

Celadonite-aluminous-glaucanite: an example from the Lake District, UK

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ABSTRACT. An occurrence of a celadonite-like mineral in a weathered basalt in the Lake District has been investigated by X-ray diffraction, X-ray fluorescence, electron microprobe, and infra-red spectroscopic methods. The bulk composition of the mineral corresponds to an aluminous-glaucanite. The data show that the mineral is most probably a celadonite-muscovite or celadonite-illite mixture, although a celadonite-phengite cannot be entirely discounted. Approximately 10% smectite layers are also present. The results suggest that re-examination of many aluminous glaucanites may show them to be mixtures of this type.

CELADONITE is an iron-rich dioctahedral mica of ideal half-unit cell composition $K(Fe^{3+}, Al^{3+})(Mg^{2+}, Fe_2^{2+})Si_4O_{10}(OH)_2$. Reports of celadonite in the British Isles are rare. Heddle (1901) gives chemical data for four occurrences in Scotland, although these data are probably unreliable in modern terms. Walker (1960) recorded celadonite as a product of zeolite-facies metamorphism in the Tertiary lavas of Ireland, but gave no further information. In morphology and colour celadonite is not unlike glaucanite and the two are often distinguished solely by mode of occurrence, celadonite occurring as infillings in veins or vesicles in basaltic lavas and glaucanite as pellets in marine sediments. Over the years there has been considerable controversy as to whether the two minerals are separate species or members of a continuous compositional series. Smulikowski (1936) coined the name skolite for an Al-rich glaucanite-like mineral, and later used the term pholidoide to encompass this general class of Al-glaucanites (Smulikowski, 1954). However, Wiewióra *et al.* (1979) have since shown skolite to be a mixed-layer illite-smectite with a large Fe content. Malkova (1956) distinguished between celadonite as a distinct species and Al-glaucanites. Pirani (1963) and Kautz (1965) reported minerals from basalts which they preferred to regard as Al-glaucanites rather than celadonites despite their mode of origin. On the other hand, Buckley *et al.* (1978) showed that carefully selected celadonites could be distinguished

from glaucanites in terms of the octahedral Fe^{3+} content in relation to both the $d(060)$ spacing and the octahedral Al^{3+} content, and concluded that the minerals should be regarded as separate species.

This paper reports the first recorded occurrence of a celadonite-like mineral in England, and considers its mineralogy and chemistry in relation to the problems outlined above. For the sake of brevity the mineral is referred to as celadonite in the body of the text.

Geological setting. The celadonite was first noticed as subrounded dark-green grains up to c. 3 mm diameter in the lower horizon (BC) of a Nercwys soil (a stagnogleyic brown earth) near Wood Hall, Bridekirk, Cumbria (Grid Reference: NY 1214 3186). Subsequent augering to depths > 2 m showed the soil passed down into a friable greyish-green material containing similar grains. Such grains were also found in a small outcrop of weathered basalt a few hundred metres to the north-west (Grid reference: NY 1192 3218) although the greyish-green friable material was absent at this site. The basalt is part of the Cockermonth Lavas which are olivine basalts of Lower Carboniferous age (Eastwood *et al.*, 1968). It is assumed that the greyish-green friable material is a weathering product of these lavas.

Morphology of the celadonite. The subrounded grains in the soil are a relatively uniform dark-green colour, occasionally showing brown staining due to alteration to iron oxides. Thin sections of the basalt showed the celadonite to be relatively fresh, few grains showing such alteration. The feldspar and olivine are rather more weathered. Hendricks and Ross (1941) reported basaltic olivine seemingly altered to or replaced by celadonite, but no cases of this were seen in the present study. The celadonite grains seen in thin section were invariably anhedral and ranged from < 50 μm to c. 3 mm diameter. All grains had irregular boundaries and some had central voids. Many grains showed zoning, being pale yellowish-green near the margins with a crystallite size too fine to be resolved by the optical

microscope, and being darker green or bluish-green towards the centre with a coarse 'speckled' appearance indicative of a larger crystallite size. There were a few cases of multiple zoning. Some grains showed creamy-white to brownish spots, particularly in the pale outer zones (fig. 1).

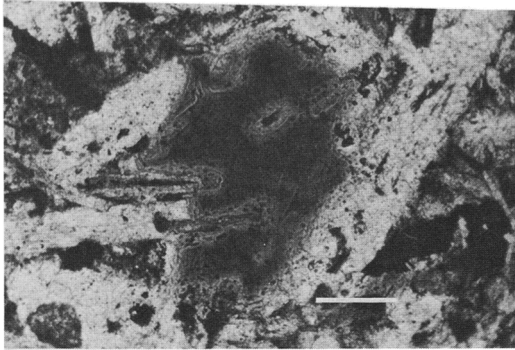


FIG. 1. Grain of celadonite showing zoning. Darker spots concentrated within the zones are thought to be a zeolite (bar = 250 μm).

