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Formation of analcime in the Dippin sill, Isle of Arran

THE Dippin sill is a Tertiary differentiated basic intrusion, 43 m thick, occurring in the SE. part of the Isle of Arran, Scotland. The sill is composed of different varieties of analcime olivine dolerite, particularly crinanite in which the analcime occurs most commonly as clear, wedge-shapes in the interstices between plagioclase laths. The interstitial analcime is characterized by low SiO_2 and Na_2O and high CaO (e.g. $\text{Ne}_{66.4}\text{Ks}_{0.2}\text{Qz}_{24.3}\text{An}_{9.1}$, wt%) and is occasionally associated with small (< 0.1 mm) nepheline grains, which are comparatively SiO_2 -rich (e.g. $\text{Ne}_{73.4}\text{Ks}_{8.1}\text{Qz}_{16.9}\text{An}_{1.6}$). Analcime also occurs along innumerable small cracks in plagioclase and as a major constituent of large patches, up to 1 cm across, in which it may be associated with brown fibrous natrolite and radiating aggregates of other zeolites. Rocks from the chilled margins of the sill are characteristically rich in lath-shaped analcime pseudomorphs (after plagioclase) and the analcime-bearing patches; the abundances of both decrease inwards from the contacts.

There can be little doubt that the analcime present as pseudomorphs and that in the patches was formed by the action of hydrothermal solutions at subsolidus temperatures. However, the origin of the wedge-shaped, interstitial analcime is more problematical. Many petrologists have interpreted the textural relations as being indicative of a late-stage 'primary' mineral, i.e. crystallized from the melt (e.g. Scott, 1916; Tyrrell, 1928; Harker, 1954, fig. 45b; Wilkinson, 1958). However, the analcime stability curve at low pressures in the system Ne-Ab- H_2O (Greenwood, 1961; Kim and Burley, 1971) lies well below the solidus for an alkaline olivine basalt and below the nepheline-alkali-feldspar minimum melting curve (fig. 1). Indeed, Roux and Hamilton (1976) showed that in the Ne-Ab- H_2O and Ne-Or-Ks- H_2O systems the assemblage analcime plus melt occurs only at pressures between 5 and 13 kb and between 640° and 600°C . Geological evidence suggests that the Dippin sill is unlikely to have been emplaced at a depth of more than 3 km below the contemporary surface, in which case it is likely to have crystallized at a confining pressure of less than 1 kb. Thus the interstitial analcime must be secondary unless its comparatively high Ca content has substantially increased its thermal stability (Roux and Hamilton, 1976). We have tested this possibility by carrying out experiments on a fresh crinanite sample (AC 649) in which the bulk of the analcime is of the interstitial variety.

Rock powder and glass made from this by melting at 1200°C for 15 hours at a log P_{O_2} of -6.4 and a pressure of 1 bar were used as starting materials in the experiments. Samples of each were sealed with excess water in separate gold capsules and were crystallized at pressures from 0.5 to 2.0 kb for 4-6 days; no attempt was made to buffer the P_{O_2} . The presence of analcime in the

products was established by X-ray diffraction methods. The temperatures above which analcime did not grow in the glass and above which analcime disappeared from the rock powder show good agreement. The results, summarized in fig. 1, show that there is little variation in the analcime thermal stability in the pressure range investigated. The most significant result is that the stability of the Ca-rich analcime in the basic rocks is much reduced relative to that for Ca-free analcime in the Ne-Ab system (e.g. at 1 kb the reaction temperatures are 380° and 520°C respectively). Thus the interstitial analcime could only have formed by alteration of pre-existing primary Na-rich phases at subsolidus temperatures.

