Journal of the Geological Society, *London*, Vol. **157,** 2000, pp. 635–640. Printed in Great Britain.

Controls on kaolinite and dickite distribution, Highland Boundary Fault Zone, Scotland and Northern Ireland

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Abstract: Kaolinite and dickite occur widely in central Scotland and Northern Ireland. Stable hydrogen and oxygen isotope compositions of both minerals are similar, suggesting that the formation of kaolinite occurred first at temperatures of <50°C from meteoric water, probably as a result of alteration of Lower Carboniferous volcanic rocks, and that dickitization followed locally as a result of local heating that accompanied the intrusion of dykes during Late Carboniferous–Permian times. This mechanism of dickite formation explains why the higher-temperature polytype dickite occurs in a region from the Firth of Clyde to Perthshire, in association with dyke swarms, whilst kaolinite occurs elsewhere. The original kaolinite precipitation was focused along the high permeability fault zone now marked by the Highland Boundary Fault Zone and its presumed trace in Northern Ireland.

Keywords: Scotland, kaolin, kaolinite, dickite, palaeotemperature.

Mineral transformations are temperature dependent and those that have well-known threshold temperatures are of value as palaeotemperature indicators in studies of sedimentary basins, ore deposits and orogenic belts. One such transformation is that of kaolinite to dickite, which occurs between 100 and 120°C (Hoffman & Hower 1979; Ehrenberg *et al*. 1993; McAulay *et al*. 1994). As most oil reserves are encountered at temperatures lower than 120°C (Bjørkum & Nadeau 1998) and much of the oil potential of hydrocarbon source rocks is exhausted at 120°C, the kaolinite–dickite transformation has received much attention and has been documented in the deeper levels of many oilfields of the North Sea, including the Dutch, Norwegian and UK sectors (Ehrenberg *et al*. 1993; McAulay *et al*. 1993; Lanson *et al*. 1996; Beaufort *et al*. 1998; Hassouta *et al*. 1999).

The kaolinite–dickite transformation has very rarely been recorded outside oilfields, yet it has the potential to provide palaeotemperature data which can be used in basin modelling, fluid-flow modelling and palaeogeothermal modelling such as is used in fission-track analysis. This study describes kaolinite and dickite distribution in basement rocks in Scotland and Northern Ireland for which the post-orogenic thermal history is undocumented. We show that a combination of field relationships, regional geological history and stable-isotope analysis are sufficient to deduce that dickite precipitated as kaolinite and was later heated by intrusions and thereby thermally altered to dickite.

Kaolin minerals, including dickite, are widespread in crustal rocks, particularly where there has been fluid flow. For example, in the British Isles, dickite occurs in limestones mineralized by hydrothermal fluids in the Isle of Man (Maliva *et al*. 1999) and Ireland (N. Moles pers. comm.), coals affected by thrust-related fluids in South Wales (R. Gayer pers. comm.), in the hydrothermal aureole of the Skye Igneous Complex, and in the Orlock Bridge Fault, a major lineament across Scotland and Ireland (J. Parnell, unpublished data). Examples of dickite occurrences elsewhere include in thrust-related alteration in Montana (Hoffman & Hower 1979), in the Betic Cordilleras, Spain (Ruiz Cruz & Andreo 1996) and in the Pyrenees (Buatier *et al*. 1997), numerous hydrothermal deposits in the former Soviet Union (Chukhrov 1968), zones affected by hydrothermal alteration around igneous intrusions in Kansas (Schroeder & Hayes 1968) and gold mineralization in South Africa (Frankel 1949).

Geological setting

The geographical distribution of kaolinite and dickite in our study area, and their relationship to the Caledonian unconformity and the Highland Boundary Fault Zone, is shown in Figs 1 and 2. The Highland Boundary Fault Zone comprises Dalradian (late Proterozoic–early Palaeozoic) metasedimentary rocks (to the north) and Upper Palaeozoic rocks (to the south), which sandwich a narrow outcrop of Highland Border Complex rocks of predominantly Ordovician age. Both unconformities and faults can be recognized between the Precambrian/Lower Palaeozoic basement rocks and the Upper Palaeozoic cover rocks (Bluck 1984). Occurrences of kaolinite and dickite are localized at the contact between Upper Palaeozoic rocks and Dalradian rocks (the 'Caledonian unconformity') in the vicinity of the Highland Boundary Fault Zone (HBFZ; Figs 1 and 2).

