# Kaolin polytype evidence for a hot-fluid pulse along Caledonian thrusts during rifting of the European Margin

J. Parnell<sup>1,\*</sup>, G. Watt<sup>1</sup>, H. Chen<sup>1</sup>, H. Wycherley<sup>1</sup>, A. Boyce<sup>2</sup>, D. Elmore<sup>3</sup>, R. Blumstein<sup>3</sup>, M. Engel<sup>3</sup> and P. Green<sup>4</sup>

<sup>1</sup> Department of Geology, University of Aberdeen, Aberdeen AB24 3UE, UK

<sup>2</sup> Scottish Universities Environmental Research Centre, East Kilbride G75 0QF, UK

<sup>3</sup> School of Geology & Geophysics, University of Oklahoma, Norman, OK 73019, USA

<sup>4</sup> Geotrack International Pty Ltd., 37 Melville Road, Brunswick West, Victoria, Australia

# ABSTRACT

Sedimentary basins developed along the European margin during the earliest, Permian, stage of proto-Atlantic rifting, during a phase of high heat flow. The proximity of some basins to Caledonian thrusts has implied that rifts locally utilized the basement fabric. New mineralogical and palaeomagnetic data show that thrust planes in the Moine Thrust Zone channelled a pulse of hot fluid in Permian time. The fluids precipitated kaolin in fractures in the thrust zone, and with decreasing intensity away from the zone. The high-temperature polytype dickite is largely confined to major thrust planes. Stable H and O isotope analyses indicate that the parent fluid included meteoric water involved in a hydrothermal system. Coeval hydrothermal hematite has a chemical remanence that dates the fluid pulse as Permian. This is direct evidence for post-orogenic activity in the thrust zone, in which the thrusts vented excess heat during regional crustal extension. The example from the European margin exemplifies the importance of deep-seated structures in the release of heat, and the value of kaolinite polytype mapping as a tool to record anomalous palaeo-heat flow.

KEYWORDS: kaolin, polytype, Caledonian, European margin, Moine thrust, dickite, hematite.

# Introduction

#### Geological setting

THE early stage of rifting in the North Atlantic region involved a combination of siliciclastic sedimentation in extensional basins and wide-spread extrusive and intrusive magmatic activity, of Permian age (Woodhall and Knox, 1979; Smythe *et al.*, 1995). The occurrence of sedimentary basins in the hanging walls of Caledonian thrusts, both inshore (The Hebrides) and offshore on the Atlantic Margin of western Europe, implies that the thrust zones were reactivated in extension during basin formation (e.g. Kirton and Hitchen, 1987; Cheadle *et al.*, 1987; Snyder, 1990; Roberts *et al.*, 1999). Basin-

\* E-mail: J.Parnell@abdn.ac.uk DOI: 10.1180/0026461046830195 bounding faults do not coincide exactly with the thrust surfaces, but they are related closely enough to suggest that zones of weakness or rheological contrast established during orogenic compression focused post-orogenic extensional faulting, particularly to accommodate Permo-Triassic basins (Cheadle *et al.*, 1987; Snyder *et al.*, 1997; Roberts *et al.*, 1999).

The Moine Thrust in the NW Highlands of Scotland is one of the most important geological structures in NW Europe. Extensive study of outcrops has shown that it accommodated crustal shortening during Caledonian deformation and ceased movement towards the end of the orogeny at ~425 Ma (Kelley and Powell, 1985; Kelley 1988). However, offshore seismic data show a basin-fill in the hanging wall (Snyder, 1990). This paper describes the results of kaolin polytype mapping which show that there was a postorogenic thermal anomaly along the thrust. Polytype mapping has been demonstrated previously as an effective tool in identifying palaeo-heat pulses (Parnell *et al.*, 2000*a*). The thermal anomaly along the thrust zone must reflect passage of hydrothermal fluids and a role for the thrust in focussing heat on the developing Atlantic Margin. Rocks in the thrust zone also exhibit widespread secondary reddening of rock surfaces by Fe-rich fluids. We also show how the timing of the thermal anomaly can be constrained by the palaeomagnetic dating of Fe minerals that have a clear paragenetic relationship with the kaolin.

# Methodology

Kaolin samples were hand-picked for analysis to minimize the inclusion of impurities. The mineralogy (kaolinite/dickite) was determined with a Siemens D5000 X-ray diffractometer using Cu-Ka radiation. Reflections important for distinguishing the polytypes include 111 just above  $21^{\circ}2\theta$ ,  $20\bar{2}$  and  $1\bar{3}1$  at  $38.44^{\circ}2\theta$  and 131at 39.31°20 for kaolinite and 132 and 204 at  $38.71^{\circ}2\theta$  for dickite, and the relative positions of 020 just below 20°2θ (Bailey, 1980). Samples for stable isotope analysis were treated with dilute acid, to remove carbonate minerals, X-ray diffraction (XRD) revealed no accessory minerals in these samples. Oxygen isotope analyses were undertaken using the method of Clayton and Mayeda (1963), which involved fluorinating samples that had previously been plasma-ashed at 650°C. Hydrogen isotope analysis was undertaken using the method of Bigeleisen et al. (1952). Isotopic data (Table 1) are given relative to the V-SMOW standard.

A preliminary sample set of palaeomagnetic cores was drilled at several sites using a hand-held drill in the field. Samples were cut to standard lengths and the natural remanent magnetizations (NRMs) were measured on a 2G three-axes cryogenic magnetometer located in a magnetically shielded room. Specimens were subsequently stepwise demagnetized by thermal demagnetization up to 700°C in a magnetically shielded Schonstedt TSD-1 oven to elicit directional information. The demagnetization data were plotted in orthogonal projections (Zijderveld, 1967) and magnetic directions of the components were calculated using the leastsquares method (Kirschvink, 1980). Site means were calculated using Fisher (1953) statistics.

