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Clay minerals in the basalts of the South Pennines

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ABSTRACT. X-ray diffraction, electron microprobe and STEM EDAX analyses of basalts from the South Pennines (Derbyshire) indicate that Fe-rich smectites are the dominant alteration products, occurring either as pseudomorphs or infilling veins and vesicles. Previously chlorite has been identified as the common alteration product but its occurrence is very infrequent.

MORE than forty basaltic lavas, tuffs, and sills interbedded with the Dinantian limestones of the South Pennines have been described by Walters and Ineson (1981) and the general distribution pattern is shown in fig. 1. For the most part they have suffered extensive deuteric and/or hydrothermal alteration and as such show all the stages of decomposition to the final product—a clay mineral assemblage. Woodward and Mello (1881), Green *et al.* (1887), Sargent (1917), Garnett (1923), Tomkeieff (1926), Ford and Sarjeant (1964), Sarjeant (1967), Wilkinson (1967), Smith *et al.* (1967), Stevenson *et al.* (1970), Ford (1977), and Harrison (1981) have reported that chlorite is the dominant alteration product. These determinations relied on either a partial analysis or an optical identification of the fine-grained phyllosilicate phases. Subsequently, Walkden (1972), employing X-ray diffraction techniques, demonstrated that the 'clays' were mixed-layer illite–smectites associated with the 'toadstone-clay' alteration of the basalts and that chlorite was absent or constituted only a minor component. An analysis of the veins and replacement products of the Calton Hill dolerite enabled Curtis (1976) to state that, at this locality, Fe-rich smectites were present.

Melson and Thompson (1973) have demonstrated that the optical identification of the phyllosilicates is unsatisfactory, for the 'basaltic clays' which exhibit the typical low birefringence of chlorites, are in fact smectites.

Smectite alteration. Phyllosilicate alteration of the South Pennine basalts occurs as either pseudomorphs after primary minerals or as a component in amygdales, joints, or veins. The alteration of primary olivine was first noted by Arnold-Bemrose (1894) who concluded that the material was 'mica like' but 'probably not iddingsite'. The terms iddingsite, bowlingite, or chlorophaeite have been applied to the products of the alteration of olivine in basalts (Wilshire, 1958); however, their status as discrete mineral species has been discredited by Sun (1957), Wilshire (1958, 1959), Smith (1959), and Baker and Haggerty (1967). X-ray diffraction analyses indicate complex mixtures of clay and iron-oxide and the apparent optical homogeneity is a function of the orientation of sub-microscopic goethite rods controlled by the lattice orientation or the primary olivine phase (Sun, 1957). The relationship between the varied colours and optical properties is essentially a function of the oxidation state, iron retention, and primary olivine composition.

The selective alteration of olivine microphenocrysts associated with unaltered augite, labradorite and Fe–Ti oxides in the relatively unaltered extrusive basalts in the South Pennines is a common feature. The olivines are initially altered along external surfaces and internal cracks leaving islands of relict olivine. The majority of the basalts, however, show the total replacement of the olivine by red or green phyllosilicates with fibrous or patchy replacement textures (fig. 2*a* and *b*). The homogeneous pseudomorphs exhibit optical continuity with pronounced pleochroism, extinction and low second-order birefringence colours, while pseudomorphs containing relict olivine indicate the 'inherited' nature of this optical orientation.

Anhedral, interstitial phyllosilicates are a ubiquitous feature of the 'unaltered' basalts and represent the 'primary chlorite' described by Tomkeieff (1926). These phases are optically similar to the

