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AN APPLICATION OF THERMOGRAVIMETRY TO QUANTITATIVE STUDIES OF FELDSPAR ALTERATION IN SOILS

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Thermogravimetry is a fast, accurate and highly sensitive method for the quantitative determination of halloysite, kaolinite and gibbsite in ~10 mg altered feldspar grains from lateritic saprolite materials. A wide range in composition occurs between grains, and is evidence of the existence of various geochemical microenvironments within lateritic saprolite. Variations in dehydroxylation temperature of gibbsite and halloysite/kaolinite between the altered feldspar grains are an analytical artefact. The dehydroxylation temperature of gibbsite and halloysite/kaolinite increased from 242 °C to 302 °C and 454 °C to 491 °C respectively with the increase in the concentration of these minerals in the altered feldspar grains.

Thermogravimetry has been little used for the analysis of soil materials [1]. Unlike the X-ray diffraction (XRD) technique which is routinely employed for the analysis of clay and oxide and oxyhydroxide minerals but provides only semiquantitative or qualitative results [2], thermogravimetry can provide reliable quantitative analyses for several soil minerals. Furthermore, the weight of samples required for semiquantitative XRD analysis is large (~1 g) if diffractometer techniques are used in preference to the cumbersome and poorly quantitative powder camera techniques [3]. In some studies of the alteration mechanism of primary minerals in soils, small (~10 mg) grains at various stages of alteration are separated from the soil matrix and, on the basis of mineralogical and chemical analyses, the alteration pathways of the primary minerals can sometimes be determined. We have found that TG is a particularly useful technique for research into such mineral alteration sequences. This paper illustrates the application of the TG method to a study of feldspar alteration in lateritic, granitic saprolite. In particular, we have measured the abundance of secondary minerals (halloysite, kaolinite and gibbsite) co-existing within individual partly altered feldspar grains.

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Experimental

Soil samples from saprolite zones of three laterite deep weathering profiles (A, B, C) developed from granitic rocks were collected from a railway cutting at Jarrahdale, 45 km south east of Perth, Western Australia. Samples were sealed in plastic bags and stored at room temperature, but no extra precautions were taken to prevent dehydration of halloysite. Some dehydration may have occurred in the field subsequent to excavation of the cutting although samples were taken from 20 cm depth below the surface of the cutting. Detailed profile descriptions of lateritic profiles at this locality were given by Sadleir and Gilkes [4]. A typical profile is about 10 m deep and consists of the following horizons: a surface horizon of sandy gravel and duricrust, ferruginous zone, mottled zone, pallid zone, saprolite and parent adamellite granite.

Feldspar grains at various stages of alteration were obtained from saprolite from all three profiles. Altered grains of feldspars were separated from the matrix by first disaggregating the bulk material (~ 10 g) by gentle shaking in 250 ml water adjusted to pH 8 with NaOH followed by hand-picking the grains under a stereomicroscope. The bulk samples and some altered feldspar grains were impregnated with resin and thin sectioned for petrographic examination. X-ray diffraction patterns of whole materials and separated altered feldspar grains were obtained with a Philips diffractometer with Cu Kα radiation and a surved graphite crystal monochromator. Clay (<2 μm) suspensions prepared from dispersed grains were deposited onto ceramic plates under suction to form oriented samples which were saturated with Mg, K and glycerol for diagnostic purposes prior to XRD [5]. Single grain, X-ray diffraction patterns of about 1 mm diameter altered grains of feldspar were made using a Gandolfi single crystal camera [6].

