MINERALOGICAL MAGAZINE, DECEMBER 1984, VOL. 48, PP. 519-27

The paragenesis of contrasting habits of calcite and aragonite-calcite associations from Kulnura, New South Wales, Australia

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ABSTRACT. Fine radiating groups of columnar aragonite crystals occur in a basaltic pipe at Kulnura, New South Wales, associated with calcite in habits varying from simple rhombohedra to complex spherulitic groups. It is proposed that the presence of impurities, especially magnesium, induced the crystallization of aragonite and was also responsible for the variety of calcite crystal habits present. Two distinct growth environments are indicated: steam-explosion breccia pipes containing aragonite and calcite showing an advanced stage of spherulitic growth; and vesicles with calcite in varying stages of spherulitic growth. This paper presents a preliminary study based on available material and on observations made *in situ* while access to the locality was still possible.

A TERTIARY volcanic neck is being quarried by Hymix Quarries Pty. Ltd. at Kulnura, near Gosford on the central coast of New South Wales. Fine specimens of aragonite and calcite, the latter occurring in a variety of crystal habits, have been recovered from the quarry. These pose some interesting problems in crystallization and paragenesis. Unfortunately detailed study of the occurrence was brought to a sudden halt by the closure of the quarry to all visitors in 1977.

Based on a preliminary study of the occurrence by the author prior to the closure, mechanisms to explain some aspects of the origin of the mineralisation, and paragenesis of the carbonate minerals are proposed. However, many questions remain unanswered and further research is required.

Geology and occurrence of the carbonates

The quarry is worked in a small intrusion of basaltic rock (Bryan *et al.*, 1966) which is brecciated in part. Towards the centre of the intrusion a series of steam explosion breccia pipes occur enclosed by zones of strongly altered vesicular basalt. The carbonates are found in the vesicular basalt and between large blocks of vesicular basalt in the steam explosion breccia pipes (fig. 1). The aragonite appears to be confined to the breccia pipes, while the calcite occurs in vesicles up to 70 cm in diameter in the vesicular basalt zones.

Source of the mineralization and formation of the carbonates

The vesicular basalt in the vicinity of the carbonate mineralization is strongly altered to a sectile mixture of major nontronite and massive analcime, with subordinate montmorillonite and minor pumpellyite, as indicated by X-ray diffraction. There is also a considerable amount of disordered material, which is presumed to be altered pumpellyite. Alteration is so extensive that thin sections of the rock appear almost completely isotropic in polarised light, although scanning electron microscopy (SEM) of polished sections shows the morphology of the original minerals has been largely preserved. Vesicles in this altered basalt are lined by spongy botryoidal crusts of blue-grey pumpellyite, on which the carbonates have crystallized, backed by a mixture of nontronite, massive analcime and montmorillonite. The pumpellyite structure has been disordered by strong leaching rendering it difficult to confirm by X-ray diffraction. Its identification is based on chemical analysis, the stoichiometry of the Kulnura material agreeing closely with that given by Fleischer (1983), with the exception of a severe depletion in calcium (0.5% CaO) and the presence of 4.5% FeO.

The extent and nature of the alteration and the presence of steam-explosion breccia pipes strongly suggests that hydrothermal alteration and leaching accompanied intrusion of the basalt. A bulk analysis of the altered basalt and analyses of its component phases shows considerable overall depletion of Ca and a general enrichment in Mg, also suggestive of early hydrothermal activity within the intrusion.

