Volume Relations between Palagonite and Authigenic Minerals in Hyaloclastites, and Its Bearing on the Rate of Palagonitization

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Abstract

Hyaloclastites are particularly suitable material for palagonitization. This process of alteration leads to the formation in broadly equal proportions of authigenic minerals and palagonite. When the palagonitization process reaches the stage where voids between fragments, and vesicles within fragments are completely filled with authigenic minerals so as to make the rock more or less impermeable to water, the rate of the palagonitization process is thought to slow down considerably. Depending upon the original texture and porosity of the hyaloclastite, sideromelane may or may not remain at this stage. This may explain why sideromelane, which otherwise would have been completely palagonitized, can be found in relatively old hyaloclastites. Further, study of palagonitization taking place around glassy vesicle walls strongly suggests that the process is post-eruptional, being initiated at the time the glass encounters an equeous environment, and proceeds at low temperatures.

Introduction

Sideromelane, the dominant constituent of hyaloclastites, is very susceptible to alteration under aqueous conditions. Hence, even in relatively young hyaloclastite formations (*e.g.* the Moberg formations in Iceland), it is the alteration product of sideromelane, palagonite, which to varying degrees characterizes such deposits. The alteration of sideromelane to palagonite may be either a relatively quick, or an extremely slow process, depending upon the relative effectiveness

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of the following physical/chemical parameters (BONATTI, 1965; MOORE, 1966; HAY and IIJIMA, 1968 *a, b*; JAKOBSON, 1972):

(1) the chemical composition of the glass (sideromelane),
(2) the nature of the aqueous environment in which te process takes place,
(3) the temperature during palagonitization,
(4) the time factor.

Opinions on the mechanism whereby sideromelane is converted to palagonite include gradual hydration and alteration (PEACOCK, 1926), lengthy diffusion-hydration (MOORE, 1966) and microsolution-precipitation (HAY and IIJIMA, 1968 *a, b*). BONATTI (1965) takes the extreme view that during subaqueous eruption, basaltic glass is immediately hydrated and converted to palagonite, and that sideromelane fragments will usualy be protected from direct contact with water by a crust of palagonite, formed during the earlier stages of the cooling process. Similarly PEIRCE (1970) states that « the field evidence in Iceland certainly suggests that palagonitization takes place during extrusion and cooling ». This implies that palagonite is not a secondary product of sideromelane, but may form directly during the interaction of hot lava with water.

MOORE (1965), NICHOLLS (1965), and MIYASHIRO *et al.* (1969) have shown that there is no difference in the water content from margin to core in fresh pillows, which give no positive evidence of reaction between the lava and the sea water. Study of the tephra in Surtsey (JAKOBSSON, 1972), revealed that outside the active thermal field, no palagonite was formed, whereas within the thermal field, at subsurface (ca. 20-80 cm) temperatures of about 60°-100° C, the palagonitization process was actively going on five years after the eruption. This observation, as emphasized by Jakobsson, suggests that the palagonitization of sideromelane is a post-eruptional process, that may take place even at relatively low temperatures. The same conclusion has been reached by many authors dealing with this problem (*e.g.* NOE-NYGAARD, 1940; JONSSON, 1961; HAY and IIJIMA, 1968 *a, b*), and is supported by the present work.

HAY and IIJIMA (1968 *a, b*) found that the amount of authigenic minerals in tuffs is generally proportional to the amount of palagonite, indicating that the formation of these minerals is related to the palagonitization process.

The aim of this account is particularly to stress the importance of this relationship as a controlling factor in palagonitization of hyaloclastites, since the precipitation of authigenic minerals will continuously change the texture and porosity of the rock making it finally more or less impermeable, and hence, locally slowing down the palagonitization rate.

Studies have been made of a number of hyaloclastites of different ages, and also showing varying degrees of palagonitization ranging from the very incipient to the final stage.

Sample Description

The material investigated comprises hyaloclastites from Iceland and Santa Maria (Azores). The Icelandic examples are all Quaternary hyaloclastites of subglacial origin, and the glass (sideromelane) is olivine tholeiite in composition. Within small areas of the same deposit, and indeed in the same hand specimen, considerable variations in the degree of palagonitization can be seen. It would seem as if when exposures face southwards, the hyaloclastites are generally more extensively palagonitized than in cases where exposures face in other directions. Also the outermost 1 cm of the deposits is often seen to be markedly more palagonitized than the material further inside, especially for exposures facing southwards.