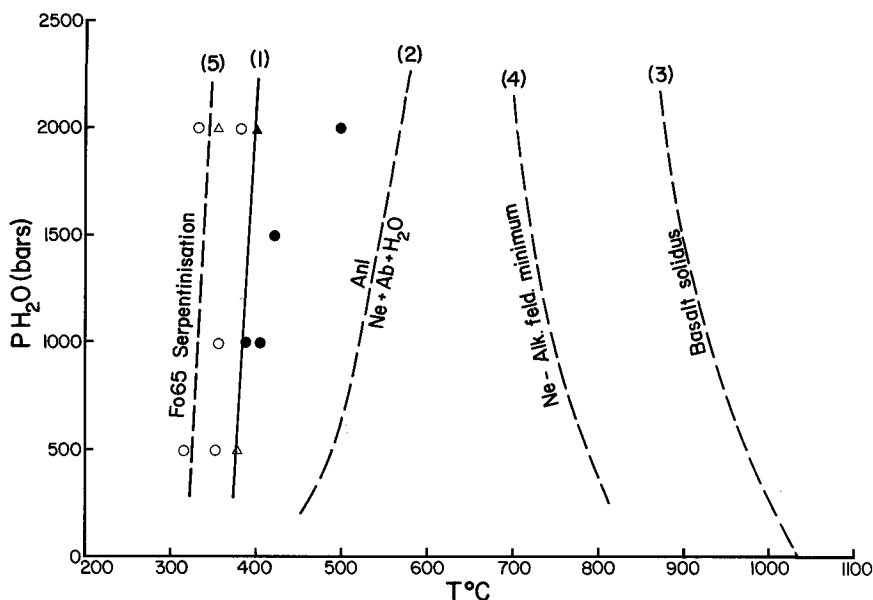


FIG. 1. The stability of analcime in Dippin crinanite AC 649. Symbols: ○ analcime present in run products for both rock powder and glass-starting materials; ● analcime absent for both rock powder and glass; △ analcime present for rock powder, absent for glass; ▲ analcime absent for rock powder, present for glass. Curves: (1) reaction boundary determined for AC 649. (2) Reaction boundary for analcime \rightleftharpoons nepheline + albite + H₂O (Greenwood, 1961). (3) Solidus for alkaline olivine basalt (Yoder and Tilley, 1962). (4) Silica-undersaturated minimum melting in the system Ne-Ks-Qz (Hamilton and MacKenzie, 1965; Taylor, 1966). (5) Calculated conditions for serpentinization of olivine of composition Fo₆₅.

Compositional relations across analcime-plagioclase interfaces were studied in crinanite AC 649 using the electron microprobe and three main types of interface were identified. The commonest type has a plagioclase crystal with an unzoned or slightly zoned core (e.g. An₆₅, mol. %) and an outer part that is continuously zoned to a comparatively sodic composition (e.g. An₃₀) at the edge of the crystal that is in sharp contact with a homogeneous analcime crystal. A less common type of interface is where a homogeneous or slightly zoned plagioclase crystal (e.g. An₆₀) is in sharp contact with analcime. An even less common relationship is where a plagioclase core (e.g. An₆₀) is surrounded by a narrow homogeneous zone of more sodic plagioclase (e.g. An₄₅), which is in turn in sharp contact with analcime. Crinanite AC 649 is from the middle of the sill but similar plagioclase-analcime relations occur throughout the whole intrusion, the only difference being in the actual composition of the feldspar. Such relations suggest that the plagioclase crystals have played little part in the formation of the interstitial analcime.

The small nepheline grains occurring in some Dippin sill crinanites are apparently remnants of larger areas that have been substantially replaced by analcime. We have also found nepheline and alkali feldspar, replaced by analcime and zeolites, in the mesostasis of a similar crinanite from the Permo-Carboniferous Howford Bridge sill, Ayr (Tyrrell, 1928). The interstitial analcime and nepheline in the Dippin sill crinanites contain acicular inclusions of apatite and it seems that apatite is a common constituent of the mesostasis of alkalic basic rocks (Tyrrell, 1928; Wilkinson, 1958, 1962). This suggests that the final product of magmatic crystallization in such rocks was interstitial alkali feldspar, nepheline, and apatite. It seems likely that in the presence of water vapour the nepheline and alkali feldspar reacted to form analcime and in many crinanites and teschenites this reaction must have gone virtually to completion. In the Dippin sill the reaction may have been further facilitated by the SiO_2 -rich nepheline being particularly unstable.

