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Analcime from the L. Lias on the W. Somerset coast

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SUMMARY. Analcime, occurring both as small, pale-brown trapezohedral crystals and pale-brown slaggy masses, is reported growing into and replacing aragonitic shell debris in a heavily faulted, 15-km long, coastal exposure of L. Jurassic marine sediments. Associated minerals include authigenic baryte, sphalerite, pyrite (some framboidal), celestine, aragonite, calcite, dolomite, quartz, and solid hydrocarbon. No other zeolites have been found. Its modes of occurrence, crystal morphology, and relationships to these minerals are described. The analcime appears to be restricted in occurrence to the W. Somerset coast. Partial chemical analysis of one sample is given. The brown colouration is suggested to be due to organic compounds. XRD analysis of five samples reveals progressive decrease in silica content towards western extremity of the exposure. No evidence of volcanic ash contamination of the sediments is found. A hydrothermal origin is discounted; formation of the analcime by purely diagenetic processes is suggested.

THIS note records the occurrence of analcime in the L. Lias of the W. Somerset coast. From Blue Anchor point (181/039437) to Stolford Rocks in the east, a 19-km coastal section exposes a continuous but heavily faulted sequence ranging from the U. Triassic red marls to the blue-grey limestone/shale alternations of the L. Lias (semicostatum Zone). Rocks of similar age are exposed on the S. Wales coastline of the Bristol Channel, approximately 25 km to the north. Many of the faults affecting the L. Lias on the W. Somerset coast are mineralized. Minerals recorded include calcite, baryte, celestine (rare), sphalerite, pyrite, and chalcopyrite. Copper was worked in this area near Doddington (181/176401) from mineralized faults in the Trias and Old Red Sandstone (Dines, 1956).

Analcime was first discovered at Kilve beach (143444) in a sample of shelly limestone from the Kilve oil shales (Rotiforme Beds, bucklandi Zone) provided by Ms M. Milton. Subsequent work revealed the presence of analcime in beds ranging from Upper bucklandi/basal semicostatum Zone (Hinkley Point 182/214472) to lower or middle angulatum Zone (Quantoxhead beach 132441) along a 15-km coastal section. The section continues from Hinkley Point to a small outcrop in Warren Bay, about 1200 m west of Watchet Harbour.

In the majority of cases the analcime occurs as opaque pale-brown single crystals or crystal groups replacing the horny-white aragonite shells of fossils, notably ammonites. These fossils either occur singly or as accumulations of shell debris in thin (1-4 cm) discontinuous shell bands, or as patchy coatings visible on the upper surface of limestone 'dogers' within the shales. Analcime is often found associated with brown or orange sphalerite, pyrite (some framboidal), baryte, and less commonly with dolomite, celestine, quartz, and solid hydrocarbon. These minerals (the hydrocarbon excepted) appear to be authigenic and have their peak abundance within the shell bands. Analcime neither replaces nor is replaced by any of these minerals. Secondary calcite as well as pyrite, sphalerite, and to a very limited extent baryte also replace shell debris. Very small amounts of glauconite are present in the shell bands and the clays.

Growth of the analcime crystals appears to have originated at the matrix/fossil interface. Some crystals are developed from discontinuities within the shell. The fossils are invariably crushed flat. Crystal growth appears to have proceeded equally from the upper and lower surfaces or from internal and external contacts where a clay filling is present. Analcime does not appear to grow freely within the clay/limestone matrix and is only sparingly developed as freely grown crystals in the body cavities of zeolitized fossils. This is in contrast to the modes of growth exhibited by the other authigenic minerals with which it occurs.

In many specimens the analcime is present as an irregular mesh consisting of trains of crystals, grown inward, along early diagenetic fractures in the shell (fig. 1). Subsequent crystal growth within the mesh spaces leads to complete shell replacement by analcime. At Hinkley Point analcime occurs also as highly irregular brown slaggy masses (up to 3 cm longest dimension) weathering out of