Fission track analyses of apatite grains from sandstone samples were undertaken using standard procedures as described by Bray *et al.* (1992) and Green *et al.* (1999). Fluid inclusion microthermometry (Shepherd *et al.*, 1985) was undertaken using doubly polished wafers in a Linkam THM600 heating-freezing stage attached to an Olympus BH-2 petrographic microscope.

# Kaolin distribution

Kaolin mineralization occurs along a 140 km length of the Moine Thrust Zone on the western seaboard of Scotland. It is particularly abundant along a 60 km segment in eastern Skye and the adjacent Scottish mainland from Loch Hourn to Loch Kishorn (Fig. 1). The thrust zone separates the deformed Caledonides to the east from relatively undeformed foreland to the west. It is bounded by the upper Moine Thrust and the lower Sole Thrust (Coward, 1982),

TABLE 1. Stable isotope data for kaolin samples, Moine Thrust Zone.

	Location	Grid Ref.	Host	Polytype	δ <sup>18</sup> O (‰)	δD (‰)
1.	Bealach na Ba	NG778416	Torridonian	Kaolinite	13.7	-65
2.	Toscaig	NG714392	Torridonian	Kaolinite	12.4	-69
3.	Loch Meodal	NG658112	Lewisian	Dickite	4.3	-118
4.	Isleornsay	NG702140	Torridonian	Kaolinite	8.8	-104
5.	Kintail Lodge	NG938198	Granite	Dickite	6.6	-52
6.	Kishorn	NG835415	Cambrian limestone	Dickite	12.1	-50
7.	Allt a' Mhuilinn	NG633067	Lewisian	Dickite	13.8	-50
8.	Loch Airigh na Saorach	NG682204	Torridonian	Dickite	4.6	-94
9.	Raasay Forest	NG572460	Torridonian	Kaolinite	17.6	-42
10.	Strath Croe	NG945212	Lewisian	Kaolinite	13.3	-70

#### KAOLIN MINERALIZATION ON CALEDONIAN THRUSTS



FIG. 1. Map of study area showing preferential distribution of the high-temperature dickite polytype relative to thrusts. Upper inset shows regional setting, Moine Thrust Zone (MTZ), Outer Isles Thrust Zone (OITZ), and Sea of Hebrides (SHB), Minch Basin (MB) and West Orkney Basin (WOB) in hangingwalls of thrusts.

termed the Kishorn Thrust in the area of study. The kaolin occurs on fracture surfaces (Fig. 2) in Lewisian, Moinian, Torridonian, Cambrian and Durness Group (Cambro-Ordovician) rocks, i.e. all those rocks in the hangingwall, footwall and thrust slices of the Moine Thrust Zone. Kaolin also occurs on the plutonic Caledonian Ratagain Complex, which postdates, and the emplacement of which may have been controlled by, the Moine Thrust (Beckinsale and Obradovich, 1973). Kaolin abundance on fracture surfaces increases markedly in the vicinity of the Moine Thrust Zone. It post-dates all deformation fabrics in the thrust zone (faults, mylonites, slickensides), and the widespread occurrence of the lowtemperature polytype kaolinite shows that it has not experienced orogenic heating. In other words, the kaolin is unrelated to processes during the Caledonian Orogeny. The occurrence of kaolin attests to a post-orogenic episode of fluid flow along the Moine Thrust Zone.

#### J. PARNELL ET AL.



FIG. 2. Kaolinite (white) coating fracture surface in Torridonian sandstone, west of Loch Kishorn. Hammer scale 39 cm.

#### Polytype distribution

In addition to an increase in kaolin abundance in the thrust zone, the high-temperature polytype dickite is present along the thrust plane. In the Sleat Peninsula of Skye, kaolin is extremely rare away from the thrust, kaolinite is common within 500 m, and dickite occurs within 50 m along each of three road sections through the thrust at Isleornsay, Loch Meodal and Kilbeg. A detailed traverse at Loch Meodal (Figs 1, 3) shows the highly restricted distribution of dickite in the hanging wall. In NE Skye and Lochalsh, kaolinite is common in the Torridonian footwall of the thrust. Dickite is, however, present instead at exposures adjacent to the thrust in Glenelg and Gleann Udalain. Kaolinite is again common in the Torridonian footwall of the Applecross Peninsula and as far NW as northern Raasay. The Moine Thrust is excised by a major fault east of Loch Kishorn, but exposures adjacent to the Kishorn Thrust at Kishorn are mineralized by dickite.

Of 14 recorded dickite occurrences, ten are along the Moine Thrust or Kishorn Thrust, two are in major normal fault zones (Fig. 1), and the other two are in the Torridonian of Skye/ Lochalsh. In the latter exposures it has been altered by contact metamorphism due to the intrusion of Tertiary dykes (36 other samples from the Torridonian outcrop are all kaolinite). The relationship between the high-temperature polytype dickite and the thrust plane(s) is thus very strong.

# Origin of kaolin

#### Petrographic relationships

Observations important to understanding the kaolin mineralization are (1) kaolin only occurs in brittle fractures and clearly cross-cuts mylonites developed in the Moine Thrust Zone, (2) kaolin commonly occurs on surfaces that are also coated with red Fe oxide, calcite and quartz which petrographic relationships indicate are coeval with the kaolin, and (3) there is no evidence for post-emplacement alteration or deformation of the kaolin.