The formation of interstitial analcime must have been almost complete before the onset of serpentinization, as many of the Dippin sill crinanites contain olivine that is only slightly serpentinized. Johannes (1968) showed that the reaction: forsterite + $\text{H}_2\text{O} \rightleftharpoons$ serpentine + brucite occurs at 360°C at 1 kb $P_{\text{H}_2\text{O}}$. We have used Johannes' data to calculate a temperature of 330°C for the serpentinization of olivine of composition Fo_{65} at 1 kb $P_{\text{H}_2\text{O}}$ (fig. 1) by assuming an average mole fraction of 0.8 for Mg in serpentine and brucite. Johannes (1969) also showed that the temperature for the pure-Mg reaction is reduced by a few degrees at 1 kb for a fluid containing up to 0.005 mole fraction CO_2 (X_{CO_2}). Magnesite forms rather than brucite for fluids richer in CO_2 and the forsterite-serpentine reaction temperature is substantially increased (e.g. to about 480°C at 1 kb, $X_{\text{CO}_2} = 0.08$). We conclude that the interstitial analcime in the Dippin sill crinanites formed between 380° and 330°C at a pressure of less than 1 kb due to the activity of a hydrothermal fluid that was poor in CO_2 . The analcime in the patches may have formed at even lower temperatures as suggested by its association with natrolite (e.g. $< 300^\circ\text{C}$, Sand *et al.*, 1957; Saha, 1961).

The analcime formation process may not have been isochemical because of introduction or removal of Na and Si (and possibly other elements) during the circulation of hydrothermal fluids within the sill. These solutions may have been responsible for forming some of the more albite-rich rims on plagioclase crystals.

It is interesting to speculate on the source of the water causing the alteration. Experiments with the crinanite sample between 700° and 1020°C in the presence of an aqueous vapour phase at 1 kb produced substantial amounts of amphibole, especially for the glass-starting material. Except for the presence of a little riebeckite in some pegmatitic rocks the Dippin sill is amphibole-free. Thus the crinanite magma must initially have been strongly undersaturated in water with the build-up of magmatic water only becoming significant very late in the crystallization process. At this stage substantial amounts of meteoric water from the sedimentary rocks may have entered the sill; this would account for the margins of the sill being more extensively altered than the inner parts.

The sediments above and below the sill show only limited effects of thermal metamorphism with induration sometimes being restricted to a zone as little as 10 cm thick. This could be consistent with intrusion of comparatively dry magma into wet sediments. Assuming that the magma was intruded at a temperature greater than 1100°C at a pressure of (say) 500 bars the water in the sediments would have been converted to a super-critical fluid. Consumption of heat in this way cooled the magma so forming the chilled margins of the sill. The super-critical fluid may have formed an envelope around the hot intrusion and acted as a medium for rapidly removing heat thus limiting the amount of thermal metamorphism in the country rocks. Significant amounts of fluid are unlikely to have entered the magma at this stage because of the

very great contrast in their viscosities and the slow diffusion rates of H₂O in silicate melts (Burnham, 1967). Thus the main influx of water from the sediments most likely occurred following fracturing in the crinanites when the sill was substantially consolidated.

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Piemontite schists from Upper Swat, north-west Pakistan

PIEMONTE schists occur near to the contact between the Palaeozoic Lower-Swat-Buner schistose group and the epidote amphibolites of the Kohistan basic complex, located about 7 km east of Khwaza Khela (34° 55' N., 72° 28' E.), NW. Pakistan. Glaucofanite schists, serpentinites, alpine ultramafites, and garnet gneisses have been previously reported along or near to this contact, which is probably a regional thrust fault. The piemontite schist horizon is at least a few hundred metres long and more than 10 m broad, and was previously described as tourmaline schist by Shah and Kahn (1971), without mention of the piemontite or other manganese-rich minerals present. The piemontite schists are associated with greenschists, calcareous schists, and quartz-mica schists of the Lower-Swat-Buner schistose group described by Martin *et al.* (1962). Epidote amphibolites are exposed about ½ km to the north of the piemontite schists, while some glaucofanite schists and serpentinites occurring within the schistose group occur a few kilometres to the east.