

PHYSICO-CHEMICAL BEHAVIOUR OF HYDRATED ALUMINIUM OXIDES AND ASSOCIATED CLAY MINERALS OCCURRING AROUND PIPRA, DISTRICT SIDHI, INDIA

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DTA techniques were employed to study the thermal and structural characteristics of hydrated aluminium oxides and aluminous clays of the Pipra pelitic rocks from district Sidhi, India. Detailed microscopic investigations, X-ray and chemical analyses reveal that these clays were derived by the localized weathering of arkosic metasediments. The chemical and normative behaviours have confirmed their formation by the isochemical metamorphism of arkose, aided by a little granitization and followed by minor retrogression. A tentative correlation between the thermal and structural changes of these oxides and clay minerals at various transition temperatures has nicely displayed the presence of kaolinite, diaspore and gibbsite. The exothermic curves of kaolinite confirm the recrystallization. The presence of kaolinite in the clay fractions indicates the detrital origin.

Identification of clay minerals

Clay minerals like kaolinite, halloysite, diaspore, gibbsite, nacrite, and dickite, etc. are practically impossible to identify with the help of an optical microscope, due to their natural occurrence in perfectly homogeneous and apparently pure condition, and it is not possible to apply any treatment to remove impurities [1]. Clay minerals are commonly too small for individual study under the petrographic microscope and only the average composite effect can be observed according to their orientation and distribution. Morgenstern and Tehalenko [2] have developed a device, introducing a photoelectric cell to obtain a quantitative measure of the intensity of the light transmitted through a sample on the petrographic microscope. They interpreted the degree of particle orientation by comparing the observations with predicted birefringent behaviour of an aggregate. In addition, it is possible to measure the refractive index and birefringence of clay mineral particles. Electron microscopy has also played a vital role in the identification of clay minerals. It reveals an approximate shape and size of the clay particles, and sometimes their thickness, but no structural detail is discernible. The large depth of focus of the electron optical system makes possible examination of rough or even curved surfaces of clay minerals. In contrast clay mineral analysis by X-ray diffraction is generally quantitative [3]. A quantitative method of X-ray analysis has also been supported by Taylor and Norrish [4]. The X-ray method

has been employed in crystal structure analysis to obtain information on the degree of disorder in the clay mineral lattice, to follow changes in mineralogical compositions induced by heat and to derive data on the minerals in a sample, but the information obtained by this method is not adequate for interpreting the genesis of Pipra clays.

Infrared spectroscopy (IR) has been extensively applied in clay mineralogy: it reveals crystal structural and bonding characteristics within the molecule and has proved useful in clay mineral identification when there is ambiguity in the interpretation of the X-ray diffraction pattern. The application of IR techniques has been described by Keller and Pickett [5] and the pioneer work of Keller, Barnes and Bradley has been of help in clay mineralogy. In clay minerals infrared absorption bands can not be assigned and interpreted, due to interactions of neighbouring ions and substantial effects from the closest neighbouring ion or ions in the second co-ordination sphere [6]. The identification of kaolin has been made by infrared analysis, kaolin displaying a band at $3.698 \pm 2 \text{ cm}^{-1}$ not shown by chlorites and kaolinites [7, 8]. The IR spectra of layer lattice silicates have been discussed by Farmer and Russel [9], but infrared absorption of the kaolinite group of minerals is not universally accepted. It is agreed that the OH group the shorter the wave length corresponding to its natural frequency of vibration. [10]. The authors have also applied this device to Pipra clays, using the Nujol technique with a Perkin-Elmer infrared spectrophotometer.

Thermogravimetry is an analytical technique concerned with measurement of weight changes in samples on heating and has been reviewed by Coats and Redfern [11]. The modifications pertaining to this technique have been described by Wendlandt [12]. The application of this technique to clay minerals has considerable value, since many reactions which affect clays on heating are accompanied by evolution or absorption of a gaseous component. Moisture is lost by many clay minerals on heating and these changes are of course accompanied by a corresponding loss in weight, as commonly evident by DTA. Some oxidation reactions in which oxygen is absorbed from the air are accompanied by a gain in weight, but the reactions which involve only energy changes, such as crystal inversion, crystallization and fusion, are not detectable with this method.

