

LÁSZLÓ PESTY*

INTERPRETATION OF PALAGONITIZATION ON THE BASIS OF ITS EXPERIMENTAL SIMULATION

(Figs. 12, Tab. 1)



Abstract: Palagonitization is a petrological process, being important also from the economic point of view. The experimental simulation of it can be successfully carried out. During palagonitization the glass structure of the original sideromelane becomes segregated due to hydration and selective dissolution. The overlapping of the devitrification-like, or crystallization process related often to hydration is responsible for the frequent contradictions found in the literature. It is suggested that the term "palagonitization" should denote only the hydration — selective dissolution process, distinguishing it from the often superimposed phenomena of devitrification and formation of up-grown crystals.

Резюме: Палагонитизация — петрологический процесс, который важным и с экономической точки зрения. Ее экспериментальная симуляция может быть успешно выполнена. Во время палагонитизации стекланная структура оригинального сидеромелана отделяется вследствие гидратации и селективного растворения. Перекрытие процесса подобного девитрификации или кристаллизационного процесса часто связанного с гидратацией является ответственным за частые противоречия, которые находятся в литературе. Предлагается, чтобы термин „палагонитизация“ обозначал только гидратацию — процесс селективного растворения, отличающий его от вышестоящих явлений девитрификации и образования выращенных кристаллов.

The concept *palagonite* was introduced by W. Sartorius, von Waltershausen having studied the samples from Sicily and Iceland and stating that it is the decomposition of the basalt glass called sideromelane. As it has been stated by several authors (e. g. Bonatti (1965), Hay-Jijima (1968); Stokes (1971); Honnorez (1972); Furnes (1974, 1978, 1980)) in the course of palagonitization the water migrates from the pores of the fresh basalt pyroclasts into the glassy material of the grains. As a consequence of this the hardly coloured or colourless sideromelane grains show darker yellow-red-brown colouration with sharp boundaries in the near-surface region. In the grains selective dissolution and devitrification is started while the grains' surface may be encrusted by automorphic crystals. The change of colour is interpreted by Hoppe (1941) and his followers by the oxidation of the iron content of sideromelane.

In the past years increased attention has been attributed to palagonitization since as emphasized by Honnorez (1978) and Huan-Jih-Lo (1978) this is an initial phase of the clay mineral and zeolitic decomposition of the vitreous volcanites, without which the process will not completely proceed and which bears economic importance, as well.

* RNDr. L. Pesty, CSc., Hungarian Academy of Sciences, Laboratory for Geochemical Research, H — 1112 Budapest, Budaörsi út 45.

Table 1

The chemical composition and O_{Fe} values of the starting basalt sample and of the basaltic glass sample

	Starting basalt sample (Analysed by Lefler J., GKL)	Basaltic glass sample (Lefler J., GKL)
SiO ₂	47.44	47.96
TiO ₂	2.19	2.45
Al ₂ O ₃	14.24	15.79
Fe ₂ O ₃	2.18	8.24
FeO	6.79	1.33
MgO	8.26	7.47
CaO	9.70	10.39
MnO	0.13	0.17
Na ₂ O	3.72	4.00
K ₂ O	2.06	2.42
-H ₂ O	0.18	0.05
+H ₂ O	1.28	0.12
CO ₂	0.68	0.07
P ₂ O ₅	0.51	0.51
	99.36	100.97
O_{Fe}	0.21	0.86

$$O_{Fe} = \frac{Fe_2O_3}{1.11 FeO + Fe_2O_3}$$

Based on the comparison of literature data it is obvious that authors denote by the term "palagonite" different formations which are not necessarily and exclusively the products of post-volcanic hydration and the subsequent effect of surface weathering is often reflected in them. Thus, e. g. the change of oxidation degree of the iron as the precursor, moreover measure of palagonitization (Furnes, 1980) has been insufficiently proved.

In the following *palagonite* is considered as the decomposition product of sideromelane, being amorphous from the optical and X-ray diffractometric points of view, which endured dissolution and change of colour due to hydration; making in this manner distinction between this and the minerals generated from it by devitrification as well as by dissolution and secondary up-grown crystal forming processes, respectively. This restriction of the concept aims to distinguish between the two or three usually interconnected processes and to resolute the contradictions deriving from them.

The experiments were carried out on a basalt glass sample produced by the oxidative melting and rapid quenching of a Hungarian basanite. The parameters were: $T = 100$ to 650°C , $P_{H_2O} = 50$ bar to 3.0 kilobar, $\tau = 8$ to 672 hours. The chemical composition, as well as the computed O_{Fe} values are found in Tab. 1.

