A celadonite–vermiculite series from the volcanic rocks of the Ochils, Stirlingshire

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SUMMARY. Spherulitic and felted green to brown minerals are described from various volcanic rocks of the Western Ochils, Stirlingshire. They fill amygdales and replace pyroxenes and appear to be an interlayered series of sheet silicates from celadonite to vermiculite. The minerals are hydrothermal in origin and suggest the presence of a potassium-rich hydrous fluid at a late stage in the volcanic history.

THE Old Red Sandstone volcanic rocks of the Western Ochils include basalts, andesites, intrusive andesites, andesitic igneous breccias, and acid tuffisites (Francis *et al.*, 1970). They contain a bright-green earthy mineral, which X-ray powder photography has shown to be glauconite or celadonite and which can be sufficiently abundant to give them a strong green colour. In thin section the green mineral is seen to merge with a brown material of similar habit but it has not proved possible to obtain a separate X-ray powder photograph of this brown phase. Electron-microprobe analyses have confirmed that the green mineral is celadonite and suggested that the brown is midway between celadonite and vermiculite. Green vermiculite and green-brown intermediate compositions can also be found in these rocks. The green of vermiculite is paler and less bright than that of the celadonite but the significance of the colour variations is not clear. The minerals occur as fibrous or felted aggregates in amygdales, as discrete fragments in tuffisite, as a replacement of pyroxene and groundmass minerals, and as replacive and dilational veins. Because of their fibrous and felted mode of occurrence, it has not been possible to measure the optical properties of the minerals precisely. The celadonite is very slightly pleochroic in shades of green but the brown mineral is not pleochroic. Both materials have refractive indices of about $\alpha = 1.57$ and β and $\gamma = 1.59$ and a birefringence of about 0.025. The absorption colours tend to produce anomalous greenish polarization colours.

Petrography. In basalts the minerals occur as small spherulites about 50 μm across, which fill amygdales of several millimetres in diameter. Individual fibres are only a few micrometres thick and are bright green in the outer parts of the spherulites but become brown towards the centres. A very small speck or rod of quartz can often be seen in the centres of the spherulites, some of which are markedly elongated. Also within these amygdales are masses of up to about 500 μm in diameter, which are cuspate in outline and consist of felted brown material in variously coloured zones parallel to the cuspate outline. The zones are about 20 μm thick, tend to become darker outwards, and have sharply defined outer surfaces. Quartz rosettes, again about 500 μm in diameter, also occur within the green spherulitic matter and the surfaces of the amygdales are coated with extremely fine-grained felted brown material. In some basalts the amygdales have calcite as the main mineral, and between the individual carbonate crystals there is often a layer of spherulites of the brown-green silicate. Andesites have similar amygdales but also contain small irregular cavities filled by the zoned, felted aggregates. These have an outer zone of fine-grained quartz about 10 μm thick within which is felted green celadonite, which fades into a central mass of brown. The green zones vary in thickness and may make up most of the

amygdales or be virtually absent. Intrusive andesites sometimes contain the bright-green spherulites in amygdales that are otherwise made of radiating quartz and in some of these rocks there are masses of green that are surrounded by brown material in a way that suggests that the groundmass of the andesite has been replaced.