Although largely depleted by hydrothermal

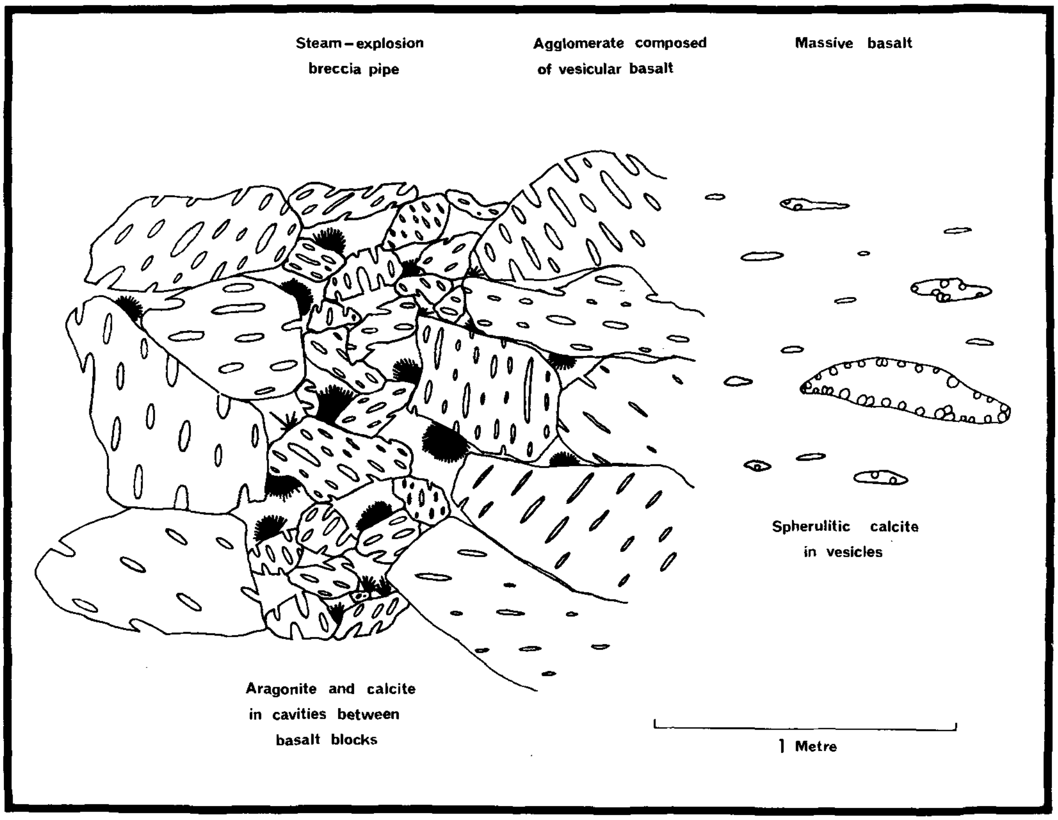

FIG. 1. Diagrammatic representation of the aragonite-calcite occurrence at Kulnura, NSW.

leaching, sufficient Ca would have become available for crystallization of the observed carbonates by later groundwater leaching of the altered basalt. The relatively low availability of Ca explains the fact that, while spectacular, carbonate crystallization at Kulnura is not abundant. In both the breccia pipes and the vesicles, carbonate crystals occur only as scattered individuals and/or groups and rarely are the cavity walls completely blanketed by crystal growths. In the vesicle environment only occasional vesicles contain crystals.

The low Ca and relatively high Mg content of the altered basalt as a whole would have resulted in high $Mg^{2+}:Ca^{2+}$ ratios in late-stage (post-alteration) mineralizing groundwater, assuming groundwater chemistry reflected that of the rock through which it migrated. Undoubtedly, this high $Mg^{2+}:Ca^{2+}$ ratio was a major factor influencing aragonite and/or calcite crystallization at Kulnura.

Analyses of the remnant phases in the altered basalt indicate that the Mg source may have been both Mg-rich magnetite and forsteritic olivine, suggesting that the original basaltic rock itself may have been Mg-rich. However, the Mg may have been introduced by the hydrothermal activity which appears to have accompanied the intrusion of the basalt.

Percolating groundwater containing CO_2 in solution would have provided a ready source of carbonate ions once the intrusion became accessible to surface waters. There is no evidence to suggest that carbonate ions were introduced during hydrothermal alteration. The presence of carbonated groundwater together with readily leachable Ca^{2+} resulted in the formation of the calcium carbonate species through the reaction:

$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_3 + H_2CO_3.$$

Changes in pH, temperature, and concentration of products and reactants will affect this equilibrium condition (Krauskopf, 1967).

Aragonite paragenesis

The problems associated with the crystallization of aragonite are complex and still not fully understood. Only occasionally does aragonite occur as a deuteric (secondary) mineral in basic volcanic rocks (Deer *et al.*, 1962). Although the stability fields for both aragonite and calcite are quite wide (Deer *et al.*, 1962, fig. 57), the P-T conditions under which secondary minerals form in volcanic rocks fall outside the stability field for aragonite, i.e. within the calcite field. Hence aragonite is uncommon in this environment, or, when it does occur, is metastable and reverts slowly to calcite. It is the stable form of $CaCO_3$ only at high pressures (4 kbar between 50 and 80 °C; Deer *et al.*, 1962, fig. 57), pressures which are unlikely to be found in the surface or near-surface environment in which the Kulnura aragonite appears to have formed. The occurrence of aragonite at Kulnura, and many similar localities, therefore presents a somewhat enigmatic problem.

Previous investigations. A few observations made by various authors may provide some indication of the paragenesis:

First, whether calcite or aragonite crystallizes may depend on the reaction or deposition rate; the metastable form being able to crystallize more quickly and hence be favoured by the more rapid precipitation of $CaCO_3$ (Krauskopf, 1967). Aragonite formation is also favoured by a high degree of supersaturation and higher temperatures (Kitano *et al.*, 1962; Kitano and Hood, 1965). Under less forced growth conditions calcite should result (Folk, 1974).

