Chemical age of detrital zircons from the basal quartz–pebble conglomerate of Dhanjori Group, Singhbhum craton, Eastern India


Chemical ages of detrital zircon concentrates from the uranium-bearing basal quartz–pebble conglomerate of Dhanjori Group from six localities have been determined based on high precision analysis of U, Th and Pb. Three of the zircons gave concordant ages of 3044–3090 Ma, which represent the minimum age of the provenance rock and older age limit of Dhanjori sedimentation. The Singhbhum Granite Complex dating between 3.3 Ga (Phases I & II) and 3.12 Ga (Phase III) are the likely provenance rocks. Chemical ages, coupled with evidences from field relations and temporal nature of uranium-bearing QPCs suggest that the sedimentary members of Dhanjori Group are likely to be older than the presently assigned age of 2300 Ma.

The Singhbhum–Orissa craton, eastern India, comprises of a complex geological assemblage of Archaean and Proterozoic age. Chronostratigraphic status of many of the lithogroups in this craton, especially the Dhanjori Group and Iron Ore Group (IOG) are still debatable, mainly because of inadequate radiogenic ages. The occurrences of uranium-bearing basal quartz–pebble conglomerates (QPC) in both Dhanjori Group and IOG are important in this context. Detrital U-bearing QPCs the world over have distinct temporal and stratigraphic positions and are generally confined to Archaean-Proterozoic transition period. Among the detrital heavy minerals in such conglomerates, zircons, because of their highly refractory nature, are considered provenance diagnostic. The ages of detrital zircon in QPCs correspond to the age of the parent rock and thereby aid in establishing provenance and stratigraphic position of the QPCs. In this communication, we report U, Th and Pb contents of detrital zircons from some QPC horizons at the base of Dhanjori Group and their chemical ages.

The volcano-sedimentary sequence of Dhanjori Group began with a basal quartz-pebble conglomerate, followed by a thick sequence of fuchsite-quartzite and an occasional phyllite. Upper part of the sequence is an extensive basic volcanic sequence. Basal QPC is exposed intermittently along the south, east and western margins of the Dhanjori basin. Conglomerate samples for the present study have been collected from six localities; Butgora in the western margin; Phuljari, Jawardih and Ashhakaoli in the southern margin; and Tirioburu and Chakri in the eastern margin of the basin (Figure 1). Zircon, chromite, rutile, monazite, pyrite, etc. are the prominent detrital heavy minerals found in all the QPC samples. Zircons recovered from these samples are characterized by their coarse (mostly 200–250 μm), stubby, unzoned nature and pink colour (Figure 2). Systematic morphometric analyses of zircon grains
reveal their uniformity in colour, habit, length–breadth ratio (1.9 to 2.1), etc. Uniform morphometric characters of zircons from various locations suggest a common provenance for the Dhanjori sediments.

Zircon-rich heavy mineral concentrates were obtained from crushed and ground QPC samples by tabling, followed by sequential heavy media separation. Magnetic separation of these concentrates on Frantz Barrier Pole Isodynamic separator yielded a zircon-rich non-magnetic fraction devoid of monazite. The non-magnetic fractions from Butgora and Phuljari contained abundant pyrite. These pyrites were converted to oxides by heating the samples to 800°C in a muffle furnace. These oxides were removed by further magnetic separation. Stereomicroscopic handpicking was resorted to ensure near 99% purity of the zircon concentrates thus obtained. Special care was taken during stereomicroscopy so that no monazite remained in the zircon concentrate.

The pure zircon separates were finely powdered and treated with conc. HNO₃ followed by conc. H₂SO₄ to remove coatings and inclusions if any. U was analysed by delayed neutron activation analysis (DNAA) after irradiating the samples and standards in the CIRUS reactor (neutron flux 10¹⁹ n · cm⁻² · s⁻¹) and by γ-ray spectrometry of the daughter product Np²⁴⁹. Th was analysed by INAA after irradiating the samples in Apsara Reactor (neutron flux of 10¹⁹ n · cm⁻² · s⁻¹) for 4 h. γ spectra were taken using 125 cc HPGe detector coupled to PC based MCA system, having 30% efficiency with respect to 3° × 3° NaI detector and system resolution of 1.9 eV for 1332 keV of ⁶⁰Co. Pb was analysed by differential pulse anodic stripping voltammetry. The errors in analysis were of the order of ±5% for U, ±2% for Th and ±4% for Pb. The U, Th and Pb content of the six samples of zircon are given in Table 1.