Methodology

Samples were collected from the localities shown in Figs 1 and 2. Subsamples were hand-picked for analysis in order to minimize the inclusion of impurities and the mineralogy (kaolinite/dickite) was determined with a Siemens D5000 X-ray Diffractometer and Cu Kα radiation. Reflections important for distinguishing the polytypes include 20-2 and 1-31 at 38.44°2θ and 131 at 39.31°2θ for kaolinite and 132 and 20-4 at 38.71°2θ for dickite (Bailey 1980). A semiquantitative expression of degree of dickitization was calculated from relative peak heights of the 110 dickite reflection divided by the combined 020 kaolinite and 020 dickite reflections (which generally merge); although semiquantitative, this value suffices to distinguish occurrences of

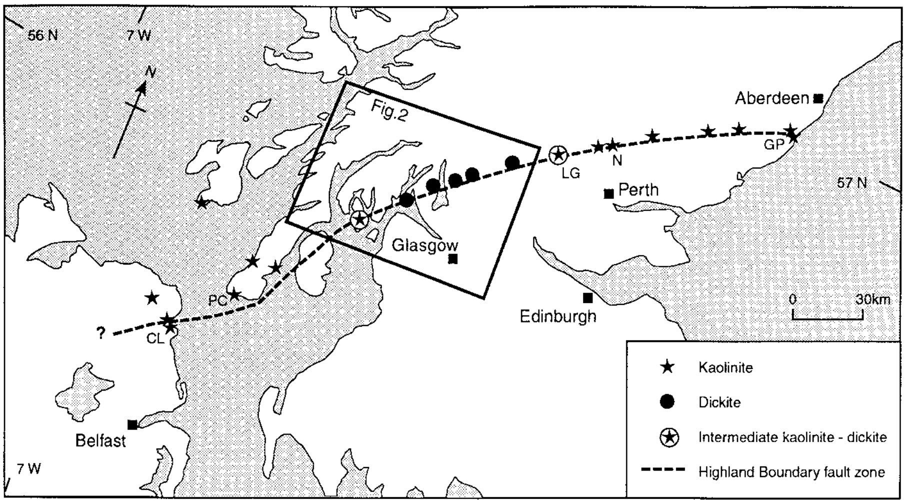

Fig. 1. Map of study area showing sample localities in vicinity of Highland Boundary Fault Zone, kaolin polytype distribution at these localities, and location of Fig. 2. CL, Cushendall; GP, Garron Point; LG, Little Glenshee; N, Newtyle; PC, Port na Cusaig.

kaolinite (values<0.8), mixed kaolinite and dickite (0.8 to 1.2) and dickite (>1.2). Full sample details, including locations, can be obtained from the Society Library or the British Library Document Supply Centre, Boston Spa, Wetherby, West Yorkshire LS23 7BQ, UK as Supplementary Publication No. SUP 18144 (3 pages).

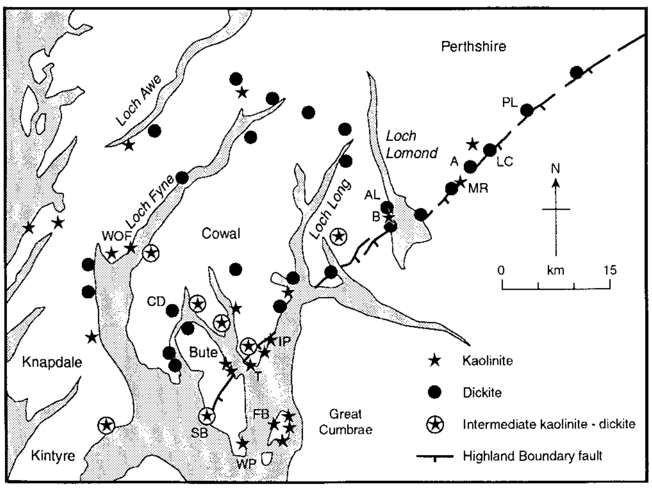

Fig. 2. Map of region from Firth of Clyde to Perthshire, showing sample localities. A, Arndrum; AL, Aldochlay; B, Bandry; CD, Creagan Dubh; FB, Fintry Bay; IP, Innellan Pier; LC, Lime Craig; MR, Maol Ruadh; PL, Pass of Leny; T, Toward; WP, White Port.