Experimental

Clods of the greenish soil were steeped overnight in deionized water. The resulting suspension was sieved at 63 μm , the > 63 μm material washed several times with acetone and air dried. Uniformly dark-green grains were hand picked from this material and cleaned further by immersion in an ultrasonic bath (150 kHz) for 30 sec., and redried from acetone. The lack of brown 'staining' in these grains, attributable to iron oxides, was interpreted as evidence of little or no weathering. A representative subsample of these grains was ground for 30 min. under acetone in an agate mortar. Thin sections of the basalt were polished and carbon coated prior to electron probe analysis.

X-ray diffraction (XRD). A subsample of the ground grains was examined as a randomly oriented powder obtained by pressing material into a holder against filter paper, and as oriented Mg^{2+} -saturated specimens prepared by sedimentation of a thick paste on to glass slides. The latter samples were examined after (a) air drying, (b) exposure to ethylene glycol vapour at 80 °C for 4 hours to reveal expandable phases, and (c) heating at 335 °C for 4 hours.

Bulk chemistry. Free Fe, i.e. non-structural, was determined by extraction with dithionite-citrate-bicarbonate solution (Mehra and Jackson, 1960). Major elements other than Na were determined by X-ray fluorescence spectrometry. The latter element was determined separately by flame photometry

of an $\text{HF}/\text{H}_2\text{SO}_4$ digest, and Fe^{2+} was determined by the method of Brinkmann (1977). Cation exchange capacity was determined by ammonia distillation.

Electron probe microanalysis (EPMA). Major elements were determined in thin sections by means of an energy dispersive electron microprobe (spot diameter *c.* 5 μm , count time 80 sec.). Several points were examined in the dark-green centres and pale outer zones of several grains, as well as a few of the creamy-white to brownish spots.

Infra-red spectroscopy (IR). A sample of the ground material was incorporated in a KBr disc and the spectrum recorded between 4000 and 4200 cm^{-1} .

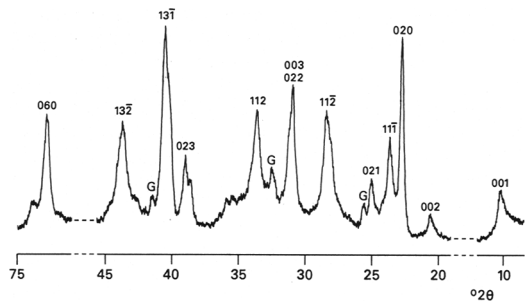


FIG. 2. XRD trace of randomly oriented powder from hand-picked material (Co radiation).

Results and discussion

X-ray diffraction. The XRD powder pattern (fig. 2) shows the sharp *hkl* reflections of a well-ordered 1M mica, although the 13 $\bar{1}$ and 130 reflections cannot be separated. This is in contrast with the type celadonite of Wise and Eugster (1964), or the example given by Buckley *et al.* (1978). Such amalgamation of these two reflections is more typical of glauconite (see, for example, Carroll, 1970), but could also be due to the presence of a more aluminous and/or K-deficient phase such as a 1M muscovite with the 130 reflection near to 2.58 Å (Yoder and Eugster, 1955), or possibly a phengite. The lack of published powder diffraction data for phengites makes this latter point speculative, but receives support from the review of the mica group by Bailey (1980). The *d*(060) spacing at 1.509 Å is very near to the celadonite-glauconite boundary (*d*(060) < > 1.51 Å respectively) proposed by Buckley *et al.* (1978).

The XRD patterns of the oriented material (fig. 3) show a strong reflection at 10 Å (air dry) with slight broadening to the low angle side, the latter disappearing on glycollation, and the former increasing sharply in intensity upon heating. Such