For calculation of chemical age, lead content in the sample is assumed to be of radiogenic origin by the decay of uranium (both ²³⁵U and ²³⁸U) and thorium. Non-radiogenic common lead content in zircons is shown to be as low as 0.01 ppm³; higher values of up to

<table>
<thead>
<tr>
<th>Location</th>
<th>U (ppm)</th>
<th>Th (ppm)</th>
<th>Pb (ppm)</th>
<th>Th/U</th>
<th>Age (Ma)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Southern margin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Jawardih</td>
<td>197</td>
<td>91</td>
<td>142</td>
<td>0.46</td>
<td>3090 ± 124</td>
</tr>
<tr>
<td>Phuljari</td>
<td>148</td>
<td>70</td>
<td>80</td>
<td>0.47</td>
<td>2538 ± 102</td>
</tr>
<tr>
<td>Asthakaoli</td>
<td>219</td>
<td>91</td>
<td>153</td>
<td>0.42</td>
<td>3048 ± 122</td>
</tr>
<tr>
<td>Western margin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butgora</td>
<td>200</td>
<td>90</td>
<td>84</td>
<td>0.45</td>
<td>2109 ± 84</td>
</tr>
<tr>
<td>Eastern margin</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tiriburu</td>
<td>248</td>
<td>134</td>
<td>152</td>
<td>0.54</td>
<td>2745 ± 110</td>
</tr>
<tr>
<td>Chakri</td>
<td>187</td>
<td>89</td>
<td>132</td>
<td>0.48</td>
<td>3044 ± 122</td>
</tr>
</tbody>
</table>

Errors in estimations are ±5% for U, ±2% for Th and ±4% for Pb. Errors in age computation are ±4%.
6.5 ppm have been reported only from rare magnetic zircons.

From the radioactive decay series of $^{238}\text{U}$, $^{235}\text{U}$ and $^{232}\text{Th}$, the atomic proportion of radiogenic lead in a mineral can be calculated using the following equation:

$$
Pb = U \times [0.999276 (\text{e}^{1/0} - 1)] + 0.007196 (\text{e}^{1/3} - 1)] + \text{Th} \times (\text{e}^{1/3} - 1),
$$

where $U$ and $\text{Th}$ are in atomic proportions. Modern abundance of $^{238}\text{U}$ is 99.276% of total $U$ and that of $^{235}\text{U}$ is 0.7196%. The decay constants given by Jaffey et al. for $^{238}\text{U}$ ($\lambda_1 = 1.55125 \times 10^{-10}$ yr$^{-1}$), $^{235}\text{U}$ ($\lambda_2 = 9.8485 \times 10^{-10}$ yr$^{-1}$) and $\text{Th}$ ($\lambda_3 = 4.9475 \times 10^{-11}$ yr$^{-1}$) are used in this calculation.

In this transcendental equation, $t$ is the time duration in years and can be solved numerically. Bowles adopted an iterative approach of solution of this equation to calculate the age of uraniuminite. We have used the Newton–Raphson method of numerical analysis for solving this equation, for which the initial approximate age was obtained using the empirical equation

$$
t = \ln \left( \frac{1.104 \text{ Pb}}{U} + 1 \right) \times \lambda_1^{-1}.
$$

A computer program in FORTRAN has been written for solving eqn (1) by Newton–Raphson method (Appendix I).

Chemical ages of the detrital zircons thus calculated are given in Table 1. Error in chemical age calculation is the cumulative manifestation of errors in chemical analysis, particularly of lead. Based on the errors in estimation of $U$, $\text{Th}$ and Pb, the age calculated will have an error of ±4%. Zircons from Jawardih, Asthakaoli and Chakri gave a very close age of 3090–3044 Ma. Tirioburu sample gave an age of 2745 Ma, whereas Phuljari and Butgora samples gave lower ages (2538 Ma and 2109 Ma respectively).