#### Importance of thrust zone

There is a clear increase in the occurrence and abundance of kaolin in the vicinity of the Moine Thrust Zone. This preferential distribution could either reflect channelling of mineralizing fluids along the thrust zone, or a widespread supergene mineralization that appears most intense in the more highly fractured ground around the thrust zone. Regardless of whether the kaolin was a supergene or hypogene deposit, the strong spatial relationship between dickite and the thrust plane shows that heat was focused along the thrust zone; the question is whether hot fluid precipitated the dickite directly or by alteration of existing kaolinite. Aspects of the distribution of kaolin suggest that it was not a supergene (surficial) deposit but was precipitated by fluids introduced along the thrust zone: (1) at Loch Kishorn, some

#### KAOLIN MINERALIZATION ON CALEDONIAN THRUSTS



FIG. 3. Selected portions of XRD traces from a traverse at Loch Meodal, Skye, showing dickite in the immediate vicinity of a thrust plane.

specimens show successive deposits of kaolinite and dickite on the same fracture surface, indicating pulsed precipitation. This suggests that the dickite was a primary hypogene precipitate, not a thermally altered supergene kaolinite. (2) Kaolin occurs along most of the western seaboard of Scotland but is only abundant in the study area of Loch Hourn to Loch Kishorn. The present-day basement surface is similar to that which existed below the Upper Palaeozoic-Mesozoic sediment cover, as shown by many examples of unconformity surfaces beneath a thin extant cover (Watson, 1984; Hall, 1991). Thus, if the kaolin was a supergene deposit we would expect it to be more regionally extensive, particularly beneath unconformities, but this is not observed. There is no enhanced development of kaolinization at a Triassic-Torridonian unconformity in Applecross, although the Torridonian sandstones in general exhibit widespread fracture-coatings of kaolin (Fig. 2). (3) Petrographic relationships indicate coeval precipitation of kaolin and quartz in some

fractures, which is unlikely in a supergene environment, but quite feasible in a hydrothermal environment. At Bealach na Ba in fractured Torridonian sandstone, mm-thick vein quartz coeval with kaolin contains primary fluid inclusions which are monophase (temperature probably <60°C) or two-phase with homogenization temperatures between 70 and 80°C. Although quartz precipitation is slow at these temperatures (Walderhaug, 1996), the volume involved is very limited and probably represents a single episode of fluid flow. The temperatures measured are clearly distinct from higher temperatures recorded in sandstones along the Moine Thrust Zone, representing pre-orogenic fluids (Baron *et al.*, 2003).

#### Stable isotope data

Stable isotope data for five dickite and five kaolinite samples from the region of Fig. 1 are shown in Fig. 4 and Table 1. All the values plot to the hotter side of the hypogene-supergene line of Sheppard and Gilg (1996), supporting the conclusion that the kaolin had a hydrothermal origin. The five kaolinite samples, and four of the dickite samples, each show linear correlation between oxygen and hydrogen isotopic compositions. The kaolinite samples have slightly heavier oxygen compositions. The positive linear correla-

tion indicates that the samples preserve their original composition and have not re-equilibrated (Fallick et al., 1993). The variations in composition within the groups of kaolinite and dickite samples suggest a mixing between two fluids. If the variation reflected temperature alone, the kaolinite and dickite compositions would instead exhibit an inverse correlation. It is very unlikely that the spread of compositions could reflect variations in relief or climate over such a limited geographic area, even if we modelled them as products of surface water. The spread of values is comparable to that found in other data sets (e.g. Sheppard and Gilg, 1996). The trend of fluid composition equivalent to the kaolinite compositions is shown in Fig. 4, assuming a temperature of deposition in the range 50-80°C, inferred from the fluid inclusions in quartz at Bealach na Ba. This trend overlaps the meteoric water line, using either the fractionation equations of Savin and Lee (1988) or Sheppard and Gilg (1996). The heavier end-member in a mixture would have a  $\delta^{18}$ O composition close to zero and could be a surface/meteoric water of late Palaeozoic age (regional data for this time reported in Hall et al., 1989; Jenkin et al., 1998). However, as in other studies a mechanism of generating low  $\delta D$  values in the other end-member is not apparent (Fallick et al., 1993). Nevertheless, a mixture of



FIG. 4. Cross-plot of O and H isotope compositions for kaolin samples from the Moine Thrust Zone, showing that all plot in the hypogene field. The projected composition of the parent fluid for the kaolinite samples plots at the meteoric water line (MWL) using the equations of both Savin and Lee (1988) and Sheppard and Gilg (1996) and assuming deposition at 50°C. Analytical procedure as in Jeans *et al.* (1997).

contemporary surface water with another component is compatible with a hydrothermal system within a thrust zone that extends from surface to kilometres depth.

#### Possible sources of heat

If hot fluids were channelled along the thrust zone, the thrust polarity implies that the source of heat is to the east, although cross-cutting major fractures such as the dickite-mineralized normal faults may have allowed the fluids to step up between thrust planes. Given the constraint of a post-orogenic origin, there are two candidates for a heat pulse evident from regional geology. Firstly, there is a dense swarm of late Carboniferous-early Permian dykes to the north of Loch Duich (Speight et al., 1982; Rock, 1983), with associated volcanic vents on both sides of the Moine thrust (Rock, 1982, 1983). Secondly, there are the products of early Tertiary magmatism, including dykes and sills, lavas and plutons. The Carboniferous-Permian intrusions occur particularly in the sector of the western seaboard where kaolin is abundant, whereas the Tertiary igneous rocks are much more widespread. Examination of many exposures of Tertiary igneous rocks in Skye shows no kaolin, except where dykes intrude Torridonian strata that contain kaolin regardless of proximity to dykes. The distribution of kaolin is therefore much more consistent with a Carboniferous-Permian heat source. Dating evidence is also more consistent with a late Palaeozoic episode of heating, as shown below.