Samples for stable isotope analysis were hand picked and treated with dilute acid, to remove carbonate minerals. XRD revealed no accessory minerals in these samples. For oxygen isotope analysis we used the method of Clayton & Mayeda (1963) which involved fluorinating samples that were plasma-ashed at 650°C. Hydrogen isotopic analysis was undertaken using the method of Bigeleisen *et al.* (1952). Isotopic data (Table 1) are given relative to the V-SMOW standard.

Settings of kaolin mineralization

Most of the kaolin is found as fracture fill as:

(i) patchy coatings on irregular fracture surfaces in Dalradian, Highland Border Complex and Lower Carboniferous sedimentary rocks;
(ii) intermixture with red dolomite in breccia-filled veins in the Dalradian;
(iii) in fractures in pebbles in Lower Old Red Sandstone (Lower Devonian) conglomerates immediately south of the Highland Boundary Fault Zone between Loch Lomond and Perth;
(iv) fracture fill in Lower Carboniferous dykes.

Paragenetic sequences for multiple fracture-fillings always show that kaolin is the final phase.

In the few cases where kaolin is not fracture-bound, it replaces clasts that were mineralogically unstable in near-surface conditions, such as clasts of volcanic rock in Old Red Sandstone conglomerates. The matrix of such conglomerates, and interbedded sandstones, is also kaolinite-rich.

Table 1. *Isotopic data for kaolin samples*

Locality	Host	Setting	Polytype	$\delta^{18}O$ (‰)	δD (‰)
Cushendall	Lower ORS	Fracture-fill	Kaolinite	+21.9	−52.5
Port na Cusaig	Dalradian	Unconformity	Kaolinite	+16.7	−55.3
West Otter Ferry	Dalradian	Breccia zone	Kaolinite	+17.7	−40.4
Creagan Dubh	Dalradian	Fracture-fill	Dickite	+13.6	−49.0
Toward	Lower Carb.	Fracture-fill	Kaolinite	+15.5	−50.3
Innellan Pier	Lower Carb.	Fracture-fill	Kaolinite	+20.8	−38.0
Fintry Bay	Upper ORS	Cement	Kaolinite	+15.5	−55.1
Bandry	Dalradian	Fracture-fill	Kaolinite	+16.2	−44.6
Arndrum	Lower ORS	Fracture-fill	Dickite	+16.9	−32.1
Pass of Leny	HBC	Fracture-fill	Dickite	+15.0	−42.4
Garron Point	Dalradian	Fracture-fill	Kaolinite	+14.8	−52.6

HBC, Highland Border Complex; ORS Old Red Sandstone.

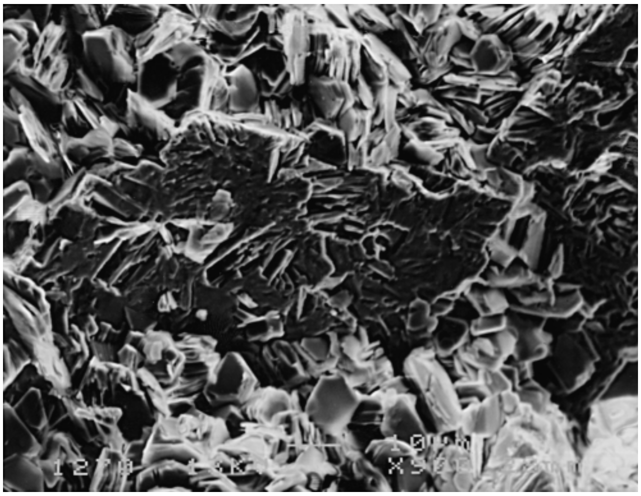

Fig. 3. Scanning electron micrograph of dolomite rhomb, suspended in dickite but also enclosing dickite plates, indicating co-precipitation, Perthshire. Field width 110 μm.

In the SW of the region, where the trace of the Highland Boundary Fault Zone is difficult to identify, there are several exposures of the 'Caledonian unconformity', i.e. where the Dalradian basement is overlain by red bed siliciclastic successions. The successions are undated, and are attributed to Old Red Sandstone (mainly Devonian), Carboniferous or Permo-Triassic successions depending on their field relationships to fossiliferous Carboniferous outcrops. Kaolinite occurs on a reddened Dalradian basement surface at many of these unconformity sites, in Kintyre, Islay and Co. Antrim. In addition to the unconformity sites, the Dalradian of Argyll contains many linear brecciated zones mineralized by red dolomite and kaolinite (see above) which probably indicates very close proximity to the reddened unconformity surface.

