

*Secondary minerals of the Tertiary basalts,
Barrington, New South Wales.*

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Summary. Secondary minerals described from Tertiary amygdaloidal basalts in the Hunter Springs area, Barrington, New South Wales, are regarded as having been deposited from cold solutions some considerable time after consolidation of the basalts. The constituents in the solutions were evidently derived from the basalts by the action of circulating meteoric waters rather than by deuteritic activity.

THE basalts that characterize the Mt. Royal and Barrington Highlands, about 50 miles north-west of Newcastle, New South Wales, are Tertiary in age. According to Browne (1933) they belong to the Newer Basalts and were poured out most probably during early Pliocene times, but David (1950) regards them as belonging to the Older Basalts and Oligocene in age. However, their exact age is immaterial as far as this paper is concerned.

Browne describes the flows as follows: 'The successive flows of basalt are indicated by flat topped terraced hills . . . the terracing . . . being due to the erosion of alternately amygdaloidal and massive layers of basalt.' For the most part, the flows are between 15 and 20 feet thick, and have a total thickness of approximately 700 feet according to Sussmilch (1940, p. 304), although Brown's estimate (1933, p. 37) is 1500 feet.

The basalts that overlie unconformably the truncated ends of the folded Carboniferous and Devonian sediments contain abundant secondary minerals.

The samples were collected from Black Cutting along the road from Moonan Flat to Tomalla in the valley of the headwater of the Hunter, the 'Escarpment', and Tubrabucca Falls. Fig. 1 indicates the approximate location of these places.

There are two types of basalt, which form alternating layers: a massive basalt with few vesicles, and a highly vesicular basalt with partially and completely filled vesicles.

The massive basalt is largely porphyritic with phenocrysts of olivine

averaging 1.0 to 1.5 mm. in length and constituting 20 % of the rock. The phenocrysts are set in an intergranular groundmass of small laths of labradorite averaging 0.5 mm. long and granular pyroxene with average grain size of 0.5 mm. The labradorite constitutes about 40 % of the rock and the pyroxene about 30 %. Scattered throughout the rock are granules of magnetite and ilmenite and minute needles of apatite, all in

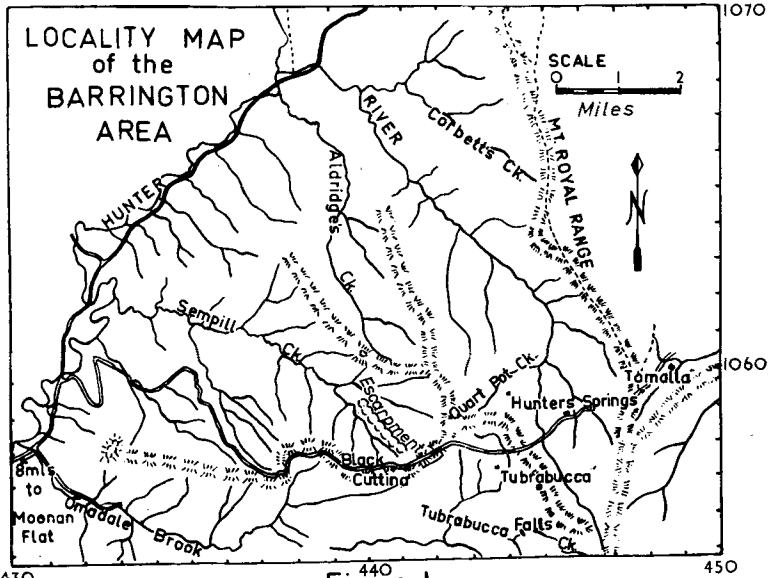


Figure 1.

subordinate amounts. In some of the basalts the olivine shows incipient alteration to chlorite along the cracks and around the rims while in the majority chlorite, in varying amounts, is intersertal. Vesicles are few in number and more regularly ovoid than those in the amygdaloidal type. Their infillings are discussed below.