Watson (1985) suggests that the small volumes of magma represented by the Carboniferous– Permian intrusions must have been delivered from their source over 20 km below the Moho along major structures such as the Great Glen Fault. This is consistent with the proposed model for heat transfer along large-scale Caledonian thrusts. No magma has been observed in association with the kaolin, but this is not surprising as the highly restricted distribution of dickite suggests that the temperature was probably not in excess of 150–200°C.

### Temperature of heat pulse

The temperature of kaolin precipitation is constrained by: (1) the kaolinite-dickite transition occurs at ~100-120°C (Hoffman and Hower, 1979; Ehrenberg *et al.*, 1993), indicating that away from the thrust where the polytype is consistently kaolinite, temperatures were probably <100°C. Along the thrust plane where dickite is found, it may have been in the range 100-200°C. (2) The fluid inclusion data for quartz coeval with kaolinite at Bealach na Ba indicate temperatures of 50-80°C. (3) If the stable isotope data for the five kaolinite samples are treated as a single group, the mean values are equivalent to a parent fluid at 50°C in equilibrium with meteoric fluid, following the method of Jeans *et al.* (1997), which identifies fluid isotopic compositions compatible with mineral isotopic compositions at each temperature. Assumptions are involved in this method, but the result is consistent with the other approaches.

# Timing of heat pulse

Reddening (hematite staining) occurs at many localities, representing alteration below a palaeoweathering surface, probably of Permo-Triassic age as staining is found at sub-Permo-Triassic unconformities (Watts, 1976). Where reddening and kaolin occur together, they show variable time relationships: in many cases hematite and kaolin occupy different sets of fractures and are clearly unrelated, but at a few localities the two are coeval. These localities are important because they have the potential for palaeomagnetic dating of the kaolin. The kaolin is a brick red colour due to a fine intergrowth with coeval hematite at the east side of Loch Kishorn. Hematite forms veins in the fractured footwall of the Kishorn Thrust in the Kishorn district, where it was mined at Rassal (MacGregor et al., 1920), indicating its incorporation in a hydrothermal system. A paragenesis from veined, brecciated Cambro-Ordovician limestones at Rassal shows that the two phases are coeval (Figs 5, 6).

The timing of the kaolin has been constrained by palaeomagnetic analysis at two localities in the Kishorn district where such a coeval relationship can be demonstrated. At Bealach na Ba, where fractures in Torridonian Sandstone are consistently both reddened and kaolin-bearing, the rocks contain two components (Fig. 7*a*). One component, removed at moderate temperatures, has southerly declinations and shallow inclinations (site BB1,  $n/n_0$  {number of specimens analysed to number processed} = 4/7, G Dec {Geographic declination} = 185.7°, G Inc {Geographic inclination} = -15.1, k {precision parameter, Fisher, 1953} = 65.9,  $\alpha$ 95 {cone of 95% confidence} = 11.4). The pole for this magnetiza-



FIG. 5. Photomicrographs illustrating aspects of mineral paragenesis in veined, brecciated Cambro-Ordovician limestones at Rassal. (a) Brecciated host limestone (BH), veined by red hematite (H2), followed by calcite (C); (b) quartz (Q) and dark hematite (H1), cross-cut by veinlets of red hematite (H2); (c) dolomite (D) in a matrix of second-stage hematite (H2).

tion is at  $167.3^{\circ}$ E and  $40.1^{\circ}$ N and lies on the Permian part of the Apparent Polar Wander path (APWP) (Fig. 8). A second component, removed at higher temperatures, has more easterly declinations and moderate down inclinations (Fig. 7*a*), and is probably a Torridonian-age magnetization (Elmore *et al.*, 2003).



FIG. 6. Mineral paragenesis in veining through brecciated Cambro-Ordovician limestone in Kishorn Thrust Zone, Rassal, Loch Kishorn. Note hematite and kaolin are coeval.

At Loch Kishorn, where kaolin-hematite intergrowths occur in veins through limestones, several sites were collected. A remanent magnetization with southerly declinations and shallow inclinations (Fig. 7b) was identified in two sites (site k15,  $n/n_0 = 3/6$ , G Dec = 190.0°, G Inc = -2.0, k = 12.8,  $\alpha 95 = 36$ ; site k11,  $n/n_0 = 2/5$ ,  $G Dec = 177.6^{\circ}$ , G Inc = -21.8) whereas a magnetization with steeper negative inclinations was identified in a third site (site k12,  $n/n_0 = 4/4$ , G Dec = 203.5°, G Inc = -49.7, k = 36.3,  $\alpha 95 =$ 15.5). The mean pole for the component with shallow inclination (169.8°E and 38.5°N) plots close to the APWP for Europe in Permian times whereas the pole for the steeper component (133.4°E and 58.6°N) suggests a Mesozoic age (Fig. 8). The results from k11 and k15 are similar to the results from the Torridonian Sandstone and indicate that a Permian component, interpreted as a chemical remanent magnetization (CRM), is present. The component from site k12 with steeper negative inclinations could be a CRM acquired in the Mesozoic or alternatively, a vector addition of the Permian CRM and a Tertiary CRM. Tertiary CRMs are reported from a number of different rock types on Skye to the south (e.g. Potts, 1990; Woods et al., 2002; Elmore et al., 2003). Resolution of this issue awaits additional studies that are currently underway.

In summary, the preliminary palaeomagnetic results indicate the presence of a Permian CRM residing in hematite in the Kishorn district. The hematite and the associated CRM are interpreted to be coeval with the kaolin. Palaeomagnetic results to the north of the Kishorn area also indicate that a Late Palaeozoic CRM occurs in rocks within the Moine fault zone (Elmore *et al.*, 2003).



