Identification of paleosols in the Precambrian metapelitic assemblages of peninsular India – A major element geochemical approach

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Al_2O_3 greater than 20%, positive correlation between Al_2O_3 and TiO_2, plot towards the Al_2O_3 corner in the Al_2O_3–K_2O–Fe_2O_3 (T) diagram and high chemical indices of alteration and weathering (CIA, CIW) distinguish the paleosols (fossil residual soils) from transported and deposited pelitic rocks like shales. Submarine weathering products are characterized by high MgO whereas the subaerial ones are not. Application of these criteria shows that majority of the khondalites of Orissa, Andhra Pradesh and Kerala are metamorphosed paleosols. They were probably formed from bauxite type lateritic soils. The protoliths of khondalites of Madras were, however, shales. Except for the biotite schists, other high alumina metapelites of Holenarasipur greenstone belt could also have been formed from paleosols. These latter being characterized by higher MgO content could represent metamorphosed submarine weathering products. The metapelites occurring at the base of the Aravalli Supergroup in Rajasthan also have chemical characters similar to residual soils. The Dharwar and Cuddapah shales stand apart from such metamorphosed probable paleosols.

STUDY of paleosols has played a key role in understanding the Precambrian atmospheric evolution and in deciphering paleoclimatic conditions[1,2]. Reports of paleosols from the metamorphosed Precambrian sequences of India have been rare. Sharma[3] interpreted the pyrophyllite–diaspore deposits of the low grade metamorphosed Palar Formation of the Precambrian of Bundelkhand province as a paleosol. Golani[4] considered that the sillimanite–corrundum deposits of Sonapahar in the Precambrian of Meghalaya may have resulted by high grade metamorphism of lateritic bauxites. Recognition of paleosols in deformed and metamorphosed Precambrian sequences is difficult because in such instances original field relations are modified, the physical fabric of the soil has been destroyed and clay minerals formed during weathering have all been metamorphically recrystallized. To help identifying paleosols in metamorphic terrains, several geochemical criteria have therefore been tried Reimer[5] suggested that metapelitic rocks with Al_2O_3 greater than 20% may represent paleosols. Taking advantage of K_2O depletion and enrichment of R_2O_3 constituents that accompanies weathering, he further used A–K–F (Al_2O_3–K_2O–Fe_2O_3) diagrams to distinguish transported clayey sediments from paleosols. Maynard[6] observed that TiO_2 and Al_2O_3, the two most insoluble major oxides, can be useful as indicator elements for distinguishing *in situ* soil profiles from allochthonous sediments. Feakes *et al.*[7] observed a positive correlation of TiO_2 with Al_2O_3 in Ordovician paleosols of Nova Scotia, Canada. We verified this relation for the data available on the paleosols from the Mt. Vulture Volcano of Italy[8], the Dominian Reef, Pongola[9] and the Hekpoort[10] of South Africa as well as the Pronto[11] and Athabaska[1] of Canada. In all cases we observed positive correlation between TiO_2 and Al_2O_3. Correlation coefficient appears to be high for high alumina paleosols and moderate for others. By contrast, the metamorphosed shales either do not show any correlation or sometimes exhibit even a negative correlation between TiO_2 and Al_2O_3. This is attributed to differential mobility of these two oxides in the transporting media.

Soil profiles characterized by high degree of weathering are enriched in hydrous clay mineral phases which, with partial desiccation, offer resistance to transport unlike the soil profiles which have witnessed partial argillitic alteration. Perhaps it is for this reason, we notice in river sands feldspar grains which are in various stages of alteration. From this, it may be inferred that the residual clays may be characterized by much higher indices of chemical weathering such as Chemical Index of Alteration (CIA=$100(Al_2O_3)/Al_2O_3$ + silicate $CaO + Na_2O + K_2O$) proposed by Nesbit and Young[12] and Chemical Index of Weathering (CIW = $100(Al_2O_3)/$ Al_2O_3 + silicate $CaO + Na_2O$) proposed by Harnois[13].