Semi-quantitative determination of the abundance of the major secondary minerals (halloysite, kaolinite and gibbsite) in whole soil materials and in 215 (7–10 mg) individual feldspar grains were made by TG. Both TG and DTG curves for single grains and also for approximately 10 mg samples of finely ground whole material were obtained in flowing air at a heating rate of 10 deg/min using a Perkin–Elmer TG 52 instrument. Grains coloured by iron oxides were discarded since goethite dehydroxylation occurs at about the same temperature as gibbsite dehydroxylation and would have prevented quantitative analysis of gibbsite. Weight losses associated with DTG maxima in the temperature ranges 60–120°, 238–315° and 455–515° due to dehydroxylation of halloysite (10 Å), dehydroxylation of gibbsite and dehydroxylation of halloysite plus kaolinite, respectively, were used to calculate mineral contents. These temperatures are similar to those reported by other workers [7, 8]. Theoretical values of weight loss for dehydroxylation of halloysite and kaolinite (13.9%), for gibbsite (34.6%) and dehydration of halloysite 10 Å (12.2%) were used to calculate the percentages of these minerals in samples. It must be noted that water lost between 60–120° will include adsorbed water so that the estimate of halloysite (10 Å) will be systematically higher than the actual content. This error was less than the equivalent amount of 2% halloysite.

The influence of sample weight on the accuracy of determination and the dehydroxylation temperature of halloysite/kaolinite was examined by running samples ranging in weight from 5 to 20 mg. The sample used for this test contained 80% halloysite/kaolinite and 20% feldspar. The accuracy of the TG technique was checked by running a standard mixture of kaolinite (Greenbushes, Western Australia), gibbsite (synthetic gibbsite prepared by ALCOA Australia Ltd.) and feldspar (labradorite). To test whether the physical nature of the sample (powder or grain) influences the dehydroxylation temperature of kaolinite and gibbsite, powder samples of standard mixtures of kaolinite and gibbsite were pressed into pellets in an IR (infrared) die at a pressure of 10 tonne/cm^2. TG data for both powder and ~10 mg fragments of pellets were obtained.

Altered feldspar grains were also investigated by scanning electron microscopy (SEM) using a Philips PSEM 500 instrument. Specimens were mounted on aluminium stubs and coated with a 5 nm layer of platinum in a vacuum evaporator. Altered feldspar grains were crushed and dispersed in water to prepare specimens of clay-size material on carbon covered grids for transmission electron microscopy (TEM) and selected area electron diffraction (SAD) using a Hitachi HUIIB instrument.

Results and discussion

Evaluation of TG procedure

Typical TG and DTG curves for single grains of altered feldspar are shown in Fig. 1. Water loss at 92° is due to dehydration of halloysite (10 Å), at 280–296° to dehydroxylation of gibbsite and at 480–516° to dehydroxylation of kaolinite and halloysite [7, 8]. From these data quantitative estimates of the amounts of these minerals in the grains can be calculated as is illustrated by the values given in Fig. 1.

It is evident from Figure 1 that the temperatures of the dehydroxylation maxima for gibbsite and kaolinite/halloysite were not constant. This effect is illustrated in Figs 2 and 3 for the data for all single grains examined. The dehydroxylation temperatures for gibbsite increased from 242° to 303° as the percentage gibbsite in grains (x) increased from 0 to 70%. This variation is well described by the asymptotic equation:

$$T\,^{\circ}\mathrm{C} = 303.3 - 61.7e^{-0.0441x}$$

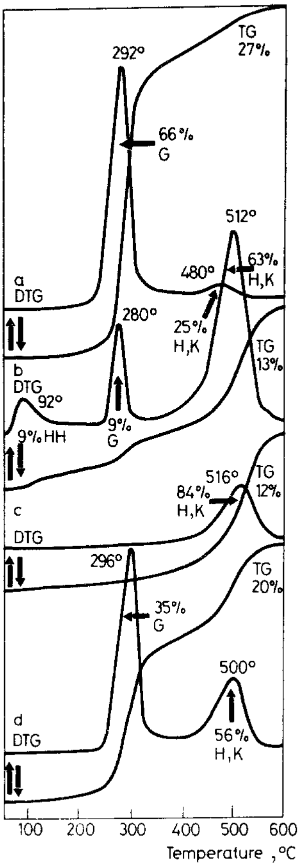

Fig. 1 Thermogravimetric curves for single grains of altered feldspar from profile C (curve A), profile B (curve B), profile A (curve C), profile A (curve D). Dehydration DTG maxima at 92 °C, 280–296 °C and 480–516 °C correspond to hydrated halloysite (10 Å), gibbsite and halloysite (7 Å)/kaolinite respectively. HH = hydrated halloysite; G = gibbsite; H, K = halloysit (7 Å)/kaolinite