Secondly, Deer *et al.* report that aragonite crystallization is induced by the presence of impurities such as Sr, Mg, Ba, Pb, Fe, $CaSO_4$, etc. in the mineralizing solutions. Of these, Mg appears to be the principal element affecting $CaCO_3$ crystallization and, as reported by Folk (1974) and others, its introduction into the growth environment in large amounts will cause aragonite to crystallize in preference to calcite.

The effect of Mg^{2+} on the structure of both calcite and aragonite has been studied in detail by Leitmeier (1910, 1915) and Folk (1974). In both species its presence has a 'poisoning' effect on lateral crystal growth, resulting in elongated and even acicular forms. This is brought about by the smaller size of the Mg^{2+} ion (1.60×10^{-10} m) in relation to Ca^{2+} (1.97×10^{-10} m). The distortion produced by this substitution may indeed favour the formation of the orthorhombic aragonite crystal lattice, which can more easily accommodate these impurity ions (Folk, 1974).

Thus, if the $Mg^{2+}:Ca^{2+}$ ratio in the mineralizing solution is over a certain value (which varies with the temperature and other conditions) the $CaCO_3$ present will form aragonite, simply because of the difficulty associated with the formation of the calcite structure in Mg-rich environments (Lippman, 1960), which includes the vicinity of basic igneous rocks (Leitmeier, 1910, 1915).

Discussion. No evidence is available from the Kulnura occurrence to lend any direct support to the proposals made by Krauskopf and Kitano *et al.* However, electron probe micro analysis (EPMA) of carefully selected clean crystals of both the aragonite and calcite forms (Table I) indicate that the presence of impurity elements, in particular Mg, may indeed have had some controlling effect on the crystallization of these carbonates at Kulnura. The presence of Fe^{2+} may have also acted in forcing aragonite crystallization, reinforcing the effect of magnesium. Levels of other impurities mentioned by Deer *et al.* were not significant and in fact fell below the limits of detection for EPMA.

TABLE I. Electron probe microanalysis of aragonite and various calcite crystal habits from Kulnura, N.S.W.

Specimen type	$MgCO_3$	$FeCO_3$	$CaCO_3$
Aragonite	2.7 0.1	0.8 0.1	96.5 98.9
Rhombohedral calcite as in Figure 5	0.1 0.2	0.1 0.2	99.9 99.5
Intermediate stage spherulitic calcite as in Figure 9	0.3 0.3	0.6 1.0	99.1 98.5
Advanced spherulitic calcite as in Figure 2	2.6 0.8	0.4 0.3	96.9 98.8

Substitution of Mg^{2+} for Ca^{2+} appears to be very limited (Deer *et al.*, 1962) and the relatively high Mg^{2+} (0.87 %) in Kulnura aragonite indicates a quite substantial $Mg^{2+}:Ca^{2+}$ ratio in the growth environment. Of the published analyses, only aragonite from a serpentinite environment in Sizvoka Prefecture, Japan (Deer *et al.*, 1962) shows a higher Mg^{2+} level (3.06 %).

The large variation in $MgCO_3$ obtained on different parts of the crystals may be due in part to unmixing and gradual expulsion of Mg^{2+} during or soon after growth of the crystals. Wray and Daniels (1957) and Folk (1974) state that under conditions of slow crystallization, which the size and perfection of the Kulnura crystals would indicate, Mg^{2+} is expelled from the structure, resulting in a gradual reversion to calcite. Energy-dispersive X-ray line scans across Kulnura aragonite crystals show a distinct edge depletion in Mg, which may indicate that reversion of at least some of the crystals is about to occur, and that the aragonite may be geologically recent in orgin.

On the other hand, Deer *et al.* state that MacDonald (1956) has shown by thermodynamical calculations that it is very unlikely that the levels of Pb, Sr, Zn (and presumably Mg and Fe) found in natural aragonites are sufficient to stabilize aragonite relative to calcite. If this is true, there would be no relationship between aragonite reversion and the loss of Mg^{2+} from the structure. Without any stabilizing effect produced by these impurities, reversion would have begun much sooner and so a fairly recent origin for the Kulnura carbonates is again indicated, since there is no obvious sign of reversion to calcite (such as the appearance of a rhombohedral cleavage or lowering of S.G.).

Although it may appear likely that the aragonite at Kulnura crystallized in the latter stages of the hydrothermal episode, geothermal data and the lack of any sign of aragonite to calcite reversion seem to preclude this possibility. Brown *et al.* (1962) state that: 'The experimental data indicate that in wet rocks with an open pore system . . .', which would approximate conditions in a breccia pipe, '. . . aragonite could survive near the surface for 100 000 years at 50 °C and for a few million years at 10 °C.' According to the experiments of Brown, *et al.*, for aragonite to survive it would require a geothermal gradient of less than 10 °C per kilometre. While it is not possible to ascertain even an approximate age for the mineralization at Kulnura, the above findings point towards a relatively recent origin. Certainly the carbonates were deposited some considerable time after cooling of the intrusive body, otherwise the aragonite would have formed in the presence of a higher than normal geothermal gradient and longer ground temperature retention times, which would have resulted in very rapid reversion to calcite.