The amygdaloidal basalt shows various degrees of weathering in contrast to the fresh massive type. Megascopically, the rock has taken on a brown colour and crumbly texture and has the appearance of a very much altered rock. Microscopic investigation reveals that the olivine and augite have altered to limonite with some granules of magnetite, still relatively fresh, interspersed, and the plagioclase has altered to albite. This basalt is extremely amygdaloidal. The vesicles and their infillings are described below. Much of the amygdaloidal basalt is of a blocky

type in which the blocks vary from 5 to 20 cm. in diameter. Some flows of this basalt reveal distinct elliptically shaped volcanic-bomb-like masses.

Nature of the vesicles and their infillings. The vesicles vary greatly in abundance and size. In the massive type they are few while in the scoriaceous material they are abundant. In size they vary from less than 1 mm. to 20 mm. and in shape from small ovoid cavities to larger irregular openings. One example showed vesicles elongated in the direction of flow and subsequently partly filled with horizontal layers of clay.

The minerals that fill the vesicles are chabazite, natrolite, montmorillonite, montmorillonite interlayered with illite, chalcedony, manganite, and calcite. They form either singly in some vesicles or in a variety of combinations as indicated in fig. 2.

The order of deposition of the minerals can only be as follows: manganite, montmorillonite interlayered with illite, montmorillonite, chabazite, natrolite, a second generation of manganite, and, finally, chalcedony and calcite. The last two also commonly infill veins that cut across the flows.

The vesicles in the massive type of lava are usually filled with one of the following combinations: chabazite; chabazite lining the vesicle and natrolite occurring in the centre; chalcedony; or radiating natrolite lining the vesicles and chalcedony filling the interior space.

Secondary minerals.

Montmorillonite occurs as two distinct forms:

As bands of clay that are cream coloured at the top grading down to mid-green with dark green at the base. X-ray analysis proved the clay to be montmorillonite and revealed practically no difference between the three varieties. There was only a very slight shift in each line of the powder photograph, and no marked difference in refractive index (n 1.499) was detected.

As a cherry red variety (like hematite), which is recorded separately from the first type of montmorillonite because it occurs in distinct layers in the vesicles and not as though it is an iron stained variety of the first type. The mineral did not react readily to qualitative tests for iron but chemical analysis carried out by G. T. See of the University of New South Wales revealed 5.10 % Fe_2O_3 .

Much of the material occurs as a powdery lining to the vesicles, but often the structures assumed are stalactitic and nodular. X-ray analysis

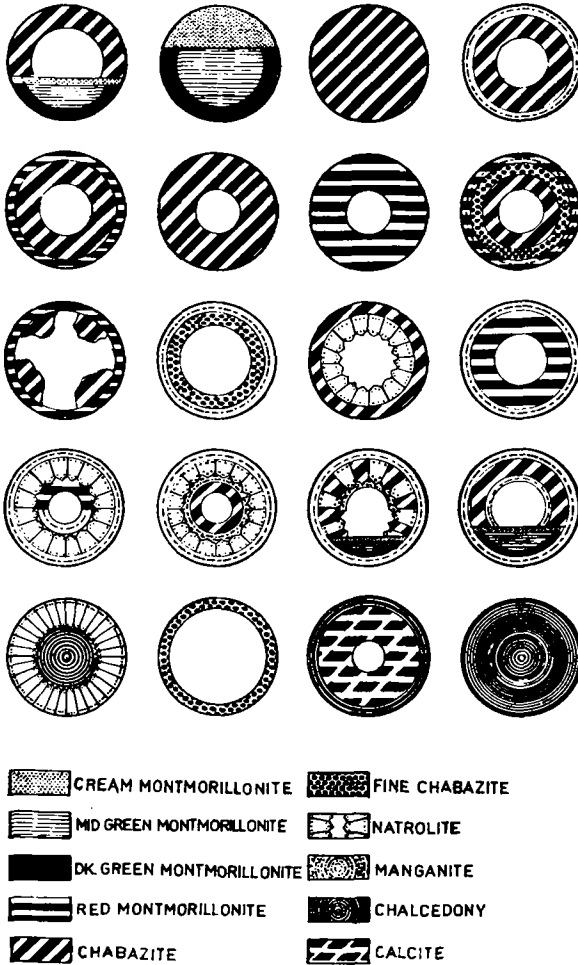


Fig. 2. Illustrates diagrammatically the combinations and arrangements of the secondary minerals in the vesicles of the highly vesicular basalt.

revealed that the mineral is montmorillonite (about 80 %) interlayered with illite (about 20 %).