Host rocks and age constraints

Along the Highland Boundary Fault Zone, kaolin minerals occur in the Dalradian, in Highland Border Group rocks including serpentinites, and in Upper Palaeozoic rocks. The youngest host rocks for kaolinite are Lower Carboniferous limestones at Innellan and Toward. At Toward, some pebbles in the Upper Old Red Sandstone have been kaolinized *in situ*. This locality is within the transitional zone of dickitization, i.e. dickitization affected rocks as young as the Upper ORS.

The facts that dickite occurs in both fractures within the Highland Boundary Fault Zone, and unconformity sites/ dolomitic breccia zones, and that the breccia zones which yield dickite are at those localities which are closest to the dickite occurrences along the Highland Boundary Fault Zone, strongly suggest that all dickite occurrences have the same origin. Many occurrences of both dickite and kaolinite, in both types of setting, contain rhombs of dolomite (Fig. 3). Thus it is probable that all occurrences originated from the same fluid, and that all dickitization of the kaolinite was a single event. There is no evidence that requires multiple episodes of kaolin precipitation.

The geographical distribution of dickite

The proportion of kaolinite to dickite varies regionally. At the western and eastern ends of the Highland Boundary Fault Zone, only the kaolinite $1T$ polytype *sensu stricto* is found. Samples between the Firth of Clyde and Perthshire, where sampling was most intense, are mostly the dickite $2M_1$ polytype. There are transitional zones both to the west and east of the dickite-bearing segment of the fault, where a mixture of dickite and kaolinite occurs (Figs 1, 2). All samples from the transitional zone are intimate physical mixtures of kaolinite and dickite (e.g. Fig. 4) rather than localized co-occurrences, and so must represent a single episode of precipitation rather than formation as successive precipitates of polytypes. At Bute and Cowal, there is a distinct kaolinite zone, bounded to the west and east by dickite occurrences (Fig. 2).

Discussion

Origins of kaolinite and dickite

Kaolinite and dickite can precipitate from acid, meteoric fluids in weathering profiles (e.g. Esteoule-Choux 1983); from basinal fluids, rich in aluminium from the dissolution of feldspars (e.g. McLaughlin *et al.* 1994); and from hydrothermal fluids (e.g. Schroeder & Hayes 1968). The dickite polytype is found where precipitation occurs at a temperature above 100–120°C (see

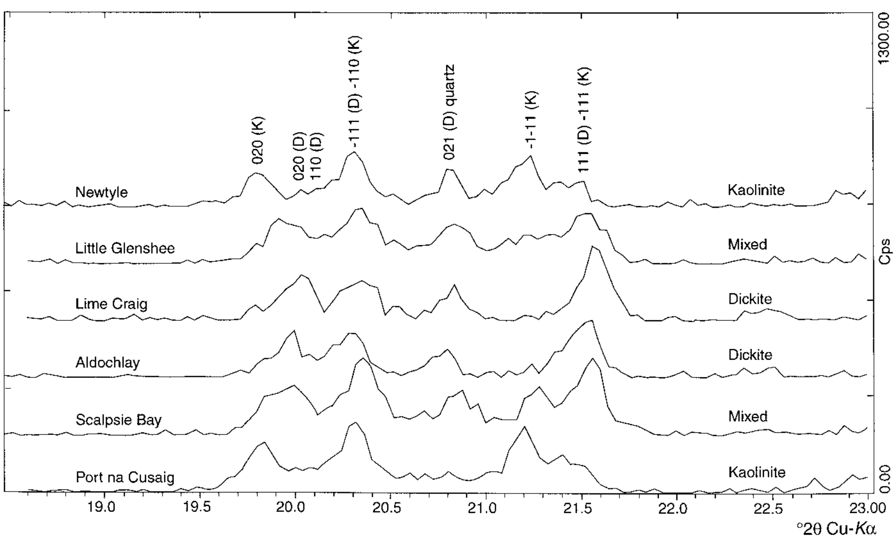

Fig. 4. X-ray diffractograms for kaolin samples from six localities which from SW to NE consist of kaolinite, mixed kaolinite-dickite, dickite, dickite, mixed kaolinite–dickite and kaolinite.

