Differential thermal analysis and thermogravimetric studies of the Kaladgi (precambrian) argillites, Karnataka

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Abstract. The Kaladgi argillites show heterogeneity in textural and physical properties. Differential thermal analysis and thermogravimetric studies have revealed that the argillites contain illite with montmorillonite, quartz and biotite. The calc-rich shale contains illite and kaolinite with total absence of montmorillonite. The mineralogical significance of the depositional environment of the Kaladgi (precambrian) sea has been discussed.

Keywords. Differential thermal analysis; thermogravimetric; Kaladgi argillites.

1. Introduction

The Kaladgi (precambrian) argillites are very fine clastic sediments. They are least described in the petrological literature because of their extremely fine grained texture where the grain is less than 0.001 mm. This makes thin section study very difficult or almost impossible. The physical properties of the argillites are also much varied and heterogeneous. They show variation in colour, bedding, lamination, induration, fissility and grain size. Based on these properties the Kaladgi argillites are classified into shale, calcareous shale, slate and claystone (Chandrasekhara Gowda 1976). The different argillite members in the Kaladgi group with their distinctive characters are given in the table 1.

2. Materials selected

The 'shale' is a layered argillite that contains essentially clay minerals. The layering or thin bedding is principally due to sedimentation process itself and the rock breaks in a distinctly platy fashion parallel to the bedding. When the shale is composed of more than 20% carbonate minerals, it effervesces with dilute HCl and hence is termed as 'calcareous shale' (Pettijohn 1957). The term 'claystone' is used for rocks less indurated than shale, but it is a consolidated clay, appearing as a massive rock body with blocky habit (Ingram 1953). The 'slate' is a low grade metamorphic derivative of shale or claystone characterised by strongly developed slaty cleavage throughout the rock. These argillites show considerable variation in colour, texture and acid reactivity in the field due to variations in their mineral content. Hence it was necessary
Table 1. Argillite members in the Kaladgi group

<table>
<thead>
<tr>
<th>Group</th>
<th>Formation</th>
<th>Member</th>
<th>Remarks</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>13. Laksanhatti dolomites</td>
<td>‘Paper shales’ and ‘silty shale’ beds are present. In intruded by</td>
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<tr>
<td>Mallapur</td>
<td></td>
<td>11. Aralikatti chert-brecia</td>
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<td>10. Kanasgeri feldspathic arenites</td>
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<td></td>
<td>9. Kadarkop claystones</td>
<td></td>
<td>Joints less developed. Appear as massive beds. No fissility. Less</td>
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<td></td>
<td>8. Petlur limestones</td>
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<td>indurated.</td>
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<td>7. Jalikatti slates</td>
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<td>Lokapur</td>
<td>6. Chikshellikeri limestones</td>
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<tr>
<td></td>
<td>5. Hebbal calcareous shales</td>
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<td>4. Chitrabhanukot dolomites</td>
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<td>Salapur</td>
<td>3. Naganur quartz arenites</td>
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<td></td>
<td>2. Jalageri shales</td>
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<td>1. Aniwal quartz-arenites.</td>
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to identify their mineral composition by suitable techniques. In the present investi-
gation typical specimens of argillites were subjected to differential thermal analysis
(DTA) and thermogravimetric (TG) studies. The following six specimens were
selected for the study: 1. grey shale, 2. red shale, 3. calcareous shale, 4. claystone,
5. slate and 6. intercalated argillite band in limestone. The location of samples is
shown in the map (figure 1).

Figure 1. Sketch map showing the location of argillite samples.
3. Experimental procedure

3.1. The argillite samples were ground to -120 mesh size (Tyler standard) and equilibrated at 55\% RH for 24 h. TG analysis was carried out on the thermogravimetric analyzer described by Venugopal et al (1976). One gm of the sample was taken in a cylindrical mullite sample holder and placed in the furnace and heated in air progressively from 20ºC to 1000ºC maintaining a rate of heating of 5ºC per min. Weight loss was recorded on Sartorius thermobalance for every 40ºC interval. At expected TG change weights have been recorded for every 20ºC. The TG curves of the argillite samples are presented in figure 2.

3.2. DTA of the argillite samples has been carried out on a 500 mg sample (-100, +120 mesh, Tyler standard) in a mullite sample holder using α-alumina as reference. The samples are heated in air at a programmed rate of 10ºC per min up to 1000ºC. The temperature \( T \) is measured on a Toshniwal recorder and the differential temperature \( T_0 \) on a moving coil amplified galvanometer using Pt-Pt/rh 13\% thermocouple. The DTA peaks are given in figure 3.

