Palagonite, Hyaloclastites and Alteration of Volcanic Glass in the Ocean *

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Abstract

Palagonite is an hydrated and often altered glass usually associated with sub-aqueous basaltic volcanites. It is commonly considered as an alteration product of normal basaltic glass (sideromelane) with which it is associated in hyaloclastites. Existing information on the diffusion rates of water in natural glasses suggests, however, that the hydration which causes the formation of palagonite takes place at relatively high temperature, that is mainly during effusion and cooling of the lava under water. It is also suggested that generally palagonite is not formed in nature to any great extent from the alteration of sideromelane. Palagonite appears to devitrify much faster than normal unhydrated glass of the same composition. This fact may explain some previously unclear data on the occurrence of volcanic glasses on the floor of the oceans; namely, the existence of totally devitrified glasses in some recent sediments and the finding of unaltered glass in older deposits.

Introduction

The term « palagonite » has been in use for more than a century in geologic literature; nevertheless it still seems to cause confusion, since it is often used with different meanings by various authors. It was originally introduced by VON WALTERSHAUSEN (1845) to indicate a glassy brown material associated with tuffs and lavas in eastern Sicily and Iceland. A clear definition of the nature of palagonite was not given until TYRELL and PEACOCK (1926) published their classic study of the petrology of Iceland. Peacock reported palagonite to be a highly hydrated volcanic glass, usually with a low index of refraction

(between 1.46 and 1.49), and in some cases, with signs of incipient devitrification. The water content of these palagonites was found by Peacock to vary between 18 and 25 per cent; strikingly high values considering that most volcanic glasses usually contain less than 4 or 5 per cent (ROSS and SMITH, 1955).

The rocks in which palagonite is typically found in Iceland constitute thick formations associated with Quaternary basalts; they consist mainly of fragments of normal basaltic glass (sideromelane) and occasionally crystalline basalt in a matrix of often partially devitrified palagonite. These rocks may superficially resemble a breccia or a tuff, hence the terms « palagonite breccia » or « palagonite tuff » frequently used to describe them. RITTMANN (1958) suggested the term « hyaloclastite » for these and similar formations to avoid confusion with normal tuffs and breccias.

Peacock (op. cit.) reported that the sideromelane associated with palagonite contains less than one per cent water, and suggested that palagonite was derived by gradual hydration and alteration of sideromelane. Hyaloclastites similar to those described by Peacock were subsequently found in several other locations. In the Columbia River basalt formation for instance, palagonite was reported as a water-rich (up to 30 per cent) glass, formed from the alteration of sideromelane, which here also contains less than one per cent water (PEACOCK and FULLER, 1932).

HOPPE (1941), HENTSCHEL (1951), NAYUDU (1962), DENAEYER (1963) and other students of hyaloclastites accordingly report palagonite as an alteration product of sideromelane glass. Sideromelane is usually regarded as a glass which originates from the rapid cooling of a basaltic melt. A certain degree of viscosity is commonly implied in any definition of glass. According to the general habit we can use the term glass when a supercooled liquid has a viscosity greater than approximately 10^{14} poise. On this basis it can be safely assumed in the majority of cases that glass will begin to form from a rapidly cooling basaltic melt in a temperature region lying several hundreds of degrees lower than the temperature of the melt at the moment of effusion. The suggestion that palagonite is an alteration product of sideromelane glass implies therefore that this alteration takes place mainly during the last stages of the cooling of the lava and/or after it. To check this concept, the conditions under which a pratically water-free glass may be altered so as to form palagonite and subsequently crystalline phases will be briefly discussed first.

Alteration of Volcanic Glass

Volcanic glass is an unstable phase on the earth's surface, but its purely thermal, anydrous crystallization proceeds at extremely low rates. MARSHALL (1961) estimates the time of complete crystallization for natural glass at 25° C on the order of 10^{60} years. RICHARDS (1939) gives for an optical glass an estimate of $> 10^{50}$ years. Natural glasses maintained at low temperatures and in non-aqueous environment appear remarkably stable; for instance an unaltered Precambrian glass has been K/Ar dated as 975 million years old (PHILPOTTS and MILLER, 1963). Due to these very low rates and to the ubiquitous presence of water on the earth's surface, anhydrous devitrification is not discussed further here.