Although weathering is dominant in subaerial environment, alteration of basalts on the seafloor has also been documented. Submarine alteration could be due to either sea water-rock interaction or alteration brought about by hydrothermal solutions connected with submarine volcanoes. Retallac[14] suggested that in the alteration affected by hydrothermal solution, MgO of the parent material is largely retained unlike in subaerially weathered mafic igneous rocks and these alteration

Table 1. Compositional parameters of Precambrian metapelites of peninsular India useful for identification of palaeosols

Rock type & area	Al_2O_3		TiO_2		CIA		CIW	
	Range	Avg	Range	Avg	Range	Avg	Range	Avg
Khondalites of Eastern Ghats								
Orissa (n = 66)[19]	8 92–36 33	18 85	0 03–2 25	1 01	68 46–98 94	85 73	79 36–99 83	95 40
Araku[22] (n = 16)	12 56–29 76	22 57	0 35–2 35	1 20	61 20–93 91	84 71	71 30–94 38	90 36
Ibrahimpatnam[23] (n = 8)	13 73–20 25	16 66	0 15–0 95	0 67	65 50–79 90	70 77	76 77–90 77	83 09
Madras (n = 10)[24]	7 50–14 60	11 53	0 03–0 87	0 37	58 90–98 47	76 21	79 30–98 65	88 55
Kerala (n = 4)[25]	15 00–20 20	16 80	0 15–0 70	0 57	63 99–74 22	68 29	80 77–88 71	81 20
Metapelites of Dharwar greenstone belts								
Holenarasipur[26] (n = 10)	6 40–33 20	22 83	0 23–0 82	0 62	77 77–85 21	81 09	95 26–98 76	96 18
Tivadahalli[27] (n = 8)	11 81–30 11	19 91	0 49–1 09	0 74	70 50–86 48	79 84	83 74–99 88	92 33
Holenarasipur[27]–Karli (n = 6)	12 15–25 62	19 18	0 48–0 68	0 61	70 23–84 10	77 95	79 20–93 59	88 16
Holenarasipur[27] biotite schist (n = 7)	17 96–24 23	20 95	0 83–0 98	0 89	62 62–71 66	69 24	70 55–84 58	79 53
Holenarasipur[27]–Chinnapura (n = 8)	7 17–17 56	13 15	0 26–0 63	0 45	65 89–89 97	79 11	71 59–93 59	88 16
Dharwar[27] shales (n = 4)	14 85–17 77	15 19	0 60–0 68	0 65	67.05–69 80	69 38	74 98–76 13	76 88
Aladahalli[28] (n = 5)	11 88–12 42	12 10	0 47–0 86	0 66	75 46–87 28	81 24	76 12–95 39	87 80
Cuddapah[27] shales (n = 3)	8 97–17 77	14 66	0 24–0 82	0 60	71.90–76 99	74 26	91 32–99 23	96 59
Metapelites of Aravalli sequence								
Debari (n = 8)[15]	9 93–28 96	17 73	0 38–1 27	0 75	53 34–68 87	61 69	77 22–86 13	84 59
Girwa (n = 8)[15]	11 29–30 22	17 82	0 02–1 12	0 61	55 88–72 05	72 05	79 95–85 82	83 66
Jharol argillites[15]								
(i) Low grade (n = 6)	11 87–25 33	22 77	0 52–0 81	0 61	71 07–76 05	74 55	87 50–91 31	89 01
(ii) High grade (n = 2)	35 32–31 61	33 47	1 54–1 87	1 71	75 44–75.70	75 57	89 19–89 72	89 45