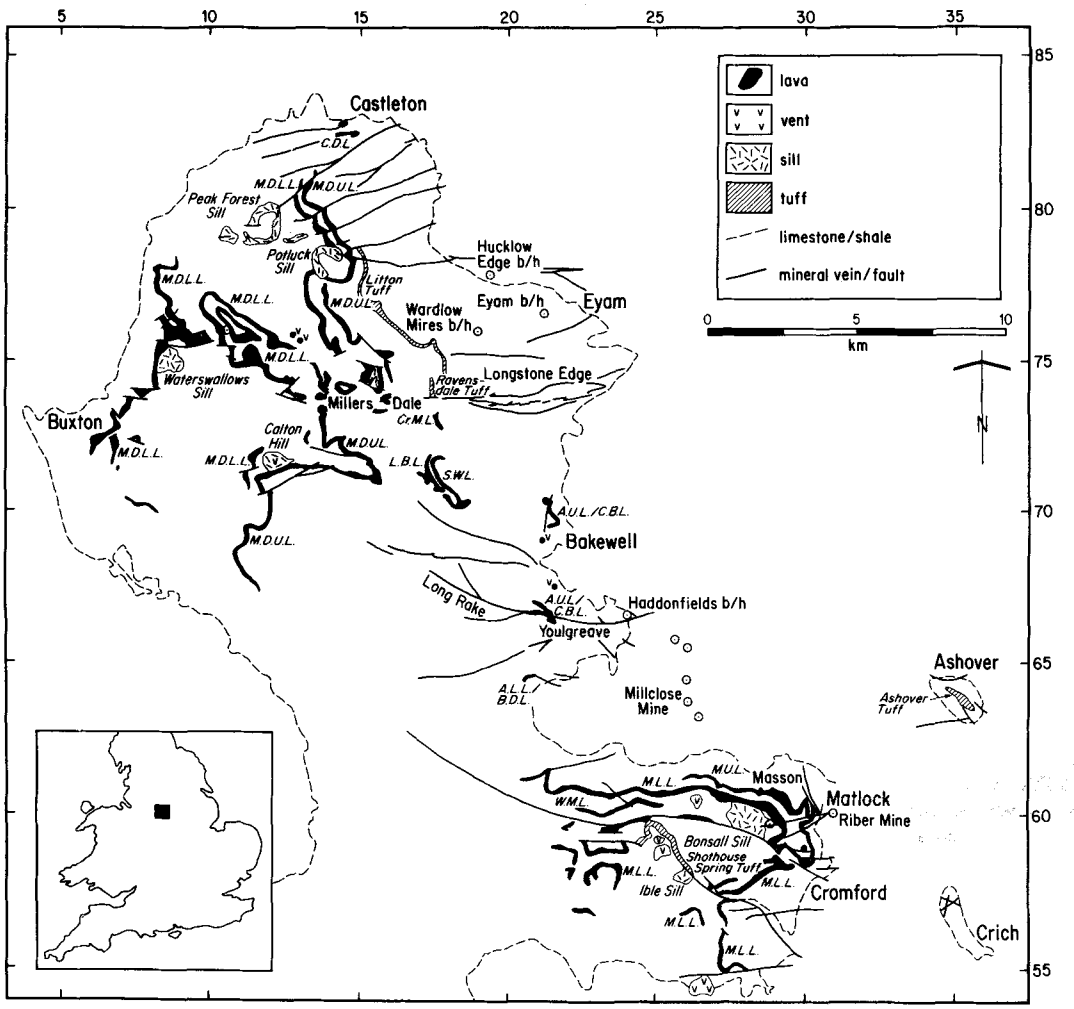

FIG. 1. Distribution of the igneous horizons in the South Pennines.
ALL—Alport Lower Lava
BDL—Bradford Dale Lava
CDL—Cave Dale Lava
LBL—Lees Bottom Lava
MDUL—Miller's Dale Upper Lava
MUL—Matlock Upper Lava
WML—Winster Moor Lava
AUL—Alport Upper Lava
CBL—Conksbury Bridge Lava
CrML—Cressbrook Mill Lava
MDLL—Miller's Dale Lower Lava
MLL—Matlock Lower Lava
SWL—Shacklow Wood Lava

smectite pseudomorphs after olivine, although pleochroism is weak or absent. They are often zoned (fig. 3*a*) with a brown fibrous periphery and a green spherulitic core. Whole-rock X-ray diffraction analyses (see Table I) confirm the presence of smectite.