The catalyzing action of water is known to play the main role in the natural devitrification of glass. According to MARSHALL (1961) water molecules contained in glass are able to break the Si-O-Si, Si-O-Al, Al-O-Al cross bonds of its structure by having hydroxyl groups each attached to a Si or Al atom. After such hydration, relatively little energy is further required to orient silica and alumina tetrahedra to form a crystalline structure. MARSHALL (op. cit.) estimates that a water content of about 15 per cent in basaltic glass is the minimum required to initiate crystallization, while in acidic glasses, water contents up to 20-25 per cent may be required because the Si-O, Al-O bonds are more numerous.

In addition, several observations by HAWKINS and ROY (1963) and by others, point to the fact that the composition of the solution in contact with a glass is also important in determining the rate and products of devitrification. It seems probable that after the first stage of the process (disruption of the glass structure), the second stage (arrangement of the silica and alumina tetrahedra into an ordered structure), will also depend, among other factors, upon the availability in the system of the cations needed to stabilize this new structural arrangement.

In most volcanic glasses, water, on the average, is not more than two or three per cent; less than one per cent is usually considered of direct magmatic origin (ROSS and SMITH, 1955; FRIEDMAN and SMITH, 1959). Diffusion seems to be the process by which introduction of water takes place. MARSHALL (op. cit.) is of the opinion that the entire water molecule diffuses into the glass; HAWKINS (1961) arrives at the same conclusion. Using this assumption, the rate of hydration of a

volcanic glass on the earth's surface is mainly conditioned by the rate of diffusion of water molecules into its structure. MARSHALL (op. cit.) estimated that the diffusion coefficient (^{1}) at 20° C is practically identical for all natural glasses, and that it is of the order of 10^{-10} cm^2/ million years. At 20° C and in a water saturated environment, hydration of volcanic glasses would proceed from the surface inwards at a very low rate, as shown in the model of Fig. 1. Consequently, devitrification also proceeds at low rates, of the order of few microns per 100 million years, as observed by MARSHALL on a great number of volcanic glasses of known geologic age. Such estimates seem much too low for some cases, when natural glasses were probable subjected to extensive chemical attack. If for instance glasses are kept in strongly alcaline environments they may devitrify at not elevated temperature much more rapidly than Marshall's model suggests, presumably by means of some microsolution-crystallization mechanism. In the case of palagonites however it appears that strong hydration is not always accompanied by extensive devitrification, and Marshall's model is probably pertinent.
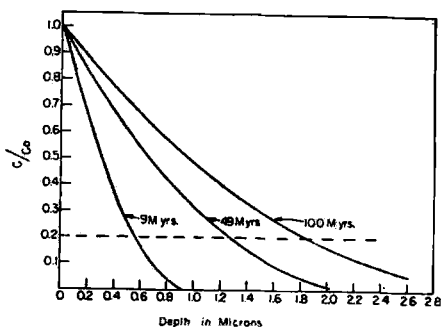

FIG. 1 - Concentration of water in volcanic glass relative to depth from a saturated surface at about 20° C. C = concentration of water in the glass. C$_o$ = fixed concentration (= 1) of water at the surface of the glass. (From MARSHALL, 1961). Dotted line added to indicate concentration at which devitrification initiates in a glass of intermediate composition.

On this basis it appears that the formation of the extensive masses of Icelandic palagonites studied by Peacock cannot be due solely to a post-eruptive process of hydration of basaltic glass taking place at athmospheric temperature. In fact, the geologic age of these materials indicates that the process would have to have taken place in less than one million years. Diffusion rates of water in glass are too low for

(^{1}) as defined by Fick's law:
$$\frac{\delta C}{\delta t} = D \frac{\delta^2 C}{\delta x^2}$$
where C = concentration of the diffusing substance;
   t = time;
   D = diffusion coefficient;
   x = space coordinate in the direction of the flow.

that, even if we admit that the original sideromelane might have been minutely fractured, thus increasing its surface of interaction with water. Similar conclusions may be applied to most palagonitic formations reported in the literature.