Chabazite varies in form from a simple rhombohedron to a more complex crystal consisting of the rhombohedron and other forms. The crystals range in size from microscopic dimensions to about 5 mm. in diameter. In some vesicles the chabazite occurs as a thin film.

Irrespective of the form, the mean refractive index is 1.490 and the sign optically negative.

Natrolite occurs as acicular crystals under 5 mm. long and as slender, hair-like crystals either surmounting other minerals or in separate radiating groups. One vesicle broken open revealed a lining of chabazite and enmeshed, doubly terminated fibres of natrolite. Natrolite occurs also in veins and cavities other than the vesicles in the basalts.

Chalcedony occurs concentrically arranged in the vesicle like the clay (montmorillonite). It shows aggregate polarization, and the refractive index and water content are more those of common opal, being n 1.488, H . 6, H_2O 13.23 % for the white chalcedony, and n 1.489, H . $6\frac{1}{2}$, H_2O 9.14 % for the cream. The water content recorded was that driven off after prolonged heating at red heat and is high relative to its refractive index. The high water content is due to some vesicles containing silica gel. The H_2O of newly exposed vesicles was observed to be very variable. With exposure to air the gel soon dried out.

Calcite is not nearly as abundant as associated chabazite and chalcedony, with which it is closely related in time of deposition. It is the transparent variety.

Manganite occurs as a black, powdery lining to some vesicles, or dusting the infillings of other vesicles; it also occurs in veins. Its chemical composition was derived by qualitative chemical tests but could not be confirmed by X-ray analysis owing to the difficulty of collecting sufficient material.

Origin of the secondary minerals.

The question arises whether the secondary minerals were deposited from deuteric solutions or from extraneous hydrothermal solutions of meteoric origin, or of later igneous origin.

Possibility of origin from deuteric solutions. The vesicles in Tertiary amygdaloidal basalts from other localities in the Barrington district are filled with chabazite, natrolite, montmorillonite, and calcite. The olivine-free Tertiary basalts that outcrop at Ardglen about 50 miles to the west have similar amygdules of chabazite, natrolite, montmorillonite of both varieties, and manganite. These examples indicate that such constituents are prevalent in basalts of this age. They point to a deuteric origin, but the associated natrolite, chalcedony, and manganite in the Barrington localities are found not only within the vesicles, but also infilling joints that were no doubt developed long after consolidation of the flow.

The highly vesicular lava indicates rather rapid consolidation so that all magmatic liquors would be expected to have crystallized and left none to move through the rock as deuteric solutions. There would thus be insufficient to satisfy the requirements of the large quantities of amygdaloidal secondary minerals observed. The recent scoriaceous basalts of the Hawaiian Islands are of comparable character. These are completely consolidated and intensely vesiculated, the vesicles being devoid of infillings except for an occasional thin layer of sublimate.

Throughout the literature on the Hawaiian lavas little mention is made of vesicle infillings. Macdonald (1949) writes: 'Pololu Volcanic Series: Olivine basalt pahoehoe, thin bedded, much weathered, reddish-brown and soft, many joint surfaces coated with a purplish-black sub-metallic substance, probably manganese oxide. Many vesicles partly filled with calcite and probably zeolites.'

This prompted one of us (B. N.) to inquire from the Hawaiian Volcano Observatory (U.S. Geological Survey) whether the bulk of the vesicles in the Hawaiian flows were filled and, if so, whether the rock was fresh or weathered; also the depth in the volcanic pile at which infillings in the vesicles become prevalent, and the age of these lavas.

Mr. G. D. Fraser (priv. comm.) informed us that the primitive undifferentiated basalts contain about 30 % void space and abundant vesicles but no zeolites at all, regardless of age and depth of burial. However, near fumarolic areas clay minerals, sulphates, and opal are common in the altered rock and in the vesicles, zeolites being rare or absent. In some areas, where zeolites have been found, the most common host rocks are unusually undersaturated or differentiated.