Smectites are not the only interstitial phase in the basalts, for primary glass and/or analcite are noted in the least-altered samples (fig. 3*a* and *b*) and indicate that they are in all probability secondary and deuteric in origin. The alteration of the pyroxenes is associated with advanced deuteric effects and/or hydrothermal processes. The primary titaniferous augites and salites are pseudomorphed by green homogeneous aggregates of smectite with a concentration of anatase at relict grain boundaries. This alteration is associated with hydrothermal processes for it is accompanied by the secondary replacement of smectite pseudomorphs after olivine by carbonates and hematite, as well as the calcitization of interstitial areas. Walters (1981) reports the low MgO and total Fe content of

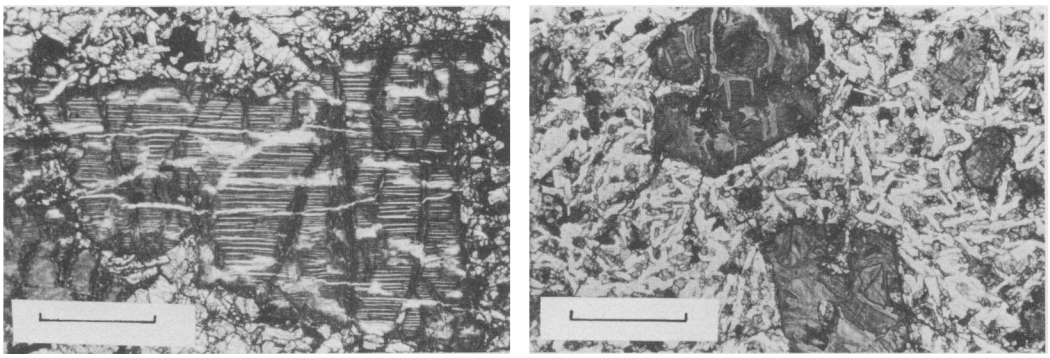

FIG. 2. (*a*, left) An olivine phenocryst pseudomorphed by smectite. Note the pronounced partings which are orientated parallel to the maximum pleochroic absorption. Waterswallows Sill, upper gabbroic horizon. (*b*, right) Two euhedral smectite pseudomorphs after olivine. The groundmass consists of randomly orientated plagioclase crystals, granular augite, opaque minerals and interstitial smectite with minor relict devitrified glass. Waterswallows Sill. Plane polarized light. Scale bars = 1.0 mm.

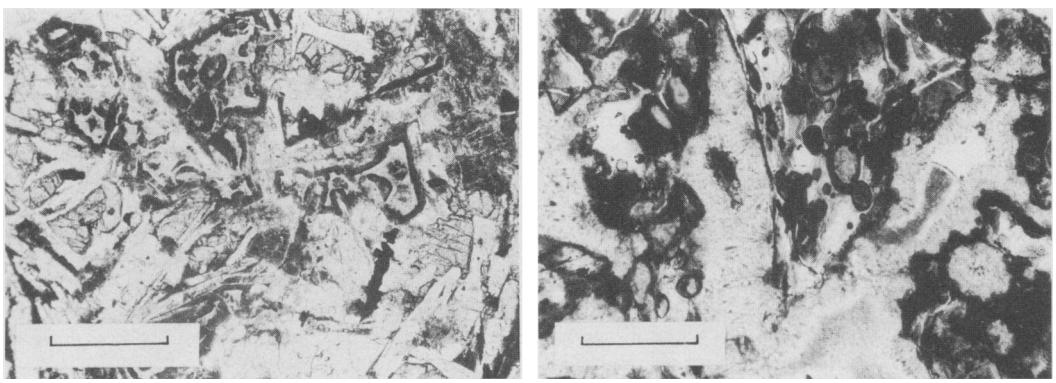

FIG. 3. (*a*, left) Advanced alteration in the groundmass of a lava. All the relict glass has been replaced by smectite as a result of deuteric alteration. The smectite has a dark (brown) fibrous rim and a (green) spherulitic centre. Haddonfields Borehole—Middle Lava of Walters and Ineson (1981). Plane polarized light. Scale bar = 0.50 mm. (*b*, right) A tuff showing secondary smectite replacement. Highly vesicular pumice fragments with regular outlines in a matrix of primary turbid analcite (dark grey) altering to fibrous smectite on the peripheries. Haddonfields Borehole of Walters and Ineson (1981)—middle horizon. Plane polarized light. Scale bar = 1.0 mm.