4. Results

4.1. Thermogravimetric analysis

The thermogram of the Kaladgi grey shale shows a smooth curve (figure 2, No. 1) up to 800ºC with a slight increase at 850ºC. The weight decreases again at 950ºC.

![Figure 2. Thermogram of Kaladgi argillites 1. Grey shale; 2. Red shale; 3. Claystone; 4. Calcareous shale; 5. Slate; 6. Intercalated argillite band in limestone.](image-url)
and the sample shows mullite phase at 950°C. From the curve grey shale appears to be a mixture of montmorillonite and illite in which the former mineral seems to be predominant. The total loss of weight of sample during the analysis is 0·04%. A steep fall in the curve till 300°C could be noticed in the thermogram of the Kaladgi red shale (figure 2, No. 2). In general appearance, it is an 'L' shaped curve which is more of hydrous mica (illite). Between the temperature 400° and 500°C a small trough has been formed due to sudden fall and rise in weight. There is no mullite phase in the red shale at 950°C and the total loss of weight is 0·35% during the analysis. The thermogram of Kaladgi claystone shows a total weight loss of approximately 1·15% per gram. The general feature of the graph (figure 2, No. 3) indicates that the rock is mostly composed of quartz and clay. Clay seems to be a binary mixture of bentonite and illite indicated by a gradual slope between 250° and 550°C. In the initial stages there is a steep fall up to 250°C which is characteristic of detrital nature of the mineral. There is a small but steep fall at 950°C which suggests that the clay mineral is more illitic in nature. However, quartz does not respond well to thermogravimetric analysis. Thus the thermogram of claystone does not indicate the formation of mullite phase even at 1000°C. There is a total loss of 9·66% per gram in the thermogravimetric analysis of Kaladgi calcareous shale. It shows a typical sigmoid (S' shape) curve (figure 2, No. 4). Dehydration in the initial stages is noticed at 350°C and there is equilibrium till 700°C. From 750°C there is a very steep fall
in weight due to extensive reactions and changes in the mineral phases. The calcareous shale is mostly composed of kaolinite with calcic phases. Due to high calcium content of the mineral, it is possible that many calcic mineral phases have been formed at high temperatures. No mullite phase has been observed in the calcareous shale. The pattern of the thermogram of the Kaladgi slate appears to be the same as that of red shale up to 900°C (figure 2, No. 5). From 900°C to 950°C there is a steep fall in the weight indicating a phase transformation. This appears to be a mixture of illite and kaolinite, predominantly composed of the former. At 950°C there is nucleation of mullite phase. The total loss of weight during the analysis is 0.71% per gram. The thermogram of the intercalated argillite band in the Kaladgi limestone shows a smooth fall till 750°C indicating the presence of montmorillonite (figure 2, No. 6). Further, there is a very steep fall till 850°C. At 850°C the nucleation of mullite starts. The intercalated argillite band in limestone shows the mullite formation much earlier than other minerals. It appears to be a mixture of montmorillonite and illite. The total loss of weight is 3.31% per gram.

4.2. Differential thermal analysis

4.2.1. The DTA pattern was characterised by endothermic and exothermic peaks. Any fall in the temperature from the standard $\alpha$Al$_2$O$_3$(T°) is endothermic in nature and any gain over the standard sample is exothermic in nature. For convenience the peaks are classified as very small ($T°<5°$), small ($T°6°-10°$), medium ($T°11°-20°$), large ($T°21°-30°$) and very large ($T°>30°$).