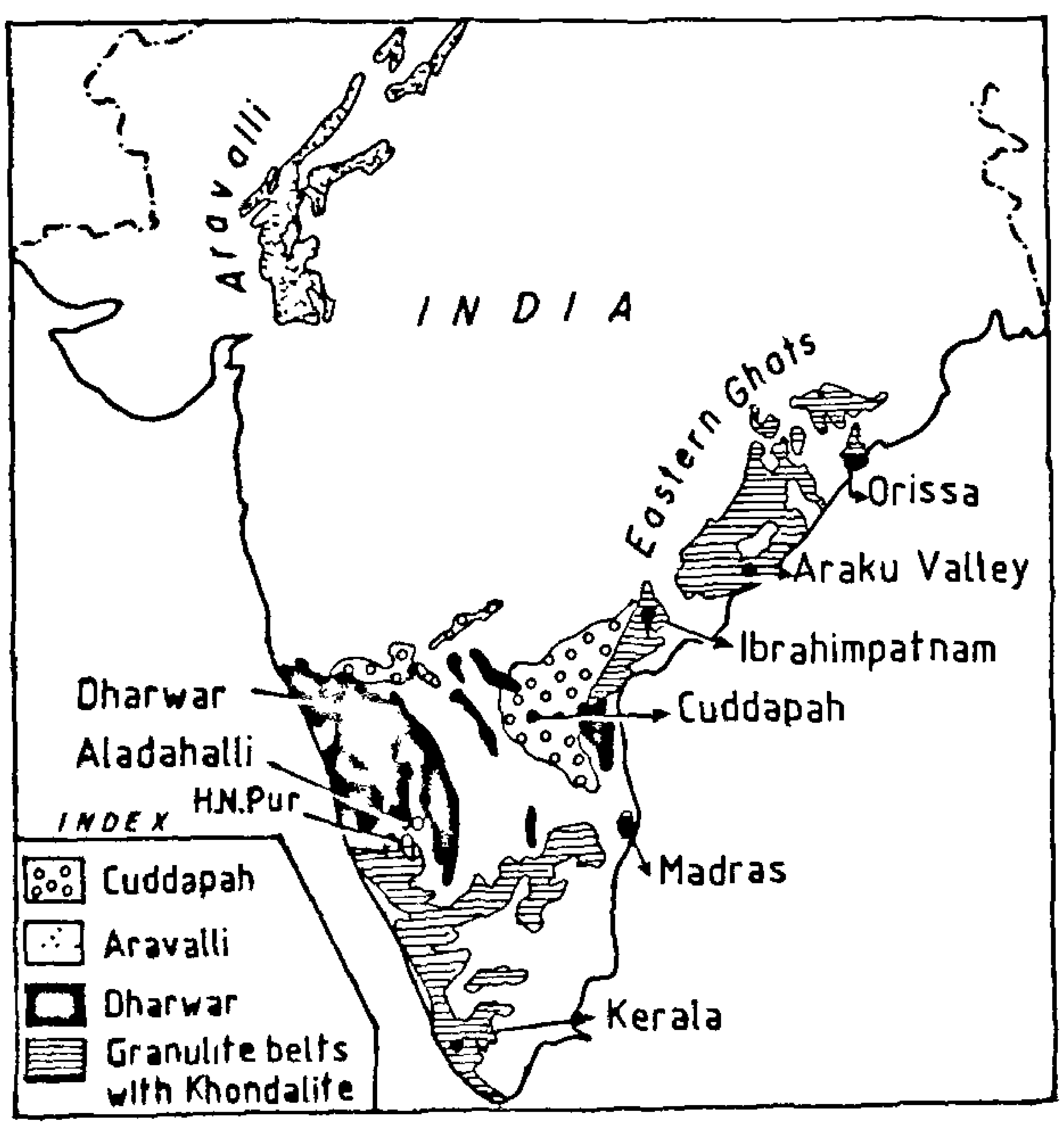

Figure 1. Sketch map of India showing the locations of metapelites whose compositions have been examined for identifying the possible paleosols

products are also enriched in certain trace elements like Cu and Zn.

In the light of the foregoing, we examine the compositions of about 300 Precambrian metapelites from peninsular India to ascertain which of them could probably represent paleosols. The database includes 117 chemical analyses of khondalites from the Eastern Ghat granulite belt, 157 metapelites from the Dharwar greenstone belts and 40 metapelites from the Aravalli belt (Figure 1). Data of a few shales from Cuddapah sequence also have been examined. References for the sources of data along with the critical parameters (Al_2O_3, TiO_2, CIA & CIW) are given in Table 1.

