 0.709 0.021 0.549 0.453 Na, O	
0.040	
0.022 0.651 0.954 0.100 0.189	
0.059 K, O -0.866 0.937 0.005 0.596 0.810 0.733 1.000	
0.001 0.0001 0.989 0.872 0.0690 0.005 0.016	
-0.131 1.000 TiO ₂ -0.420 -0.191 0.915 -0.181 -0.056 -0.056 0.009	
0.227 0.596 0.878 0.980 0.0002 0.718 0.616 0.878	
-0.773 0.527 0.369 0.571 P_2O_5 0.556 0.553 0.569 0.389 0.333 1.000	
0.095 0.117 0.294 0.347 0.009 0.097 0.086 0.266 0.085	
-0.578 0.932 -0.095 -0.031 0.128 0.182 0.971 0.518 1.000 Sc -0.015 0.071	
0.080 0.794 0.846 0.724 0.126 0.967 0.0001 0.932 0.615 0.0000	
1.000 V 0.435 0.568 0.575 0.605 0.229 0.895 0.394	
0.499 0.645 0.279 -0.691	
0.027 0.142 0.209 0.087 0.082 0.436 0.524 0.260 0.044 0.063 0.0005	
0.497 -0.103 -0.745 0.893 -0.091 0.080 0.456 0.764 0.905 0.633 0.064 0.683 1.000 Cr	
0.013 0.803 0.826 0.0101 0.144 0.776 0.049 0.030 0.001 0.185 0.0003 0.861	
0.381 -0.525 -0.800 0.428 -0.238 1.000 -0.662 0.364 -0.697 -0.350 0.337 -0.462 -0.639 Co -0.660	
0.278 0.037 0.302 0.119 0.025 0.006 0.321 0.038 0.218 0.509 0.341 0.178 0.047	
-0.527 0.347 0.076 0.323 0.205 0.024 0.426 0.294 0.450 0.403 0.836 0.405 0.641 0.446 1.000 Ni	
0.947 0.116 0.220 0.326 0.834 0.410 0.362 0.192 0.248 0.570 0.003 0.245 0.046 0.196	
-0.711 0.690 0.206 0.115 0.571 0.495 0.728 0.730 0.018 0.817 0.772 0.747 -0.371 1.000 0.246 0.788 Cu	
0.021 0.567 0.752 0.009 0.013 0.291 0.027 0.084 0.146 0.017 0.017 0.961 0.004 0.493 0.007	
0.529 -0.523 -0.026 -0.187 -0.379 -0.591 -0.226 -0.463 -0.052 -0.285 -0.091 -0.239 -0.381 0.326 -0.024 -0.114 1.000 Zn	
0.116 0.944 0.605 0.072 0.530 0.178 0.887 0.425 0.277 0.357 0.754 0.121 0.280 0.803 0.506 0.948	
-0.875 0.809 0.271 0.155 0.657 0.775 0.129 0.845 0.353 0.803 -0.437 0.754 0.950 -0.319 1.000 0.658 0.863 0.791 Ga	
0.001 0.005 0.449 0.670 0.039 0.039 0.009 0.001 0.722 0.002 0.317 0.007 0.005 0.206 0.012 0.0000 0.368	
0.772 1.000 Rb -0.850 0.864 0.127 0.051 0.517 0.720 0.691 0.919 0.076 0.283 0.758 0.918 -0.506 0.680 0.899 -0.374 0.953	
0.002 0.001 0.726 0.889 0.125 0.019 0.029 0.835 0.009 0.428 0.011 0.0002 0.135 0.031 0.0004 0.287 0.0000 0.0002	
-0.563 -0.101 0.209 0.545 0.389 0.709 0.329 0.700 1.000 Sr 0.375 0.471 0.241 0.365 0.540 0.463 0.146 0.872 0.192 0.695 0.565	
0.089 0.090 0.286 0.170 0.782 0.503 0.561 0.103 0.300 0.022 0.107 0.178 0.353 0.687 0.024 0.595 0.266 0.001 0.026	
Y -0.855 0.732 0.002 0.264 0.425 0.372 0.604 0.746 0.726 0.856 0.637 0.508 -0.013 0.565 0.539 -0.222 0.689 0.652 0.684 1.000 0.441	
0.995 0.221 0.290 0.134 0.002 0.203 0.016 0.462 0.013 0.017 0.002 0.048 0.971 0.088 0.108 0.537 0.028 0.041 0.029 0.065	
-0.572 -0.026 0.072 0.263 0.067 0.796 0.204 0.179 0.114 0.029 -0.078 -0.062 -0.221 0.142 Zr 0.126 0.663 0.305 0.758 0.164 0.198 0.746	1.000
0.084 0.728 0.944 0.854 0.572 0.013 0.037 0.843 0.462 0.391 0.006 0.011 0.621 0.753 0.936 0.830 0.865 0.540 0.650 0.695 0.583	
-0.287 0.880 -0.181 -0.175 -0.173 0.984 0.223 0.927 -0.196 -0.090 -0.312 -0.303 -0.114 0.128 0.502 0.119 0.088 -0.005 -0.050 0.314 0.666 Nb	0.772
0.422 0.380 0.0008 0.617 0.395 0.629 0.633 0.753 0.0000 0.535 0.0001 0.724 0.587 0.139 0.744 0.806 0.809 0.990 0.891 0.377 0.035	0.009
0.442 -0.637 0.719 0.004 0.019 0.408 0.530 0.605 0.772 -0.084 0.693 0.121 0.730 0.858 -0.451 0.671 0.917 -0.221 0.869 0.935 0.471 Cs	-0.147