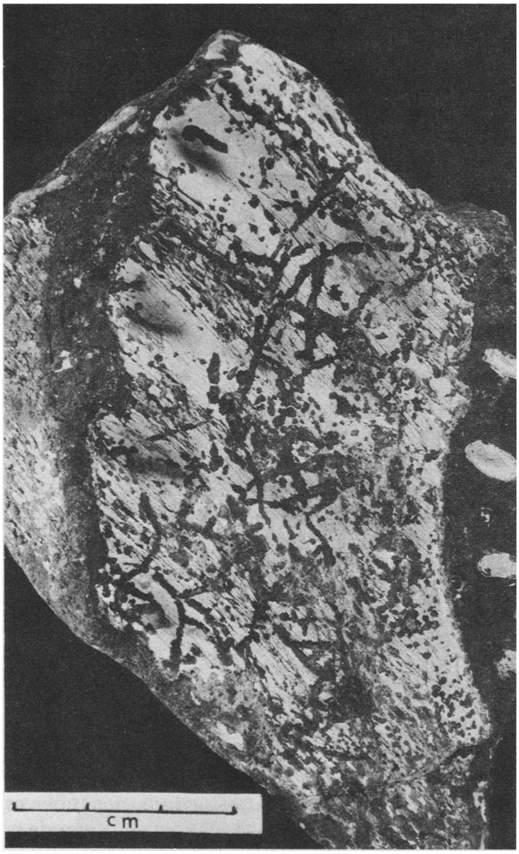


FIG. 1. Trains of analcime crystals replacing ammonite shell along fractures. Kilve.

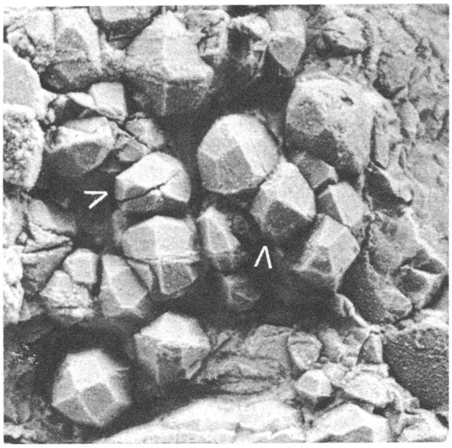
diffuse shell bands exposed in a low stack on the foreshore (209463). This 'slaggy analcime' comprises a mixture of large clasts of shell debris replaced by analcime and numerous small globular masses of analcime (usually < 0.5 mm diameter) in an analcime 'cement'. The globular masses are frequently hollow and these may show the outlines of small shells on broken surfaces. Minute gasteropods, perfectly pseudomorphed in brown analcime, and of similar size to the globular masses, occur in association with this material. In addition small euhedral, pale-brown analcime crystals are occasionally found but these are generally uncommon in the slaggy analcime. These observations suggest that much of the globular analcime represents concentrations of minute shells which have been replaced and cemented together by analcime. Water-clear analcime, which occurs both as cavity fillings and freely grown euhedral crystals, is occasionally found in the body cavities of some of the replaced shells.

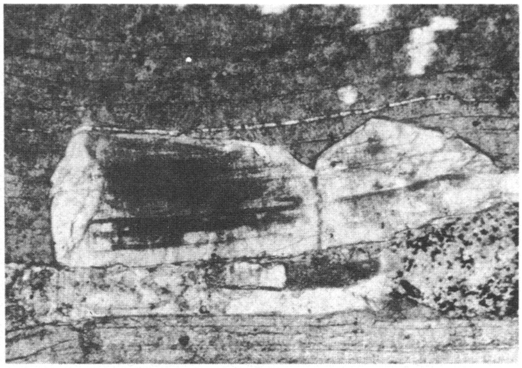
On the W. Somerset coast individual crystals attain a maximum diameter of 3 mm (Hinkley Point) with an average of about 1 mm. The majority are half crystals with the trapezohedron as the dominant form, but the cube modification is seen in some specimens (fig. 2). Stepped crystals are also developed. The surface in contact with the matrix is flat or slightly convex. Staples (1965) noted similar forms in freely grown analcime in zeolitized fossils from the Oligocene Eugene Formation, Oregon. In some cases in W. Somerset crystal growth was intermittent. The interruptions of crystal growth were very occasionally of sufficient duration to permit pyrite to develop as thin films, blebby masses, or euhedral growth on the analcime crystal surfaces. The pyrite became incorporated into the analcime when growth recommenced. Patches of shattered shell debris, subsequently replaced by analcime, are sometimes found engulfed in authigenic sphalerite. Water-clear authigenic baryte, developed in some of the large rotiforme Zone ammonites, occasionally contains analcime-bearing shell debris, pyrite crystals, and rare euhedral sphalerite.