At least one major question remains unanswered in regard to the Kulnura occurrence. If a high $Mg^{2+}:Ca^{2+}$ ratio provided favourable conditions for aragonite to develop in preference to calcite, why is not all the carbonate mineralization in the form of aragonite?

Although further on site research is required before this problem can be solved conclusively, the following hypothesis is presented in an attempt to explain the phenomenon.

The breccia pipes, to which the aragonite appears to be confined, would have provided ready access to migrating groundwater containing impurity elements leached from the overlying basalt, as well as from external sources. It is therefore quite feasible that an environment of this type could have allowed a very high $Mg^{2+}:Ca^{2+}$ ratio to develop in the growth area; a ratio considerably above the present value of 2.5:1 indicated by bulk analysis of the altered basalt. This situation would not necessarily have resulted in a higher ion concentration (which would have slowed aragonite crystallization; Wray and Daniels, 1957), since the pipes acted as open channelways in which there would have been little or no opportunity for permanent storage of solution and hence negligible build-up of ion concentration.

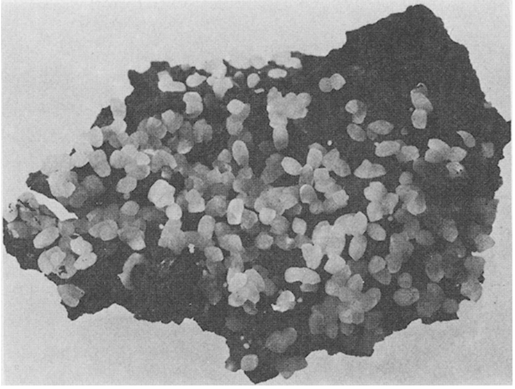

FIG. 2. Advanced spherulitic calcite, found in direct association with aragonite in steam explosion breccia pipes at Kulnura. Specimen is 6 cm in diameter.

The direct association of calcite in an advanced spherulitic form (fig. 2) with the aragonite indicates a quite significant change in environment, a change which allowed a more recent calcite stage to develop. This most likely took the form of a distinct lowering of the local $Mg^{2+}:Ca^{2+}$ ratio, although a relatively high level of Mg must still have been present to have produced advanced spherulitic growth. This is confirmed by an analysis of this calcite, shown in Table I. In all specimens examined by the author, the calcite is more recent in origin than the aragonite. Change in the $Mg^{2+}:Ca^{2+}$ ratio may have been the result of a limited short-term abundance of Mg in the mineralizing groundwater. Alternatively, once groundwater flow had ceased, further nutrients for crystal growth would have had to be drawn from the altered basalt of the immediate walls of the cavity by groundwater seepage. Although analysis of the altered basalt shows that a high $Mg^{2+}:Ca^{2+}$ ratio presently exists, this may not have been sufficiently high to have induced aragonite crystallization in preference to calcite.

On the other hand the vesicles, which contain an abundance of spherulitic calcite with virtually no aragonite, represent an almost completely closed (i.e. stagnant) environment in which groundwater remained trapped, hence presenting a totally different environment from the open breccia pipes in which aragonite predominates.

So two quite distinct growth environments are indicated at Kulnura, each displaying its own peculiar paragenesis; a phenomenon which adds to the variety of specimens and unique character of the locality.

Morphology of the carbonate species

Aragonite. The aragonite was distinguished from calcite by its crystal forms and characteristic twinning, lack of rhombohedral cleavage, and higher specific gravity (2.94). At Kulnura the aragonite occurs as radiating groups of white to colourless columnar crystals ranging from 1 cm to over 8 cm in length (fig. 3A and B). Specimens show no evidence of cleavage, although several sources quote a prismatic cleavage for this mineral (Deer *et al.*, 1962). However in thin section the crystals commonly show incipient parting parallel to (110).

Single crystals comprise the prism *m* (110) and the brachypinacoid *b* (010), terminated by dome *k* (011) faces. The prism and brachypinacoid faces are usually tapered.

Twinning in Kulnura aragonite is ubiquitous and varies from the simple contact variety to complex twinned intergrowths, with *m* (110) as the twin plane. Simple cyclic twins characteristic of aragonite have not been observed at Kulnura. Polysynthetic twinning on (110) is very evident in all crystals and is expressed externally as striations on the prism and brachypinacoid faces. Successive removal of component crystals towards the termination of the twins due to tapering of the prism and brachypinacoid faces has been observed (fig. 4). Thin-section microscopy of basal sections of the aragonite sprays near their point of attachment with the cavity wall revealed that both individual and twinned crystals in each divergent group are related either by twinning or parallel growth.

