ZEOLITES AND PALYGORSKITE AS WEATHERING PRODUCTS OF PILLOW LAVA IN CURAÇAO[1]

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ABSTRACT

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Infillings between pillows in the lavas of Curaçao consist of zeolites, notably offretite, as well as the clay minerals palygorskite and smectite. The material is dissected by veins of analcite. The zeolites have been formed from the glassy crust of the pillow lava upon subaerial weathering in a dry and hot climate creating a pseudo-closed system. Under these conditions, hydrolysis of the glassy basaltic material generates a saline alkaline environment favourable for zeolite formation. Behind the weathering front the altered material will be exposed to gradually less saline and less alkaline interstitial fluid and the zeolites are transformed to palygorskite. Next, at a still greater distance, palygorskite is transformed to smectite. Analcite is precipitated from a brine formed by evaporation of the interstitial fluid in fissures.

INTRODUCTION

The Island of Curaçao consists for a large part of pillow lavas and hyaloclastites, that make up the Curaçao Lava Formation as defined by BEETS (1972). These lavas have been dated radiometrically by SANTAMARIA & SCHUBERT (1974), who reported K/Ar ages of 126 ± 12 Ma and 118 ± 10 Ma. Between the pillow lavas, a small sedimentary intercalation was discovered at Ronde Klip hill. Fossils from six ammonite genera from this deposit indicate an Upper Middle Albian age (WIEDMANN, 1978).

For a description of the Curaçao Lava Formation, the reader is referred to BEETS (1972). The more than 1000 metres of basaltic pillow lavas and related hyaloclastites underwent a major tectonic phase in the early Cenozoic, when they were faulted and uplifted above sea level. The overlying Seroe Domi Formation (Miocene-Lower Pleistocene reef talus) at Seru Pretu starts with a transgression conglomerate that contains relatively unweathered basalts. Most of the Curaçao Lava Formation consists of strongly weathered rocks, and it is likely that most of the weathering has occurred in the late Cenozoic.

The Curaçao Lava Formation is exposed in several road-cuts. In these exposures, the weathered material has retained its pillow lava fabric resulting in 'giraffe skin' patterns (Fig. 1). The less weathered rock is being quarried at several sites, e.g.
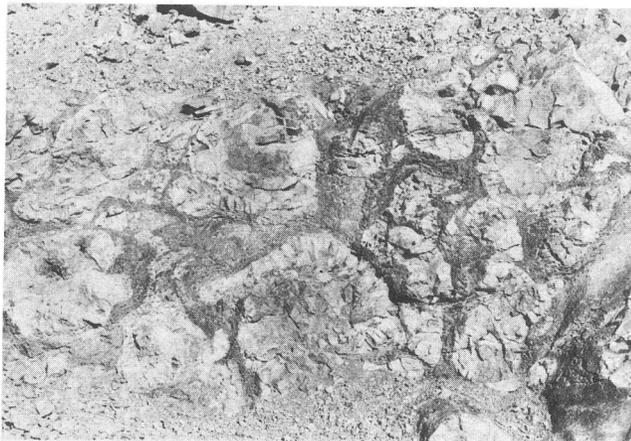

Fig. 1.
Weathered pillow lava with brown material between the pillows Koraal Tabak, Curaçao. Pillows are approx. 0.5 m across.

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Sua and Koraal Tabak. In these exposures, alteration products are found between the pillows. The materials consists of brittle, resin-like material with a vitreous lustre and may show a conchoidal fracture. In cross-section, the material is most abundant where three pillows join. The brown material is fisurred by white veins and is normally referred to as 'volcanic glass'. In this study the actual nature of this material and its genesis was investigated.

METHODS

The material was separated into dull brown earthy, dark brown vitreous and white subsamples. The white material could be obtained in a virtually pure state, but the separation of the brown material was very difficult, and samples of approximately 75% purity were the maximum attainable. X-ray diffraction photographs were made with a triple Guinier camera using Co-Kα radiation. Thermogravimetric analysis were carried out with a DuPont 951 termobalance. Chemical analysis of the two brown fractions and of a mixed sample, was carried out by X-ray fluorescence. Ferric and ferrous iron were not determined separately.

Thin sections were prepared of undisturbed, synolite impregnated material. One of these sections was used for microscopy, the second one was used for scanning electron microscopy and X-ray microanalysis (EDAX).