The dehydroxylation temperature of kaolinite/halloysite increased from 454° to 491° as the concentration of kaolinite/halloysite (x) increased from 0 to 85%. This variation was also well described by an asymptotic relationship:

$$T\,^{\circ}\mathrm{C} = 491 - 36.6e^{-0.0654x}$$

These variations in dehydroxylation temperature could reflect systematic differences in gibbsite and kaolinite/halloysite properties that occur between grains [9] as the degree of feldspar alteration increased or could be an instrumental effect due to differing grain weights or concentration of these minerals within grains.

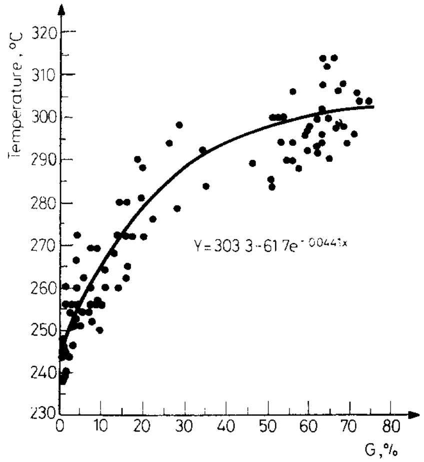

Fig. 2 Relationship between % gibbsite in grain and dehydroxylation temperature of gibbsite for altered feldspar grains

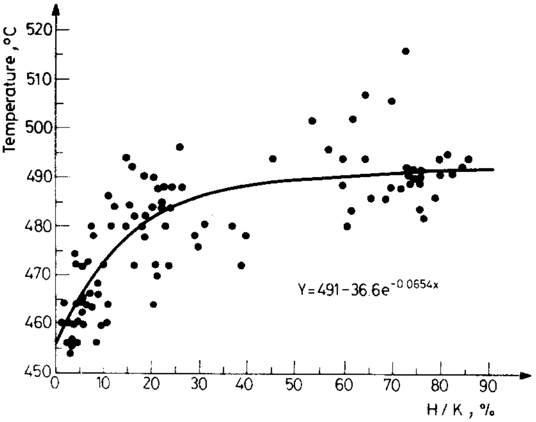

Fig. 3 Relationship between % halloysite/kaolinite in grain and dehydroxylation temperature of halloysite/kaolinite for altered feldspar grains

These possibilities were examined by TG measurements made on various synthetic mixtures of kaolinite, gibbsite and feldspar.

The first experiment investigated the influence of sample size on both dehydroxylation temperature and the accuracy of quantitative analysis for a powdered mixture of 80% kaolinite and 20% feldspar. For a 5–20 mg range in sample weight there was only a very minor but statistically significant increase in dehydroxylation temperature (about 0.30 deg/mg sample weight, $r=0.74$) and no systematic trend in the measured kaolinite content (all values were $80\pm3\%$) (Fig.

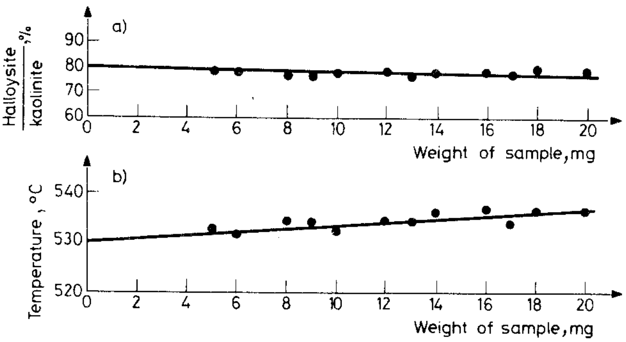

Fig. 4 (A) A plot of weight of sample *vs.* % halloysite/kaolinite determined by TG for a fine ground sample of highly altered feldspar; (B) A plot of the weight of sample *vs.* the dehydroxylation temperature of halloysite/kaolinite for the same sample