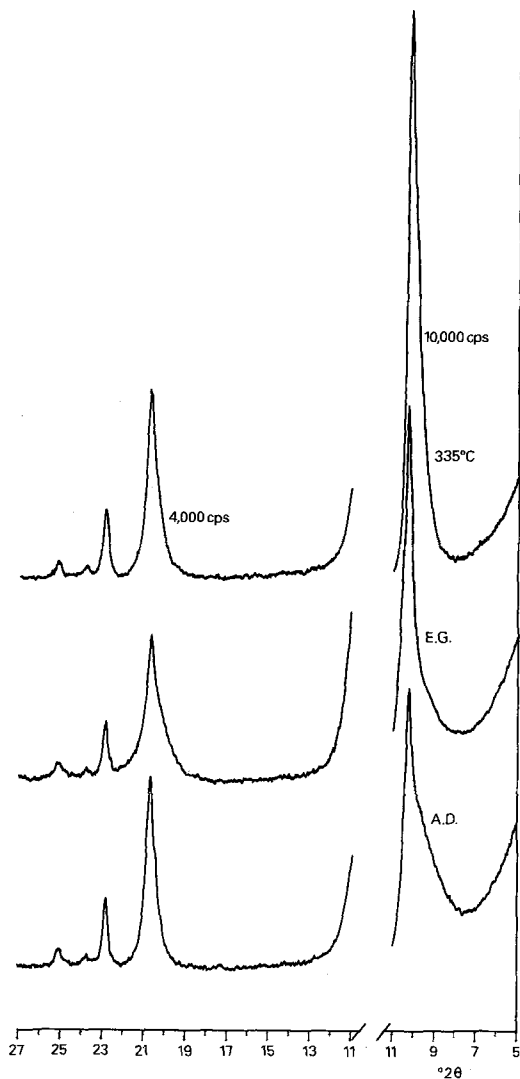


FIG. 3. XRD traces of oriented Mg^{2+} -saturated hand-picked material. (AD = air dry, EG = ethylene glycol; Co radiation).

behaviour indicates the presence of an expandible phase—probably a smectite, interstratified with the 10 Å phase. The absence of a specific series of reflections different to those attributable to the 10 Å mineral(s) and comparison with calculated diffraction profiles for glauconite-smectites (Reynolds, 1980) suggests that less than 10% of the expandible phase is present. The XRD patterns also show a strong reflection at 5 Å, which is more typical of muscovite or illite-like micas than glauconite or celadonite.

Bulk chemistry and EPMA. The chemical analyses and structural formulae are given in Table I. The calculation of the structural formula of the bulk sample was adjusted for free Fe content, and in all samples P was offset against Ca as $Ca_5(PO_4)_3(F,OH)$.

Table I. Chemical analyses and structural formulae

	A	B	C	D
SiO ₂	51.57	48.87	55.2	54.10
TiO ₂	0.11	0.12	0.16	0.12
Al ₂ O ₃	13.70	20.51	8.55	18.67
Fe ₂ O ₃	10.19	10.01	16.21	10.38
FeO	2.14	nd	nd	nd
MnO	nd	nf	nf	nf
MgO	4.50	2.63	5.58	2.84
CaO	0.52	0.16	nf	0.14
Na ₂ O	0.64	nf	nf	nf
K ₂ O	8.17	7.85	8.71	8.32
P ₂ O ₅	0.02	nf	nf	nf
LOI	8.15	nd	nd	nd
Total	99.71	90.15	94.42	94.57
CEC (mEq/100g)	14.9	nd	nd	nd
Fe ₂ O ₃	1.70	nd	nd	nd
Number of ions on the basis of 22(O,OH,F)				
Si	3.73	3.48	3.85	3.66
Al	0.27	0.52	0.15	0.34
Al	0.90	1.20	0.55	1.14
Fe ³⁺	0.46*	0.54	0.85	0.53
Fe ²⁺	0.13	-	-	-
Mg	0.48	0.28	0.58	0.29
Ti	<0.01	0.01	0.01	0.01
Ca	0.04	0.01	-	0.01
Na	0.09	-	-	-
K	0.75	0.71	0.77	0.72
$\sum R^{3+}R^{2+}$	1.97	2.03	1.99	1.97
$\sum R^{3+}$	1.36	1.75	1.41	1.68
$\sum A$	0.88	0.72	0.77	0.73

nd = not determined; nf = not found; * = corrected for free Fe₂O₃ content; A = bulk sample (by XRF); B, C = means of dark green centres of very different Al contents D = mean of pale green zones (by EPMA).

The bulk sample is more aluminous than the celadonites and glauconites of Buckley *et al.* (1978) and Weaver and Pollard (1973), but other differences in composition are small. In terms of the Fe³⁺/060 relationship the bulk sample is nearer to celadonite than glauconite, but the octahedral Al³⁺/Fe³⁺ relationship places it nearer to the

glaucanites (fig. 4). The cation exchange capacity of the bulk sample (Table I) is indicative of an expansible (smectite) layer content of *c.* 10% by comparison with data for glauconite-smectites (Manghnani and Hower, 1964)—there are no published data for celadonites. This accords with the XRD estimate of a maximum smectite content of about 10%.

The EPMA results showed that the dark-green grain centres formed two groups with large differences in Al contents. The paler grain margins also had large Al contents. These differences are clearly shown in fig. 4.