Table 4. Correlation coefficient (r) and significance level (P) of the Dhanjori quartzite (number of sample, n = 10).

O CaO Na₂O K₂O TiO₂ P₂O₅ Sc V Cr Co Ni Cu Zn Ga Rb Sr Y Zr

320

 $SiO₂$

 Al_2O_3 Fe₂O₃ MnO MgO

Table 4. Contd....

DISCUSSION

Provenance

Several authors have used geochemistry (including REEs, HFSEs, and TTEs) of sedimentary rocks to know their source character (e.g., Cullers et al., 1988; Taylor and McLennan, 1985; Armstrong-Altrin et al., 2004; Mir et al., 2015). In the discrimination function diagram (after Roser and Korsch, 1988), studied samples of the Dhanjori Group fall in quartzose sedimentary field (Fig.8a). Roser (2000) stated that the recycled material of felsic igneous rocks does not plot in the igneous fields; however, such sediments do plot in the quartzose field. Zr vs. $TiO₂$ diagram (Hayashi et al. 1997; Fig.8b) shows that the analyzed samples plot in the felsic and mafic fields. According to Hayashi et al. (1997), $\text{Al}_2\text{O}_3/\text{TiO}_2$ ratio ranges from (3 to 8), (8 to 21) and (21 to 7) in mafic, intermediate, and felsic igneous rocks respectively. In present samples, $\text{Al}_2\text{O}_3/\text{TiO}_2$ value ranges from 6.47–64.90 (except sample No. U-16/R = 0.28). Hence, high values of Al_2O_3/TiO_2 indicate felsic igneous rocks are the dominated source for Dhanjori quartzite. $\operatorname{Al_2O_3}$ $TiO₂$ values of studied quartzites are computed in the following equation of Hayashi et al. (1997)

$$
SiO_2 (wt. %) = 39.34 + 1.2578 (Al_2O_3/TiO_2) - 0.0109 (Al_2O_3/ \nTiO_2)^2.
$$

Therefore, the derived $SiO₂$ contents (39.69 to 75.06, average 60.31) wt. %) from the equation implies felsic igneous rocks as the source of

Fig.8. (a) Discriminant function plot (Roser and Korsch, 1988) and **(b)** TiO₂-Zr plot (Hayashi et al., 1997) for the studied Dhanjori quartzites.