Al_2O_3 content

The khondalites whose analyses have been examined here are from Orissa, Andhra Pradesh (Araku valley and Ibrahimpatnam), Madras and Kerala regions. Forty-two per cent of the analyses of the Orissa and Araku valley khondalites are characterized by Al_2O_3 content greater than 20%, and the rest from this region have Al_2O_3 ranging between 15 and 20%. Khondalites of Ibrahimpatnam and Kerala show Al_2O_3 content ranging from 13.73 to 20.20%. The Madras khondalites have the lowest Al_2O_3 falling in the range of 7.50 to 14.60%.

The metapelitic rocks of the Dharwar greenstone belts, barring rare exceptions like those of Holenarasipur schist belt have low Al_2O_3 content. Twenty-five per cent of the Dharwar metapelites, almost all from the Holenarasipur schist belt are characterized by high Al_2O_3. Similarly shales of Cuddapah have low Al_2O_3 ranging from 7.80 to 17.86%. More than 44% of argillites from the Aravalli belt are of high Al_2O_3 type. Argillites of Jharol region appear to be enriched in Al_2O_3 compared to the argillites of Girwa valley and Debari areas.

Al_2O_3 and TiO_2 correlation

Figure 2 is the Al_2O_3 vs TiO_2 plot for the various metapelites of peninsular India. The khondalites of Orissa, Araku valley, Ibrahimpatnam and Kerala exhibit a strong positive correlation between Al_2O_3 and TiO_2 ($r = +0.6348$, $+0.7720$, $+0.6273$ and $+0.8127$). Madras khondalites, by contrast show a strong negative correlation ($r = -0.7883$).

Except for the biotite schists ($r = 0.0660$), strong positive correlation ($r = +0.9007$ and $+0.9529$) characterizes the high alumina metapelites of Holenarasipur