Calcite. Apart from the advanced spherulitic habit associated with the aragonite in the steam explosion breccia pipes, calcite is virtually restricted to vesicles in the vesicular basalt zones. The most notable feature of the calcite at Kulnura is the diversity of crystal habits present. Crystals vary from simple rhombohedral forms to complex spherulitic groups, often with adjacent vesicles containing crystals of completely different habit. This presents interesting problems in paragenesis which remain to be fully explored. However, it is proposed in this present study that differing levels of impurities in the growth environment played a major part in producing the wide range of crystal habits. The most important contaminants appear to be Mg^{2+} and Fe^{2+} (Table I) and certainly the effect of Mg^{2+} on the crystallization of $CaCO_3$ has been well documented.

Leitmeier (1910, 1915) showed that the crystallization of calcite under low $Mg^{2+}:Ca^{2+}$ ratios produced only the simple rhombohedron. With higher Mg^{2+} levels, 'poisoning' of lateral crystal growth occurs, favouring the development of steeper rhombohedra, scalenohedra, and finally prism faces. Because of its lower ionic radius compared to calcium, Fe^{2+} is assumed to have a similar effect to Mg^{2+} and both ions probably have an additive effect on the $CaCO_3$ structure. pH values may have also had some controlling effect, although no documentation of their influence on carbonate crystallization could be found in the literature, apart from a brief reference by Lebedev (1967) which indicates that simple rhombohedral crystals are the stable form at pH values below 7.4. The formation of spherulitic structures is discussed below.

Single crystals of calcite are uncommon at Kulnura. They usually take the form of simple rhombohedra *e* $(01\bar{1}2)$, commonly modified by

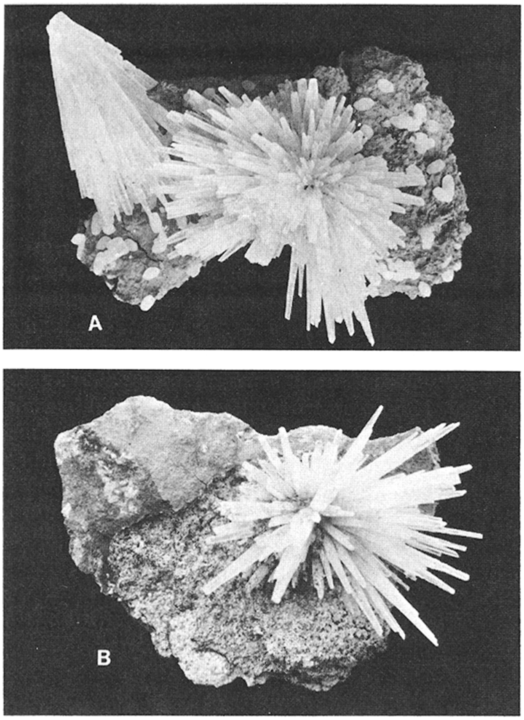

FIG. 3. Aragonite crystals in divergent groups on altered basalt. Note the presence of spherulitic calcite in specimen 'A' similar to that shown in fig. 2.