the highly altered basalts and suggests the formation of a montmorillonite in contrast to the nontronites and saponites which have resulted from deuteric processes. He also records that the excess of potassium, invariably associated with the hydrothermal alteration of basalts, results in the formation of mixed-layer illite–smectites adjacent to mineralization. The continuation of Long Rake Vein into the Conksbury Bridge Lava at an open cast mineral site near Youlgreave (Walters and Ineson, 1980) is a typical example of a sequence of hydrothermal alteration zones. Veinlets in these zones, however, contain a clay with increased birefringence and pleochroism in comparison with typical smectites or illite–smectites. X-ray diffraction analysis indicates that the clay is pure illite with a sharp peak at 10.0 Å which is unaffected by glycolation or heating (450 °C).

Smectite analyses. X-ray diffraction analyses of extracted olivine pseudomorphs, whole-rock smear samples and clay mineral fraction mounts are shown in Table I. The response to glycolation and heat treatment indicate the presence of smectite. Quantitative STEM EDAX analysis was carried out using the ratio technique as described by Cliff and Lorimer (1975). A comparison was made between the green pleochroic olivine pseudomorphs and green interstitial phyllosilicates. Selected area electron diffraction and lattice imaging in the TEM showed both areas to be made up

TABLE I. X-RAY DIFFRACTION OF CLAY MINERALS

Sample Locality	X.R.D. Sample	Air Dried (4-30° 2θ)	Glycolated (4-10° 2θ)	Heat Treated to 450°C (4-10° 2θ)
Waterswallows Sill (Lower Horizon)	Smear mount of whole rock	15.10(vs), (mb), 3.04(ws)	16.80 (vs)	9.83 (mb)
Waterswallows Sill (Middle Horizon)	Smear mount of whole rock	15.00(vs),7.50(mb)	16.20 (vs)	10.00 (mb)
Waterswallows Sill (Upper Horizon)	Olivine pseudomorph	14.80(vs), 7.40(mb)	16.30 (vs)	9.80 (sb)
Waterswallows Sill (Fibrous Vein at Basal Contact)	Smear mount of whole sample	15.20(vs), 7.50(mb)	16.80 (vs)	9.80 (mb)
Cressbrook Dale Lava	Olivine pseudomorph	15.10(vs), 7.40(wb), 3.04(ws)	16.83 (ws)	9.83 (mb)
Shacklow Wood Lava	Olivine pseudomorph	15.20(vs), 7.50(mb)	16.80 (vs)	10.00 (mb)
Shacklow Wood Lava	Smear mount of whole rock	14.60(ms), 7.50(mb)	16.70 (ms)	10.00 (mb)
Matlock Upper Lava	Smear mount of whole rock	14.50(ms), 7.50(mb)	16.50 (ms)	9.95 (mb)
Ible Sill	Olivine pseudomorph	15.00(vs), 7.40(mb)	16.20 (ms)	10.00 (mb)

vs - strong, sharp peak
mb - medium, broad peak
ms - medium, strong peak
ws - weak, sharp peak

of a phyllosilicate with a basal spacing of 10 Å probably representing a collapsed smectite. Chemical analyses of these two phases proved to be very similar, for they are an Fe–Mg-rich, low-Al_2O_3 smectite, suggesting a saponite–nontronite with little deviation from the SiO_2–FeO–MgO ratio of normal olivines when compared with published analyses. The STEM EDAX analyses are shown in Table II. Hydration and oxidation therefore represent the dominant alteration processes. Electron microprobe analyses of the red pleochroic 'iddingsitic' olivine pseudomorphs from the Potluck Sill dolerite (Table III) indicate a greater degree of MgO depletion. These variations are similar to those reported by Scheidegger and Stakes (1977) who recorded that the red 'iddingsitic' phases associated with altered basalts tend to be nontronite enriched compared with the green or brown saponitic aggregates, and therefore relatively depleted in MgO. Minor whole-rock MgO depletion associated with samples containing predominantly red 'iddingsitic' phases, however, indicate that only MgO was mobilized during the alteration of olivine and was incorporated in the interstitial deuteric phases.