4). The influence on dehydroxylation temperature of the concentrations of gibbsite and kaolinite mixed with feldspar in 10 mg powdered and pressed samples was also investigated (Fig. 5). For both kaolinite ($\Delta T = 21°$) and gibbsite ($\Delta T = 23°$), the dehydroxylation temperature increased (ΔT) as the concentration of mineral in the powdered sample increased from 5 to 100% (Fig. 5). For the same samples pressed into 10 mg pellets the dehydroxylation temperatures for both gibbsite and kaolinite were systematically higher (by between 1 and 8°). The corresponding increases in

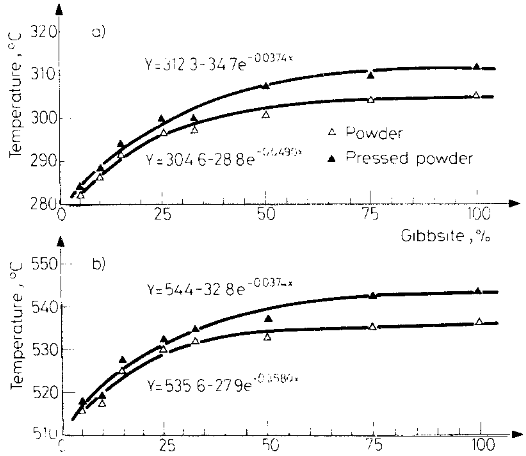

Fig. 5 (A) A plot of % gibbsite in 10 mg sample *vs.* the dehydroxylation temperature of gibbsite for powdered and pressed samples; (B) A plot of % kaolinite in 10 mg sample *vs.* the dehydroxylation temperature of kaolinite for powdered and pressed samples. △ Powder; ▲ Pressed powder

dehydroxylation temperature with increasing kaolinite and gibbsite contents were 27° and 29°. The temperature increments for the altered feldspar grains derived from the statistically fitted curves (Figs 2 and 3) were about 29° and 50° respectively, indicating that much of the variation in dehydroxylation temperature observed for altered grains was an analytical artefact and not an expression of systematic trends in crystal properties of the two minerals for different extents of feldspar alteration.

To confirm that variations in dehydroxylation temperatures of gibbsite or halloysite/kaolinite is an analytical artefact, the point of commencement of DTG peak was used to determine the true (initial) temperature of reaction (as suggested by anonymous referee). Figure 6 shows that the dehydroxylation temperature of gibbsite is constant (~222°) when the point of commencement of the DTG peak is used as an indication of the temperature of reaction. Figure 6 included the data only from those samples where the point of commencement of DTG peak could be accurately measured. A similar trend was observed for halloysite/kaolinite, however a much larger error occurred in locating the point of commencement of the DTG peak due to the relatively small magnitude of this peak. We therefore conclude that the variation in dehydroxylation temperature of gibbsite described in Figs 2 and 3 is an analytical artefact and not indicative of the differences in intrinsic properties of these minerals.

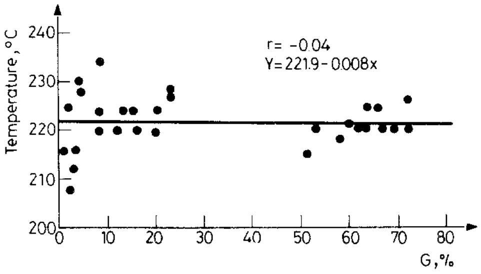

Fig. 6 Relationship between % gibbsite in grain and dehydroxylation temperature of gibbsite using the point of commencement of the DTG peak as an indicator of temperature of reaction for altered feldspar grains