RESULTS

Description of the material; analysis of thin section

The material consists of small domains, varying from several millimetres to several centimetres across, of dull brown, earthy material that is surrounded by a thin rim, generally less than a millimetre thick, of dark brown, vitreous material. The domains are separated by irregular veins, generally less than 2 mm thick, of a white, crystalline material that may form aggregates. In thin section (Fig. 2a, b) the white material is colourless and isotropic. The dull brown material is isotropic to weakly anisotropic, microcrystalline, and has unaltered isotropic (vitric) cores in several places. Birefringence increases gradually from the cores outward but the material remains largely unoriented (Fig. 2c). The outer zones with the vitreous lustre are strongly birefringent and are reminiscent of clays that form by *in situ* weathering of primary rocks or minerals.

Embedded in the dull brown earthy material, some scattered colourless lath-like crystals of phillipsite occur (Fig. 3a, b). In a few places two types of crystal spherulites were found,

one with a banded or radial structure consisting of phillipsite and occurring in the earthy matrix and the other embedded in the analcite having thin walls of radially oriented epistilbite crystals (Fig. 3a, b). The former sometimes have a thin coating of oriented clay and are very similar to the phillipsite spherulites described by SHEPPARD & GUDE (1968, their Fig. 10B) in altered vitric tuff.

The conspicuous fissure filling domains of partly oriented clay-size material (Fig. 2c, d) could not be separated and identified but probably consists of an assemblage of zeolite, palygorskite, and smectite.

X-ray diffraction analysis

The diffraction patterns of the white material indicate that this material consists of pure analcite. The dull brown earthy material consists of the zeolite offretite as the most abundant phase and not the closely related erionite which is often reported to be present in diagenetically altered vitric tuff (DEFFEYES, 1959 a&b; SHEPPARD & GUDE, 1968). Offretite was identified using the detailed data of SHEPPARD & GUDE (1969) which discriminate between offretite and erionite on basis of the diffraction line (*d*-values) at 0.907, 0.751 and 0.534 nm present in erionite and absent in offretite.

The main component of the vitreous rim material was smectite with a small amount of palygorskite. Because of the imperfect separation of the material, some smectite was present in the 'earthy' offretite sample and some offretite in the 'vitreous' clay sample. Both phillipsite and epistilbite are present in too small amounts to show up clearly in the X-ray photograph.

Chemical analysis

Chemical analysis of the altered material and the parent rock are presented in Table I. There are no major differences between the earthy sample (high offretite, low smectite) and the vitreous sample (low offretite, high smectite), and these samples will be called the 'altered material' in the following.

All samples have similar contents of SiO_2, Al_2O_3, Fe_2O_3 (including FeO), MnO, TiO_2 and P_2O_5. The altered material has higher contents of MgO and K_2O, and lower contents of Na_2O and CaO than the host rock. The sodium content is highest in the mixed sample (5), which is due to an admixture of fissure analcite. Assuming 29% Na_2O in analcite, the mixed sample would contain about 5% of this mineral.

Comparing the chemical analysis of the Curaçao offretites (3) with the offretite from Montbrison (6) it is apparent that recalculation of the Curaçao analyses to fit the formula of the Montbrison offretite (approximately $(M^+, \frac{1}{2}M^{++})_4 Al_4Si_{14}O_{36}$)