Chemistry of the clay minerals

The authors have taken recourse to the rapid methods of silicate analysis [13, 14] in analyzing these clays and refractory minerals. Clay samples were separated by standard methods. Silica and alumina were determined spectrophotometrically, and alkali metals on a flame-photometer, while a Spekker absorptiometer was used for the calorimetric determination of iron and titanium. Calcium and magnesium were analyzed by volumetric methods against ethylenediaminetetraacetic acid (EDTA) using screened calcein and O-cresolphthaleine complexone indicators, respectively, whereas MgO was determined against a standard dichromate solution. H₂O was determined by the modified Penfield method. The instru-

mental techniques, the underlying principles and the accuracy of the results in the analysis of clays and refractory minerals have already been described by Mehrotra *et al.* [15–18]. All the chemicals used in the chemical analysis were of analar grade.

The partial chemical analysis of clay minerals (Table 1) has been compared with the other analyses [19]. Amorphous silica and alumina are common constituents of the kaolinite group of minerals and considerable care has been taken in interpreting the significance of the Al/Si ratio of kaolinites. The clay minerals of the present area contain slightly more alumina than silica. This may be due to the presence of diasporite and/or gibbsite besides kaolinite in the clay fractions [16]. Kaolinite has the same $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio as halloysite, but the water content is lower. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio for the various kaolinite samples suggested that

Table 1
Chemical analysis of kaolinite, diasporite and gibbsite
(weight per cent oxides)

Oxides	1	2.	3.	4.	5.	6.	7.	8.	9.	10.
SiO ₂	43.30	44.06	44.81	43.84	2.64	1.37	—	2.80	1.03	2.78
Al ₂ O ₃	41.03	39.44	37.82	38.85	79.10	84.23	77.95	61.57	64.92	62.80
Fe ₂ O ₃	0.40	0.80	0.92	0.46	1.78	—	6.60	0.56	tr.	0.44
MnO	—	—	—	—	—	—	—	—	—	—
MgO	0.22	0.26	0.35	0.36	—	—	—	0.06	tr.	0.03
CaO	0.14	0.06	0.43	*	0.12	0.10	—	0.14	0.17	0.20
K ₂ O	n.d.	n.d.	n.d.	*	—	—	—	—	—	—
Na ₂ O	n.d.	n.d.	n.d.	*	—	—	—	—	—	—
TiO ₂	0.16	—	0.37	1.03	—	—	—	—	—	0.04
*Others	—	—	—	0.77	—	—	—	—	—	—
H ₂ O	14.80	15.22	15.37	13.54	16.44	14.67	15.00	35.02	34.12	38.74
Total	100.05	99.84	100.07	98.85	100.08	100.37	100.00	100.15	100.24	100.03

1. Average chemical analysis of Pipra kaolinites (average analysis of 30 kaolinite samples) [15, 17].
 2. Kaolinite, in vermicular grains from kaolin seams in bauxite, Saline County, Ark., U.S.A.; Analyst F. A. Gonyer [31].
 3. Kaolinite associated with arkosic sand from Mexia, Texas, U.S.A.; Analyst F. A. Gonyer [31].
 4. Chemical analysis of kaolinites from Macon, Georgia, U.S.A. [32].
 5. Average chemical analysis of Pipra diasporites (average analysis of 20 diasporite samples) [16].
 6. Diasporite, Pyrophyllite deposit, Shokozan, Bingo Prov., Japan (Yoshiki, 1933) [33].
 7. Diasporite (ferrian), Ural Mts. (quoted by Palache *et al.*, 1944) (Includes P₂O₅ 0.45) [33].
 8. Average chemical analysis of Pipra gibbsites (average analysis of 15 gibbsite samples) [16, 17].
 9. Gibbsite, Klein-Tresny, Moravia (Kovar, 1901) [33].
 10. Gibbsite, Kodikanal, Madras, India (Warth, 1902; See Palache *et al.*, 1944) [33].
- n.d. = not determined.

most of the variations are due to impurities. The average Fe_2O_3 content of the kaolinite samples is higher than the standard average values for halloysite, but is considerably higher still than the value of the well-crystallized kaolinites. The TiO_2 content of kaolinite is apparently dependent on the source of the mineral. When feldspar is the major source of the clay and is of hydrothermal origin, the TiO_2 content of kaolinite is low; when the source is a biotite-schist or biotite granite, the TiO_2 content is relatively high. In the clay samples of the present area the TiO_2 content is usually less than 1%. MgO , CaO , K_2O and Na_2O are usually present in kaolinite samples. Weaver and Pollard [20] have stated that most kaolinites contain appreciable amounts of MgO . Electron-probe studies [21] indicate that some of the MgO is related to TiO_2 , Fe_2O_3 material and some is present in biotite, as revealed by the clay samples of the area. Therefore, the chemical analysis of the kaolinites from the lowest metamorphosed unit, namely quartz-kaolin-sericite schist, co-ordinates with the results of DTA. It has been shown that the progressive regional metamorphism (isochemical metamorphism) of these clays leads to the formation of sillimanite and corundum-bearing rocks of the area.