This suggests that the process may be accelerated by diurnal temperature fluctuations.

The material from Santa Maria (Azores) is from a shallow marine pillow lava/hyaloclastite delta, situated upon Mid-Miocene calcareous sediments, and now elevated about 200 m above sea level.

The pillows are alkali basaltic in composition. In this deposit the degree of palagonitization increases progressively with depth in the delta. This is thought to be a reflection of the length of time the various parts of the delta were below sea level.

The lowest part must necessarily have been submerged for a longer time than the upper part of the delta, and hence been in a more favourable situation for palagonitization.

Texture of the Hyaloclastites

The grains of hyaloclastites are mostly characterized by a very irregular shape, which, in some cases, may give information about the genesis of the deposit. Along the edges of grains, embayments sometimes occur, indicating that the grains formed by breaking along vesicles. In the hyaloclastites dealt with here, vesicularity is very variable, and vesiculation alone cannot account for the disintegration of the lava. PECKOVER *et al.* (1973) demonstrated that processes of the fuel-coolant interaction type may play an important role in the breaking up of lava down to a water depth of about 700 m. Other mechan-

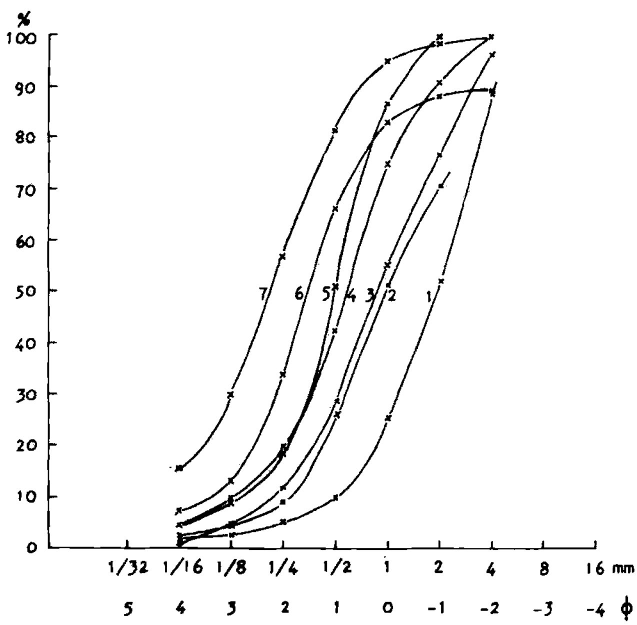

FIG. 1 - Grain-size distribution curves of hyaloclastites. 1-3 represent reworked shallow-marine hyaloclastite from Santa Maria (Azores), and 4-7 subglacial hyaloclastite from Iceland.

isms for disintegrating basalt glass to form hyaloclastites, unrelated to depth, are described elsewhere (JONES, 1968; FURNES, 1972).

JAKOBSSON (1972) found that more than 90 % of the tephra in Surtsey has a grain size between 0.05-5 mm, and that the grain size curves in most cases had three maxima. Grain size distribution curves of hyaloclastites are shown on Fig. 1. Nos. 1-3 are on the field evidence reworked hyaloclastites (Santa Maria), and this may be reflected in the distribution curves (Fig. 1) as they have less fine material than nos. 4-7 (from Iceland) which, from both field and microscopic evidence, are undisturbed. They are all, however, unimodal.

HAY and IIJIMA (1968 *a*) presented data on the porosity of a number of tuffs from Oahu, Hawaii, ranging from fresh glass to dense palagonite tuff, and there is a marked departure in porosity from about 36 % to 8 %, respectively.

Palagonite Thickness around Shards and Vesicle Walls

MOORE (1966) demonstrated that the thickness of palagonite coating the outermost glassy margins of dredged fragments of pillow lava of known age, is a simple function of time.

In the case of hyalocastites, and especially those of shallow-marine or subglacial origin, it is difficult, if not impossible to relate palagonite thickness directly to the age of the deposit. This is because the chemical/physical properties of the aqueous environment are likely to fluctuate considerably. Also, and probably just as important as any of the commonly quoted factors (1-4 on p. 174) affecting the palagonitization process at some stage, is the original texture of the rock.