Mineralogy of whole materials and clay fractions

X-ray diffraction patterns of whole saprolite samples showed them to consist of various mixtures of feldspars, mica, quartz, halloysite (10 Å), kaolinite/halloysite (7 Å) and gibbsite. Quantitative TG of ground samples of whole material demonstrated that the secondary minerals (halloysite, kaolinite and gibbsite) increased in abundance upwards throughout the saprolite zones in all profiles with

Table 1 Abundance (%) of secondary minerals in granitic saprolite

Profile	Zone	Depth, m	Halloysite, 10 Å	Halloysite 7 A. and/or kaolinite	Gibbsite	Total secondary minerals
A	Lower saprolite	12–11	1	9	2	12
	Middle saprolite	11–10	2	15	1	18
	Upper saprolite	10– 9	2	25	1	28
B	Lower saprolite	12–11	3	12	2	17
	Middle saprolite	11–10	5	14	1	20
	Upper saprolite	10– 9	6	18	2	26
C	Lower saprolite	6.5–6	0	10	14	24
	Middle saprolite	6 –5.5	0	12	17	29
	Upper saprolite	5.5–5	0	14	23	37

the amount of gibbsite relative to kaolinite/halloysite increasing in profile C (Table 1). Halloysite (10 Å) was absent from profile C. The TG technique is particularly sensitive and could detect less than 1% gibbsite, halloysite or kaolinite in ~10 mg samples. These results demonstrate that the TG method provides excellent quantitative analyses for this particular mineral assemblage.

Residual feldspar, quartz and mica in whole material samples were identified by XRD. Feldspar became less abundant upwards throughout the saprolite zones due to increased alteration to halloysite, kaolinite and gibbsite. Halloysite (10 Å), kaolinite/halloysite (7 Å), gibbsite and small amounts of geothite, quartz and feldspars were present in clay fractions of A and C profiles (Fig. 7). Halloysite 10 Å), halloysite (7 Å), kaolinite, gibbsite and small amounts of geothite, quartz, feldpars and mixed-layer micaceous minerals (12.3 Å) were present in the clay fraction of saprolite of profile B (Fig. 7). On glycerol treatment, the 10 Å reflection expanded to 11.3 Å which confirmed the identification of halloysite [4]. The 10 and 7.4 Å reflections moved to 7.2 Å on heating at 120° for 1 hour which is a characteristic of halloysite [4]. Samples were heated at 300° for 1 hour, the diffractograms showed that the 4.84 Å reflection had disappeared, confirming the identification of gibbsite.

Morphology and mineralogy of altered feldspar grains

Thin section photographs show that various degrees and styles of alteration of feldspar grains occurred within the saprolite (Fig. 8A–1). Biotite flakes had altered to exfoliated pseudomorphs consisting mostly of kaolinite, gibbsite and goethite (Fig. 8A–2). Magnetite grains had altered to hematite (Fig. 8A–3). Quartz was

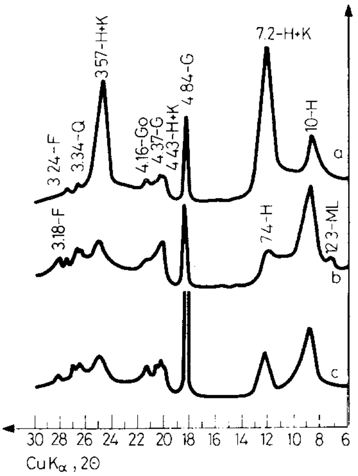

Fig. 7 XRD patterns of basally oriented Mg saturated clay fractions (<2 μm) of lowersaprolite from profiles A, B and C. Spacings in Ångstrom units. H = halloysite (10 Å); H+K = halloysite (7 Å) and/or kaolinite; G = gibbsite; Go = goethite; Q = quartz; F = feldspar; ML = mixed layer mineral

resistant to chemical weathering, but grains had separated along pre-existing fractures (Fig. 8A–4). Feldspar grains had altered to a fine grained clay material which was a mixture of halloysite, kaolinite and gibbsite. Altered feldspar grains identified in thin sections were grouped according to their degree of alteration, which was estimated as the percentage of each feldspar grain that had been replaced by clay. Large differences in the degree of alteration of individual feldspar grains exist between adjacent grains within single saprolite specimens. Furthermore, the general extent of alteration differed between saprolite specimens from the three profiles.