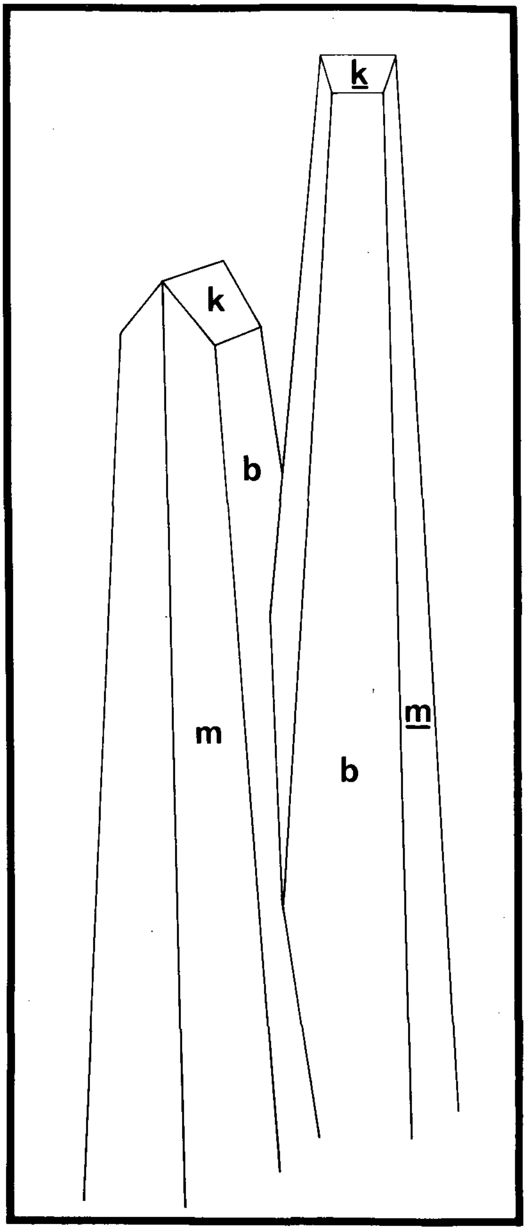

FIG. 4. Removal of component crystals towards the termination of twinned aragonite due to tapering of the prism and brachypinacoid faces. Length of crystal is 2 cm.

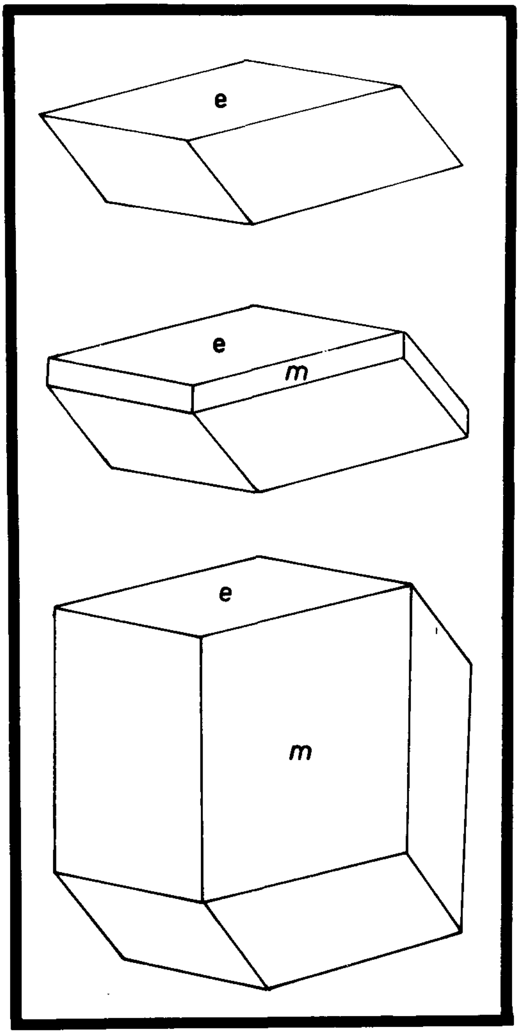

FIG. 5. Habits shown by single calcite crystals from Kulnura.

the prism *m* (10$\bar{1}$0) (fig. 5). Rare scalenohedra terminated by the rhombohedron *e* (01$\bar{1}$2) are also present. In a few vesicles, relatively small (3-4 mm) simple rhombohedral crystals are scattered among typical spherulites (fig. 6) which they obviously post-date. This indicates a latter stage of crystallization in which the Mg^{2+} and Fe^{2+} levels had been lowered to such an extent that single crystals, without any sign of spherulitic development, were able to form. This is verified by the analysis of rhombohedral calcite shown in Table I, assuming that the levels of impurity elements or isomorphous compounds absorbed by the crystals are directly proportional to impurity levels in the mineralizing groundwater.

The range of spherulitic habits developed in the calcite at Kulnura provides most of the variety seen in specimens. In calcite, spherulitic forms are developed from the simple rhombohedron as a result of disruption of the atomic structure along

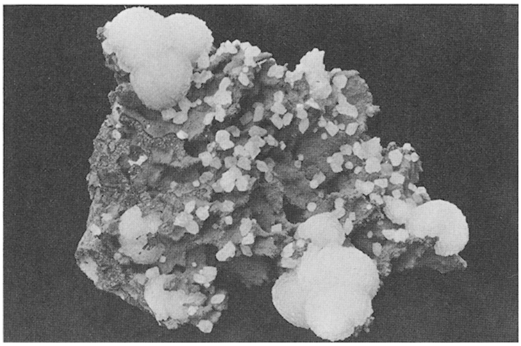

FIG. 6. Fully developed calcite spherulites with single calcite crystals on altered basalt. Specimen is 10 cm in diameter.

the rhombohedral cleavage directions. This is caused by sectorial enrichment of some element or isomorphous compound on those planes (Lebedev, 1967). The greater the enrichment, the more the crystal tends towards a complete spherulite.