Fig.9. (a) Al_2O_3 vs. Ti O_2 diagram (after Ekosse, 2001),and **(b)** La/Sc vs. Th/Co diagram (after Cullers, 2002)for the studied Dhanjori quartzites.

studied quartzites. Al_2O_3 vs. Ti O_2 plot had been used by Ekosse (2001) to differentiate between granite and basaltic source rocks; such a plot supports the presence of mixed provenance for the studied Dhanjori quartzite (Fig.9a). Further, La/Sc vs. Th/Co (after Cullers, 2002) plot also supports mixed (felsic plus mafic) provenance (Fig.9b) for the studied samples. Furthermore, some useful trace elemental ratios of analyzed samples indicate that these are felsic, mafic, and upper continental crust derived sediments. Further, ratios like Eu/Eu* (~ 0.68), La/Sc (~ 4.42), Th/Sc (~ 0.61), La/Co (~ 0.11), Th/Co \sim 0.03) and Cr/Th (\sim 141.62) also suggest that studied samples have been derived from mixed (felsic plus mafic) source rocks (Table 3).

The triangular diagram of La-Th-Sc (Taylor and McLennan, 1985) is utilized to determine the nature of the source. The average compositions of the granite, TTG, andesite, basalt, komatiite (Condie, 1993), and UCC (Taylor and McLennan, 1985) are used for the assessment of the provenance characteristics of the studied samples. The studied samples when plotted on La-Th-Sc ternary diagram, show close association with TTG, granite, UCC and andesite compositions (Fig.10); such an association implies that the sediments for the studied samples have been derived from the source that had major amounts of felsic and minor amounts of mafic rocks. From the above discussion, it is concluded that mixed (felsic plus mafic) provenance is suggested for the studied samples of the Dhanjori Group. The poorly mixed source is also suggested by earlier workers like De et al. (2015) for the Dhanjori Group. Since the Dhanjori Group is surrounded in the east by the Older Metamorphic Group (OMG) and in the

Fig.10. La-Sc-Th plot for the studied Dhanjori quartzites; UCC values are taken from Taylor and McLennan, 1985; Granite, Basalt, Andesite, TTG and Komatiite are after Condie, 1993. Passive margin field (Bhatia and Crook, 1986).

south by the Singhbhum granitoid complex (SBGC), both of them older than the Dhanjori Group. Therefore, it is inferred that the metasediments and ortho-amphibolites of OMG, Singhbhum granitoid complex (SBGC), and associated Archaean metavolcanic suites may have been the probable source areas for the studied Dhanjori quartzites.

Table 5. The recovery values (%) of the analytes

Analyte	GSR-4 (CV)	GSR-4 (OV)	SD	Recovery values $(\%)$
Sc	4.20	4.26	0.07	101.45
V	33.00	32.59	0.15	98.77
Cr	20.00	19.92	0.19	99.60
Co	6.40	6.39	0.03	99.91
Ni	16.60	16.85	0.21	101.52
Cu	19.00	19.06	0.15	100.30
Zn	20.00	20.15	0.10	100.76
Ga	5.30	5.43	0.18	102.37
Rb	29.00	28.71	0.07	99.00
Sr	58.00	57.61	0.13	99.33
Y	21.50	20.99	0.08	97.60
Zr	214.00	209.72	1.79	98.00
Nb	5.90	5.77	0.06	97.85
Cs	1.80	1.86	0.05	103.40
Ba	143.00	144.39	2.23	100.97
La	21.00	20.79	0.30	99.02
Ce	48.00	48.11	0.67	100.22
Pr	5.40	5.36	0.08	99.26
Nd	21.00	20.88	0.21	99.42
Sm	4.70	4.68	0.07	99.48
Eu	1.02	1.03	0.02	101.05
Gd	4.50	4.56	0.06	101.41
Tb	0.79	0.79	0.01	99.93
Dy	4.10	4.06	0.03	99.04
Ho	0.75	0.75	0.02	100.02
Er	2.00	1.97	0.02	98.52
Tm	0.32	0.31	0.01	97.63
Yb	1.92	1.92	0.02	100.14
Lu	0.30	0.29	0.00	97.33
Hf	6.60	6.52	0.18	98.77
Ta	0.42	0.41	0.01	98.69
Pb	7.60	7.63	0.03	100.45
Th	7.00	6.87	0.07	98.15
U	2.10	2.08	0.01	99.04