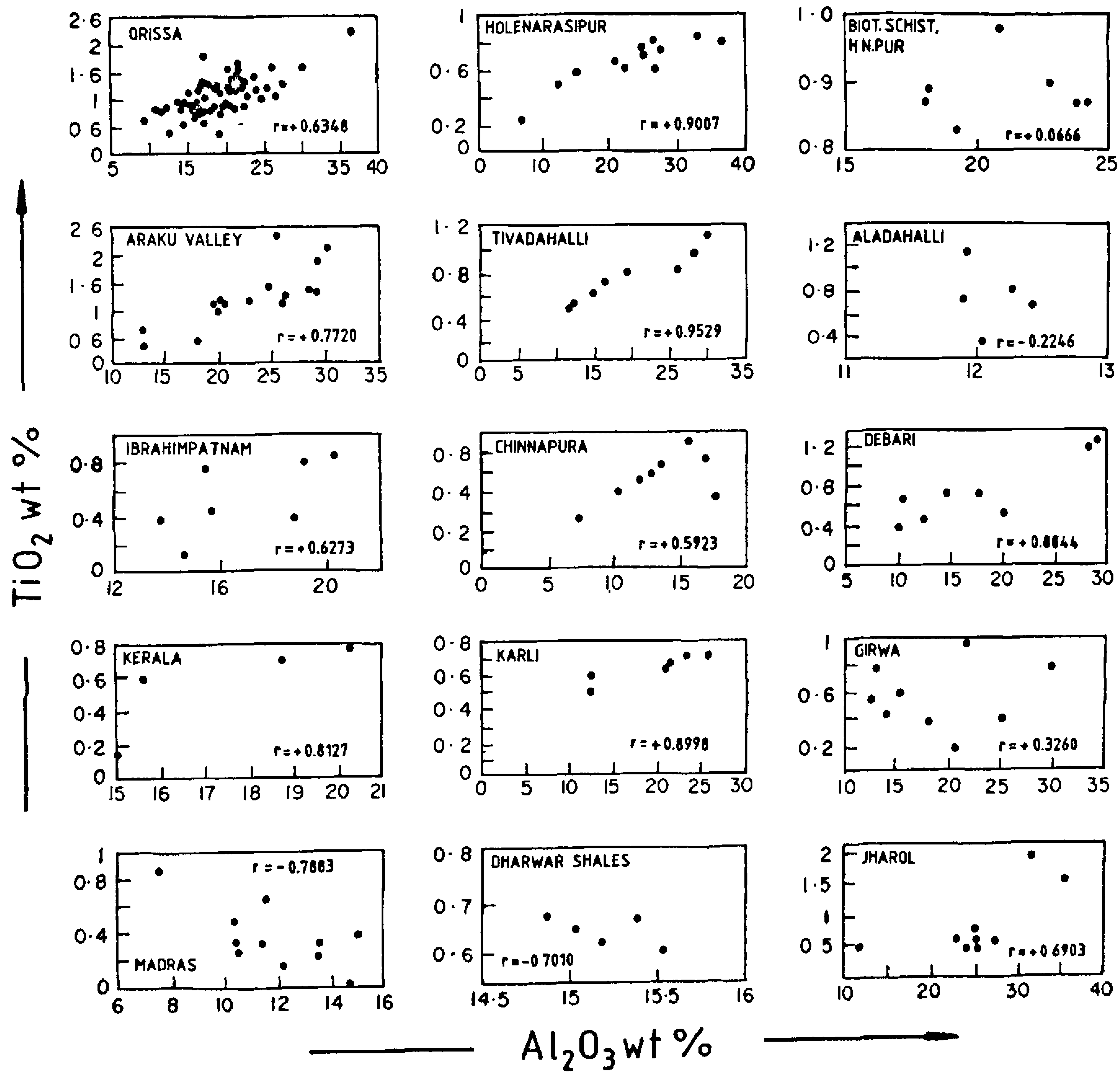

Figure 2. Al_2O_3 vs TiO_2 plot for some of the Precambrian metapelites of peninsular India.