4.2.2. DTA pattern of the Kaladgi grey shale (figure 3, No. 1) revealed the presence of kaolinite, illite and montmorillonite. The presence of illite was indicated by two small peaks at 107°C and 550°C. Montmorillonite was revealed by very large peaks at 140°C and 730°C and a small peak at 850°C. A very small peak at 104°C and a very large peak at 590°C indicated the presence of kaolinite. A small exothermic reaction of montmorillonite was observed at 920°C which indicated the presence of both illite and kaolinite. The sample of Kaladgi red shale consists of illite showing a very small endothermic peak at 106°C and a very large exothermic peak at 945°C (figure 2, No. 2). A medium endothermic peak at 570°C was partly due to the presence of illite and biotite. The presence of biotite was confirmed by a small endothermic peak at 890°C. The Kaladgi claystone shows small endothermic peak at 110°C and a medium peak at 650°C indicating the presence of illite (figure 3, No. 3). Beidellite was revealed by a very large endothermic peak at 150°C and a medium exothermic peak at 920°C which also had an overlapping of montmorillonite. The presence of montmorillonite was also confirmed by a small endothermic peak at 860°C. Beidellite and illite showed an overlapping small peak at 550°C. The Kaladgi calcareous shale showed the presence of kaolinite by a small endothermic peak at 109°C and very large exothermic peak at 980°C (figure 3, No. 4). Illite was revealed by a very big peak at 660°C which was endothermic in nature. At 560°C a very large endothermic peak indicated both kaolinite and illite. The Kaladgi slate sample contains illite as indicated by a small endothermic peak at 545°C and a very large peak at 690°C (figure 3, No. 5). A very large peak at 570°C indicated the presence of kaolinite. A small endothermic peak at 107°C and very large exothermic peak at 950°C showed the presence of both illite and kaolinite. The sample
of the intercalated argillite band in the Kaladgi limestone contains illite as indicated by very small endothermic peaks at 120°C and 570°C (figure 3, No. 6). The presence of montmorillonite was shown at a very large endothermic peak at 150°C, a large peak at 690°C and a small peak at 880°C. A small exothermic peak at 930°C was also due to the presence of montmorillonite.

5. Discussion

5.1. Although TG and DTA studies revealed the presence of similar minerals in certain cases, a clear picture of the argillite composition has been revealed by DTA like presence of biotite in the Kaladgi red shale. Further, DTA studies showed clear and sharp peaks. A detailed study of thermograms reveals that in most of the samples there is weight gain till 200°C. This is probably due to oxidation of iron content from ferrous to ferric enhancing the iron phase in the argillite samples under study.

5.2. The DTA and TG studies reveal the preponderance of illite in all the argillite samples studied followed by montmorillonite or beidellite and kaolinite in the order of importance. As a general rule these clay minerals show small endothermic peaks below 200°C when —OH molecules are expelled. Between 400° and 700°C medium to large peaks were exhibited by the samples as a result of phase changes. Above 900°C exothermic peaks of medium to large size indicate lattice changes due to structural destruction and resultant mullite nucleation. Since the presence of montmorillonite and beidellite was observed by DTA in claystone XRD and chemical analysis were carried out (Chandrasekhara Gowda et al 1977). Montmorillonite did not reveal the first principal reflection in the powder photographs. But the second and third principal planes showed medium intensity reflections of \( d \) 4·395 Å and 1·484 Å. Similarly strong reflections of \( d \) value of 3·944 Å and 1·508 Å indicated the presence of beidellite in claystone. Chemical data showed that in the claystone the tetrahedral layer value was 4·65 and the octahedral layer was 1·63 and the interlayer was 0·28. The layer charge of the claystone was 1·36. The above data also seem to point out presence of beidellite in the claystone. However, since the samples are not monomineralic, the chemical and x-ray data were not more conclusive as DTA for the presence of beidellite (figure 3, pattern No. 3).

6. Conclusion

The above studies have revealed that the argillites of Kaladgi group are mostly illitic argillites with montmorillonite and beidellite and to a lesser extent kaolinite and biotite. The predominant occurrence of illite in all the argillite samples studied shows that the rocks were formed under potash rich marine condition. The association of montmorillonite and beidellite of bentonitic nature is suggestive of a sedimentary environment (Millot 1970). Preservation of montmorillonite in sedimentary petroliferous suites has been reported by Weaver (1960). Montmorillonite seems to be indifferent to the salinity of its genetic environment. It can occur in calcareous and hypersaline seas. Although abundance of potassium and sodium salts has no influence on the mechanism of its growth, an alkaline environment is
mandatory (Millot 1970). It appears from the above study that the Kaladgi sea was in potash rich alkaline environment, as a result of which illitic clays were formed and the residual alkalinity resulted in the formation of bentonite type of montmorillonite and beidellite. The total absence of montmorillonite in Kaladgi slates is due to the sensitivity of the mineral to the phenomenon of diagenesis where it disappears before the onset of low grade metamorphism resulting in the formation of slate (Millott 1970). The association of kaolinite with illite in calc rich shale seems to suggest that the former is derived primarily from acid feldspars and micas existing in adjacent areas and transported and sedimented in hypersaline condition (Tooker 1962). The biotite and quartz seems to be of detrital origin.

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