With progressive palagonitization and accompanied growth of authigenic minerals around edges of sideromelane shards, the ratio of maximum to minimum thickness of palagonite rinds becomes increasingly variable (Fig. 2). For each ratio worked out, the maximum and minimum thicknesses have been measured on the same grain. None of the four earlier-mentioned palagonitization factors are therefore likely to be responsible for this behaviour, as the physical/chemical conditions would always be identical or nearly so over small distances, usually in the order of a few microns, as seen on Fig. 3 A. However, at the incipient stage of palagonitization, or in cases where small or negligible amounts of authigenic minerals have been precipitated, but an appreciable palagonite rind has been formed, the thickness is very constant (Fig. 3 B). In cases where the maximum and minimum thickness is very variable, evidence can sometimes be found that the thickness at some early stage of palagonitization was constant. This is reflected by zones of constant thickness following the edges of grains (Fig. 3 A).

How zoning in palagonite is produced is unclear, but JAKOBSSON (1972) suggested that fluctuations in the temperature and the amount of steam may possibly explain the zoning in the palagonitized tephra in Surtsey. However, an example studied in the present work showed

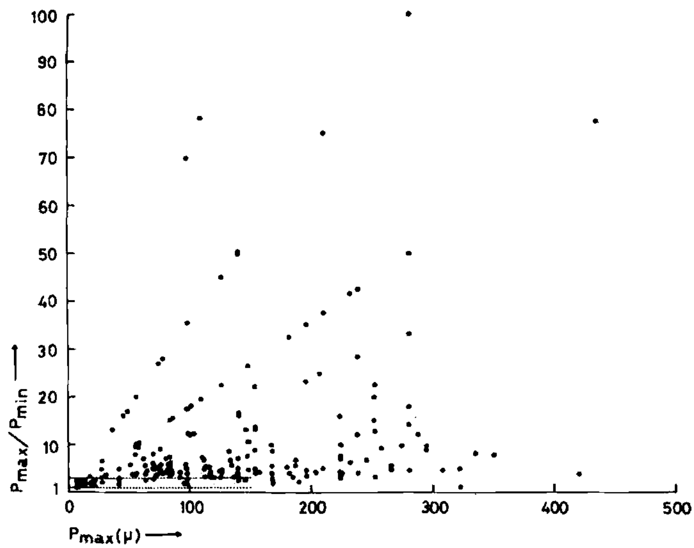

FIG. 2 - P_{Max}/P_{Min} as a function of P_{Max} to show how the ratios become increasingly variable with increasing P_{Max} around shards. In all semples investigated the ratio of authigenic minerals to palagonite is close to one.
P_{Max} = maximum thickness of palagonite.
P_{Min} = minimum thickness of palagonite.
The stippled lines show the superimposed position of Fig. 4.

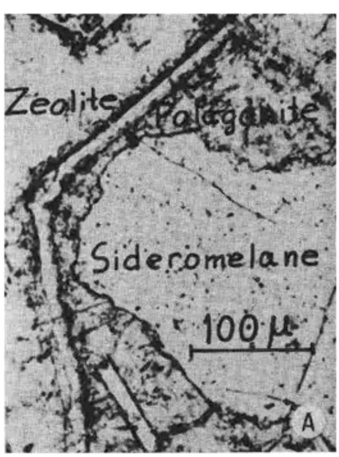

FIG. 3 A - Microphotograph showing the variable thickness of palagonite surrounding part of a fragment from a subglacial hyaloclastite. The voids between the fragments are mostly filled with zeolites. Note the thin rind of constant thickness along the edge of the grain, and which represents the beginning stage of palagonitization.
B - Partly palagonitized fragments of sideromelane (S), where the thickness of palagonite (P) is constant. The voids between the fragments are empty.

only two zones, an outer one of constant thickness, followed by an inner one of irregular thickness (Fig. 3 A), and temperature fluctuations seem unlikely to have produced such a pattern. PEACOCK (1926) divided palagonite into two types, *gel-palagonite* and *fibro-palagonite*, representing palagonite with increasing crystallinity, respectively. STOKES (1971) also distinguished between various types of palagonite according to their crystallinity, and showed how zoning (two zones) might be produced by an outer microcrystalline, anisotropic zone of palagonite, and an inner isotropic phase adjacent to the glass. Although both zones of Fig. 3 A are isotropic, it is considered most likely that they reflect various degrees of crystallinity of the palagonite.