SEM micrographs of broken surfaces of altered feldspar grains show various mixtures of ~0.5 μm crystals of tubular halloysite (Fig. 8B–1) and ~0.2 μm platy crystals of kaolinite and/or gibbsite (Fig. 8B–2) arranged in a random porous fabric. TEM photographs of the clay fraction of altered feldspar grains show clearer detail of these mostly irregular crystals of tubular halloysite (Fig. 8C–1) and platy sub-hexagonal crystals of kaolinite and/or gibbsite (Fig. 8C–2). The identity of the crystals of halloysite, kaolinite and gibbsite was confirmed by the use of selected area electron diffraction (SAD). SAD patterns of halloysite crystals show them to be elongated along the *b* axis (Figure 8D, E). Kaolinite SAD patterns consist of a hk0 net of reflections with an 060 spacing of 1.49 Å (Fig. 8F, G). Gibbsite crystals gave typical arched hk0 reflections with a 330 spacing of 1.46 Å (Fig. 8H, I). These SAD patterns were calibrated by reference to the SAD pattern of an external gold standard.

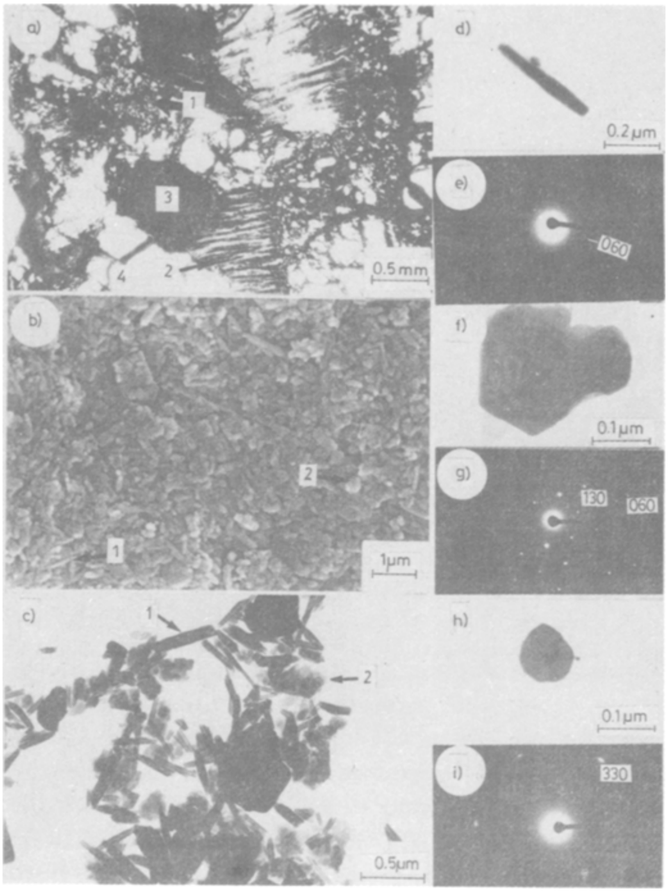

Fig. 8 (A) Micrographs of saprolite materials, altered feldspar (1); altered biotite (2); opaque mineral (3); and quartz (4). (B) SEM, tubular halloysite (1) and platy kaolinite and gibbsite (2). (C) TEM, tubular halloysite (1) and platy hexagonal crystals kaolinite and gibbsite (2). (D, F, H) TEM micrographs of halloysite, kaolinite and gibbsite, respectively, and their indexed SAD patterns (E, G, I). The halloysite tube is elongated along its *b* axis