The behavior of the diffusion coefficient as a function of temperature is shown by the well known relation: $D = D_o e^{-E/RT}$. The activation energy E for the diffusive process was estimated by MARSHALL (op. cit.) from hydrothermal experiments to be of the order of 30 kcal/mole. This value is in good agreement with that of 25 kcal/mole measured by HAWKINS (op. cit.) in a soda-lime glass, and with the range of 19-31 kcal/mole given by SHOLZE and MULFINGER (1959). Using these values one may estimate the rate of diffusion of water in glass at various temperatures. In Fig. 2 (from MARSHALL) the rate of reconstruction of a perlitic glass to a depth of 100μ from its surface is shown as function of
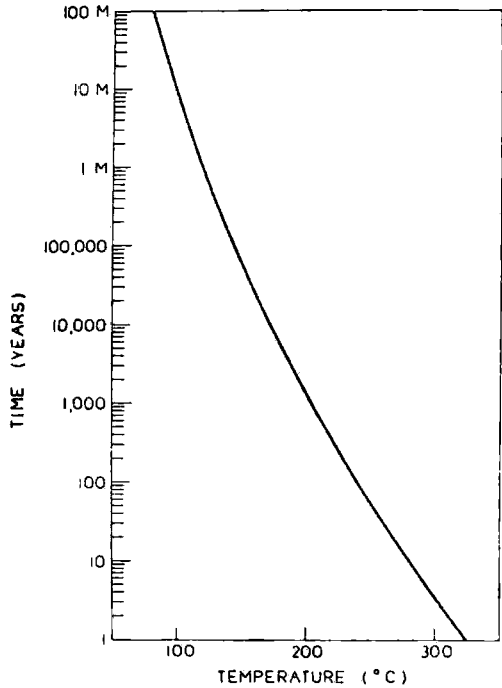

FIG. 2 - Time required for the hydrothermal reconstruction of perlite to a depth of 100 microns as a function of temperature. (From MARSHALL, 1961).

temperature. Extrapolating the function of Fig. 2 we would find that hydration effects of the order of those achieved in many million years at 20° C might be achieved at 500° C in times of the order of hours or less.

The behavior of the diffusion of water as a function of temperature suggests that the high water content of palagonitic glasses (such as those from Iceland) can be accounted for if it is assumed that hydration took place mainly at elevated temperature, that is, most lilely, during the effusion and cooling of the lava. Such hydration may be achieved if the effusion takes place in a water-rich envi-

ronment. In this connection, it is significant that all occurrences of palagonitic rocks are reported in the literature as being associated with ancient underwater volcanic eruptions: in most cases, submarine, such as in the hyaloclastites of Sicily (RITTMANN, 1958) or of the Pacific Ocean (MURRAY and RENARD, 1891; NAYUDU, 1962); in other cases sub-lacustrine (FULLER, 1931; DENAEYER, 1963); in the Icelandic case, the eruption took place under ice (PEACOCK, 1926).

FULLER (1932) found in the Columbia River basalts evidence that formation of palagonite was syngenetic with effusion. In some instances, this is suggested by the fact that the hyaloclastites are intermingled with partially consolidated sediments, captured when the fluid basalt flow advanced into a lake. The glass of the hyaloclastites is palagonite, while the glass grains contained in the sediments are unhydrated and fresh. The same author also recognized a definite boundary between the part of the lava flow which cooled under water and that which cooled subaerially; he reports palagonite being formed only in the subaqueous part of the flow (FULLER, 1932). In this case, therefore, we have strong evidence indicating that the water of the palagonite is not magmatic in origin but was derived from hydration of the lava in the lake.

In such underwater eruptions, the part of the lava directly interacting with water may be hydrated during cooling at very fast rates, depending on temperature, as shown in Fig. 2. Hydration is probably most rapid at the highest temperatures when the lava is still in a molten state. Such lava will rapidly cool reaching the viscosity range of glasses. During this stage the hydrated lava will directly form hydrated glass (palagonite), while the portions of lava not directly reached by water will form a normal unhydrated glass, such as sideromelane. More hydration will probably affect both kinds of glass during the subsequent final stages of cooling. Accordingly, some sideromelane may also be hydrated at these lower temperatures. In general, however, the amount of this latter sideromelane-derived palagonite will be insignificant if compared with the quantity of primary palagonite for two reasons:

a) Hydration decreases very rapidly towards lower temperatures, as shown in Fig. 2, and

b) Sideromelane fragments will usually be protected from direct contact with water by a crust of palagonite, formed during the earlier stages of the cooling process, as just described.