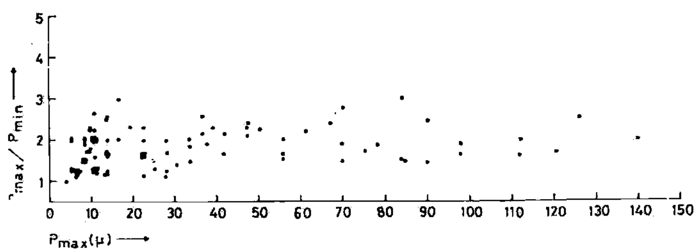

FIG. 4 - P_{Max}/P_{Min} as a function of P_{Max} to show that the ratios remain constant with progressive palagonitization and authigenic mineral formation around vesicles.
P_{Max} = maximum thickness of palagonite.
P_{Min} = minimum thickness of palagonite.

In contrast with the general situation of progressive palagonitization and authigenic mineralization around shards, the ratio of maximum to minimum thickness of palagonite formed around vesicles remains constant with progressive palagonitization and associated mineral growth (Fig. 4).

These observations (Fig. 2, 3, 4) indicate that the rate of the palagonitization process at a given time in the early stage is fairly constant. It has been pointed out that the grains are mostly irregular in shape, and, further, that palagonitization is normally accompanied by secondary mineral growth, which decreases the total porosity of the rock. These effects are thought to account for the increasing variations in P_{Max}/P_{Min} (Fig. 2) with progressive palagonitization, and can be explained as follows. Initially water can reach a grain at any point. When authigenic minerals start to precipitate and cement the grains, the distance water has to travel to reach the glass, will become increasingly variable with progressive alteration and cementation.

In the case of vesicles, the distance water has to travel will also increase with progressive palagonitization and authigenic mineral formation, but this distance will be approximately the same in any direction normal to the vesicle wall.

Relationship between the Amount of Palagonite and Authigenic Minerals

Total Rock.

When sideromelane is converted to palagonite, a certain amount of the major elements are lost either as oxides or ions, and in this isovolumetric reaction, water influx compensates for the loss (HAY

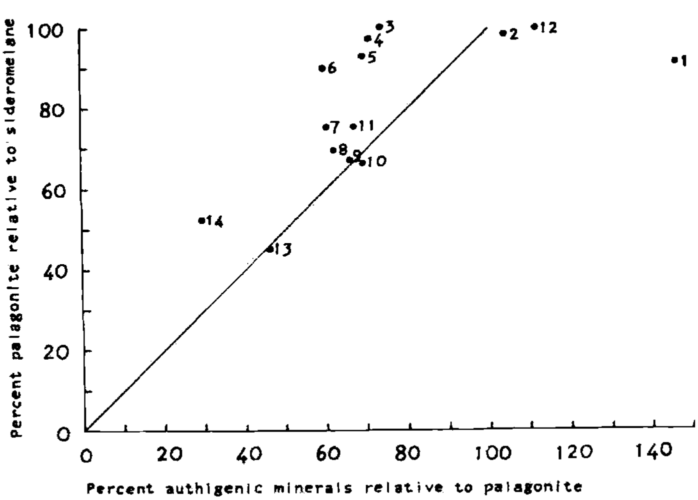

FIG. 5 - Relationship between the amount of authigenic minerals and palagonite. 1-9: Post-Mid-Miocene palagonitized hyaloclastite of shallow marine origin. Santa Maria, Azores. 10-12: Quaternary palagonitized hyaloclastite of subglacial origin. Eiriksjökull area, Iceland. 13: Palaeocene palagonitized hyaloclastite. Skye, Scotland. 14: Post-erosional palagonitized hyaloclastite of subglacial origin. Mosfell, Iceland.

and IIJIMA, 1968 *a, b*; JAKOBSSON, 1972). Formation of authigenic minerals accounts for the components lost from the glass (sideromelane), and these minerals may be precipitated adjacent to the palagonite. Fig. 5 shows the relationship between authigenic minerals and palagonite for hyaloclastites of very different ages, and also various stages in the palagonitization process. Indeed, in a number of cases there is a good relationship between the two. The same relationship was found by HAY and IIJIMA (1968 *a, b*), indicating that authigenic minerals are produced in the palagonitization of sideromelane. However, anomalous examples are found where there may be an appreciable amount of palagonite but no authigenic minerals. In such cases the