FIG. 7. Orthogonal projection diagrams (Zijderveld, 1967) of representative stepwise thermal demagnetizations of specimens. Open symbols: vertical projection; solid symbols: horizontal projection. (*a*) Torridon Group sandstone west of the fault zone showing removal of the component with southerly declination and shallow inclination at moderate temperatures and an easterly component at higher temperatures. (*b*) Durness Group limestone near Kishorn thrust showing removal of southerly and shallow component.

Fission track data help to interpret both the age of the heat pulse and its magnitude. Samples of Torridonian sandstone have yielded new fission track data from apatite grains at two dickitebearing localities. A sample from Kilbeg, Skye, yielded just two apatite grains (no confined tracks), but with very similar fission track ages (109, 112 Ma), conferring confidence in these data. The simplest interpretation of the data is a maximum temperature of ~100 to 120°C at some time between 170 Ma and the present, which regional evidence constrains to early Tertiary heating around the Skye igneous centre. This is comparable with other apatite fission track data in eastern Skye (Lewis *et al.*, 1992; Thomson *et al.*, 1999), including from localities where the kaolin polytype is kaolinite rather than dickite. This indicates that although the temperature in eastern Skye may have just reached that needed for dickitization during early Tertiary time, dickite distribution is not controlled by proximity to the Tertiary igneous centre. Therefore the dickite is not constrained to be of Tertiary age, except where it is clearly related to Tertiary dykes. In fact, the predominance of kaolinite rather than dickite near the igneous centre on Skye implies that Tertiary magmatic activity was not responsible for the kaolin precipitation.



FIG. 8. Apparent polar wander curve for Europe, showing pole positions for CRMs from sites mineralized by hydrothermal hematite and kaolin. The poles for most sites plot at or near the curve in Permian time. Analytical procedure as in Parnell *et al.* (2000*b*). Circle, pole for the BB1 site at Bealach na Ba; Square, pole for the mean from sites k11 and k15 at Kishorn; Triangle, pole for site k12 at Kishorn.

A sandstone sample from adjacent to a dickitebearing fault zone in Glen Shieldaig vielded 15 apatite grains with a mean track length of 12.3±2.21 µm and a mean fission track age of 353±19 Ma. This is amongst the oldest recorded in northwest Scotland (Lewis et al., 1992; Thomson et al., 1999). The combined age and track length data are consistent with a temperature of no greater than 100°C since Devonian time. There is no evidence for heating to 120°C since the Caledonian Orogeny, implying that the hot fluid that precipitated dickite was so rapid that it did not heat the country rock for long enough to affect the kinetically-dependent fission track data. If there had been prolonged heating (>~0.1 Ma) of the rock at 100°C during that time, the tracks would have been largely annealed. No anomalous heat flow during the Tertiary, identified elsewhere off western Europe (Green et al., 1999; 2002), is evident in this analysis.

#### Discussion

Several other studies show that kaolinization may be focused along thrust zones (Hoffman and Hower, 1979; Lin and Wang, 1989; Ruiz Cruz and Andreo, 1996; Buatier *et al.*, 1997). Features in common with the Moine Thrust Zone include an increased intensity of kaolinization near the thrust zone, precipitation of the dickite polytype along the thrust, and evidence that dickite postdated the main thrust movement.

Models for dickite precipitation in these occurrences include: (1) heating of pre-existing kaolinite by tectonic burial (thrust-stacking to increase burial depth and therefore temperature) (Ruiz Cruz and Andreo, 1996; Hoffman and Hower, 1979); (2) channelling of hydrothermal fluids along thrust surfaces which exhibit enhanced permeability (Lin and Wang, 1989); and (3) the combination of high strain and fluid flow through sheared rock (Buatier et al., 1997). The post-orogenic timing of the Moine Thrust dickite occurrences indicates that the hydrothermal model is appropriate in this case. The Permian age of the mineralization associated with the hydrothermal pulse suggests that it is an expression of the regional high heat flow in NW Europe at that time. Although the thrust planes were structurally dormant, they possessed enough permeability to vent excess heat as 100+°C fluids. As the present-day surface is similar to the Upper Palaeozoic surface (Hall, 1991), the fluids would have emerged as boiling springs or steam vents. The confinement of dickite to fault planes shows that heat dissipated rapidly in the surrounding rock. Even at moderate permeabilities, the retention of high fluid temperatures along thrust surfaces with enormous rock/fluid ratio, probably extending to depths of several kilometres, required a markedly anomalous degree of heating. The flow volume must have been substantial, to precipitate abundant kaolin in the adjacent fracture systems. The fission track data imply that heating must have been very rapid: this is not surprising as prolonged heating would be difficult to sustain. In other cases where fission track data do not record hot fluids inferred by other techniques, the maximum time of heating that can be modelled is no more than 1000 y (e.g. Middleton et al., 2001).

We can speculate that similar venting of heat may be a feature at plate margins and other deepseated structures elsewhere. At the present day, there is evidence for anomalous heat along major faults from direct physical measurements (e.g. Quattrocchi *et al.*, 2002) and from satellite infrared data (Tronin, 1996; Srivastav *et al.*, 1997). Mineralization along lineaments by episodes of fluid flow subsequent to the original tectonic activity could help to weaken the lineaments and make them susceptible to reactivation. In NW Scotland, the Outer Hebrides Fault Zone similarly shows evidence of early thrust motion, followed by phyllonite development due to fluid flow, then reactivation (Butler *et al.*, 1995). The nature of the mineralization is different in this case, but emphasizes the potential for the preferential break-up of crust along pre-existing structures during extension.