XRD patterns of individual altered feldspar grains were taken with a Gandolfi camera with patterns being obtained for both still and rotating grains. XRD powder patterns of kaolinite and gibbsite were also taken for reference purposes (Fig. 9A, B). Single grain X-ray diffraction patterns of partly altered feldspar grains consist of various mixtures of feldspar, halloysite, kaolinite and gibbsite (Fig. 9C, D, E, F). For still (i.e. stationary) grains reflections due to residual feldspar occur as spots, but reflections due to halloysite (10 Å) at 10.1 Å, kaolinite/halloysite (7 Å) at 7.2 Å and gibbsite at 4.85 Å form continuous rings. Thus the secondary minerals

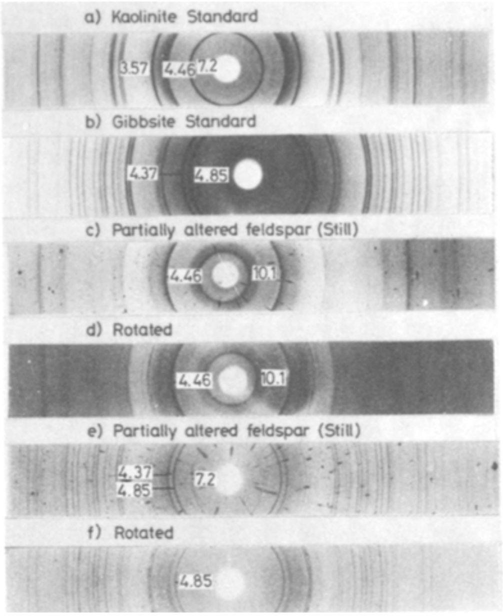

Fig. 9 (A, B) Powder X-ray photographs of mineral standards kaolinite and gibbsite. (C, D, E, F) Gandolfi camera XRD patterns of a single partially altered feldspar grains. Patterns were obtained with the grain not rotating (C, E) and rotating (D, F). Spacings are indicated in Ångstrom units. The 10.1 and 4.46 Å reflections in pattern C are due to halloysite. The 7.2 and 4.85 Å reflection are due to kaolinite and gibbsite respectively

are randomly oriented within the altered feldspar grains which is coosistent with the textures seen in optical and electron micrographs (Fig. 8A, B). A large number of grains were examined using this procedure, and although results are only semiquantitative, it was apparent that the relative proportions of secondary minerals in altered grains varied considerably. There was therefore a clear need for the application of a technique (i.e. TG) that would provide quantitative analyses of the abundance of secondary minerals in single grains of altered feldspar.

TG analysis of single grains

The optical microscopy, XRD, SEM and TEM analyses of altered feldspar grains established the nature and morphology of alteration products but were unable quantitatively to determine the relative abundance of alteration products within single grains of altered feldspar. This information was essential for the development of a quantitative model of feldspar alteration pathways and was provided by TG of 215 single grains of altered feldspars. The weight of feldspar grains ranged from 7 to

10 mg, but as discussed earlier, this small variation in the weight of the sample did not affect the accuracy of analyses. A summary of the distribution of secondary minerals for each profile is given in Fig. 10. Most of the feldspar grains in profiles A and B had altered to mixtures of halloysite (10 Å) and halloysite (7 Å)/kaolinite. However, the secondary minerals suite in some grains contained little halloysite (10 Å), about 50% gibbsite for profile A and 15% gibbsite for profile B. In profile C, the secondary minerals included no halloysite (10 Å), consisting of various mixtures of gibbsite and halloysite (7 Å)/kaolinite. Evidently co-existing single feldspar grains in lateritic saprolite have altered to different assemblages of secondary minerals, which is a surprising result and indicates that discrete and quite different geochemical microenvironments exist within adjacent ~10 mg grains. The reasons for these differences are not known, but electron microprobe analyses of residual feldspar fragments within grains have shown that the variations are not due to the differences in parent feldspar composition, i.e. plagioclase *vs.* alkali feldspar [10].