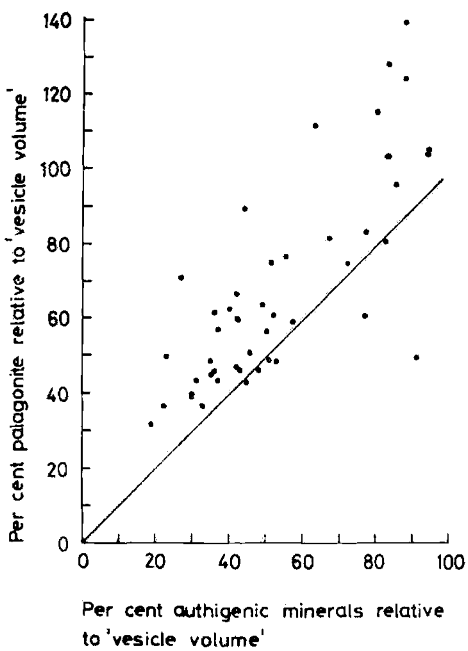

FIG. 6 - Relationship between the amount of palagonite and authigenic minerals for partially filled vesicles.

rock has behaved as an open system, and components extracted from the glass (sideromelane) have not been precipitated as authigenic minerals adjacent to the source.

Vesicles Partially Filled with Authigenic Minerals.

In shards of partly palagonitized hyaloclastites, vesicles of different size showing degrees of palagonitization varying from the very incipient stage, are commonly seen. Also, amygdales surrounded by palagonite can be found close to completely « fresh » vesicles.

The palagonite rind around vesicle walls is as previously mentioned, very constant in thickness, and the amount of palagonite can therefore easily be calculated. For a number of vesicles the amount of palagonite and authigenic minerals have been calculated, and as seen from Fig. 6, there is a fairly good relationship between the two. Generally there is more palagonite than authigenic minerals, and this feature may be explained as follows: the palagonite formed must remain in situ, whereas part or all of the solution carrying the leached components may be transported away to form authigenic minerals elsewhere. Precipitation of zeolites at low pressure is controlled by the properties of the solution such as pH, the activity of silica and the concentration of alkalis and alkaline earths, etc. (HAY, 1966; HESS, 1966; IIJIMA and HARADA, 1969). Hence, as reflected in Fig. 6, it would be expected that less authigenic minerals than palagonite would be present.

Vesicles Apparently Filled with Authigenic Minerals.

Fig. 7 shows the volumetric relationship between palagonite and authigenic minerals for apparently filled vesicles (amygdales) of var-

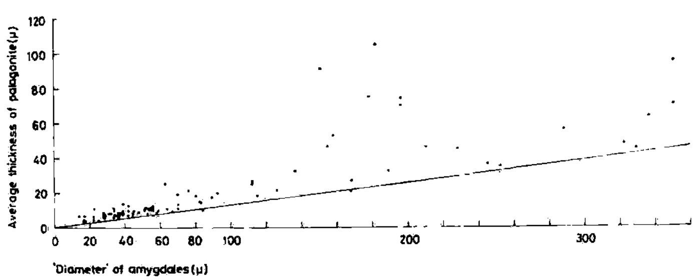

FIG. 7 - Relationship between « diameter » and average thickness of palagonite around amygdales. The solid line represents the position where the volume of authigenic minerals and palagonite is equal.

ious sizes. The solid line on the diagram represents the position where the plots should fall if the volume of palagonite equaled that of authigenic minerals (*i.e.* type 2-amygdale on Fig. 8 A). The interpretation of Fig. 7 is difficult since six possibilities, as shown on Fig. 8 A, may be represented, and each, therefore, has to be taken into consideration. Fig. 8 B shows where randomly cut sections through any of these possible amygdales/vesicles on Fig. 8 A may plot on Fig. 7, and only types 1 and 4 of Fig. 8 A can plot below the line $V_1 = V_2$ (Fig. 7 and 8 B). On Fig. 7 none of the measurements plots markedly below the line $V_1 = V_2$, and hence it is assumed that examples of 1 and 4-type amygdales/vesicles are not represented. If this assumption is jus-