The brown and green minerals are most abundant in the tuffisites and in the matrices and xenoliths of some igneous breccias where they may make up to 10% of the rocks. Most of the tuffisites have blue-green mineral fragments some 50 μm across, together with interstitial, extremely intricately shaped aggregates of celadonite some 100 μm in diameter. Some samples have aggregates of cuspate outline, which have dusty, opaque outer zones some 10 μm thick inside which are green zones about 20 μm thick that merge into central coarser-grained greenish brown and then brown material. Some extremely flattened amygdales and a few of normal shape are made of radiating quartz crystals and chains of green spherulites each about 30 μm across. Some of the matrices of the igneous breccias contain cuspate masses up to a millimetre in diameter, which are zoned with, from outside inwards, 10 μm of fine-grained quartz, 20–40 μm of fine-grained felted brown material, 20–40 μm of green, and central coarser-grained green material merging into light-brown flakes. The celadonite can also be seen in places to have grown across feldspar crystals and rock fragments without causing obvious dilation but in other places thin veins of the green mineral clearly brecciate the igneous rocks. In all rocks the pyroxenes may be partly or wholly replaced by the green flakes (but not the brown).
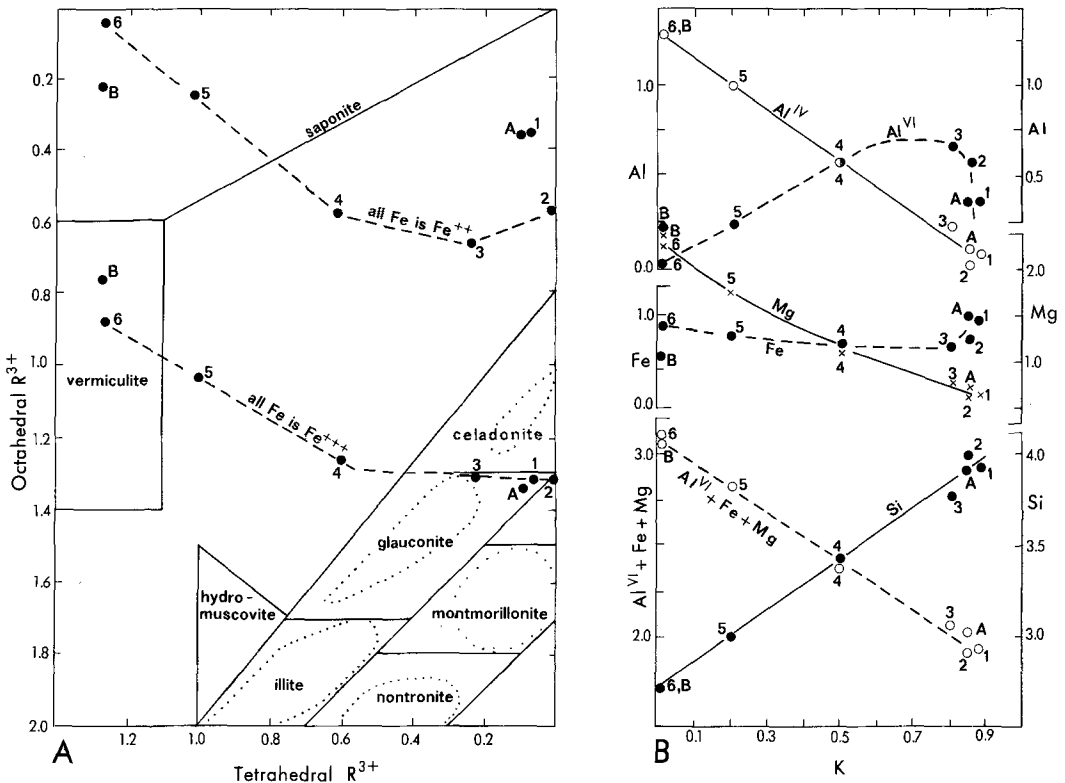

FIG. 1. Chemical variations in celadonite and related minerals. A, tetrahedral R^{3+} versus octahedral R^{3+}; dotted lines are from Yoder and Eugster (1955) and full lines are based on data from Deer *et al.* (1962), Wise and Eugster (1964), Young *et al.* (1968), and Kohler and Köster (1976); Points A, B, and 1–6 are from Table I. B, cations calculated to twenty-two charges plotted against potassium, data from Table I.

Orthopyroxene tends to be altered peripherally to dull green vermiculite and in some rocks the small orthopyroxenes are replaced by single crystals of the vermiculite. Clinopyroxene tends to be altered to more flaky aggregates of the bright green celadonite.

Composition of the minerals. Distinguishing between celadonite and glauconite is not easy. The X-ray data for the minerals studied do not allow distinction to be made between celadonite and glauconite. According to Wise and Eugster (1964), it is possible to deduce from the atomic spacings the oxygen fugacity at which a given celadonite grew, but the present X-ray data give a maximum fugacity from some spacings and minimum from others. The infra-red spectrum is also ambiguous, for, though Wise and Eugster (1964) suggest that the spectrum can be diagnostic of celadonite, Manghnani and Hower (1964) have shown that the peak indicating celadonite also appears in the spectra of glauconites that have low proportions of expandable layers. The spectrum of the Stirling mineral indicates the presence of about 10 % of expandable layers. Because of these difficulties the distinction between celadonite and glauconite is commonly based upon the assumption that only celadonite occurs in volcanic rocks, but Yoder and Eugster (1955) have suggested that there are systematic compositional differences between the two minerals. Fig. 1A shows the compositional areas indicated by these authors for the two phases and for other relevant sheet silicates. Their diagram has been modified to include more recent data and enlarged fields are shown for celadonite and glauconite. The boundary between these minerals is drawn as the best visual discriminant through an area of some overlap. Electron-microprobe analyses of the present green and brown minerals are given in Table I and are plotted in fig. 1A. The bright-green minerals plot close to the boundary between celadonite and glauconite in fig. 1A if all the iron is presumed to be trivalent. However, the ferric to ferrous ratio (determined for individual small grains by the method of French and Adams, 1972) varies

TABLE I. *Electron-microprobe analyses of celadonites and related minerals*

	A	1	2	3	4	5	6	7	B
SiO_2	54·38	56·30	55·99	52·82	48·32	41·57	—	33·30	33·82
TiO_2	0·14	n.f.	n.f.	0·17	n.f.	n.f.	—	n.f.	1·84
Al_2O_3	5·41	5·26	6·67	10·57	14·35	14·60	—	12·59	15·82
FeO_3	18·17	18·19	13·92	11·93	12·87	14·57	—	23·97	8·74
MnO	0·25	n.f.	n.f.	n.f.	n.f.	0·20	—	n.f.	n.f.
MgO	6·40	5·92	5·57	7·04	10·86	16·66	—	19·26	19·17
CaO	0·42	n.f.	0·22	0·17	0·47	0·82	—	0·23	0·56
K_2O	9·23	9·87	9·33	8·81	5·46	2·91	—	0·13	0·10
Total	94·40	95·54	91·70	91·51	92·33	90·61	—	87·01	80·05