Fig.2a, b, c, d (facing page)
Thin sections of the brown material. a. plain light, b. crossed polarizers, c. and d. crossed polarizers. Legend: (1) unaltered volcanic glass; (2) offretite; (3) strongly birefringent smectite (+ palygorskite?); (4) analcite; (5) fissure filling domains surrounded by oriented clay; (6) phillipsite spherulite coated by thin clay film; (7) epistilbite spherulite; (8) iron segregation along cracks; (9) phillipsite crystals in clay matrix.
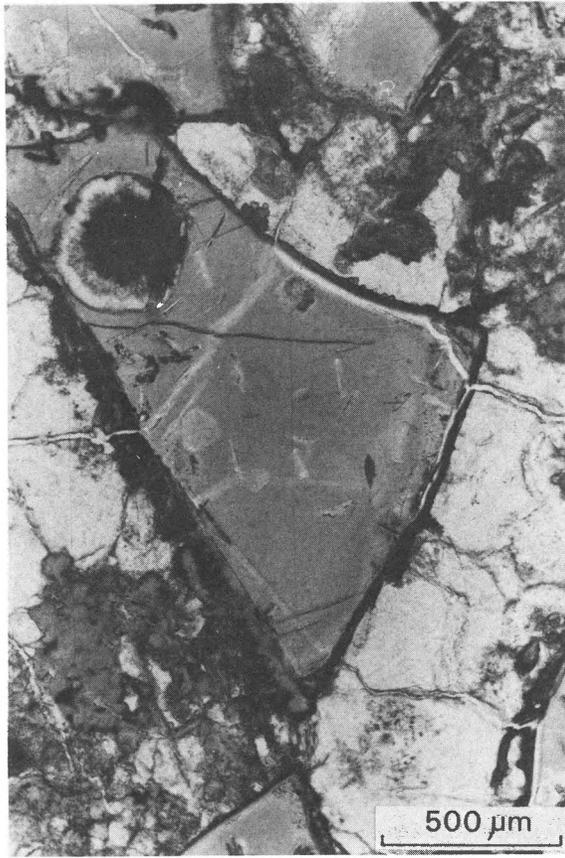
a

b

c

d
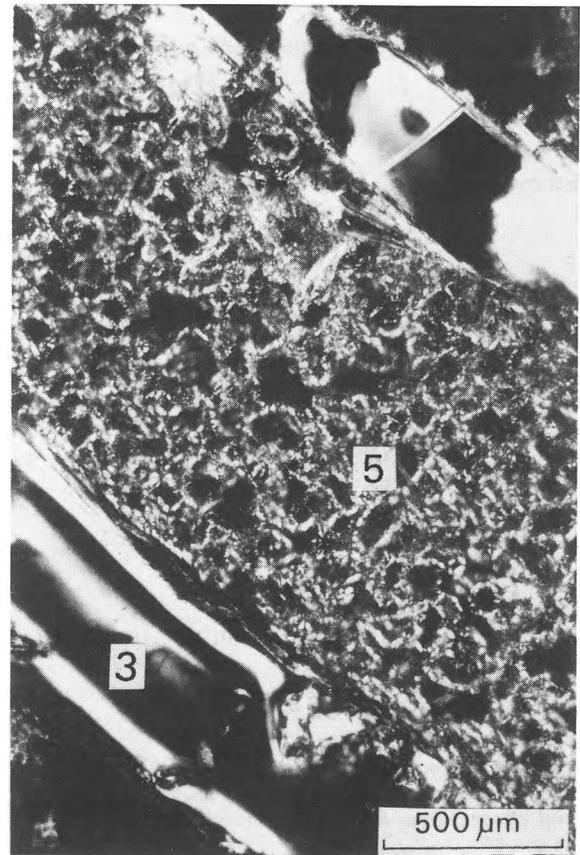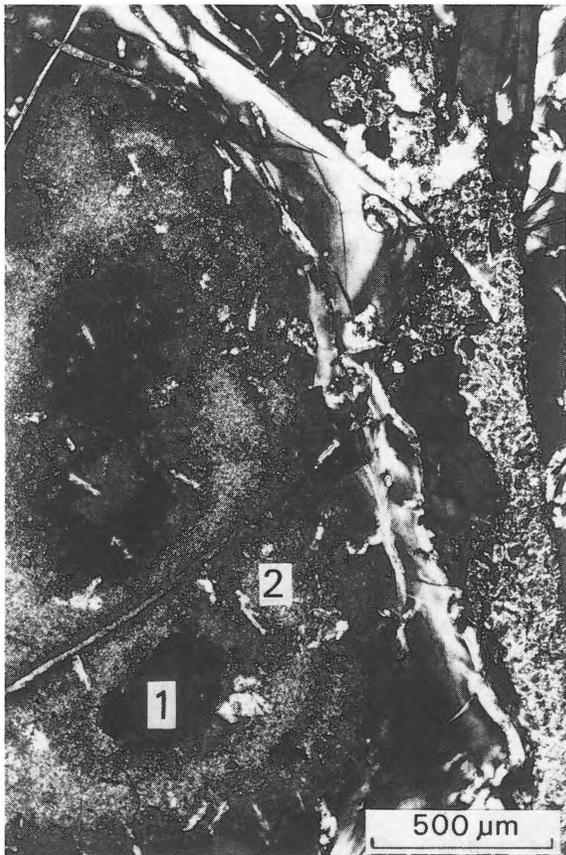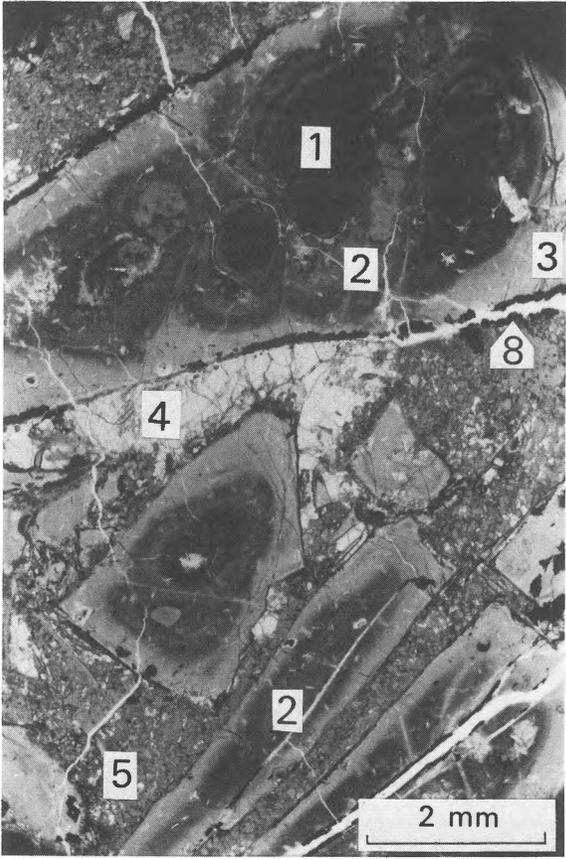
Fig. 3a, b
Thin section of vitreous material with analcite vein. a. plain light, b. polarizers at 85°C. Legend see figure 2.