TABLE II. ENERGY DISPERSIVE X-RAY ANALYSES (EDAX) OF SMECTITES FROM THE WATERSWALLOWS SILL, BUXTON, DERBYSHIRE

	Bladed clays in olivine pseudomorphs		Interstitial clays		
SiO_2	56.48	56.61	60.15	53.48	53.85
Al_2O_3	4.73	3.31	2.69	4.41	2.99
*FeO	19.33	18.68	16.51	20.03	22.41
MgO	17.98	18.52	20.17	2.126	19.63
CaO	1.48	2.88	0.48	0.29	1.12
Na_2O	0.00	0.00	0.00	0.53	0.00
Total	100.00	100.00	100.00	100.00	100.00

The analytical technique results in an artificial total of 100% which does not account for H_2O or other minor volatile components.

*Total Iron as FeO

Analyst: B.J. Ireland

Chlorite. Of the 200 localities investigated in the South Pennines, at only three localities has chlorite been identified. Chloritic pseudomorphs of devitrified and highly fragmented shards are recorded in a phreatomagnetic tuff which overlies the Cressbrook Dale Lava beneath Hucklow Edge (fig. 4*a*), while in the same general area chlorite and spherulitic silica constitute the matrix of an autobrecciated horizon in the lower part of the Cressbrook Dale Lava intersected by the Eyam Borehole. These occurrences are considered to be atypical examples in the South Pennines and may indicate high-temperature sea-water reactions, as described by Seyfried and Bischoff (1981), in contrast with the predominantly subaerial extrusive nature of most of the material, for 'normal' smectite has been developed in the coarse grained tuffs above the Cressbrook Dale Lava (fig. 4*b*) in this area.

The third locality at which chlorite has been described (Walters and Ineson, 1982) is from the Ible Sill in the Via Gellia (see fig. 1) where it occurs in a subvertical fissure cutting the olivine-dolerite sill. X-ray diffraction and petrological analyses indicate an Fe-rich chlorite replacing primary augite and smectite pseudomorphs after olivine. Walters and Ineson (1982) indicated that the stability of chlorite as opposed to smectite, at this

TABLE III. ANALYSES OF "SMECTITES"

	1	2	3	4	5	6	7	8	9	10	11	12	13
SiO_2	42.80	45.70	38.00	52.33	35.92	42.58	41.70	36.24	43.05	39.11	46.83	43.98	45.12
TiO_2	-	-	-	-	-	0.01	-	-	-	0.18	0.64	0.16	0.23
Al_2O_3	4.10	4.00	-	4.13	12.20	7.69	6.09	13.10	6.40	3.29	8.95	10.15	5.13
Fe_2O_3	-	-	-	-	7.59	9.50	5.55	-	17.86	31.49	7.87	7.85	11.14
FeO	28.90*	28.30*	28.10*	18.06*	4.66	1.95	5.05	21.06*	0.10	0.96	4.88	5.32	4.77
MgO	7.90	8.30	34.00	23.87	21.82	17.52	20.36	17.18	4.46	8.05	11.08	18.02	17.06
CaO	2.00	1.90	0.30	1.62	1.82	1.74	2.10	trace	2.92	2.28	2.78	2.78	0.21
Na_2O	0.10	0.10	-	-	-	0.03	0.01	-	-	-	1.71	-	2.68
K_2O	-	-	-	-	-	0.01	0.05	-	-	-	1.93	-	0.85
H_2O^+	14.10$^\phi$	11.50$^\phi$	-	-	9.20	18.44	19.04	11.68	23.93	16.27	5.39	9.24	13.60
H_2O^-			-	-	6.50						6.81	6.24	
Total	100.00	100.00	100.70	100.01	99.71	99.59	99.95	99.26	100.04	101.63	98.87	100.39	100.83