It is proposed that varying levels of sectorial enrichment by Mg and Fe carbonates produced the range of spherulitic forms observed in the Kulnura calcites. This is indicated by the increasing levels of Mg^{2+} and Fe^{2+} found in crystals of increasing spherulitic development (Table I). This sectorial enrichment causes splitting of the crystals along the rhombohedral cleavage directions during growth. The more contaminant carbonate absorbed in the structure, the greater this splitting effect (fig. 7), until eventually the corners of the rhombohedron curl alternately up and down towards the *c*-axis forming an almost complete sphere (fig. 8). This curling of the rhombohedron edges in alternate directions produces a continuous narrow depression on the surface of the sphere, separating two interlocking trigonal dumb-bell-like areas. This is a characteristic seen on all calcite spherulites. Usually distinct rhombohedral faces are only visible in depressions at either end of the *c*-axis. An intermediate stage in spherulite development is shown in fig. 9. Lebedev (1967) indicated that pH values may also play some part in encouraging spherulite development. pH values of greater than 7.4 to 7.6 are quoted as being favourable for spherulitic growth, while below this value recrystallization to normal rhombohedral calcite occurs. Verification of these findings with respect to the Kulnura occurrence was not possible.

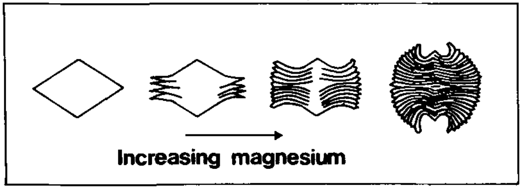

FIG. 7. The effect of increasing Mg on spherulitic structure. Crystals are sectioned through the *c*-axis and opposite edges of the rhombohedron.

All stages between simple crystals and completely developed spherulites have been observed at Kulnura.

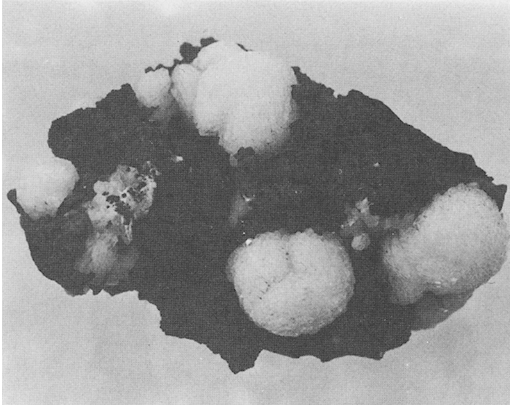

FIG. 8. Fully developed calcite spherulites on altered basalt. The centre of the trigonal depression in the spherulite towards the base of the specimen represents the exit point of the *c*-axis. Specimen is 10 cm in diameter.

The vesicle environment and the role of pumpellyite in calcite crystallization

Pumpellyite is virtually absent from the breccia pipes but is common as vesicle linings in the zones of altered vesicular basalt surrounding them. Its presence in the vesicles appears to have had a significant influence on calcite crystallization.

The formation of pumpellyite vesicle linings during hydrothermal alteration would have absorbed much of the Ca and Mg released by decomposition of the plagioclase and olivine components of the basalt adjacent to the vesicles. Thus the pumpellyite provided an immediate local source of both Ca^{2+} and Mg^{2+} which would be readily available by carbonated groundwater leaching to both induce $CaCO_3$ crystallization and influence the crystal habits produced.

As previously stated, the carbonates at Kulnura appear to be relatively recent in origin and indeed carbonate formation could not have commenced until meteoric waters intersected the intrusion, assuming that the hydrothermal alteration episode which produced the pumpellyite played no part in introducing carbonate ions into the system.

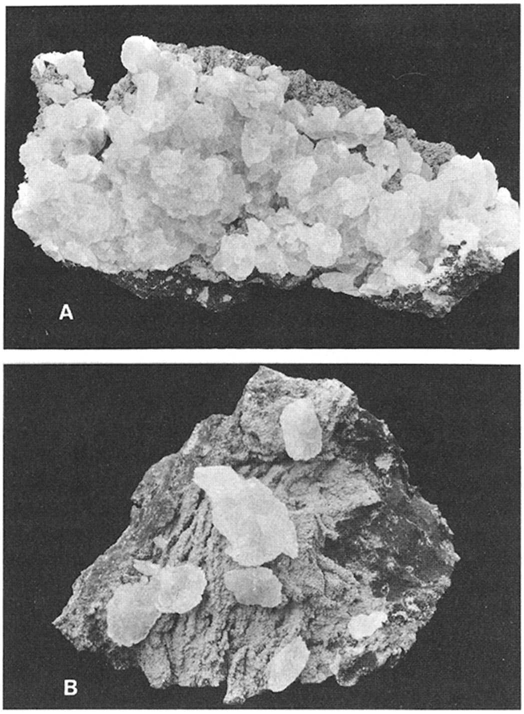

FIG. 9. Specimens showing an intermediate stage of spherulitic growth. Note the presence of the pumpellyite vesicle lining. Specimen A is 18 cm in diameter; specimen B is 7 cm in diameter.