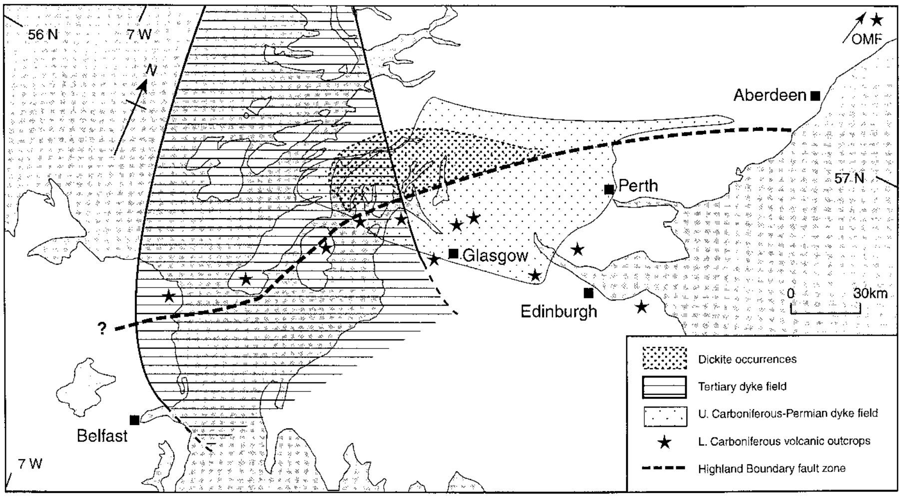

Fig. 5. Distribution of three main episodes of magmatic activity, and distribution of dickite polytype, which shows close comparison with distribution of upper Carboniferous–Permian dykes. OMF, Outer Moray Firth.

above), although kinetic factors may cause some deviation from this range. The presence of dickite in parts of the study area therefore suggests that these temperatures were reached locally.

We examine three mineral parageneses. Kaolinite and dickite might have precipitated at the same time but at different depths, and so temperatures, below the surface; kaolinite might have precipitated everywhere and been converted to dickite subsequently and locally; kaolinite and dickite were precipitated at different times from different fluids.

We discount the precipitation of kaolinite and dickite at the same time, as it would require a very unusual pattern of faulting to explain the distributions of kaolinite and dickite in the Dalradian rocks west of Glasgow. There is also no reason to expect physical mixtures if they were coeval. If the two polytypes were precipitated at different times, there should be numerous localities where both occur together, instead of the exclusivity of precipitation shown in Figs 1 and 2, and it is very unlikely that both polytypes would occur coeval with dolomite in the breccia zones through the Dalradian. We therefore favour the idea that kaolinite precipitation was followed by local conversion to dickite. This would explain the pattern of exclusivity, with physical mixtures of the two at the boundaries between dickitized and non-dickitized kaolinite. It also explains why the kaolin minerals are abundant in the Highland Boundary Fault Zone, but the dickite occurrences west of Glasgow are not controlled by the Highland Boundary Fault Zone. Precipitation of the kaolin minerals would have been focussed along the high-permeability conduit provided by the fault zone, but the dickitization would have required a source of heat capable of producing temperatures over 100°C, which need not have been fault-controlled.

Relationships between heat sources and kaolin minerals

Since clasts in the Old Red Sandstone are altered, heat for dickitization must have occurred after deposition of this unit. Episodes of igneous activity that could have provided the heat include basalt extrusion (Clyde Plateau Lavas) and associated intrusions in Early Carboniferous time, intrusion of quartz dolerite dykes during the late Carboniferous–early Permian, and dyke intrusion in Palaeocene time (Cameron & Stephenson 1985).

Lower Carboniferous volcanism extended across the whole of central Scotland (Francis 1991) where kaolin minerals occur (Fig. 5). Upper Carboniferous–Permian intrusions cut across the central portion of the Highland Boundary Fault Zone and were emplaced into it to the northeast (Smythe *et al.* 1995). This distribution is clearly comparable with the distribution of dickite. Dykes of this swarm are exposed at several localities in the Highland Boundary Fault Zone where dickite was sampled. The westward termination of the dense swarm of quartz dolerite dykes in the Loch Fyne region is coincident with the change from dickite to kaolinite. In central Knapdale, where several prominent dykes can be traced westwards to the Atlantic coast, the dickite polytype occurs. There is no positive relationship between kaolin mineral occurrences and the Tertiary dyke swarm: the dykes cross-cut the western part of the dickite-rich region, but not the eastern part, and in Northern Ireland where Palaeocene magmatic activity was intense there was no dickitization of kaolinite.