Thus the general features of hyaloclastitic rocks (fragments of sideromelane and/or crystalline volcanites in a matrix of more or less altered palagonite) can be explained by admitting a syngenetic origin of both the hydrated (palagonite) and the non-hydrated (sideromelane) glass.

The only cases where palagonite may originate in great quantity from sideromelane is when the latter, formed during a volcanic episode, subsequently undergoes prolonged hydrothermal action connected with the same or later volcanic episodes (FULLER, 1932; SILVESTRI, 1963). This mechanism may be important in a few particular cases. Generally, however, underwater cooling of lavas is rapid, and according to the previous discussion, palagonite is not a secondary product of sideromelane, but is formed directly during the interaction of hot lava with water.

It has to be pointed out that not all subaqueous effusions of lava give rise to palagonite. In some instances, it appears that very little interference takes place between lava and water, and little or no palagonite is formed. The reasons for such behaviour are discussed elsewhere (BONATTI, in prep.).

Volcanic Glass on the Ocean Floor

Since the alteration of volcanic glass is conditioned by its hydration state and since low temperature hydration is extremely slow, it is clear that an originally highly hydrated glass (palagonite) will devitrify at much faster rates than an anhydrous glass under low temperature conditions. In fact, the different rates of alteration of genetically different glasses may give some clue to understanding the components. ARRHENIUS (1963, p. 698 states: « The conditions determining the rate of decomposition and devitrification of volcanic glass in marine sediments are still obscure. While some minute glass shards in Mesozoic sediments are unaltered, some Quaternary deposits of ash and pumice have been entirely altered to montmorillonoid minerals or to phillipsite ».

This apparent contraddiction is resolved if we assume we are observing two genetically different kinds of volcanic glass on the sea floor:

a) glass formed by the direct interaction of the lava with sea water during a submarine volcanic eruption. Such glass (palagonite)

is highly hydrated and will decompose into crystalline phases on the ocean floor at very high rates if compared with a normal unhydrous volcanic glass of the same composition;

b) glass formed during subaerial eruptions (and later transported into oceanic deposits) or in the process of submarine eruptions while the lava was prevented from directly interacting with water during cooling. Such glass will hydrate and crystallize at very low rates, of the order estimated by Marshall (op. cit.).

The rate of alteration (by alteration is meant hydration plus crystallization) will certainly also depend on the composition of the glass. Data by SCHOLZE and MULFINGER (1959) and by HAWKINS (1961) suggest that the activation energy for the diffusion of water into glass decreases with the decrease in acidity of the glass. The dependence of diffusion coefficients on the viscosity of the medium is well known, therefore, the lower activation energy for basic glasses is probably caused by their lower viscosity, that is, by their more disrupted silica network due to higher content of cations. The difference in diffusion rates of acidic and basic glasses because of this effect is probably negligible at temperatures of the ocean bottom and for time ranges up to the order of millions of years, while it may become sensible at higher temperatures.

The rate of alteration also depends on composition because in acidic glasses more water is required to disrupt the Si-O, Al-O network, as already mentioned. This effect is probably the main one which causes marked differences in alteration rate between an acid and a basic glass at the low temperature environment of the ocean floor. According to Marshall this factor causes the alteration rate to be about 20 per cent higher in a basaltic than in an acidic glass. This difference in rate is minor when compared to the difference in alteration rate between a palagonitic and a normal glass of the same chemical composition.

It should be pointed out, incidentally, that determinations of composition of glass grains in sediments, usually based on refractive index measurements, are uncertain because the index varies not only with composition but also with the water content of the glass.