The lack of knowledge of non-radiogenic lead content leads to overestimation of age. But chemical ages calculated on individual uranium-bearing minerals having practically little initial lead content, using high precision analytical data, are found to be close to the isotopic age, and zircon is one such mineral. Since zircons from all the QPCs have similar optical and morphometric characteristics as well as similar U/Th ratios (see Table 1), it is reasonable to assume that their provenance is the same, and that the concordant age of 3044–3090 Ma obtained for three of the samples (Jawardih, Asthakaoli and Chakri) should be close to the age of the provenance rock. The lower ages of the samples from Butgora, Tirioburu and Phuljari are the result of natural lead loss or unintended lead loss that occurred during preparation of pure zircon separates. Though it is logical to assume that all the lead in zircon is radiogenic, post-crystalline lead loss, especially in broken zircon grains is definitely a possibility, which would yield lower values in chemical age calculations. Accordingly, the discordant age of 3040–3090 Ma may be taken as the minimum age of the provenance rock. Isotopic age of zircons, and hence that of the provenance rocks, can be expected to be close to this age on the higher side, i.e., ≥3100 Ma, taking into account minor lead loss. The ≥3100 Ma also represents the maximum age limit of commencement of sedimentation in the Dhanjori basin.

The heavy mineral suite of the Dhanjori QPCs is dominated by the presence of zircon, monazite and chromite. Quartz and quartzitic pebbles, abundance of detrital zircon and monazite, and geochemical characteristics of the QPCs including their REE pattern (paper under preparation) suggest the predominance of a granitic rock unit in the provenance for Dhanjori sediments. Detrital chromite suggests the occurrence of some ultramafic rocks also in the provenance. The palaeocurrent and basin analysis based on sedimentary structures, and textural maturity of the QPC, indicate a fluvial to deltaic depositional environment on a peneplaing granite–greenstone terrain. Among the probable older rocks of the Singhbhum craton that could be the source for zircons in the QPCs, the most widespread is Singhbhum Granite Complex belonging to three successive and closely related phases. The other older rocks are the Older Metamorphic Tonalite Gneiss (OMTG) and Older Metamorphic Group (OMG). Singhbhum Granite phase III has been dated by Pb–Pb whole rock isochron method as 3130 ± 28 Ma and by Sm–Nd method as 3120 ± 100 Ma, while the Phase I is c3300 Ma old. OMG rocks have been dated by Pb–Pb method as ≥3400 Ma or older. The Pb–Pb age data on zircons from OMG16 gave ≥3550 Ma as the older age limit for OMG sedimentation. We have compared the morphometry of zircons in OMG samples from Champua and OMG samples from Saraikela with those of Dhanjori QPCs and found that the Dhanjori zircons are distinctly different from those found in OMG and OMG samples. On the other hand, several samples of Singhbhum Granite are found to contain appreciable amounts of zircon morphometrically similar to those found in Dhanjori QPCs. It is reasonable to infer from these observations that the prominent source rock for Dhanjori Group sediments is Singhbhum Granite; however it is difficult to decipher at this stage whether Phases I and II (Singhbhum Granite A) are the major contributors or phase III (Singhbhum Granite B).

Dhanjori Group of rocks are assigned an age of c2300 Ma by Saha et al. However, the following considerations indicate that the sedimentary members of Dhanjori Group of rocks are likely to be older in age: (i) Uranium-bearing basal QPCs are generally confined to late Archean–early Proterozoic transition period. (ii) The provenance rocks are of 3100 Ma or of older age. (iii) There is striking similarity in the geological
setting of QPC units of Dhanjori with Bababudans of Dharwar Super Group of Karnataka, of age estimated to be between 3000 and 2800 Ma. The 555 m level crosscut of the Jaduguda uranium mine now exposes a continuous rock succession in the dip direction from Dhanjori metabasics through the uranium-bearing lodes to the schists and quartzites of Singhbhum Group. This conformable and continuous succession with Dhanjori at the base also indicates that Dhanjoris are older than Singhbhum Group of rocks, an observation also made earlier by Mukhopadhyay in the Rakha Mines. The Singhbhum Group of rocks has been assigned the age of c.2300 – 2400 Ma. It is also interesting to note here that the basal QPCs of IOG also contain detrital heavy minerals including zircons similar in character to those found in QPCs of Dhanjori. Because of these mineralogical similarities, we believe that the provenance of both IOG and Dhanjori Group was the same, and the sedimentation in IOG and Dhanjori basins was more or less coeval.