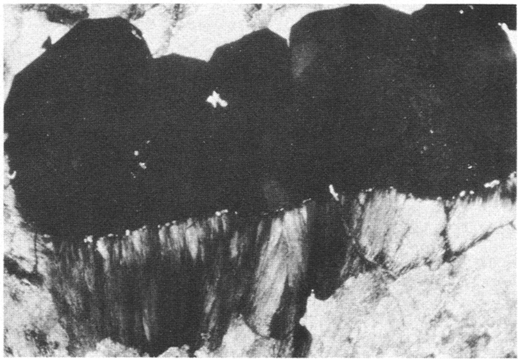
The complete crystals are much smaller, frequently colourless or else turbid white, and may be developed on the pale-brown analcime. This relationship is well displayed in the slaggy analcime at Hinkley Point. Water-clear analcime is occasionally found grading into the pale-brown variety at this locality.

Crude zoning is found in most crystals although exceptions appear to be the turbid white/colourless crystals. The zoned crystals have a lighter coloured opaque centre and a transparent dark-brown periphery. A few specimens from Quantoxhead (132441) show development of narrow growth zones parallel to the crystal boundaries. These zones appear to be due to preferential dissolution operating in certain zones in the crystal as a result of weathering. Similar features have been noted in partially altered analcime from the Lizard, Cornwall (Seager, 1978). The turbidity of the crystal centre is due to calcite inclusions. In thin section the original prismatic and lamellar shell structure is usually visible as calcite remnants in the replacing analcime (figs. 3, 4). Authigenic, fibrous aragonite, developed between the microfossils in the Hinkley Point 'slaggy analcime' has also suffered patchy replacement. In thin section the fibrous aragonite can be seen as inclusions within the pale-brown analcime (fig. 5). The replaced areas, in section, may show globular outline. This suggests that, in addition to shell replacement, some of the globular analcime may have formed by replacement of authigenic aragonite.

Alteration of analcime to halloysite, commencing along fractures in the crystals, has been noted







FIGS. 2–5. FIG. 2 (*top left*). Analcime crystals. 'V' points to crystals showing {100} × 14. Kilve. FIG. 3 (*top right*). Analcime crystals replacing shell material. Shows relict shell structure within the crystals. Plane polarized light × 60. Kilve. FIG. 4. (*bottom left*). As fig. 3, crossed polars × 40. Kilve. FIG. 5 (*bottom right*). Analcime (pale-brown variety) showing fibrous internal structure (due to fibrous aragonite inclusions) associated with isotropic, euhedral (water-clear) analcime. × 40. Crossed polars. Hinkley Point 'slaggy analcime'.

on some specimens from Quantoxhead. Elsewhere these fractures, visible in both single crystals and totally replaced shells, usually contain calcite or secondary analcime, but pyrite and occasionally baryte may also be present.

No other zeolites have been found. In view of the close association of the analcime with calcium carbonate, the Ca-analogue wairakite might be expected but none was found. A partial chemical analysis of a sample from Hinkley Point (basal semicostatum Zone) gave the following: SiO_2 50.3 %; Al_2O_3 19.65; Na_2O 11.22; CaO 4.77; H_2O 7.47; CO_2 (carbonate only) 2.27; total carbon 1.23 %; total H 0.89 %; sulphur 0.59 %. No iron was detected. Assuming that all the CO_2 was derived from $CaCO_3$, a maximum of 5.15 % $CaCO_3$ is present, leaving a residue of 1.89 % CaO and 0.62 % C. This result, coupled with a partial chemical analysis of analcime from Kilve, and X-ray powder photographs of Kilve and Hinkley Point (basal semicostatum Zone) analcime suggest that calcium substitution for sodium is occurring only on a very limited scale. Recalculating total H as H_2O leaves a residue of 0.07 % H. The carbon and hydrogen residues, high sulphur content, and the appearance of an oily scum during acid digestion of the analcime suggest the presence of organic compounds. The lack of iron suggests that these may be responsible for the brown colouration. Na, Al, Ca were determined by atomic absorption; silicon colourimetrically; iron by XRF; C, H by Perkin-Elmer CHN elemental analyser; sulphur, CO_2 titrimetric; H_2O absorptiometric.