Devitrification both of palagonitic and of normal glass of similar composition presumably gives rise to the same phases on the ocean floor. When in pelagic deposits highly altered grains of glass are observed, it becomes impossible to decide by purely petrological

criteria if we are dealing with devitrified palagonite or with very ancient volcanic glass gradually devitrified during geologic time. However, if the knowledge of the drastically different alteration rates of the two types of glass is coupled with stratigraphic considerations, the distinction often becomes possible. For example, highly altered grains of glass are one of the major components of large areas of the South Pacific Ocean floor. Grain dimensions vary from a few microns to a couple of millimeters in diameter. Most grains are greatly altered, the products being mainly two water-rich phases: the zeolite phillipsite, and phyllosilicates of the smectite group (BONATTI, 1963).

An example of a completely devitrified grain of this type is shown in Fig. 3. Phillipsite crystals with radial structure have developed in the grain. Some of the larger grains of this kind show the presence of a core of unaltered sideromelane. An example is given in Fig. 4. The entirely devitrified grain of Fig. 3 is approximately 200 microns in radius, while devitrification in the grain of Fig. 4 proceeded to a depth of approximately 400 microns. If hydration and devitrification of these glasses had occurred at low temperatures on the sea floor, times of the order of hundreds of millions of years must be required according to Marshall's estimates. These, and great quantities of similar grains, were recovered from the upper few centimeters of the bottom deposits; consequently they are not older than one or at most a few million years.

It is probable that these grains originally consisted of palagonite and were produced by high temperature hydration during and soon after submarine volcanic effusions. The core of some of the bigger grains such as the one shown in Fig. 4, was probably protected during eruption and cooling from direct contact with water by the outer palagonite-forming crust; it therefore gave rise to a normal basaltic glass. A further example of this association is in Fig. 5 from a hyaloclastic rock dredged from the East Pacific Rise.

These hyaloclastites from the Pacific Ocean seem very similar to those present in impressive formations on the Iblean Mountains of Sicily. The Sicilian hyaloclastites, presumably formed through granulation or pulverization of the lava upon contact with sea water, also consist of more or less altered palagonitic glass; the larger grains occasionally contain a small central nucleus of normal unaltered basaltic glass (HONNOREZ, 1963).

It is known that phillipsite and smectites (nontronite) are among the dominant components of the surface layers of large areas of the

Pacific floor (ARRHENIUS, 1963; BONATTI, 1963; PETERSON and GRIFFIN, 1964). On the basis of the preceding discussion it is suggested that these oceanic minerals are derived by gradual alteration of palagonitic glass, with only minor contribution from normal, originally, unhydrated glasses or from other silicates.

Hydrothermal experiments by HAWKINS (1961) confirm that glasses of intermediate and basic composition tend to form structures of the smectite group, provided that suitable cations are present in the system. Lack of proper ions limits the ease of crystallization of hydrated glasses. In this connection, Hawkins points out the particularly important role of Mg^{2+}. This requirement, however, is not likely to be a limiting factor for devitrification on the ocean floor because of high concentration of cations in sea water.

X-ray diffraction analyses of some samples of apparently fresh palagonite from the Columbia River Plateau and the Oregon Coast formation revealed the presence of smectites as the only crystalline components, as did samples of palagonite from Iceland (BONATTI and NAYUDU, unpubl. results). In addition to their gradual formation at low temperature, it is probable that structures of the smectite group may be formed during very early stages of alteration of palagonite and during cooling of the hydrated submarine lava. Presence of water at relatively high temperature and pressure may allow some of the silicon-oxygen tetrahedra to arrange themselves at fast rates into smectitic nuclei together with volcanic and/or water derived cations. The possibility of high temperature formation of montmorillonite is well established (HAUSER and REYNOLDS, 1939). This process is likely to preferentially affect basic lavas for the reasons before mentioned.

Phillipsite appears to be formed prevalently through a low temperature-gradual alteration process of palagonite. This is suggested particularly by the stratigraphic distribution of the mineral in certain deposits of the Pacific (BONATTI, 1963) and also by the fact that at high temperature other zeolites are more likely to form, as suggested by the work of HAWKINS and ROY (1963).