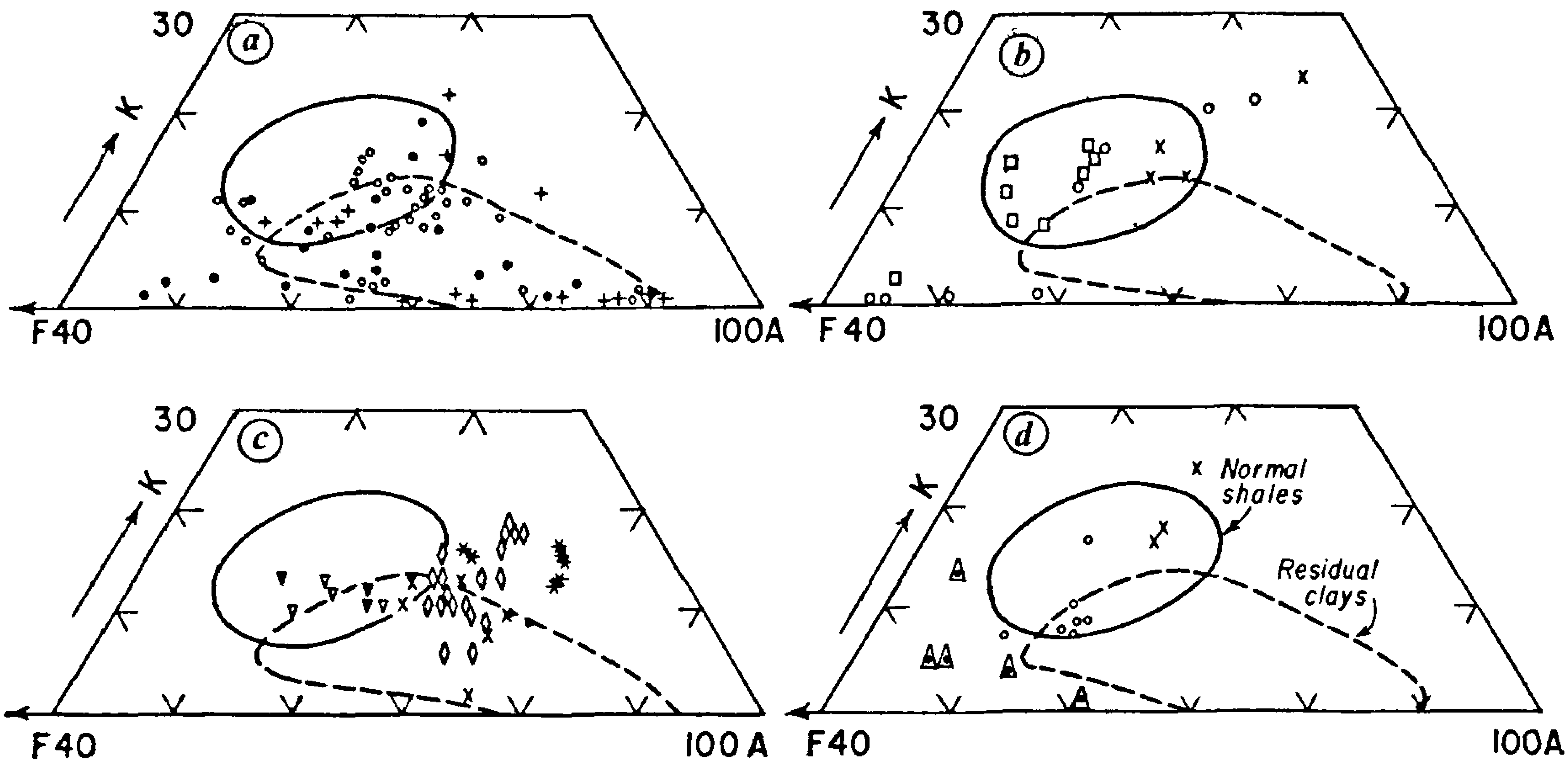

Figure 3. Al_2O_3–K_2O–Fe_2O_3 (T) diagrams for some metapelites of peninsular India (*a*) open circles, Orissa; plus, Araku valley; (*b*) squares, Ibrahimpatnam, open circles, Madras; crosses, Kerala; (*c*) diamonds, high Al_2O_3 schists of Holenarasipur and Tivadahalli, stars, high alumina schists of Karli of Holenarasipur belt; inverted triangle, high alumina biotite schists of Holenarasipur; (*d*) open circles, Dharwar shales; crosses, Cuddapah shales; triangles, Aladahalli metapsammopelites.

and Tivadahalli areas of the Holenarasipur greenstone belt. Similarly a strong positive correlation is observed in the Debari argillites, whereas it is moderate and weak in the case of Jharol and Girwa valley argillites of the Aravalli belt. The shales of Dharwar, psammopelites of Aladahalli as well as Cuddapah shales show a depletion of TiO_2 with increase in Al_2O_3.

A–K–F diagrams

It can be seen in the A–K–F diagram that the khondalites of Orissa and Araku valley plot in the zone of residual clays (Figure 3 *a*). But the other khondalites including Ibrahimpatnam, Madras and Kerala fall outside the field of residual clays being enriched in K_2O (Figure 3 *b*). Some of the Madras khondalites plot on the Al_2O_3–Fe_2O_3 join and more towards Fe end due to the enrichment of Fe_2O_3. In all these cases while the R_2O_3 (especially Al_2O_3) constituents are enriched, MgO is depleted.

High alumina metapelites of the Holenarasipur greenstone belt comprising the Holenarasipur and Tivadahalli schists plot in the field of residual clays (Figure 3 *c*), some of them as well as the Karli schists from this belt are enriched in K_2O and therefore plot outside the field of residual clays. The high alumina schists of Holenarasipur, unlike the residual clays resulting from subaerial weathering, show retention of MgO ranging from 1.66 to 5.42. The biotite schists of Holenarasipur, although characterized by moderate to high alumina, plot outside the field of residual clays. The psammopelites of Aladahalli are enriched in iron compared to the Holenarasipur metapelites, and therefore show a scatter towards F corner of the A–K–F diagram (Figure 3 *d*). The Dharwar and Cuddapah shales plot in the field of normal shales.