Similar information was sought for the geologically young lavas of New Zealand and New Guinea. Mr. D. Kear of the Geological Survey of the Dept. Sci. Indust. Research in New Zealand indicated that many of the Auckland basalts (Holocene to Upper Pleistocene in age) are highly vesicular. A few of the vesicles are reputedly filled with calcite but in general the vesicles are void of minerals. The vesicles in some of the older weathered lavas are sometimes coated with a mere white film that may prove to be zeolitic. Mr. Kear also remarked that the Upper Pleistocene and Recent basalt flows on Samoa are unweathered, unaltered by thermal solutions, and have no vesicle infillings.

Dr. G. Baker of the Mineragraphic Investigations Section, Commonwealth Sci. Indust. Res. Organ., Melbourne, sent similar information on lavas in New Guinea. Baker (1946) indicated that the vesicles in lavas from the Goropu volcanic eruptions of December 1943 to August 1944

are not infilled and the rocks show no hydrothermal alteration. Again, Baker (1948) pointed out that any vesicles in young basalt from Oiava-ai on Goodenough Island and in andesites from the Amphlett Group are not infilled. Similarly, the volcanic rocks (Quaternary to Recent) of Mt. Bogana, Bougainville Island, Solomon Islands (Baker, 1949), do not have their vesicles infilled and are not hydrothermally altered to any extent. However, the older Aitape lavas in the Bismarck Archipelago, which are Lower Miocene in age, have many infilled vesicles (Baker, 1954).

The data point to the fact that when lavas are first consolidated, and for some considerable time thereafter, their vesicles remain unfilled. Both Fraser and Baker (priv. comm.) suggest that fumarolic action may play some part locally in the alteration of lavas and in the infilling of some of their vesicles. Such action, no doubt, would be limited in geographic distribution. Similar infillings of vesicles are fairly universally distributed in the Tertiary basalts of eastern Australia and do not occur in isolated patches, as one would expect, as the result of fumarolic effects. Evidently the infillings post-dated consolidation and were thus not a direct result of deposition from deuteric solutions, so that extraneous secondary solutions must have been responsible.

Possibility of origin from extraneous secondary solutions. Extraneous secondary solutions could be either of magmatic origin, that is, emanating from an igneous intrusion injected some time after the consolidation of the basalts, or of meteoric origin, from circulating subterranean solutions.

As there has been no post-basalt igneous intrusion of a magnitude to produce such solutions the possibility of the solutions being magmatic could not hold, hence the only possibility is meteoric. The only igneous rock type in the region is basalt, hence such solutions must result from the action of meteoric waters percolating through the basalt, dissolving some of its constituents and redepositing them in vesicles and joint planes. The nature of the alteration of the original rock suggests the possibility that products of this type of alteration gave rise to the secondary minerals listed in tables I and II.

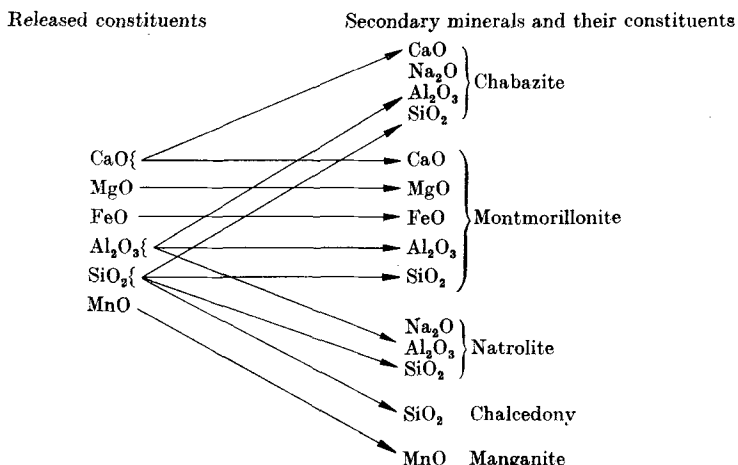
All of the released constituents listed in table I are necessary for the formation of the majority of the newly formed minerals of secondary origin, as is shown schematically in table II.