In some cases chemical analyses of palagonite and closely associated sideromelane (whose composition should be close to that of the original melt) have been carried out. Table 1 gives some of the results. Palagonites are generally characterized by a decrease in Mg and Ca and sensible changes in the alkalis, usually an increase in K and a decrease in Na, except in case *a* where they are both very enriched. Also shown is a complete oxidation of Fe^{+2} to Fe^{+3}, and in

TABLE 1 - Chemical data from hyaloclastic rocks.

	a			b			c			d			e
	1	2	3	1	2	3	1	2	3	1	2	3	
SiO_2	46.76	44.73	49.1	46.39	35.34	46.83	49.54	36.36	41.6	51.9	33.0	46.1	25.81
Al_2O_3	17.71	16.26	17.8	16.27	11.15	14.78	16.47	16.20	18.5	14.7	8.3	11.5	19.35
Fe_2O_3	1.73	14.57	16.0	1.35	10.28	13.62	2.30	16.56	18.9	1.6	15.2	21.2	15.05
FeO	10.92	—	—	9.96	2.19	2.90	7.55	0.93	1.0	8.6	—	—	0.63
Mn_2O_3	—	2.89	3.2	—	—	—	—	—	—	—	—	—	—
MnO	0.44	—	—	tr.	0.22	0.29	0.19	1.25	1.4	—	0.1	0.15	0.15
MgO	10.37	2.23	2.4	9.77	6.52	8.64	7.91	4.86	5.6	8.7	5.0	7.0	1.29
CaO	11.56	1.88	2.1	13.00	7.01	9.29	11.43	6.77	7.7	10.4	7.0	9.8	1.25
Na_2O	1.83	4.50	4.9	1.40	0.16	0.21	2.62	2.01	2.3	2.6	0.7	1.0	1.68
K_2O	0.17	4.02	4.4	0.15	0.19	0.25	0.30	0.94	1.0	2.4	0.3	0.4	0.89
H_2O^+	{ —	9.56	—	0.15	8.90	—	0.95	6.31	—	0.20	9.3	—	} 31.02
H_2O^-			—	0.10	15.50	—	0.27	6.26	—	0.16	18.3	—	

a. South Pacific (MURRAY and RENARD, 1891). 1 = sideromelane; 2 = palagonite; 3 = palagonite on a water-free basis.

b. Iceland (PEACOCK, 1926. 1 = sideromelane; 2 = palagonite; 3 = palagonite on a water-free basis.

c. Atlantic ocean (CORRENS, 1930). 1 = sideromelane; 2 = palagonite; 3 = palagonite on a water-free basis.

d. Palagonia, Sicily (HOPPE, 1941). 1 = sideromelane; 2 = palagonite; 3 = palagonite on a water-free basis.

e. Glass from North Atlantic (NICHOLLS and BOWEN, 1961).

some cases, definite changes in the concentration of Si and Al. The high concentration of Mn in the palagonite of column *a* is probably due to segregations of manganese oxides which often are associated with palagonites. In column *e* data from a glass recovered from the North Atlantic are reported for the sake of comparison. Studies of the chemical gradients within hyaloclastites are presently being carried out (ARRHENIUS et al., in prep.).

Already from these data it is apparent that interaction of hot lavas and great masses of water is accompanied by high mobility of several elements, as also suggested by geochemical calculations of BOSTRÖM (1964). Interactions of this sort have influenced the chemistry of large areas of the Pacific. For example, Mn and Fe leached out of basaltic lavas during and after their effusions on the ocean floor seem to be mainly responsible for the extensive deposits of ferromanganese oxides of the Pacific bottom, presumably formed according to a mechanism suggested by BONATTI and NAYUDU (1965).