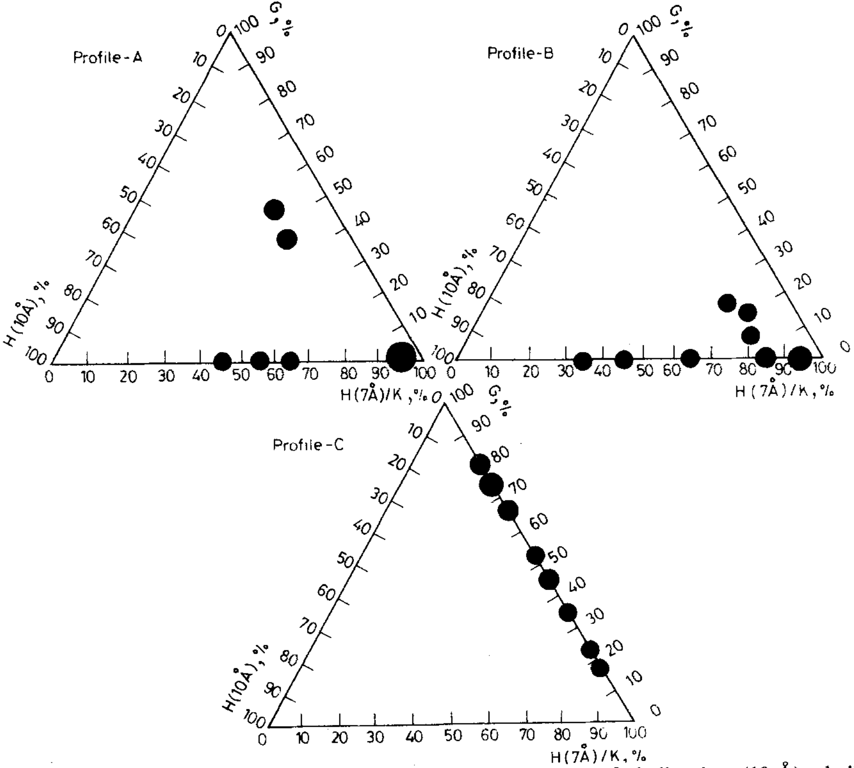

Fig. 10 Triangular diagrams showing the relative amounts of halloysite (10 Å), halloysite (7 Å)/kaolinite and gibbsite in individual altered feldspar grains from profiles A, B and C (schematic). ● 55% grains, ● 30% grains, ● 20% grains, ● 10% grains, • 5% grains

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Zusammenfassung — Die Thermogravimetrie ist eine schnelle, genaue und hochempfindliche Methode zur quantitativen Bestimmung von Halloysit, Kaolinit und Gibbsit in Feldspatkörnern von lateritischen Saproplit-Materialien. Die Zusammensetzung der Körner schwankt in weiten Grenzen, was auf die Existenz von verschiedenen geochemischen Mikroumgebungen innerhalb des lateritischen Saprolits hinweist. Unterschiede in der Dehydroxylierungstemperatur von Gibbsit und Halloysit/Kaolinit haben sich als Artifakte herausgestellt. Die Dehydroxylierungstemperatur von Gibbsit bzw. Halloysit/Kaolinit stieg mit zunehmender Konzentration dieser Minerale in den Feldspatkörnern von 242 auf 302 °C bzw. von 454 auf 491 °C.

Резюме — Термогравиметрия является быстрым, точным и наиболее чувствительным методом количественного определения галоизита, каолинита и гиббсита в 10 мг зерен измененного полевого шпата в латерито-сапролитных минералах. Широкая область изменения состава зерен свидетельствует о наличии различных геохимических микроокружений внутри латерито-сапролитных минералов. Изменение температур дегидроксилирования гиббсита и галоизит/каолинита, наблюдаемое в различных зернах измененного полевого шпата, является аналитически случайным явлением. Температура дегидроксилирования гиббсита и галоизит/каолинита увеличивается, соответственно, от 242 до 302° и от 454° до 491° с увеличением концентрации этих минералов в зернах полевого шпата.