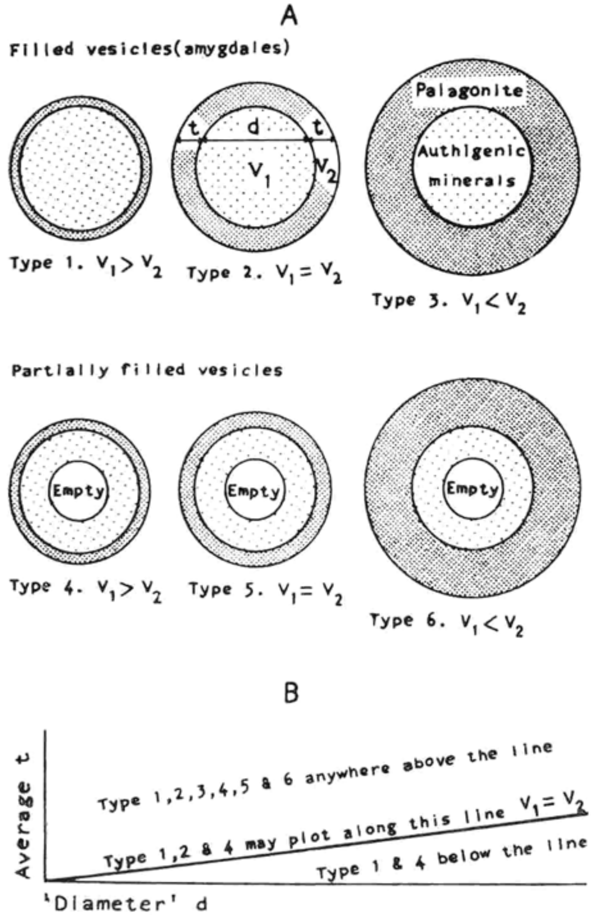

FIG. 8 - A shows the six possibilities of amygdales/vesicles that may be represented on Fig. 7, and B shows where they may plot on the diagram.

tifiable, it means that only examples of type 2 (Fig. 8 A) are represented close to and on the line $V_1 = V_2$. If, however, all the plots on Fig. 7 were of type-2 amygdales, all the measurements should be uniformly distributed between 0 and 1 (Fig. 9). Fig. 9 shows that they are not, and hence some examples of type 3 and/or 5 and/or 6 (Fig. 8 A) must be represented. It is, however, unlikely that any high proportion of type 3 and 6 should be present as the samples selected for measurements show, as far as the total rock is concerned, very good correlation between palagonite and authigenic minerals (nos. 7-11 of Fig. 5). A crude check on the likely abundance of types 3 and 6 can be

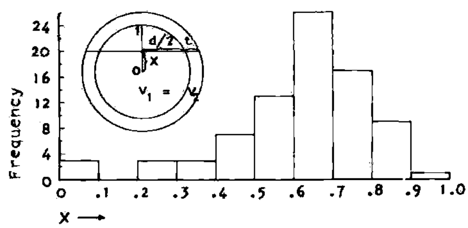

FIG. 9 - Frequency distribution of the data plotted on Fig. 7. Inset figure (upper left corner) shows how X of each « amygdale » has been calculated.

$$X = \sqrt{\frac{F^{2*}\,2^{2/3} - 1}{F^2 - 1}}\ , \text{ where } F = \frac{2\,t + d}{d}$$

made by calculating the amount of vesicles/amygdales that have been cut through the palagonite rind. If only type 2 amygdales were present, such sections should comprise about 26 % of the total amount, and if type 3 and 6 were present in any appreciable amount, a considerably higher percentage should be expected. In most of the samples, however, the amount of « palagonite-sections » is considerably less than 26 %, indicating that type 5 is present in an appreciable amount, rather than types 3 and 6.

The conclusion that types 2 and 5 (the only $V_1 = V_2$ types) are the majority represented on Fig. 7, indicates that palagonite and authigenic minerals are present in roughly equal amounts at any stage during progressive alteration around vesicles. Further, when a vesicle is filled with authigenic minerals, palagonite growth stops, or at least the rate slows down considerably.

Summary and Conclusions

The main observations of progressive palagonitization of hyaloclastites may be summarized as follows:

1. P_{Max}/P_{Min} becomes increasingly variable with progressive palagonitization and authigenic mineralization around shards.

2. P_{Max}/P_{Min} around shards remains fairly constant with progressive palagonitization when no authigenic minerals are formed.
3. P_{Max}/P_{Min} remains constant with progressive palagonitization and authigenic mineralization around vesicles.
4. Around vesicles, and usually for the total rock, there seems to be a good relationship between the amount of palagonite and authigenic minerals formed.
5. Palagonitization around vesicles starts at any time when water is accessible, and the rate of the process apparently slows down considerably or ceases when they become filled with authigenic minerals.