Experimental

Differential thermal analysis

Differential thermal analysis has been found to be an important tool for the study of the structural changes occurring in solids during thermal treatment and this technique is employed most commonly for qualitative analysis of clay minerals; however, some attempts at quantitative analysis have also been made. The parameters which affect the quantitative application of DTA have been described by Barral and Rogers [22] and Yammamoto [23]. DTA supplements the information obtained by optical microscopy, X-ray diffraction studies, infrared spectroscopy, thermogravimetry and the determination of magnetic susceptibility, but even then difficulty arises in identifying clay minerals associated with impurities which obscure the other effects by undergoing oxidation. In such cases these techniques fail to give a clear picture. By the application of DTA, with control of the furnace atmosphere, such effects can be annulled. This technique has proved useful in revealing more specific information which is not adequately available by other methods.

The peaks resemble "spectral bands" and bear three points of interest, namely the initiation of the reaction, the significance of the peak apex and the area under the peak.

Factors controlling the nature of the thermal curves

The nature of the thermal curves depend mainly on various factors, including the particle size of the samples, the mode of packing of the samples, the heating rate and the dilution of the samples. The furnace atmosphere has a pronounced

effect on DTA results. Full control of the atmospheric composition and pressure greatly increases the versatility, but does not yet give the technique full self-sufficiency as an analytical procedure for clay mineralogy. Thus, the alternate use of inert and oxidizing atmospheres will permit differentiation of thermal decomposition from oxidative degradation. Within reasonable limits, pressure will have little effect on a condensed-phase transition, but it will strongly influence reactions where gaseous matter is evolved. For example, operation with increasing pressures of water vapour will inhibit a dehydration reaction, thereby permitting precise identification of the peak associated with such reactions.

DTA of Pipra clay minerals

After separation of clay minerals by utilizing standard methods, the Pipra clays were subjected to DTA. This method of thermal analysis has been regarded as a valuable adjunct to the other methods for the study of the thermal and structural characteristics of these clays. The instrumental technique and its applications

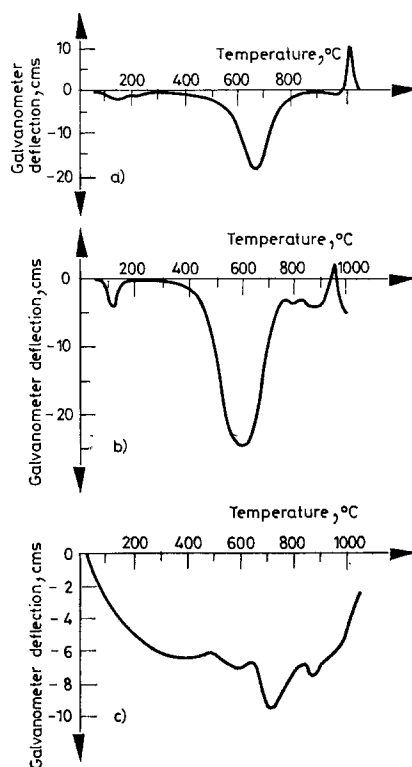


Fig. 1a. DTA curve of kaolinite and gibbsite

Fig. 1b. DTA curve of kaolinite

Fig. 1c. DTA curve of kaolinite, gibbsite and diaspore

have already been described by Ramchandran and Bhattacharya [24], and Mehrotra *et al.* [15–18]. The various curves (Fig. 1a–e) thus obtained reveal the physico-chemical and structural details of the clay mineral of the area.