Kaolin is found on 'basement' surfaces elsewhere in Europe, particularly in Scandinavia (Söderman, 1985; Lidmar-Bergström, 1995), and is present in fracture zones (Lundqvist, 1985, Lidmar-Bergström, 1995). These occurrences are assumed to represent weathering profiles rather than hydrothermal activity. However, they do emphasize that kaolin minerals are widespread and have potential in the reconstruction of regional heat flow histories, including in 'basement' terrains where there may be a useful supplement to fission track data.

Hot fluids imply a deep source, for most geothermal gradients. There are few independent methods of indicating a deep-seated origin, although noble gas data can indicate a mantle source, and hence a deep origin, such as along the San Andreas Fault (Kennedy et al., 1997). However, in the geological past, evidence for heat venting depends upon palaeotemperature parameters in the fault zone. Fluid inclusion data can indicate the passage of hot fluids (e.g. Xie et al., 2001), but suitable phases for fluid inclusion microthermometry are not always present. In the case of the Moine Thrust Zone, the kaolin data give us evidence from localities where there is almost no potential for microthermometry. The kaolin polytyping, therefore, is a tool which increases our capability to document anomalous palaeo-heat flow.

# Conclusions

The combination of kaolin-polytype data, petrography, fluid-inclusion analysis, stable-isotope analysis, palaeomagnetism and fission-track analysis constrains the nature of the hot fluid pulse along the Moine Thrust Zone.

(1) The thermal anomaly was strongly localized along the thrust zone.

(2) The temperature of the hot fluid exceeded 120°C, but was probably no hotter than 200°C.

(3) The hot-fluid pulse was of Permian age, coincident with a phase of high heat flow on the European margin.

(4) The hot-fluid pulse was very rapid.

(5) There is no consistent evidence for a later thermal overprint along the thrust zone during Tertiary magmatic activity.

# Acknowledgements

The manuscript benefited from constructive reviews by K. Brown and Q. Fisher. We are grateful to J.B. Fulton, P. Gaffikin and C. Wood for skilled technical support, and to A.E. Fallick for helpful discussion.

# References

- Bailey, S.W. (1980) Structure of layer silicates. Pp. 1–123 in: Crystal Structures of Clay Minerals and their X-ray Identification (G.W. Brindley and G. Brown, editors). Monograph 5, Mineralogical Society, London.
- Baron, M., Parnell, J. and Bordas Le Floch, N. (2003) Preservation of pre-orogenic palaeofluids within the Caledonides of northwest Scotland. *Journal of Geochemical Exploration*, 78–79, 27–31.
- Beckinsale, R.D. and Obradovich, J.D. (1973) Potassium-argon ages for minerals from the Ross of Mull, Argyllshire, Scotland. *Scottish Journal of Geology*, 9, 115–147.
- Bigeleisen, J., Perlman, M.L. and Prosser, H.C. (1952) Conversion of hydrogenic materials to hydrogen isotopic analysis. <u>Analytical Chemistry</u>, 24, 1356–1357.
- Bray, R.J., Green, P.F. and Duddy, I.R. (1992) Thermal history reconstruction using apatite fission track analysis and vitrinite reflectance: a case study from the UK East Midlands and the southern North Sea.
  Pp. 3–25 in: *Exploration Britain: Into the Next Decade* (R.F.P. Hardman, editor). Special Publication, Geological Society of London.
- Buatier, M.D., Trave, A., Labaume, P. and Potdevin, J.L. (1997) Dickite related to fluid-sediment interaction and deformation in Pyrenean thrust-fault zones. *European Journal of Mineralogy*, 9, 875–888.
- Butler, C.A., Holdsworth, R.E. and Strachan, R.A. (1995) Evidence for Caledonian sinistral strike-slip motion and associated fault-zone weakening, Outer Hebrides Fault Zone, NW Scotland. *Journal of the Geological Society, London*, **152**, 743–746.
- Cheadle, M.J., McGeary, S., Warner, M.R. and Matthews, D.H. (1987) Extensional structures on the western UK continental shelf: a review of evidence from deep seismic profiling. Pp. 445–465

in: *Continental Extensional Tectonics* (M.P. Coward, J.F. Dewey and P.L. Hancock, editors). Special Publication, **28**, Geological Society of London.