Bhattacharya[15] observed that the Debari paleosol and the associated argillites have compositions different from residual clays. These and the Girwa valley argillites are enriched in K_2O. Jharol argillites are stated to have residual clay compositions.

Weathering indices

Chemical index of alteration (CIA)

The Orissa khondalites are characterized by very high CIA values as in highly weathered soil profiles (avg. 85.73). More than 40% of the Orissa khondalites show CIA values greater than 80 and 30% show this index greater than 90. Similarly the Araku valley khondalites are also characterized by very high CIA (avg. 84.71). Fifty per cent of samples show CIA greater than 85 and 44% of samples, greater than 90. Compared to these, the khondalites of Ibrahimpatnam show a range of CIA values varying between 65.5 and 79.9, average being 70.77 which is not outside the range of shales. The Kerala khondalites also have moderate CIA values, ranging between 63.00 and 74.22, average being 68.29. In the case of Madras khondalites extreme variation of CIA from 58.9 to 98.47 has been observed. This is due to the large variation of alkali content in these khondalites.

The CIA values of the Dharwar metapelites show a wide range. The high aluminous metapelites of Holenarasipur in spite of their high Al_2O_3 nature show a moderate range of CIA values varying between 70.5 and 85.21. This is due to their high K_2O content. The shales of Dharwar area show a range between 62.16 and 71.88. The metapelites of Aladahalli, Karnataka exhibit CIA values ranging between 75.46 and 87.28. The shales of Cuddapah sequence show a range between 71.90 and 76.99 typical of sedimentary shales. The Debari, Jharol and Girwa valley meta-argillites show a low to moderate range of CIA values varying between 53.34 and 76.05 although they are rich in Al_2O_3.

Chemical index of weathering (CIW)

Since many soil profiles as well as shales undergo diagenetic changes, their alkali content, especially the K_2O content, has been found to be altered[2,16]. In the case of metapelites post-metamorphic hydrothermal alteration also could contribute to the enrichment of K_2O (ref. 17). Therefore, Harnois[13] considers that the alteration index calculated on K_2O-free basis will represent better the intensity of weathering. The revised index is designated as Chemical Index of Weathering (CIW). Condie[18] considers CIW as a best measure of intensity of chemical weathering.

The CIW just as CIA values is found to be maximum for khondalites of Orissa (avg. 95.40 and range 79.36–99.83) and Araku valley (avg. 90.36 and range 71.30–94.38). However, the Madras khondalites which show low CIA values are characterized by high CIW (avg. 88.55) suggesting that the low CIA may be due to post-depositional enrichment of K_2O in these khondalites. The Ibrahimpatnam and Kerala khondalites exhibit lower CIW (avgs. 83.09 and 81.20 respectively) when compared to the other khondalites.

Although the high alumina Holenarasipur metapelites are characterized by a moderate range of CIA values, they exhibit very high CIW values ranging between 83.49 and 99.89, suggesting post-depositional K_2O enrichment. The biotite schists of Holenarasipur are an exception in having lower CIW (avg. 79.53). The iron-enriched metapelites of Aladahalli similar to the high alumina metapelites exhibit high CIW (avg. 87.80). CIW of the Dharwar shales matches with their low CIA values. Despite their moderate CIA the Cuddapah shales are characterized by high CIW ranging between 91.32 and 99.23. In the Aravalli sequence, the argillites of Girwa valley, Jharol and Debari exhibit moderate values of CIW ranging between 77.22 and 91.31.