Paleoweathering

The degree of separation of mobile elements (like Ca, Na, & K) against immobile ones (like Al & Ti) depends on the composition and strength of the parent rock, climatic conditions, and time (Nesbitt and Young, 1982). The chemical index of alteration (CIA) by Nesbitt and Young (1982) is utilized to calculate the intensity of chemical alteration of the provenance by the following equation: $CIA = [Al_2O_3/$ $\text{(Al}_2\text{O}_3+\text{CaO*}+\text{Na}_2\text{O}+\text{K}_2\text{O})\}\times 100$ in molar proportions CaO* symbolize the Ca of silicate fraction. In the present work, CaO* is rectified by the method of McLennan (1993). According to this method, CaO* is equal to CaO when CaO is lesser than Na₂O and when CaO is greater than Na₂O then CaO $*$ is supposed to be equal to Na₂O. For unweathered rocks, CIA values are <50 to nearly 100 for highly altered products (initial 50 to 60, moderate 60 to 80 and severe >80; Fedo et al., 1995). The studied samples show CIA values ranging from 41.44 to 84.78 (average 69.41) which suggests moderate to intense

Fig.11. $\text{Al}_2\text{O}_3\text{-(CaO+Na}_2\text{O})\text{--K}_2\text{O}$ (A–CN–K) diagram for the studied Dhanjori quartzites (after Nesbitt and Young 1984). OMTG: Older metamorphic tonalite gneiss, OMG: older metamorphic group, SG: Singhbhum granite.

Fig.12. SiO₂ vs. $\text{Al}_2\text{O}_3 + \text{K}_2\text{O} + \text{Na}_2\text{O}$ plot for the studied Dhanjori quartzites (Suttner and Dutta, 1986).

weathering conditions (except two samples whose CIA value is less than 50). To note the weathering trends and provenance nature, studied samples have been plotted on a triangular diagram Al_2O_3 - $(CaO+Na₂O) - K₂O$ (A–CN–K) (Nesbitt and Young, 1984). In this diagram, most of the studied samples fall near the $\operatorname{Al_2O_3}$ corner which implies moderate to high degrees of chemical weathering of the provenance (Fig.11). Chemical index of weathering (CIW), which excludes K-metasomatism possibility, is calculated from the equation as CIW = $[A_2O_3/(Al_2O_3 + CaO^- + Na_2O)] \times 100$ (Harnois, 1988). The studied samples exhibit values of CIW ranging from 57.38 to 96.67 (average 89.19) which further indicates that the source terrain of the studied samples have experienced moderate to severe weathering conditions. Such weathering degrees are also supported by the plagioclase index of alteration PIA= $[(Al_2O_3 - K_2O)/(Al_2O_3 + CaO_3)]$ $+Na_2O - K_2O$] × 100; (Fedo et al. 1995) which ranges from 30.73 to 95.49 (average 80.15) for the studied samples. Like the CIA, CIW, PIA, and A–CN–K ternary diagram, the Rb/Sr ratio (0.70-7.10) of studied samples too suggests moderate to intense chemical weathering. The strength of chemical weathering depends on the climate and tectonic uplift (Wronkiewicz and Condie, 1987). SiO_2 vs. $Al_2O_3 +$ K_2O+Na_2O plot is used to determine the climatic conditions of the studied Dhanjori quartzites (Suttner and Dutta 1986). The plot shows that the studied Dhanjori Group sediment samples have been derived from a source that has experienced semi-humid climatic conditions (Fig.12). These results corroborate with the conclusions of De et al. (2015). De et al. (2015) have also suggested moderate to severe chemical weathering of the Dhanjori Group.

CONCLUSION

Based on petrography and geochemical character, the studied quartzite samples of Dhanjori Group are categorized into quartz-arenite and sub-arkose. The high quartz abundance of studied samples infers sluggish upliftment in an association of strong weathering of source terrain and deposition in the stable platform. Calculated values of the geochemical indices like CIA, CIW, and PIA infer that the source terrain of the studied samples of the Dhanjori Group have experienced moderate to intense chemical weathering under the humid to semihumid climatic conditions. In addition to La/Sc, Th/Sc, La/Co, Th/Co ratios, the REE profile showing enrichment in LREE with negative Ce anomalies and flat HREE with negative Eu anomaly indicates the derivation of the sediments for the studied sample of the Dhanjori Group from the mixed source (felsic plus mafic) probably from the OMG, SBGC, and associated Archaean metavolcanic terrains.

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