From these observations it may be inferred that the textual changes (decreasing porosity) resulting from authigenic mineral growth when sideromelane is palagonitized, are very important in controlling the rate of the process. Around the same grain it may result in considerable variation in the rate of palagonitization, which is reflected in the sometimes highly variable thickness of the palagonite. Hence if the voids between fragments have become filled with authigenic minerals while there is still sideromelane left (as could be the situation in coarse-grained hyaloclastites), such residual sideromelane may remain unaltered for an abnormally long time. Consequently in most cases it is not possible to use the extent of palagonitization in hyaloclastites as a measure of their ages.

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References

BONATTI, E., 1965, *Palagonite, hyaloclastites and alteration of volcanic glass in the ocean.* Bull. Volcanol., *28*, p. 257-269.

FURNES, H., 1972, *Meta-hyaloclastite breccias associated with Ordovician pillow lavas in the Solund area, west Norway.* Norsk Geol. Tidsskr., *52*, p. 385-407.

HAY, R. L., 1966, *Zeolites and zeolitic reactions in sedimentary rocks.* Geol. Soc. Amer. Spec. Pap., *85*, 130 pp.

——— and IIJIMA, A., 1968 *a*, *Nature and origin of palagonite tuffs of the Honolulu Group on Oahu, Hawaii.* Geol. Soc. Amer. Mem., *116*, p. 331-376.

——— and ———, 1968 *b*, *Petrology of palagonite tuffs of Koko Craters, Oahu, Hawaii.* Contr. Mineral. and Petrol., *17*, p. 141-154.

HESS, P. C., 1966, *Phase equilibria of some minerals in the K_2O-Na_2O-Al_2O_3-SiO_2-H_2O system at 25°C and 1 atmosphere.* Amer. J. Sci., *264*, p. 289-309.

IIJIMA, A and HARADA, K., 1969, *Authigenic zeolites in zeolitic palagonite tuffs on Oahu, Hawaii.* Amer. Mineralogist, *54*, p. 182,197.

JAKOBSSON, S. P., 1972, *On the consolidation and palagonitization of the tephra of the Surtsey volcanic island, Iceland.* Surtsey Progr. Rep., *VI*, p. 1-8.

JONES, J. G., 1968, *Intraglacial volcanoes of the Laugarvatn region, south-west Iecland, I.* Quart. Jour. Geol. Soc. Lond., *124*, p. 197-211.

JONSSON, J., 1961, *Some observations on the occurrence of sideromelane and palagonite.* Bull. Geol. Inst. Univ. Uppsala., *40*, p. 81-86.

MIYASHIRO, A., SHIDO, F and EWING, M., 1969, *Diversity and origin of the abyssal tholeiite from the Mid-Atlantic Ridge near 24° and 30° north latitude.* Contr. Mineral. and Petrol., *23*, p. 38-52.

MOORE, J. G., 1965, *Petrology of deep-sea basalts near Hawaii.* Amer. Jour. Sci., *263*, p. 40-53.

———, 1966, *Rate of palagonitization of submarine basalt adjacent to Hawaii.* U. S. Geol. Surv. Prof. Pap., *550-D*, p. 163-171.

NICHOLLS, G. D., 1965, *Basalts from the deep ocean floor.* Min Mag., *34* (Tilley Vol.), p. 373-388.

NOE-NYGAARD, A., 1940, *Sub-glacial volcanic activity in ancient and recent times.* Fol. Geogr. Dan, Tom. 1, no. 2.

PEACOCK, M. A., 1926, *The petrology of Iceland. Part. I. The basic tuffs.* Trans. Roy. Soc. Edinb., *55*, p. 51-76.

PECKOVER, R. S., BUCHANAN, D. J. and ASHBY, D. E. T. F., 1973, *Fuel-coolant interactions in submarine volcanism.* Nature, *245*, p. 307-308.

PEIRCE, J. W., 1970, *Chemical changes during palagonitization under marine and non-marine conditions.* Science in Iceland, *2*, p. 31-36.

STOKES, K. R., 1971, *Further investigations into the nature of the materials chlorophaeite and palagonite.* Min. Mag., *38*, p. 205-214.

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