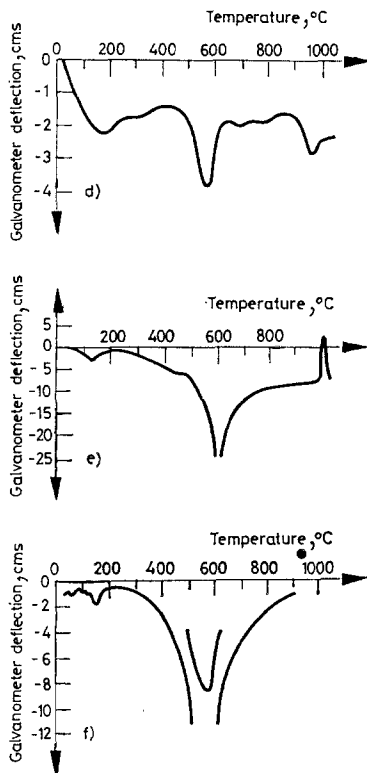


Fig. 1d. DTA curve of gibbsite and diaspore

Fig. 1e. DTA curve of kaolinite and gibbsite

Fig. 1f. DTA curve of Georgia-kaolinite (after Gillot)

Results and discussion

The most characteristic DTA of kaolinite is depicted in Fig. 1a, which refers to a kaolinite sample. With the start of heating loss of mechanical water is seen within the temperature range 50 to 180° and is followed by the appearance of aluminium hydrate (gibbsite) between 180 and 440°. On further heating, disordered kaolinite with a characteristic endothermic curve appears in the temperature range 440 to 750°. This endothermic curve is followed by the exothermic curve of recrystallized (ordered) kaolinite, the peak temperature being 998°. As shown in Fig. 1b, a small endothermic peak occurs with kaolinite at about 105°, caused by the evolution of adsorbed water. At 520° the main endothermic peak com-

mences, with the tip of the peak at about 600° this corresponds to the decomposition of the mineral and elimination of hydroxyl groups as water. A further peak, which is exothermic, occurs at about 1000° , this is probably associated with recrystallization. Figure 1c is the curve of the third clay sample. The appearance of gibbsite covers a large integral in the diagram up to the range 490 to 630° . This indicates a larger quantity of gibbsite compared to diasporite in the sample subjected to DTA. The endothermic curves of gibbsite and diasporite are followed by the endothermic curve of kaolinite (disordered) in the temperature interval 630 to 820° . On further heating, recrystallization starts, as shown by the exothermic curve of kaolinite in the range of 1020° . Figure 1d refers to the DTA of sample IV. The portion of the curve between 50 and 160° pertains to the mechanical water adsorbed during preparation of the sample. On further heating, the gibbsite fraction appears, within the temperature range 160 to 425° (endothermic). Diasporite is less hydrated than gibbsite and therefore, with further rise of the temperature, its corresponding endothermic curves appear between 425 and 640° . Therefore, the sample contains a mixture of diasporite and gibbsite. Impurities of the natural clay fractions are detected within the temperature ranges 640 to 750° (Mg-Fe carbonates) and 750 to 1000° (CaCO_3), the nature of the curve being endothermic. The curve of the last sample is shown in Fig. 1e, where the loss of mechanical water appears up to 130° and is followed by the endothermic curve of gibbsite (130 to 450°). The diasporite component is not seen in this diagram and the endothermic curve of disordered kaolinite is observed in the temperature range 450 to 910° , followed by ordered (recrystallized) kaolinite, showing an exothermic peak at 1005° .

On the basis of the DTA of the clay minerals, including aluminium hydroxides, and interpretation of the patterns of the curves [10, 16, 25], it is seen that these exceptionally high aluminous clays are strictly contained in the lowest metamorphosed unit, i.e. quartz-kaolin-sericite schist comprises diasporite ($\alpha\text{-AlOOH}$), gibbsite ($\gamma\text{-Al(OH)}_3$) and kaolinite ($\text{Al}_2\text{O}_3, 2\text{SiO}_2, 2\text{H}_2\text{O}$). Both disordered and ordered kaolinites are present in the samples of clay fractions. The assumption of the authors that the present sillimanite and corundum-bearing rocks have been formed by the progressive regional metamorphism (isochemical metamorphism) of diasporic clays (derived from the localized weathering of arkose) is supported by the presence of diasporite and gibbsite. The diasporite fraction appears within the temperature range 425 to 640° and the nature of the peak being endothermic. Diasporite is less hydrated than gibbsite and the endothermic curves of gibbsite commence within the temperature range 160 to 440° . The endothermic curves of kaolinite (disordered) cover the temperature range 440 to 750° followed by the exothermic curve at 998 to 1020° confirming recrystallization. The presence of kaolinite in the clay fractions indicates the detrital origin [15].