Table I
Chemical composition of Curaçao lava and its weathering products (wt%)

Sample	1	2	3	4	5	6
SiO_2	48.7	49.6	48.2	47.8	48.9	53.0
Al_2O_3	13.9	13.7	13.5	12.9	14.3	18.1
Fe_2O_3	4.7	6.2 ⎫	12.7	14.0	12.2	0.0
FeO	6.7	4.9 ⎭				
MgO	6.9	6.9	9.5	10.9	9.6	2.0
CaO	10.1	10.7	4.7	4.3	3.7	4.1
K_2O	0.05	0.1	0.6	0.4	0.4	3.6
Na_2O	3.9	1.9	0.0	0.0	1.5	0.0
MnO	0.2	0.2	0.1	0.1	0.1	–
TiO_2	1.2	1.2	1.4	1.4	1.2	–
P_2O_5	0.1	0.1	0.1	0.1	0.1	–
H_2O+	3.8	4.8	10.4	9.4	8.9	18.8
Total	100.2	100.3	101.2	101.3	100.9	

1. basalt with variolitic texture (BEETS, 1972)
2. basaltic glass (BEETS, 1972)
3. dull brown, earthy material
4. dark brown, vitreous rim
5. mixture of weathered material, including analcite
6. natural offretite from Montbrison, France (SHEPPARD & GUDE, 1969)

would result in insufficient ions for the tetrahedral positions and a surplus of compensating monovalent and divalent cations. Especially the Mg surplus offers a problem. Alteration of the original vitric material implies hydration reactions as indicated by a significant increase in the H_2O+ content. It is noteworthy that the present vitric material has a higher water content (4-5%, see Table I) than lavas usually have (less than 1%, MUELLER & SAXENA, 1977, their table 15.1). This could point to a low–grade metamorphosis as described by BEETS (1972) or possibly to an early submarine palagonitization of the lava.

The reversibility of the dehydration of zeolites (VAN REEUWIJK, 1974) was used to estimate the zeolite content of the samples. Rehydration after dehydration to 600°C on the thermobalance indicated a zeolite content of about 70% for the brown earthy material using the natural offretite from Montbrison as reference material. Considering the contribution of other phases in the sample, the offretite content may be estimated at over 50%. The vitreous rim material appeared to contain about 25% offretite.