The broad-scale relationships are complemented by the field relationships of kaolinite with the three dyke swarms which are all very well-exposed on the Islands of Bute and Great Cumbrae, both close to the Highland Boundary Fault Zone. On both islands, the sandstone/conglomerate wallrocks of NNE-trending Lower Carboniferous dykes are impregnated with dolomite, and where brecciated are also mineralized by kaolinite, but the Upper Carboniferous–Permian and Tertiary dykes show no spatial association with kaolinite. These observations very strongly relate the kaolinite to the Lower Carboniferous igneous rocks.

Isotope data: temperature implications

A combination of hydrogen and oxygen isotopic compositions of clays can be used to distinguish between clays with hypogene and supergene origins (Sheppard *et al.* 1969; Sheppard & Gilg 1996), and a supergene-hypogene line (equivalent to kaolinite in equilibrium with meteoric waters at about 35°C) effectively separates kaolinites and dickites of hydrothermal and weathering origins (Fig. 6). The isotopic compositions for oxygen are representative of the waters from which kaolin precipitated.

The stable isotopic compositions (Fig. 6) allow the samples to be divided into three subgroups (1) two supergene

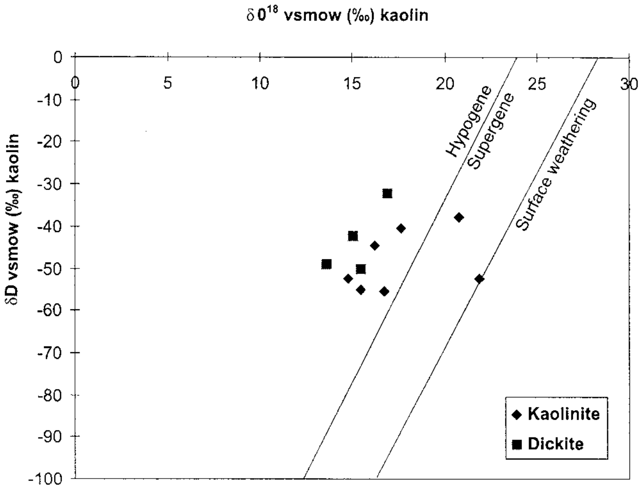

Fig. 6. Cross-plot of oxygen and hydrogen isotope compositions of kaolin samples, with hypergene-supergene line of Sheppard *et al.* (1969).

kaolinites, which plot to the right of the hypogene–supergene line; (2) all dickite samples, which plot to the left of the hypogene–supergene line; (3) hypogene kaolinites, which plot to the left of the hypogene–supergene line. Supergene kaolinites are from the stratigraphically highest host rock, the Lower Carboniferous (Innellan) and from what may be the top of a Devonian volcanic body (Cushendall). These two samples represent conditions closest to the surface during mineral formation.

From the isotopic composition of the minerals, the isotopic composition of the source fluid can be calculated using the equations given below:

$$1000\ln\alpha \text{ (kaolinite–water) } O^{18} = (2.76 \times 10^6 \times T^{-2}) - 6.75 \quad (1)$$

$$1000\ln\alpha \text{ (kaolinite–water) } D = (-2.2 \times 10^6 \times T^{-2}) - 7.7 \quad (2)$$

We assume the same fractionation factor (α) for both kaolinite and dickite as there is no evidence for a fractionation in either oxygen or hydrogen isotopes between kaolinite and dickite (Lombardi & Sheppard 1977; Marumo 1989; Gilg & Sheppard 1996).

Figure 7 shows calculated source composition for temperatures of 20, 30, 40, 50, 60 and 100°C using the mean isotopic

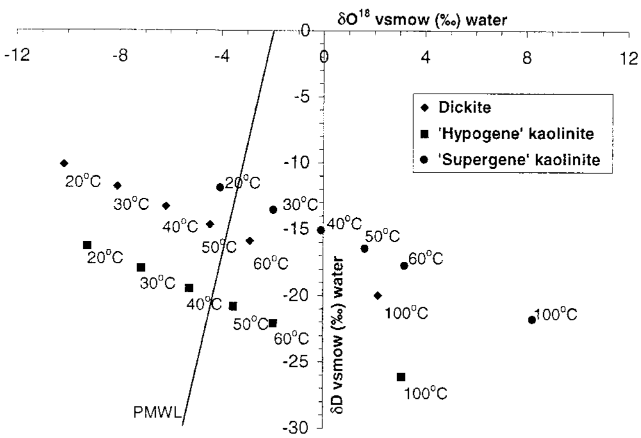

Fig. 7. Oxygen and hydrogen isotope compositions of parent fluid predicted from mineral isotopic compositions at six temperatures for three groups of kaolin samples. PMWL is the present day meteoric water line.