*Total Iron as FeO Anhydrous Total

$^\phi$Total H_2O Calculated by Subtraction from 100%

1 & 2 Microprobe analyses, red 'iddingsite' olivine, pseudomorph in the Potluck Sill (Walters, 1981)

3 Microprobe analysis - primary olivine pseudomorph in the Potluck Sill (Walters, 1981)

4 EDAX analysis of bladed clays in olivine pseudomorph, middle horizon, Waterswallows Sill, see Table 2.

5 Chlorite var delessite - infilling vesicles - Calton Hill (Tomkeieff, 1928).

6 Chlorite var. delessite - fibrous vein infill at Calton Hill (Sarjeant, 1967)

7 Saponite - fibrous vein infill at Calton Hill (Curtis,1976)

8 Chlorite var. diabantite - infilling vesicles, Matlock Upper Lava, Millclose Mine (Garnett, 1923)

9 Fe-rich nontronite in altered basalt (Weaver & Pollard,1973)

10 Average of five 'iddingsite' analyses (Ross and Shannon, 1925)

11 Mixed nontronite/saponite infilling vesicular basalt (Schneidegger and Stakes, 1977)

12 & 13 Saponite in altered basalt (Weaver & Pollard, 1973) & (Seyfried et al.,1978).

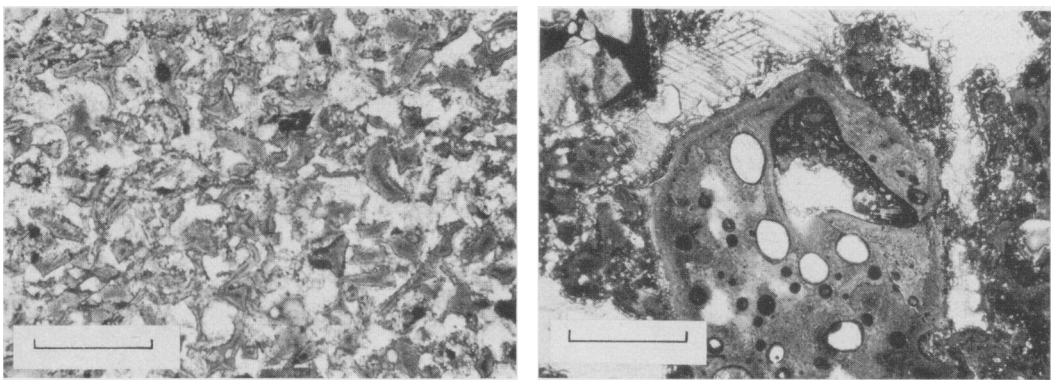

FIG. 4. (*a*, left) Fine grained and fragmented tuff, with devitrified cuspate shards, the matrix of which is replaced by aggregates of silica, carbonate, and analcite. The shards are being replaced by chlorite. Top of the Cressbrookdale Lava. Hucklow Edge No. 11 Borehole. Plane polarized light. Scale bar = 0.5 mm. (*b*, right) Tuff with anchnelithic lapilli—note the presence of clear euhedral analcite associated with coarse-grained carbonates. Tuff at the top of the Cressbrookdale Lava, Hucklow Edge No. 11 Borehole. Plane polarized light. Scale bar = 1.0 mm.

locality, was related to excessive and localized hydrothermal wall-rock reactions between the olivine-dolerite and invading mineral fluids.

Conclusions. Previous publications of Melson and Thompson (1973), Scheidegger and Stakes (1977), Seyfried *et al.* (1978) and Papavassiliou and Cosgrove (1981) have all demonstrated that Fe-rich smectites are the typical products of the deuteric or low-temperature alteration of basalts. The investigation of similar material from the South Pennines agrees with these findings as well as concluding that the previous and frequent reports of 'chlorite' were incorrect.

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