WEATHERING MECHANISM AND PARAGENESIS

The alteration of volcanic rocks in various environments has

been rather well documented in recent years. Most attention appears to have been given to the diagenetic alteration of tuffs and lavas by alkaline and saline marine, lake or connate water (e.g. DEFFEYES, 1959a; HAY, 1966; SHEPPARD & GUDE, 1968; GOODWIN, 1973; SHEPPARD, 1973; SURDAM & SHEPPARD, 1978).

The most commonly formed zeolites in these alteration processes are phillipsite, erionite, chabazite, clinoptilolite and analcite whereas other species seem to occur less abundantly. Particularly reports on epistilbite and offretite are scarce. However, because of the similarity of offretite and erionite, the former may often have been unnoticed (SHEP-PARD & GUDE, 1974)

MUNSON & SHEPPARD (1974) classify the various occurrences of zeolitic sedimentary rock as follows: (1) hydrothermal (in geothermal areas), (2) burial metamorphic (vertical succession of zeolite types due to hydration and temperature gradient), (3) weathering, (4) open system (reaction of volcanic rock with subsurface meteoric water, and (5) closed system (reaction with connate water trapped during sedimentation in a saline, alkaline lake).

The occurence of zeolites described here clearly belong to the weathering class (3), a type that according to MUNSON & SHEPPARD is of minor importance but is probably often overlooked. The most familiar examples of zeolite formation by weathering are those resulting from percolating ground water through soils and sediments (HAY, 1966; BALDAR & WHITTIG, 1968; HAY & IIJIMA, 1968; HOOVER, 1968; IIJIMA & HARADA, 1968; FRANKART & HERBILLON, 1970). Percolation of water through vitric material leads to an increase in cation content and pH which may bring about zeolitization of the material at some depth due to stagnation of water. In the present setting, the climate can be considered the key factor. Curaçao has a hot tropical climate with evaporation exceeding precipitation (Köppen: BSh; Troll: V.4) (MUELLER, 1982). The annual precipitation is between 500 and 600 mm with the highest rainfall in winter (about 100 mm in November and December). Therefore, sufficient water is available for chemical weathering while there is no or very occasional leaching. Under these conditions, minerals and particularly vitric material may hydrolyze without the reaction products being removed. This inevitably leads to a saline and alkaline environment (KRAUSKOFF, 1967, p. 115; DEFFEYES, 1959a) which is a prerequisite for the formation of zeolites. The type of zeolite formed is a function of the pH, the Si/Al ratio in the solution and the concentrations of the alkali and alkaline earth cations (HAY, 1966; SHEPPARD & GUDE, 1968). The Si/Al ratio and pH are inversely related; with increasing pH, the Al concentration increases at a faster rate than the Si concentration (MARINER & SURDAM, 1970). Thus, at higher pH values less siliceous types of zeolite will be formed than at lower pH values. The zeolites reported in this study are all less siliceous types.

The microscopic study reveals the following sequence of

formation of minerals. First, the glass is transformed to offretite. Upon continuation of the weathering process the distance between the first formed zones and the fresh unaltered material augments and the chemical environment changes accordingly. Both salinity and alkalinity will be reduced and conditions will become favourable for the formation of palygorskite. This mineral is also formed under saline alkaline conditions but the ratio Si/Al should be high and the presence of Mg ions is essential (MILLOT, 1964; SINGER & NORRISH, 1974; VELDE, 1977; ZELAZNY & CALHOUN, 1977). The increase in Si/Al ratio results from the decrease in pH while Mg dissolved out of the glass remains available since it is not used in the construction of the zeolite frameworks. Continuation of this process may lead to further dilution of the interstitial fluid and lowering of the pH which induces transformation to smectite. Thus, apart from local variations, there is a chemical gradient from the glass cores outward resulting in a mineralogical zonation.
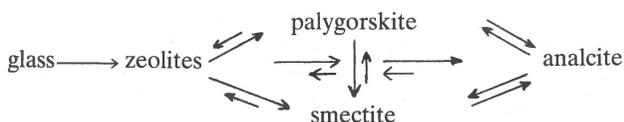
The analcite, occuring as fissure filling, is formed by precipitation during evaporation of water which will mainly take place at the matrix-fissure interface. During evaporation both salinity and alkalinity increase strongly and favour the precipitation of analcite from the brine. Similar occurences of analcite in vitric basaltic rock were reported by IIJIMA & HARADA (1968) and LO (1978).

