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What was hydrophilite?

HYDROPHILITE was described by J. F. L. Hausmann (Handb. Mineral. (1813), 857) as a coating on gypsum from the Lüneburg boracite deposit; he states that its constituents are calcium chloride and water, and that it is hygroscopic, deliquescent, very soluble in water, soluble in alcohol, and has an intensely bitter taste. Few authors have mentioned it; it does not appear in the first three editions of Dana's System, but in the 4th (p. 506) and 5th (App. II, p. 29) it appears as chloride of calcium. In the 6th edition, 1892, p. 161, it is equated with Scacchi's chlorocalcite, formulated $CaCl_2$ (ignoring the water mentioned by Hausmann), and adopted as the species name. In the 7th edn. (2, 41) it appears as a doubtful chloride of calcium, with several additional localities besides Lüneburg, and the comment that it was possibly chlorocalcite, now formulated $KCaCl_3$: this it certainly was not, for $KCaCl_3$ is decomposed by alcohol, with separation of insoluble KCl, and Hausmann specifically mentions solubility in alcohol. Hydrophilite was evidently one of the several hydrates of $CaCl_2$, and may have been an early find of antarcticite ($6H_2O$) or sinjarite ($2H_2O$), but remains undefined.

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Zoned glauconite from the Upper Greensand

CAYEUX (1906) specifically associated the alteration of glauconite grains with the formation of brown iron oxides. The process is usually thought of as proceeding from the outside of the grain inwards, and the literature abounds with references to such grains with 'iron rims'. Bentor and Kastner (1965) reported grains in which the reverse appeared to be true, i.e. a brown centre and a green rim, and referred to them as 'internally oxidized grains', but gave no further chemical or mineralogical data.

This note reports the existence of glauconite grains with green rims completely surrounding a brown centre, in the glauconitic sand of the Upper Greensand (Jukes-Browne and Hill, 1900) of the Vale of Pewsey, Wiltshire, U.K. The grains are rare, approximately one in three thousand 'normal' dark green glauconite grains. They can be observed only in thin section because whole grains are usually too optically dense for the central browning to be seen. In outline, size, and optical properties the grains resemble the bulk of their fellow glauconites being *c.* 125-250 μm in diameter, roughly spherical or ovoid, occasionally fissured and with R.I. = 1.62 (fig. 1).

Under high-power optical examination (×420) the rims are clearly optically continuous with the centre, implying that the former are not separate

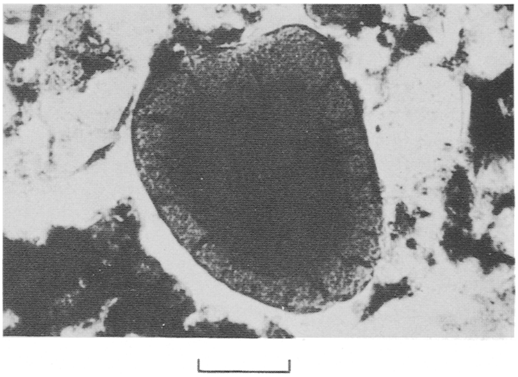

FIG. 1. Glauconite grain showing brown (dark) centre and green (lighter) rim (Bar = 250 μm).

features formed penecontemporaneously or later, as has been reported for some rim structures in glauconite grains (Zumpe, 1962; Odom, 1976). The brown coloration is removed by treatment with dithionite-citrate-bicarbonate reagent (Mehra and Jackson, 1960), indicating the presence of non-structural iron oxides. Several points in both rims and centres were analysed by energy dispersive electron microprobe and the averaged results are given in Table I. Bulk samples of glauconite were obtained by magnetic separation and analysed by X-ray fluorescence spectroscopy and again the averaged analyses are given in Table I. Ferrous iron was determined in the bulk samples by the method of Brinkmann (1977) and adjusted to an ignited basis. The extremely low values thus found were confirmed by Mössbauer spectroscopy (R. E. Meads, pers. comm.; Loveland, 1978).