Although the decomposition of the basalt could release the constituents needed for the mineral infillings of the vesicles in the Hunter Springs localities at Barrington and in other localities, it is only a

TABLE I. Suggested alterations, and constituents released thereby.

| Original minerals in fresh basalt | Constituents of minerals | Present minerals in altered basalt | Constituents of minerals | Constituents released during alteration |
|-----------------------------------|---|------------------------------------|--|--|
| Olivine | MgO, FeO, MnO, SiO ₂ | Limonite | FeO | MgO, MnO, SiO ₂ |
| Augite | MgO, FeO, MnO, CaO, Al ₂ O ₃ , SiO ₂ | Limonite | FeO | MgO, MnO, CaO, Al ₂ O ₃ , SiO ₂ |
| Labradorite | CaO, Na ₂ O, Al ₂ O ₃ | Albite | Na ₂ O, Al ₂ O ₃ , SiO ₂ | CaO |

TABLE II. Scheme of formation of secondary minerals.



Note: Na₂O would be released if any of the feldspar (labradorite or albite) is kaolinized.

localized feature and does not explain the infillings in the fresh basalt. However, it is not improbable that downward percolating solutions containing the constituents from weathered basalt at a higher level could affect the fresher and apparently unaltered material. Evidence of this was seen in the traces of solution channels, now filled with secondary minerals, that extend downwards from the weathered section of the rock through the vesiculated area.

Temperature of the secondary solutions. Walker (1951), when discussing the distribution of zeolites, especially chabazite, in the Garron Plateau Area, County Antrim, called upon the agency of hot water solutions to explain the observed distribution of the different habits of that mineral. He did not consider the possibility of cold water solutions, citing only

the generally accepted opinion of other workers in the field, namely that zeolites normally form above 100° C. He deals with the possible sources of heat or mechanisms for the production of heat. One suggestion put forward, but not accepted for the Garron basalts, was that the heat was supplied by the lavas themselves, that is, possibly due to the progressive accumulation of heat in the lava pile by a succession of small additions from each flow erupted. In theory this may seem feasible but in practice and from studies of the recent lavas, it does not happen. Walker finally appealed to the self-generation of heat in the lava pile during zeolitization of the feldspars and hydration of the olivines and pyroxenes. However, such a theory may not be tenable because many of the basalts under discussion are too fresh. For example, the massive basalts from Barrington and the Ardglen basalts were little weathered and show little sign of having been affected by hydrothermal solutions. This fact is borne out by the freshness of the minerals observed in thin sections. The only mineral affected is olivine, as indicated earlier. Secondary chlorite also appears interstitially.

It was reported locally that deposition of a white mineral (probably chalcedony, perhaps with some calcite) and a red mineral (no doubt montmorillonite interlayered with illite) in cavities in the basalts near Tubrabucca Falls from the stream water, which flows over the basalt and has a temperature of about 5° C., had been observed.

More evidence indicating continued deposition of these minerals from cold solutions is provided by the finding of cold solutions actually in the cavities of parts of freshly broken massive basalt. It was impracticable to sample these solutions in the field because the precise position of the containing vesicles could not be detected before the rock was broken open. Upon breaking the rock, the solution immediately trickled over its surface and was lost. However, some of the rock was taken back to the laboratory. Filter paper was specially treated by washing with dilute hydrochloric acid to free it of any impurities. As soon as the specimen was broken and a vesicle containing solution was revealed, the solution was mopped up by the paper. The constituents of the solution held in the paper were then converted to soluble chlorides by treatment with dilute hydrochloric acid. Flame photometry revealed no trace of sodium while qualitative spot tests revealed no trace of calcium, magnesium, iron, aluminium, or silicon. Although the tests used are normally sensitive, the abundances of the salts in solution were evidently too low to reveal even a trace.

The solution-bearing vesicles were lined with a thin layer of a zeolite,

possibly chabazite. This was spotted with small mammillary 'blebs' of chalcedony about 3 mm. in diameter. Some vesicles contained a thin layer of banded dark green montmorillonite.

Additional evidence that these solutions act in the cold is provided by the appearance of a damp rim surrounding vesicles completely filled with chalcedony or with natrolite and chalcedony or with clay. When the rock was freshly broken the original rim was about 2 mm. wide and completely surrounded the filled vesicle. Within 24 hours the width of the rim had expanded to 4 mm. due to surface effects. A piece of rock containing these damp rims was placed in an oven at 105° C. for 6 hours. The rim dried out, but it left a yellowish stain indicating that something more than water was present. The constituents in the solution have not yet been determined.