By local migration of ions phillipsite and epistilbite (and possibly other, undetected phases) can form. Such different chemical environments can arise from non-uniform changes in moisture content of the material and differences in mobility of ions in solution. Also, preferential uptake of ions by different phases leads to local variations. It is likely that the small amounts of available K are mainly incorporated in the phillipsite since this mineral is not formed in the absence of K (IIJIMA & HARADA, 1968).

According to the chemical analysis (Table I) both the Na and Ca contents decrease during the alteration reactions whereas Mg increases. Apparently, in wet periods, some Na and Ca is lost from the system. The overall transformation of volcanic glass to smectite must involve a loss of both Ca and Na (BOLES & COOMBS, 1975) while others such as Si, Al anf Mg can remain relatively constant. The significant increase of Mg, therefore, poses a problem. The increase in Mg, however, may be due to influx to wind-blown salt from seawater, as was suggested in the case of Na by IIJIMA & HARADA (1968).

The shift in composition from offretite to clay was confirmed by X-ray microanalysis (Fig. 4). While the content of Si remains the same, that of Na and Mg is lower in the clay (probably due to some palygorskite) whereas the Mg content was markedly higher. The higher Fe content can be ascribed to local concentration of precipitated ferric oxides. This is visible in thin section by the brown staining of the clay, especially along fissures.

In the present setting the paragenetic sequence of transformations can schematically by presented as follows:

$$glass \longrightarrow zeolites \rightleftarrows \begin{array}{c} palygorskite \\ \rightleftarrows \downarrow\uparrow \rightleftarrows \\ smectite \end{array} \rightleftarrows analcite$$

Except for the hydrolysis of the glass, all reactions are considered reversible. Since the chemical environment may vary considerably, reversal of reactions is possible. The mineralogical equilibria, therefore, will be local and labile. Theoretically, the primary reaction is not from glass to zeolite, but rather from glass to smectite because in first instance the pH and salinity are not immediately high enough for zeolite formation (BOLES & COOMBS, 1975; SHEPPARD & GUDE, 1968). The occurrence of both pre-zeolite and post-zeolite montmorillonite was discussed by HAY (1966, p. 82) and VELDE (1977, p. 138).
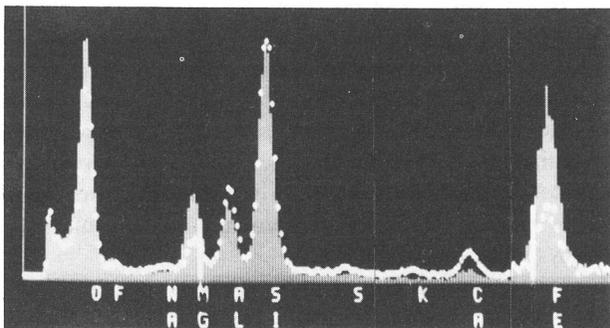

Fig. 4
X-ray microanalysis (EDAX) of offretite zone (area under dotted line) and clay zone (hatched area). Peak area is proportional to content of elements.

The absence of calcite is remarkable especially since Ca ions seem to be amply available. Internal adsorption by the zeolites, however, may preclude precipitation of calcite. The chemical analyses (Table I) indicate that the offretite is indeed a Na-free and therefore predominantly Ca-(Mg-)saturated species.

The described paragenesis is in accordance with the geological evidence of a subaerial raher than a submarine weathering. Particularly the absence of enrichment of the altered material with potassium (little phillipsite, no illite) points to a non-marine environment. Also, the occurrence of analcite as fissure filling and not as a more uniformly distributed cement is difficult to reconcile with submergence.

CONCLUSIONS

Weathering of the glassy crust of pillow basalt under the dry and hot climatical conditions of Curaçao appears to take place in a pseudo-closed system in which hydrolysis of the basaltic material by rain-water leads to sufficiently high salinity and alkalinity enabling the formation of zeolites, notably offretite.

At some distance from the weathering front, the alkalinity is sufficiently reduced to allow formation of palygorskite. At still greater distance conditions are favourable for the forming of smectite while zeolites and palygorskite disappear. Analcite is formed by precipitation in fissures from a brine formed by evaporation of the migrating interstitial fluid. The chemical budget indicates the loss of some Ca and Na and the influx of Mg.

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