Not unexpectedly the centres contain more iron than the rims. Presumably this excess is present mostly as the non-structural iron oxides removed by the dithionite-citrate-bicarbonate reagent. The most striking aspect of the bulk samples analysis is the low ferrous iron content which gives a Fe^{3+}/Fe^{2+} ratio of 45:1. This is in marked contrast to the ratio of 5:1 given both by Weaver and Pollard (1973) for sixty-nine glauconite analyses from a range of geological formations, and Buckley *et al.* (1978) for six glauconites mostly from the Gault facies of the Upper Greensand. In view of the evidence from Mössbauer spectroscopy, however, the difference in the ratios seems to be real. The analyses of rims and centres cannot be compared precisely because of the difficulty of allowing for the non-structural iron oxides. However, if the difference between the Fe_2O_3 contents of rims and centres is taken to be due to non-structural iron oxides and the analysis of the centres is adjusted to allow for this 'diluting' effect (Table I), it can be seen that the rims contain slightly more silica, alumina, potassium, and magnesium than the centres.

The structural formulae (Table I), calculated on the basis of twenty-two charges per unit half cell illustrate further the low ferrous iron contents. The marked effect of making even a notional adjustment for non-structural iron can be seen in the values of octahedral Al for the centre and adjusted centre formulae. It is interesting to note that, whilst all the structural analyses plot within the glauconite compositional field given by Weaver and Pollard (1973), the rim and adjusted centre analyses plot very close to the results of Buckley *et al.* (1978) obtained by electron microprobe, whereas the non-adjusted centre and bulk analyses plot well away from the results of the latter authors. Buckley *et al.* (1978) also comment on the fact that electron microprobe analysis seems to give consistently lower octahedral R^{3+} contents for glauconites than other forms of analysis and this work, albeit on a very small number of samples, seems to confirm this trend.

It seems unlikely that the centres of glauconite grains could be weathering before the outsides. It seems more likely that an original excess of iron over the structural requirements of the mineral has oxidized. Such an excess could conceivably arise by the following mechanism: glauconite is thought to form commonly by adsorption of potassium and iron (not necessarily together) by a poorly crystalline substrate followed by subsequent 'crystallization'. Such adsorption is believed to happen frequently inside foraminiferal tests or faecal pellets (Burst, 1958; Boyer *et al.*, 1977), i.e. where reducing conditions prevail due to the presence of decaying organic matter. Under such conditions iron would mobilize as Fe–II and presumably adsorb most strongly in the region of maximum reducing conditions, i.e. near the centre of the decaying organic matter. Subsequent 'crystallization' of the ferruginous substrate to form glauconite requires slightly

TABLE I. *Electron microprobe and bulk analyses and structural formulae**

	Rim	Centre	Adjusted centre	Bulk
SiO_2	49.51	46.12	48.87	49.56
Al_2O_3	7.40	5.81	6.16	9.60
Fe_2O_3	20.69	26.72	20.47†	20.47
FeO‡	0.47	0.47	0.47	0.47
MgO	4.06	3.85	4.08	3.86
CaO	0.19	0.23	0.24	0.86
Na_2O	0.23	0.28	0.30	0.23
K_2O	9.05	8.37	8.87	6.78
P_2O_5	0.25	0.41	0.43	n.d.
Total	91.95	92.29	89.89	91.83
Si	3.68	3.51	3.73	3.64
Al	0.32	0.49	0.27	0.36
Al	0.33	0.03	0.29	0.47
Fe^{3+}	1.16	1.53	1.18	1.13
Fe^{2+}	0.03	0.03	0.03	0.03
Mg	0.45	0.44	0.46	0.42
K	0.86	0.81	0.86	0.63
Na	0.03	0.03	0.04	0.03
ΣA	0.89	0.84	0.90	0.67
ΣR^{3+}	1.49	1.56	1.47	1.60

* Ca and P were assumed to be present as a phosphate and thus omitted from the calculation.

† Taken from the bulk analysis.

n.d. Not determined.

‡ Corrected for free Fe and Si; ignited basis.

oxidizing conditions. Thus any grains with iron in excess of structural requirements would tend to form a zone of iron oxides in the area of greatest excess, i.e. the grain centre. Whilst it may thus be reasonable to refer to such grains as 'internally oxidized', it is equally clear that such oxidation has not affected the mineral glauconite but only the adsorbed iron. The larger question as to why the glauconite in this part of this Upper Greensand facies should have such a low ferrous iron content remains unanswered. It probably points to rather unusual conditions at the time of formation, but exactly what these were is not known.

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