compositions of the three sample groups given above (cf. Jeans *et al.* 1997). Also plotted is the present day meteoric water line (PMWL). The water precipitating kaolin was probably ultimately meteoric, so the temperature of precipitation can be estimated from the intersection of the temperature curves with the meteoric water line. The temperatures obtained for all three groups of samples are in the range 40–60°C, which would be consistent with near-surface meteoric waters in a low-latitude climate. The low temperature of formation of the dickite samples imply that dickite formed by conversion from precursor kaolinite. The slight isotopic differences between the fluid compositions calculated for hypogene dickite and hypogene kaolinite may reflect limited hydrogen exchange during dickitization, as kaolin may exhibit significant post-formational hydrogen isotope exchange (Bird & Chivas 1988; Longstaffe & Ayalon 1990; Sheppard & Gilg 1996), but not isotopic exchange of oxygen at temperatures below 350°C (O'Neil & Kharaka 1976).

Kaolin-mineralizing waters

The data for oxygen isotope compositions of fluids in Fig. 7 implies a low negative value for the fluid from which the kaolin was precipitated. These values are consistent with previous determinations of the stable isotopic composition of meteoric water in the area during Upper Palaeozoic time viz. −0.4‰ from altered Lower Carboniferous lavas in the eastern Midland Valley, which may represent seawater or low latitude meteoric water (Hall *et al.* 1989), −5‰ to −2‰ for Upper Carboniferous meteoric water in Ireland (Jenkin *et al.* 1998), and −5‰ for Devonian meteoric water in central Scotland (Fallick *et al.* 1985).

The close association of kaolinite with Lower Carboniferous dykes suggests that the dykes were conduits for fluid movement during Lower Carboniferous time. The dykes are related to extrusion of thick basalt lavas, which were subaerially exposed. Alteration of the feldspar-rich basalts would have provided abundant aluminium and silicon for the precipitation of kaolinite. There is ample small-scale evidence for hydrothermal alteration of the basalts, with resultant mineralization (e.g. Hall *et al.* 1989; Gribble 1992). However hydrothermal activity is not essential to the alteration process and precipitation of kaolinite, which could have been achieved by low-temperature weathering. Southwest of Glasgow, barite and copper mineralization within the Lower Carboniferous lavas is spatially associated with Carboniferous-Permian dykes (Stephenson & Coats 1983; Gribble 1992), emphasizing the role of the dykes in focusing mineral precipitation.

Conclusions

Field, petrographic and isotopic evidence places a number of constraints on the relationship between kaolinite and dickite along the Highland Boundary Fault Zone and in adjacent areas.

(i) The exclusivity of occurrences of kaolinite and dickite, but physical mixtures of the two polytypes at the boundaries between their distributions, suggests that there was a single episode of kaolin mineralization, and that dickite distribution was temperature controlled. As kaolin minerals occurs in rocks as young as Early Carboniferous in age, mineralization occurred after this time.

(ii) The distribution of dickite is coincident with a dense distribution of Upper Carboniferous–Permian dykes, implying that the intrusions were a source of heat to cause dickitization of pre-existing kaolinite.

(iii) Kaolinite precipitation was partially focused along the Highland Boundary Fault Zone, which would have possessed high fracture permeability. However as dickitization was promoted by heating, dickite distribution is not restricted to the most permeable regions.

(iv) Oxygen and hydrogen isotope data suggest deposition of all kaolin samples at low temperatures (<50°C), probably from meteoric water. The timing constraints and the associations with Lower Carboniferous dykes suggest that kaolin may have formed from interaction of meteoric water with Lower Carboniferous volcanic rocks.

(v) In regions with a complex thermal history (i.e. more than one heat pulse), stable isotopic analysis provides an understanding of the relationship between kaolin polytypes, and hence allows their use as a palaeotemperature indicator.

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Received 4 January 1999; revised typescript accepted 22 September 1999.
Scientific editing by John McArthur.