- Clayton, R.N. and Mayeda, T.K. (1963) The use of bromine pentafluoride in the extraction of oxygen from oxides and silicates for isotopic analysis. *Geochimica et Cosmochimica Acta*, 27, 43–52.
- Coward, M.P. (1982) Surge zones in the Moine thrust zone of NW Scotland. *Journal of Structural Geology*, **4**, 247–256.
- Ehrenberg, S.N., Aagaard, P., Wilson, M.J., Fraser, A.R. and Duthie, D.M.L. (1993) Depth-dependent transformations of kaolinite to dickite in sandstones of the Norwegian continental shelf. <u>Clay Minerals</u>, 28, 325–352.
- Elmore, R.D., Blumestein, R., Engel, M. and Parnell, J. (2003) Paleomagnetic dating of fluid-flow events along the Moine Thrust Zone, Scotland. *Journal of Geochemical Exploration*, **78**–**79**, 45–49.
- Fallick, A.E., Macaulay, C.I. and Haszeldine, R.S. (1993) Implications of linearly correlated oxygen and hydrogen isotopic compositions for kaolinite and illite in the Magnus Sandstone. <u>Clays and Clay</u> <u>Minerals</u>, 41, 184–190.
- Fisher. R.A. (1953) Dispersion on a sphere. *Proceedings* of the Royal Society of London, A217, 295–305.
- Green, P.F., Duddy, I.R., Hegarty, K.A. and Bray, R.J. (1999) Early Tertiary heat flow along the UK Atlantic margin and adjacent areas. Pp. 349–357 in: *Petroleum Geology of Northwest Europe: Proceedings of the 5<sup>th</sup> Conference* (A.J. Fleet and S.A.R. Boldy, editors). Geological Society, London.
- Green, P.F., Duddy, I.R. and Hegarty, K.A. (2002) Quantifying exhumation from apatite fission-track analysis and vitrinite reflectance data: precision, accuracy and latest results from the Atlantic margin of NW Europe. Pp. 331–354 in: *Exhumation of the North Atlantic Margin: Timing, Mechanisms and Implications for Petroleum Exploration* (A.G. Doré, J.A. Cartwright, M.S. Stoker, J.P. Turner and N. White, editors). Special Publication, **196**, Geological Society, London.
- Hall, A.J., Banks, D., Fallick, A.E. and Hamilton, P.J. (1989) A hydrothermal origin for copper-impregnated prehnite and analcime from Boylestone Quarry, Barrhead, Scotland. *Journal of the Geological Society, London*, 146, 701–713.
- Hall, A.M. (1991) Pre-Quaternary landscape evolution in the Scottish Highlands. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, 82, 1–26.
- Hoffman, J. and Hower, J. (1979) Clay mineral assemblages as low grade metamorphic geothermometers: Application to the thrust faulted disturbed belt of Montana, U.S.A. Pp. 55–79 in: Aspects of Diagenesis (P.A. Scholle and P.R. Schuger, editors). SEPM, Tulsa, Oklahoma.

- Jeans, C.V., Fallick, A.E., Fisher, M.J., Merriman, R.J., Corfield, R.M. and Manighetti, B. (1997) Clay- and zeolite-bearing Triassic sediments at Kaka Point, New Zealand: Evidence of microbially influenced mineral formation from earliest diagenesis into the lowest grade of metamorphism. <u>Clay Minerals</u>, 32, 373–423.
- Jenkin, G.R.T., Mohr, P., Mitchell, J.G. and Fallick, A.E. (1998) Carboniferous dykes as monitors of post-Caledonian fluid events in West Connacht, Ireland. *Transactions of the Royal Society of Edinburgh: Earth Sciences*, **89**, 225–243.
- Kelley, S.P. (1988) The relationship between K-Ar mineral ages, mica grain sizes and movement on the Moine Thrust Zone, NW Highlands, Scotland. Journal of the Geological Society, London, 145, 1-10.
- Kelley, S.P. and Powell, D. (1985) Relationships between marginal thrusting and movement on major internal shear zones in the Northern Highland Caledonides, Scotland. <u>Journal of Structural</u> Geology, 7, 161–174.
- Kennedy, B.M., Kharaka, Y.K. and Evans, W.C. (1997) Mantle fluids in the San Andreas Fault System, California. *Science*, **278**, 1278–1281.
- Kirschvink, J.L. (1980) The least-squares line and plane and the analysis of paleomagnetic data. *Geophysical Journal of the Royal Astronomical Society, London*, 62, 699–718.
- Kirton, S.R. and Hitchen, K. (1987) Timing and style of crustal extension N of the Scottish mainland. Pp. 501-510 in: *Continental Extensional Tectonics* (M.P. Coward, J.F. Dewey and P.L. Hancock, editors). Special Publication, 28, Geological Society of London.
- Lewis, C.L.E., Carter, A. and Hurford, A.J. (1992) Lowtemperature effects of the Skye Tertiary intrusions on Mesozoic sediments in the Sea of Hebrides Basin. Pp. 175–188 in: *Basins of the Atlantic Seaboard* (J. Parnell, editor). Special Publication, **62**, Geological Society of London.
- Lidmar-Bergström, K. (1995) Relief and saprolites through time on the Baltic Shield. <u>*Geomorphology*</u>, 12, 45–61.
- Lin, S.B. and Wang, Y.R. (1989) Mineralogy and tectonic implications of the dickites from Hengchun Peninsula, southern Taiwan. Acta Geologica Taiwanica, 27, 19–32.
- Lundqvist, J. (1985) Deep-weathering in Sweden. *Fennia*, **163**, 287–292.
- MacGregor, M., Lee, G.W. and Wilson, G.V. (1920) The Iron Ores of Scotland. *Geological Survey of Scotland Special Report on Mineral Resources*, 11.
- Middleton, D.W.J., Parnell, J., Green, P.F., Xu, G. and McSherry, M. (2001) Hot fluid flow events in Atlantic margin basins: An example from the

Rathlin Basin. Pp. 91–105 in: *Petroleum Exploration of Ireland's Offshore Basins* (P.M. Shannon, P.D.W. Haughton and D. Corcoran, editors). Special Publication, **188**, Geological Society of London.