Most of the vesicles observed at Kulnura were found to contain groundwater on opening, indicating that crystallization occurred from aqueous solution in an effectively closed system, in which the nutrients for crystal growth would have been provided by goundwater leaching of the vesicle walls. Also, with the very low Ca content of the altered basalt as a whole, the pumpellyite would have represented the only local easily available source of Ca.

Further evidence for this hypothesis is provided by the observed relationship between the degree of spherulitic development and the presence or absence of pumpellyite in the vesicle. An examination of several hundred Kulnura specimens, both *in situ* and collected material, shows without exception that once the fully developed spherulitic stage has been reached, the pumpellyite vesicle lining is totally absent. Presumably intermediate stages of spherulitic growth on pumpellyite matrix, as shown in fig. 9, would have eventually formed complete spherulites, with accompanying loss of pumpellyite matrix, had growth been allowed to continue.

Examination of specimens of the type shown in fig. 6, where small more recently developed single calcite crystals showing no spherulitic development are directly associated with fully-developed spherulites deposited directly on to the altered basalt of the vesicle wall provides a further interesting hypothesis on calcite crystal paragenesis at Kulnura.

The nucleation and initial stages of calcite growth in the vesicles would have taken place under the influence of a very low $Mg^{2+}:Ca^{2+}$ ratio (around 0.3 : 1, as essentially governed by the pumpellyite stoichiometry, since the vesicles represent an effectively closed system). Hence growth would have initially proceeded virtually without the disturbing influence of high impurity levels. However, as Ca^{2+} is absorbed by the growing crystals, the local $Mg^{2+}:Ca^{2+}$ ratio would be gradually increased and hence the tendency towards increased sectorial enrichment by $MgCO_3$ and complete spherulitic development would also increase as leaching of the pumpellyite vesicle lining proceeded. Eventually complete spherulites would result. Examination of progressive morphology changes in sections of complete spherulites lend support to this hypothesis.

With the pumpellyite source decomposed and completely removed from the system, further nutrients for crystal growth could only be provided by leaching of the altered basalt of the vesicle walls. Hence, once again, crystal growth is nucleated under the influence of a relatively low $Mg^{2+}:Ca^{2+}$ ratio (governed by the pumpellyite/nontronite of the altered basalt groundmass), so that small single crystals result. As before, the absorption of Ca^{2+} by crystal growth would result in a gradual increase in the local $Mg^{2+}:Ca^{2+}$ ratio which would eventually reach a sufficiently high value to produce a second generation of spherulitic growth by enforced sectorial enrichment in $MgCO_3$. This would mean that the small single crystals seen in fig. 6 represent an early stage in the development of second generation calcite spherulites.

This finding also lends support to the hypothesis that the nutrients for crystal growth in the vesicle environment were provided by progressive groundwater leaching of the pumpellyite lining and altered basalt wallrock of the host vesicle.

Thus, the observed variation in calcite crystal habits between vesicles at Kulnura is easily explained in terms of different phases in spherulitic development resulting from different stages of progressive groundwater leaching of the vesicle walls.

Conclusions

The basalt in which the carbonate mineralization occurs at Kulnura was hydrothermally altered to nontronite/pumpellyite prior to carbonate precipitation. The limited extent of mineralization observed is a direct result of the low Ca^{2+} content of the altered basalt. Two distinct growth environments are indicated; steam explosion breccia pipes and vesicular basalt zones, each displaying different $CaCO_3$ species and crystal habits.

The aragonite at Kulnura was forcibly crystallized at close to normal pressures and temperatures by the presence of a very high $Mg^{2+}:Ca^{2+}$ ratio in the particular growth environment. The lack of any physical sign of aragonite to calcite reversion indicates a recent origin for the carbonate mineralization.

The variety of calcite crystal habits present can be directly related to varying Mg content of groundwater in the growth environment. The nutrients for calcite crystal growth in the vesicle environment were provided by direct groundwater leaching of the pumpellyite vesicle linings and the observed variation in calcite habits between vesicles can be explained in terms of different phases in spherulitic development resulting from different stages in progressive groundwater leaching of vesicle walls.

No evidence is available to enable any relationship to be postulated between ion concentration or pH values and carbonate crystallization, although these factors may have been important.

Acknowledgements. Appreciation is expressed to the Management of the Broken Hill Proprietary Company Limited, Central Research Laboratories for the use of the equipment and resources of the Laboratories; also to Richard Depledge, School of Earth Sciences at Macquarie University, Sydney, for his critical review of the original manuscript and helpful suggestions.

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[*Manuscript received 27 September 1983; revised 6 February 1984*]