In order to check for any compositional variations in the analcime, five samples (Hinkley Point; slaggy analcime; Kilve beach; Quantoxhead;

Warren Bay) were analysed, using the back reflection XRD method of Saha (1959). Silicon is used as an internal standard. The value of $\Delta 2\theta$ analcime$_{639}$-$\Delta 2\theta$ silicon$_{331}$ increases with increasing silica content. The values obtained, respectively, 1.887, 1.876, 1.873, 1.873, 1.864, suggest a progressive decrease in silica content towards the western extremity of the coastal section.

No analcime has been found in rocks of similar age on the S. Wales coast, in the Bristol-Mendip region, or in the coastal exposures of the L. Lias (U. bucklandi/L. semicostatum Zones) at Hock Cliff near Gloucester. No analcime was found during examination of beds of Rhaetic-Lias (turneri Zone) on the Dorset coast *c.*60 km SSE of the area under study. Inland exposures of the L. Lias in the south-west of England are few, but inspection of the available sites supplemented by examination of ammonites (planorbis-semicostatum Zones) in the extensive collections of the Bristol City Museum produced no positive results. This would suggest that the analcime development in the L. Lias is a local phenomenon, restricted to the W. Somerset area.

The authigenic sulphides and baryte have a much more extensive lateral and vertical distribution. On the W. Somerset coast they occur throughout the Rhaetic and L. Lias. Authigenic galena (Wobber, 1965) occurs in considerable amounts in the near-shore facies of the L. Lias along the S. Wales coast. Pyrite $\pm$ baryte $\pm$ sphalerite has been noted on many L. Lias fossils from various localities in Gloucestershire, Avon, and Somerset. They also occur lining cracks in septarian nodules near Lyme Regis (L. Lias) and in the internal cavities of flattened white aragonitic ammonites in the bituminous shales near Kimmeridge (U. Jurassic).

The total stratigraphic range of the analcime could not be determined with certainty, since erosion has removed all beds younger than the U. semicostatum Zone (Palmer, 1972) in the immediate area of the occurrence. Analcime appears to be absent from the Trias, Rhaetic, and planorbis Zone succession. Abundant white aragonitic ammonites ('Arietitid bed'—Palmer, 1972—Mid semicostatum Zone) occurs in Donniford Bay (079432) near Watchet. Analcime is not present, although the circumstances appear to be in all respects identical to those obtaining in the case of the analcime-bearing ammonites. These 'Arietitid bed' fossils locally contain abundant water-clear baryte and minor sphalerite. Examination of ammonites representative of higher Lias zones in the Gloucestershire, Avon, and Somerset region proved negative. The absence of analcime from the 'Arietitid bed' could be taken as indicating a M. semicostatum Zone upper limit to its occurrence.

The heavy faulting which affects the Lias in this area seems to have no influence on the concentration or distribution of analcime. In many cases where zeolites occur in sediments they have arisen as a result of alteration of volcanic detritus. Examination of thin sections of the limestone bands in which analcime is developed revealed no glass shards (cf. Jeans *et al.*, 1977) or any other evidence to suggest contamination by volcanic debris.

A preliminary XRD analysis of the clays proved inconclusive. Samples from Rhaetic-semicostatum Zone were examined. Samples adjacent to analcime-bearing ammonites in mid angulatum, bucklandi, and lower semicostatum Zones were also analysed, and the results compared with data from a sample taken at Hock Cliff. All specimens showed similar clay mineralogy, comprising a major proportion of illite and variable amounts of chlorite and kaolinite. The illite is interlayered with an expanding clay, the identity of which could not be established. No discrete smectite phase was detected.

The lack of evidence of contamination of these sediments by volcanic dust weighs against a volcanic origin for the analcime. The absence of analcime from the Trias, Rhaetic, and planorbis Zone sequence argues against hydrothermal origin. So, too, does the lack of any evidence of faults having had an influence on distribution. Analcime and the associated minerals can all occur purely diagenetically without any thermal influence. A diagenetic origin for this occurrence is thus tentatively suggested. On this basis the observed restriction of this assemblage to the W. Somerset area may be the result of a favourable combination of permeability, pH, and salinity during the early diagenetic history of these sediments.

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