Problem of origin

The origin of clay minerals is a most controversial and fascinating problem in clay mineralogy. The kaolinite and halloysite group of minerals appear to be the

result of a genetic process; leaching by sulphuric acid produced by the alteration of pyrites [1] seems to be one of the more common weathering processes. In the alteration of granitic rocks and pegmatites, mica is more likely to alter to kaolinite and feldspar to halloysite [26]. Mica contains a more appreciable quantity of titanium than the feldspars, which would account for the differences in their alteration products. Souza *et al.* [27] are of the opinion that kaolinites and halloysites were formed by weathering of porphyritic granite. Konta [28] described kaolinite as a residual weathering product from leucocratic granite, high in muscovite. The pioneer clay mineralogist Keller *et al.* [29] reported on the occurrence of these minerals, formed by the action of hot spring water on rhyolitic volcanic rocks in Mexico, and suggested that high concentrations of Si and Al in solution, low pH (about 3.5) and sulphate as the solvent anion, allow the formation of halloysite rather than the other kaolinite minerals. A few clay mineralogists have stated that kaolinite is formed by the leaching of alkaline rocks, primarily the feldspars and micas, but practically any silicate rock or mineral will alter to kaolinite if the leaching conditions are sufficiently favourable for a long period of time. Brindley [27] has performed investigations on the crystal structural relations of kaolinite and halloysite minerals and has strongly pleaded a similar origin. The Pipra clays were subjected to various modern scientific techniques, and it was found that these exceptionally high aluminous clays were derived by the localized weathering of arkosic metasediments, which have been assumed the parent of the granitic rocks of the area. These granitic rocks were formed by the isochemical metamorphism of arkose, aided by a little granitization and followed by a minor retrogression. The presence of kaolinites in the clay fractions indicates a detrital origin [15, 16]. The clays are of wide-ranging industrial importance in the ceramic and refractory industries. These clays can be suitably utilized as fire clays and for the manufacture of porcelain ware, etc. [3, 30].

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RÉSUMÉ — Les caractéristiques thermiques et structurales des oxydes d'aluminium hydratés et des argiles des rochers pélitiques Pipra du district de Sidhi (Inde) contenant de l'aluminium ont été étudiées par ATD. Les examens au microscope et par rayons X ainsi que l'analyse chimique ont révélé que ces argiles proviennent de l'érosion localisée des métasédiments arkosiques. Les comportements chimiques et normatifs ont confirmé leur formation par métamorphisme isochemique de l'arkose, facilitée par une faible granitisation et suivie d'une rétrogression mineure. Une tentative de corrélation, à diverses températures de transition, entre les changements de comportement thermique et de structure de ces oxydes et minéraux argileux a montré nettement la présence de kaolinite, de diaspore et de gibbsite. La présence de kaolinite dans les fractions d'argile indique son origine détritique.

ZUSAMMENFASSUNG — Die DTA wurde zur Untersuchung der thermischen und strukturellen Charakteristika hydratisierter Aluminiumoxide und aluminiumhaltiger Tonarten der Pipra Pelitfelsen aus dem Bezirk Sidhi, Indien, eingesetzt. Die eingehenden mikroskopischen Untersuchungen, die Röntgen- und chemische Analyse zeigt, daß diese Tonarten durch die lokalisierte Erosion arkositischer Metasedimente entstanden sind. Das chemische und das normative Verhalten bestätigten ihre Bildung durch isochemischen Metamorphismus von Arkose, unterstützt durch ein wenig Granitisation und darauffolgende geringe Retrogression. Ein Versuch der Korrelation zwischen den thermischen und strukturellen Änderungen dieser Oxide und Tonmineralien bei verschiedenen Übergangstemperaturen zeigte deutlich die Anwesenheit von Kaolinit, Diaspora und Gibbsit. Die exothermen Kurven von Kaolinit bestätigen die Rekrystallisierung. Die Gegenwart von Kaolinit in den Tonfraktionen weist auf ihren Gebränchs-Ursprung hin.

Резюме — Использованы методы ДТА для изучения термических и структурных характеристик гидроокисей алюминия и алюминиевых квасцов в горных породах на района Сидхи в Индии. Детальные микроскопические исследования, рентгенографический и химический анализы свидетельствуют, что образование алюмоквасцов произошло вследствие выветривания аркозных метаосадков. Их химическое поведение также подтверждает, что они образовались вследствие изохимического метаморфизма аркозы, протекающего с вклиниванием гранитов с последующим незначительным регрессом. Экспериментальная корреляция между термическими и структурными изменениями гидроокисей и глиноземов с различными температурами перехода ясно показала присутствие каолинита, диаспоры и гиббсита. Эндотермические кривые каолинита подтвердили его рекристаллизацию. Присутствие каолинита в глиноземных фракциях подтверждает его происхождение как следствие изнашивания горных пород при трении.