Appendix

C NEWTON–RAPHSON METHOD FOR DETERMINATION OF CHEMICAL AGE BY

C SOLVING EQUATION FOR RADIOGENIC LEAD

C

REAL LU238, LU235, LTH
CHARACTER NCODE*10
C NCODE = SAMPLE CODE
OPEN (UNIT = 15, FILE = 'CHEMAGE.OUT', STATUS = 'OLD')
WRITE (*, 5)
5 FORMAT (10X, 'Please Enter the Sample Code:')
READ (*, *) NCODE
WRITE (*, 10)
10 FORMAT (1X, 'Enter the increment in Time and Accuracy check value:')
READ (**, **) DELT, EPSI
U238 = 0.99276
U235 = 0.007196
C U238 AND U235 ARE CRUSTAL ABUNDANCE OF THE ISOTOPES
WRITE (*, 20)
READ (**, **) U1, TH1, PB1
C U1, TH1 & PB1 = CHEMICAL ASSAYS OF U, Th & Pb IN THE SAMPLE
20 FORMAT (1X, 'Enter the assays of U, Th, Pb')
C
U = U1/(U238*238 + U235*235)
TH = TH1/232
PB = PB1/206
C U, Th & Pb = ATOMIC PROPORTIONS OF U, Th, and Pb IN THE SAMPLE
LU238 = 1.5513E-10
LU235 = 9.8485E-10
LTH = 4.9475E-11
C LU238, LU235 & LTH = DECAY CONSTANTS OF U238, U235 AND TH
TA = (LOG(1.104*PB/U + 1))/LU238
T = TA
C
FOFT=U*(U238*EXP(LU238*T) - 1) + U235*
(1 - U235*EXP(LU235*T) - 1) + Th*(EXP(LTH*T) - 1)
PB = FOFT
FOFTN = FOFTN - PB
WRITE (*, 35) FOFTN
35 FORMAT (10X, 'Pb(Cal) - Pb(Exp) = ', E15.4)
IF (FOFTN*FOFTN) 70, 40, 60
TFN = TFN
WRITE (*, 50) TFN, FOFTN
50 FORMAT (10X, 'AGE IS = ', E15.6, 10X, 'ERROR = ', E15.6)
STOP
T = TN
GOTO 30
70 FOFTN = U*(U238*EXP(LU238*T) - 1) + U235*
(1 - U235*EXP(LU235*T) - 1) + Th*(EXP(LTH*T) - 1)
PBC = FOFTN
FOFTN = FOFTN - PB
DFOFTN = U*U238*EXP(U238*LU238*T) + U*U235*L
U235*EXP(U235*LU235*T) + Th*LTH*EXP(TLH*T)
TN1 = TN1 - DFOFTN/DFOFTN
IF (ABS(TN1-TN) - EPSI) 90, 90, 80
TN = TN1
GOTO 70
90 TFN = TN1
90 FOFTN1 = U*(U238*EXP(LU238*T) - 1) + U235*
(1 - U235*EXP(LU235*T) - 1) + Th*(EXP(LTH*T) - 1)
PBC = FOFTN
FOFTN1 = FOFTN1 - PB
WRITE (*, 25) TA
25 FORMAT (10X, 'Approximate age in years = ', E15.4)
WRITE (*, 50) TN1, FOFTN1
ERROR = PBC - PB1
WRITE (15, 200) NCODE
200 FORMAT (25X, 'The Rock Sample code:', A10/I)
WRITE (15, 250)
250 FORMAT (10X, 'Element', 12X, 'U', 14X, 'Th', 14X, 'Pb')
WRITE (15, 300) U1, TH1, PB1
300 FORMAT (10X, 'Assay in ppm', 3(F10.3, 5X/I)
WRITE (15, 25) TA
300 FORMAT (10X, 'The Pb calculated (atomic prop.) = ', E15.7)
WRITE (15, 500) PB
500 FORMAT (10X, 'Experimental value of Pb (atomic. prop.) = ', E15.7)
WRITE (15, 600) ERROR
600 FORMAT (10X, 'The Error = ', E15.7)
WRITE (15, 700) TFN
700 FORMAT (10X, 'The calculated chemical age in years = ',
E15.7/I)
STOP
END


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