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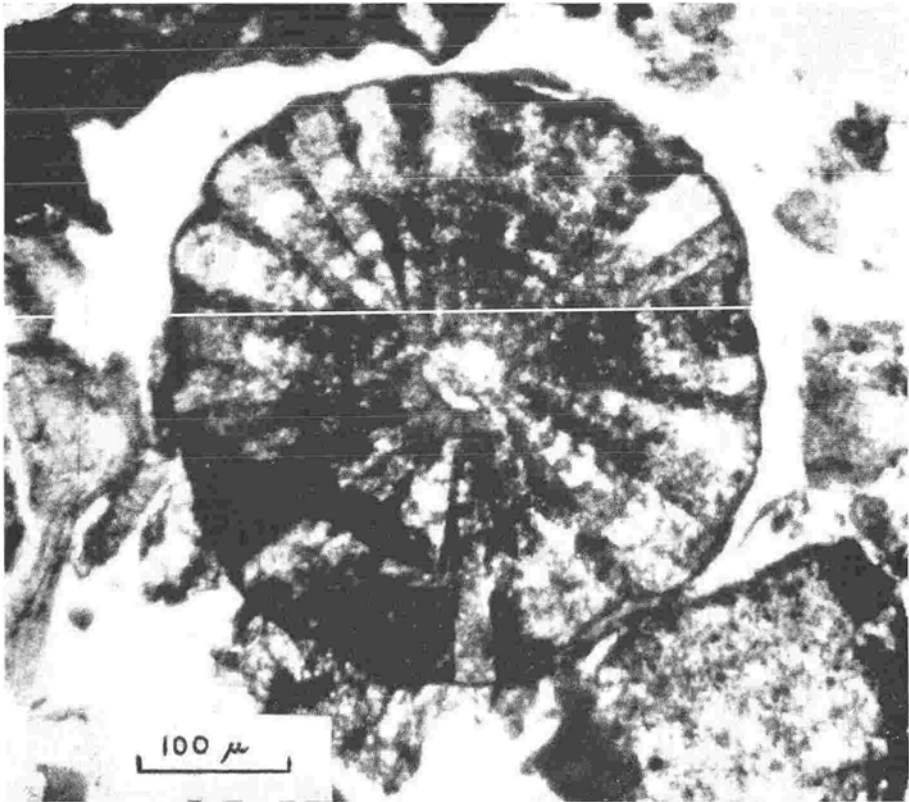
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Fig. 3 - Thin section of an altered grain of palagonite from the South Pacific. Phillipsite crystals growing radially.

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FIG. 4 - Thin section of a hyaloclastic grain from the South Pacific, showing core of sideromelane, and crust of altered palagonite. Phillipsite crystals are visible. Dark material is nontronite, with some Fe and Mn oxides.
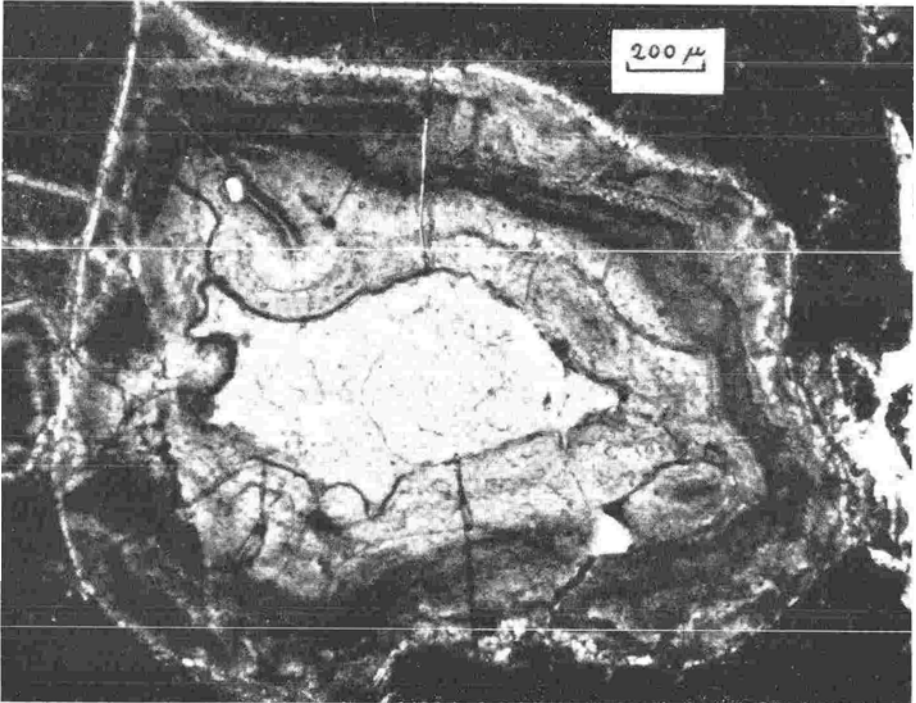
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FIG. 5 - Hyaloclastic grain from the East Pacific Rise, showing core of sideromelane and thick crust of palagonite. A felspar inclusion is present in the sideromelane. (Thin section).