Cations to $O_{10}(OH)_2$ excluding Ti and Mn

	A	1	2	3	4	5	6	7	B
Si	3·90	3·93	4·00	3·77	3·40	3·00	2·73	2·52	2·72
Al^{iv}	0·10	0·07	0·00	0·23	0·60	1·00	1·27	1·13	1·28
Al^{vi}	0·36	0·36	0·57	0·67	0·58	0·24	0·01	0·35*	0·22
Fe	0·98	0·96	0·75	0·64	0·68	0·79	0·87	1·01	0·54
Mg	0·68	0·62	0·60	0·75	1·14	1·79	2·24	2·18	2·30
Ca	0·03	0·00	0·02	0·01	0·04	0·07	0·08	0·03	0·10
K	0·84	0·88	0·85	0·80	0·49	0·20	0·00	0·00	0·00
$Al^{vi} + Fe + Mg$	2·02	1·94	1·92	2·06	2·40	2·82	3·12	3·19	3·06

A, celadonite, sample 15 of Wise and Eugster (1964); B, vermiculite from Walker and Cole (1957); 1, bright-green mineral in spherulitic amygdale in andesite; 2, blue-green fragment in tuffisite; 3, 4, 5, successive zones inwards through a zoned felted amygdale in tuffisite; 6, composition of the end member of the series if K = 0; 7, vermiculite replacing orthopyroxene. Analyses are recalculated to a total of twenty-two charges equivalent to $O_{10}(OH)_2$ assuming that the iron is all trivalent.

* Fe allocated to tetrahedral site. Analyses were made by electron microprobe at Cambridge with a Harwell E.D.S.

from about 5 to 1 to about 12 to 1, and this small amount of ferrous iron is sufficient to take the 'green' compositions clearly into the celadonite field. The brown and dull-green material falls outside the celadonite field towards either vermiculite or saponite composition depending upon whether the iron is assumed to be dominantly ferric or ferrous. Although saponites are known (Miyamoto, 1957) with total iron contents comparable with the Stirling minerals, vermiculite is favoured since it seems more likely that the iron oxidation state will be similar to that of celadonite, and Al^{iv} is much greater than is appropriate for saponite. It is therefore most probable that the series is from celadonite towards vermiculite in composition. Fig. 1B shows that certain ions and sums of ions vary linearly through the mineral series. The celadonite has typically high Si and K and both of these elements decline through the series towards vermiculite. Al in tetrahedral coordination rises as K falls and at zero K the Al^{iv} content is 1·27 atoms per formula unit. This is almost exactly the value found on extrapolating total Al to zero K indicating that all the Al is in tetrahedral coordination in the vermiculite end-member. The sum of Al^{vi}, Fe, and Mg varies linearly with K and is close to 2 at the K-rich end of the series and 3 at zero K. The composition of a K-free end-member has been calculated and is given in Table I. The numbers of cations found are almost exactly equal to those necessary to fill the tetrahedral and octahedral sites if the zero-K end-member molecule is trioctahedral, with a small residue of interlayer cations. The minerals therefore resemble an interlayered series from a dioctahedral celadonite molecule to a trioctahedral vermiculite-like end-member. The celadonite molecule has Al, Fe, and Mg in octahedral sites and Si almost alone in tetrahedral sites. This produces a negatively charged layer of pyrophyllite-type in which K^+ is the main balancing interlayer cation. The trioctahedral end-member molecule has Mg and Fe in the octahedral sites, and Si and substantial Al in the tetrahedral sites. This talc-like layer is virtually electrically neutral and the layers may be linked by interlayer water molecules.

The vermiculite end-member has not been found in amygdales but in certain rocks the replacement product of orthopyroxene has a composition that is very close to the end-member molecule (Table I). This mineral is rather iron-rich compared with common vermiculites but its octahedral and tetrahedral R^{3+} ions, its total octahedral site occupancy, and its optical properties are those of vermiculite.

The formation of the minerals. The occurrence of the celadonite–vermiculite series appears to indicate a low-temperature hydrothermal origin. The minerals are associated with silica minerals, often as banded agate, chlorite, and carbonate. Wise and Eugster (1964) have shown that celadonite can occur with numerous other low-temperature phases including carbonates and that the mineral can be synthesized over a considerable range of pressures and oxygen fugacities if the temperature is below about 400 °C. Experiment also shows that vermiculite is unlikely to be precipitated above 300 °C (Roy and Romo, 1957) and it seems possible that the trioctahedral mineral is a lower-temperature phase than the green celadonite. Potassium for these minerals may be derived from the groundmasses of the volcanic rocks, which tend to be potassium-rich. However, in certain tuffisites the celadonite is the only abundant potassium-bearing mineral and is itself so abundant in amygdales that it must be presumed that the hydrothermal fluid was itself rich in K. Since celadonite occurs in early basalts, in fragments and matrices in the later igneous breccias, and in the even later tuffisites, it seems likely that the fluid was available at several stages and became especially abundant late in the volcanic history.

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