- Parnell, J., Baron, M. and Boyce, A. (2000a) Controls on kaolinite and dickite distribution, Highland Boundary Fault Zone, Scotland and Northern Ireland. *Journal of the Geological Society, London*, 157, 635–640.
- Parnell, J., Baron, M., Davidson, M., Elmore, D. and Engel, M. (2000b) Dolomitic breccia veins as evidence for extension and fluid flow in the Dalradian of Argyll. <u>Geological Magazine</u>, 137, 447-462.
- Potts, G.J. (1990) A palaeomagnetic study of recumbently folded and thermally metamorphosed Torridon Group sediments, Eishort anticline, Skye, Scotland. *Journal of the Geological Society, London*, **147**, 999–1007.
- Quattrocchi, F., Favara, R., Capasso, G., Pizzino, L., Bencini, R., Cinti, D., Galli, G., Grassa, F., Francofonte, S. and Volpicielli, G. (2002) Thermal anomalies and fluid geochemistry framework in occurrence of the 2000–2001 Nizza-Monferra area seismic sequence (northern Italy): Episodic changes in the fault zone heat flow or chemical mixing phenomena? http://ftp.dipteris.unige.it/geofisica/ esc2002/RIASSUNTI/POSTERS/SS2/nizzaesc.htm
- Roberts, D.G., Thompson, M., Mitchener, B., Hossack, J., Carmichael, S. and Bjørnseth, H.-M. (1999)
  Palaeozoic to Tertiary rift and basin dynamics: mid-Norway to the Bay of Biscay a new context for hydrocarbon prospectivity in the deep water frontier. Pp. p. 7–40 in: *Petroleum Geology of Northwest Europe. Proceedings of the 5<sup>th</sup> Conference* (A.J. Fleet and S.A.R Boldy, editors). Geological Society, London.
- Rock, N.M.S. (1982) Petrography and age of agglomeratic vents near Toscaig, Applecross, Scotland. <u>Proceedings of the Geologists' Association</u>, <u>93</u>, <u>305–308</u>.
- Rock, N.M.S. (1983) The Permo-Carboniferous camptonite-monchiquite dyke-suite of the Scottish Highlands and Islands: distribution, field and petrological aspects. *Report of the Institute of Geological Sciences*, No. 82/14.
- Ruiz Cruz, M.D. and Andreo, B. (1996) Genesis and transformation of dickite in Permo-Triassic sediments (Betic Cordilleras, Spain). <u>Clay Minerals</u>, 31, 133–152.
- Savin, S.M. and Lee, M. (1988) Isotopic studies of phyllosilicates. Pp. 189–223 in: *Hydrous Phyllosilicates* (S.W. Bailey, editor). Mineralogical Society of America, Washington.

Shepherd, T.J., Rankin, A.H. and Alderton, D.H. (1985)

A Practical Guide to Fluid Inclusion Studies. Blackie, Glasgow, UK.

- Sheppard, S.M.F. and Gilg, H.A. (1996) Stable isotope geochemistry of clay minerals. <u>Clay Minerals</u>, 31, 1–24.
- Smythe, D.K., Russell, M.J. and Skuce, A.G. (1995) Intra-continental rifting inferred from the major late Carboniferous quartz-dolerite dyke swarm of NW Europe. Scottish Journal of Geology, 31, 151–162.
- Snyder, D.B. (1990) The Moine Thrust in the BIRPS data set. *Journal of the Geological Society, London*, 147, 81–86.
- Snyder, D.B., England, R.W. and McBride, J.H. (1997) Linkage between mantle and crustal structures and its bearing on inherited structures in northwestern Scotland. *Journal of the Geological Society, London*, **154**, 79–83.
- Söderman, G. (1985) Planation and weathering in eastern Fennoscandia. *Fennia*, **163**, 347–352.
- Speight, J.M., Skelhorn, R.R., Sloat, T. and Knapp, R.J. (1982) The dyke swarms of Scotland. Pp. 449–459 in: *Igneous Rocks of the British Isles* (D.S. Sutherland, editor). John Wiley, Chichester, UK.
- Srivastav, S.K., Dangwal, M., Bhattacharya, A. and Reddy, P.R. (1997) Satellite data reveals preearthquake thermal anomalies in Killari area, Maharashtra. *Current Science*, **72**, 880–884.
- Thomson, K., Underhill, J.R., Green, P.F., Bray, R.J. and Gibson, H.J. (1999) Evidence from apatite fission track analysis for the post-Devonian burial and exhumation history of the northern Highlands, Scotland. <u>Marine and Petroleum Geology</u>, **16**, 27–39.
- Tronin, A.A. (1996) Satellite thermal survey a new tool for the study of seismoactive regions. *International Journal of Remote Sensing*, 17, 1439–1455.
- Walderhaug, O. (1996) Kinetic modelling of quartz cementation and porosity loss in deeply buried sandstone reservoirs. *American Association of Petroleum Geologists Bulletin*, 80, 731–745.
- Watson, J.V. (1984) The ending of the Caledonian orogeny in Scotland. *Journal of the Geological Society, London*, **141**, 193–214.
- Watts, N.L. (1976) Paleopedogenic palygorskite from the basal Permo-Triassic of northwest Scotland. *American Mineralogist*, **61**, 299–302.
- Woodhall, D. and Knox, R.W.O'B. (1979) Mesozoic volcanism in the northern North Sea and adjacent areas. Bulletin of the Geological Survey of Great Britain, 70, 34–56.
- Woods, S., Elmore, R.D. and Engel, M. (2002) Paleomagnetic dating of smectite-to-illite conversion: testing the hypothesis in Jurassic sedimentary rocks, Skye, Scotland. *Journal of Geophysical Research*, 107, 10.1029/2000JB000053, EPM 2-1-2-12.

- Xie, X., Li, S., Dong, W. and Hu, Z. (2001) Evidence for episodic expulsion of hot fluids along faults near diapiric structures of the Yinggehai Basin, South China Sea. <u>Marine and Petroleum Geology</u>, <u>18</u>, 715–728.
- Zijderveld, J.D.A. (1967) A.C. demagnetization of rocks: Analysis of results. Pp. 254-286 in:

Methods in Palaeomagnetism. (D.W. Collinson, K.M. Creer and S.K. Runcorn, editors). Elsevier, Amsterdam, The Netherlands.

[Manuscript received 24 May 2002: revised 18 September 2003]