Discussion

The high Al_2O_3 content, strong positive correlation of TiO_2 with Al_2O_3, the A–K–F ratios similar to residual soils, low potassic nature and high values for CIA and CIW indicate that the protoliths of the khondalites of Orissa and Araku valley were of the nature of paleosols. Similarity of their compositions with the aluminous laterites of Brazil has also been suggested by Dash *et al.*[19]. The Ibrahimpatnam and Kerala khondalites in respect of having moderately high content of Al_2O_3, and positive correlation of Al_2O_3 with TiO_2 also could have been paleosols. However, higher K_2O content in them indicates that if indeed these were lateritic soils like the Orissa khondalites, they have later been affected by K-metasomatism. Granitization of khondalites in various parts of the Eastern Ghats and the southern Indian granulite terrain has been known for a long time (cf. Krishnan[20], p. 108). Because of higher K_2O content the Kerala and Ibrahimpatnam khondalites plot outside the field of residual clays in A–K–F diagram. The Madras khondalites seem to be different from the other khondalites in respect of having low Al_2O_3, negative correlation of TiO_2 with Al_2O_3 and higher K_2O content. They also plot outside the field of residual clays in A–K–F diagram. In all these respects their composition seems to be similar to those of transported argillitic sediments rather than residual soils. We, therefore, consider that the protoliths of khondalites comprised residual laterites as well as sedimentary shales.

High alumina metapelites from the Holenarasipur greenstone belt in respect of their Al_2O_3 content, strongly positive Al_2O_3 and TiO_2 correlation and very high CIW values are similar to paleosols. Unlike the paleosols produced by subaerial weathering they do not show MgO depletion. In this respect they resemble submarine weathering products. Kimberly[21] suggested the possibility of formation of these clays by alteration associated with volcanic exhalations. The biotite schists of this belt, however, differ from the associated high alumina schists in respect of very low correlation coefficient between Al_2O_3 and TiO_2 and lower CIA and CIW values; they also plot outside the field of residual clays. Their protolith may be a transported pelitic sedimentary rock. However, they have high Al_2O_3 than in normal shales. But as in the case of some khondalites and Precambrian paleosols of other regions, the Holenarasipur metapelites are characterized by higher K_2O content, which renders the composition of these rocks to plot in the field outside that of residual clays in the A–K–F diagram. However, breakdown of high alumina silicate minerals like kyanite to sericite and/or paragonite noticed in these rocks at several places point to K and/or Na metasomatic alteration.

Shales of the Dharwar area, Cuddapah and metapelites of the Aladahalli formation – are all characterized by less than 20% Al_2O_3, negative correlation of TiO_2 with

Al_2O_3, lower CIA values and plot outside the field of residual clays indicating that their pelitic protoliths were lithified sediments which had been transported from the site of weathering.

The Debari argillites of Aravalli mountain belt located close to the interface of granite gneiss (Banded Gneissic Complex) and the Aravalli Supergroup, are characterized by moderate Al_2O_3 content, a strong positive correlation between Al_2O_3 and TiO_2 and moderate values for CIA and CIW. These indicate that they could probably be paleosols. Weak correlation between Al_2O_3 and TiO_2 and their occurrence in the heart of sedimentary sequence above the base of Aravalli belt rule out the possibility of Girwa valley argillites being paleosols. The Jharol argillites exhibit high Al_2O_3, moderate positive correlation between Al_2O_3 and TiO_2, moderate CIA values and high CIW values similar to paleosols. Their plot in the zone of residual clays in the A–K–F diagram corroborates such an inference. However, their occurrence well within the sedimentary sequence of Aravalli mountain belt contradicts this inference. Further studies are essential to understand the reasons for their chemical characteristics. All the meta-argillites of Aravalli sequence are characterized by higher alkali content which may be attributed to the post-depositional alkali enrichment.

Conclusions

Application of criteria such as Al_2O_3 content, Al_2O_3–TiO_2 ratios, A–K–F proportions, chemical indices of alteration (CIA and CIW) and MgO retention has led to identification of the following rock formations as having resulted by the metamorphism of paleosols: 1. Khondalites of Orissa and Araku valley; 2. Metapelites of the Holenarasipur greenstone belt except for the biotite schists; these however could be submarine alteration products; 3. Debari argillites of the Aravalli mountain belt.

Although it is possible that some of the khondalites such as Kerala and Ibrahimpatnam could be paleosols, their original alkali content, especially the K_2O content has largely been altered by post-depositional processes. This is also true for the metapelites of Holenarasipur and Aravalli belts.

Detailed studies could be directed towards some of these occurrences which potentially are metamorphosed Precambrian soil profiles for understanding the Precambrian exogenic processes.

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