The problem delineates itself thus: On the one hand there are reports in the literature of hot water solutions being responsible for the deposition and habit distribution of zeolites, while on the other hand there are the actually observed vesicles filled with cold water in contact with chalcedony and montmorillonite, which presumably were deposited from it. The authors have not as yet proved that this cold-water solution was always cold, or that it is capable of further deposition or that it is in any way connected with the more prolific and varied deposition of minerals present in the more vesicular and weathered basalt.

A more fundamental problem that applies to the deposition of all minerals from solution has yet to be solved, and this is the cause and mechanism of precipitation. The commonly accepted possible causes of precipitation appear to be: Reaction of the solution with the wall of the vesicle, reaction of the solution with a previous sublimate either by using it as a nucleus or by actual chemical reaction, slow cooling of a saturated solution, and reaction of hot ascending solutions with descending meteoric solutions.

By way of actual evidence the authors note: that the large and perfectly formed crystals of chabazite tend to favour slow crystallization from an aqueous solution with no marked evidence of co-precipitation; that the radial growth of natrolite crystals around an unidentifiable foreign nucleus indicates slow crystallization; that the red montmorillonite and chalcedony commonly show colloform texture; and that a recognizable, if imperfectly understood, sequence of deposition is apparent, with strictly localized deposition of some minerals or mineral associations.

The first, second, and fourth of these points indicate that the secondary

minerals were precipitated from different solutions. For example, chabazite was deposited from one solution, natrolite from another different solution, and so on. Such different solutions are necessary to explain non-contamination by overlap of crystallization during what must have been a considerably long time. Even when chabazite and natrolite grow side by side they are not structurally intermingled.

The second point indicates the activity and effect of nucleation on the crystallization of natrolite.

The colloform texture of red montmorillonite and chalcedony seems to indicate deposition from colloidal solution, but Krauskopf (1956) contends that silica is transported in true solution in the form of the monosilicic acid, H_4SiO_4 , and not as a colloidal solution. He does indicate, however, that over a period of time the true solution is transformed into a colloidal solution. Such a transformation possibly occurred in the vesicles or in the veins or both. The deposition of concentrically layered chalcedony followed. Similar effects may have caused deposition of the red montmorillonite.

The perfection of form of some of the individual crystal species, together with the size and arrangement of the clusters of crystals in an otherwise empty vesicle, seem to indicate slow crystallization from a cold yet saturated solution. These solutions are considered to be still actively depositing mineral matter.

Conclusions.

This study of the secondary minerals in selected examples of Tertiary basalts in New South Wales was conducted with a view to solving some of the physico-chemical problems associated with the movement of secondary solutions through already consolidated lavas. Little success attended considerations of the problems relating to the composition, concentration, rate of movement, and causes of precipitation of secondary mineral matter in the vesicles and joint planes of these basalts, but the following conclusions have been drawn from observations in the field and laboratory: The solutions depositing the secondary minerals were evidently not deuteric but extraneous, namely, percolating meteoric waters. The constituents in the solutions were evidently derived during processes of weathering of the basalts. And the secondary minerals were deposited from cold solutions. This process is still taking place in the Barrington area at a temperature of approximately $5^{\circ}C$.

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References.

- BAKER (G.), 1946. Journ. Geol., Chicago, vol. 54, p. 19.
——— 1948. Trans. Amer. Geophys. Union, vol. 29, p. 656.
——— 1954. Proc. Roy. Soc. Queensland, vol. 64, p. 15.
BROWNE (W. R.), 1933. Journ. Roy. Soc. New South Wales, vol. 67, p. 9.
DAVID (T. W. E.), 1950. Geology of the Commonwealth. Edited by W. R. Browne. Arnold, London.
KRAUSKOPF (K. B.), 1956. Geochimica Acta, vol. 10, p. 1.
MACDONALD (G. A.), 1949. U.S. Geol. Surv. Prof. Paper, 214-D.
SUSSMILCH (C. A.), 1940. Proc. Linn. Soc. New South Wales, vol. 65, p. 301.
WALKER (G. P. L.), 1951. Min. Mag., vol. 29, p. 773.
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