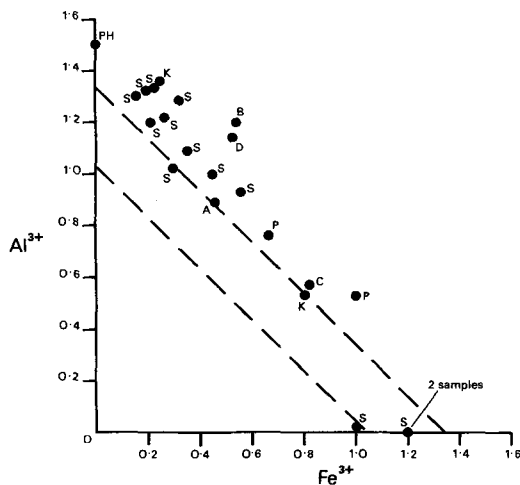


FIG. 4. Relationships between octahedral Al^{3+} and Fe^{3+} per half unit cell for celadonite in this study and Al-glaucanites from other workers. A, B, C, D as in Table I; PH = ideal phengite; S = Smulikowski, 1954; P = Pirani, 1963; K = Kautz, 1965. Dashed lines indicate average octahedral R^{3+} compositions of 1.04 for celadonites and 1.34 for glauconites (after Buckley *et al.*, 1978).

The creamy-white spots are considerably more siliceous than surrounding material and this may indicate the presence of a zeolite, although in the absence of XRD data this cannot be confirmed.

Infra-red spectroscopy. The spectrum (fig. 5) is characterized by very sharp OH stretching adsorption bands in the $3605\text{--}3530\text{ cm}^{-1}$ region, and a very sharp OH bending band at 800 cm^{-1} . These features are typical of the IR spectra of celadonites as opposed to glauconites. The spectrum is very like that of sample E of Buckley *et al.* (1978). The broad OH band centred around 3618 cm^{-1} and the broad SiO stretching bands around 1075 and 1000 cm^{-1} are indicative of the presence of an illite-like mineral.

The bulk chemistry is unequivocal and can

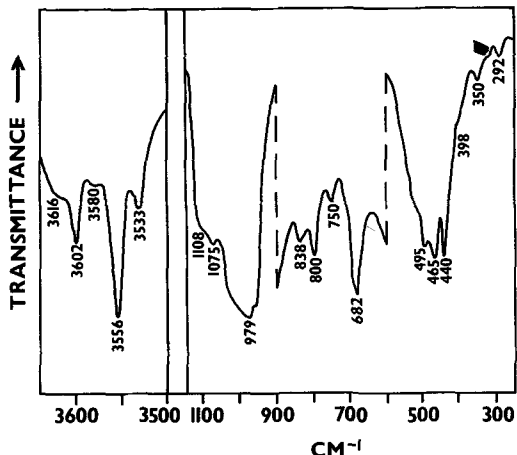


FIG. 5. Infra-red spectrum of hand-picked material.

be interpreted as celadonite or Al-glaucanite depending on which parameter is given most weight, and in this sense accords with previous reports of Al-glaucanites, the compositions of several of which are plotted in fig. 4. The EPMA results reveal considerable variation in composition among the grains, and even the least aluminous fragments have a composition nearer to glauconite than celadonite in terms of octahedral $\text{Fe}^{3+}/\text{Al}^{3+}$. Simple proportionation of the octahedral R^{3+} contents in terms of an idealized phengite ($R^{3+} = 1.5$) (Bailey, 1980) and celadonite ($R^{3+} = 1.04$) would give sample C in this study (Table I), i.e. that with the smallest octahedral Al content by EPMA, a composition of approximately 75% phengite and 25% celadonite. This phengite content is thought to be too large particularly as no allowance has been made for the probable presence of aluminous smectite layers. Similar calculations in relation to sample C based on Al_2O_3 contents of 30.3, 26.4, and 3.5% for muscovite (Deer *et al.*, 1962), illite (Weaver and Pollard, 1973), and celadonite (Buckley *et al.*, 1978) respectively, give celadonite contents between 75 and 80%.

The mineral under discussion is undoubtedly a mixture. The IR and XRD evidence suggests celadonite, another—more aluminous— 10 \AA mica and a small amount of a smectite. The 10 \AA mica is difficult to identify with certainty, but the evidence suggests that an illite or muscovite is most likely, although a phengite cannot be discounted entirely. These minerals may exist either as separate phases, i.e. as a simple physical mixture, in domains smaller than the area examined by the electron probe beam, or as two- or three-component interstratifications. The XRD results indicate quite strongly

that a randomly interstratified smectite-mica is present, but the identity of the mica cannot be stated with certainty.

The data in this paper suggest that many of the reports of Al-glaucconites could be of celadonite-aluminous-mica mixtures, and the re-examination of such materials by a wider range of methods than was readily available at the time could be worthwhile, as, for example, was done for skolite by Wiewióra *et al.* (1979). The formation of the present occurrence of celadonite is probably by crystallization at a late stage of the basalt intrusion.

Finally, it is worth recording that Thomas (1928) [In Eastwood *et al.*, 1968] reported chlorophaeite in these lavas close to the area of the work reported in this paper. Examination of Thomas's thin sections showed that the present mineral and chlorophaeite are quite different.

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