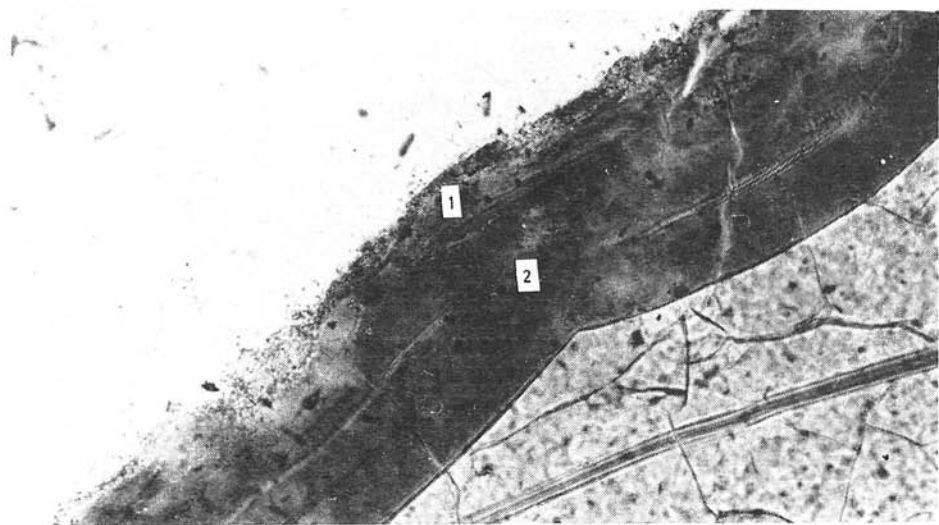


Fig. 1. Change of colour of basalt glass sample due to water diffusion at $T = 350^\circ\text{C}$, $P_{\text{H}_2\text{O}} = 0.5$ kbar and $\tau = 168$ hours. Thin section, $M = 300\times$.

Explanations: 1 — devitrification along the surface; 2 — the layer analogous to the palagonitized one due to water diffusion; 3 — unchanged basalt glass.

As we have stated (Pesty, 1980; 1982; 1983) in the course of experiments the water diffuses into the basalt glass by centripetal orientation producing the colouring analogues to that of palagonite. The colour changing takes place with a marked boundary when the water front of diffusion going through (Fig. 1). Simultaneously with this the dissolution of centrifugal orientation of the ions constituting the glassy material proceeds. Consequently, palagonitization proves to be an *interdiffusion* process, since the simultaneous migration of the water and of the dissolving ions is of opposite orientation. Since at the front of diffusion the change of colour follows, the depth of water diffusion can be measured under microscope in thin sections made from the samples after experiment. The formation of crystals by devitrification takes place solely in the near-surface parts of the sample endured the water diffusion, by means of crystal germs bound the phase interfaces. Having compared the results obtained with the publications mentioned above it has been stated that the experiments simulate fairly well the natural processes. If the experimental PT-range exceeding the presumed natural temperature of about 100°C , the quality of the process is the same, but more intense. Qualitative differences can be observed only in the mineral composition produced by the crystallization related to palagonitization itself. Thus, when interpreting palagonitization in narrow sense, the conclusion drawn from the experiments of higher PT than the natural can also be incorporated.

The experimentally produced palagonitization can be divided into three (simultaneous and overlapping) sub-processes. The water diffusing into the glass, destroys (Storrey: depolymerizes) the weak chemical bonds of it and initiates the processes below: 1. the selective dissolution of rock glass, i. e. pala-

gonitization of narrow sense; 2. devitrification bound to phase interfaces; and 3. recrystallization of the ions dissolved from the palagonitized glass at the external surface of the grains.

In the following the palagonitization of narrow sense as well as the kinds of crystallization processes will be discussed separately.

Palagonitization

1. After Hoppe (1941); Furner (1980) and others the conspicuous change of colour shown by the hydration of sideromelane is caused by the oxidation of iron content of the rock glass. Nevertheless, in our case only 15 percent of the iron ions proved to be ferro-ion, the strating glass sample is just colourless. The sudden colouring at the moment of passage of the water diffusion front could not be caused by the oxidation of ferro-ion of small quantity, even this would take place there and completely.

As to our opinion the change of colour is caused not by the oxidation of the system, but rather by the rearrangement of the submicroscopic structure of the glass material due to hydration, in the course of which the infinite disoriented silicate structure is broken up. According to Harding the process of hydration of the silicate glass consisting of the disoriented SiO_2 tetrahedra (after Zahariassen and Hess) and of the secondary cations between them, is as follows: the water is built in the glass structure partly in form of hydroxide as proved by the infrared studies of Greenwald—Exarhos (1978) and Drurechenski et al. (1979), Fig. 2. This process means the incorporation of the hydrogen and hydroxyl ions in the positions of the secondary cations (Boulos—Kreidl, 1972; Freer, 1981) which leads to the selective dissolutions of them, to the disaggregation of the glass structure, i. e. to the change of the physical properties.

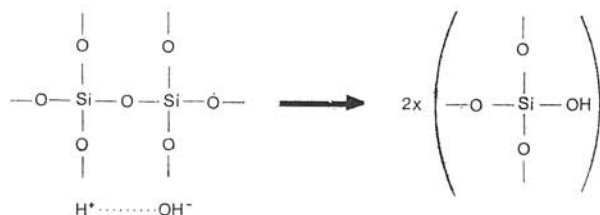


Fig. 2. Breaking up of silicate glass structure due to hydration (Harding, 1972).

As it was stated by Furnes (1980; 1984) the selective dissolution of palagonitization is of isovolumetric character, though the dissolved cations may be substituted by water up to 30 percent. Consequently, the disaggregation of the original infinite silicate glass structure did not cause its collapse, because the hydrogen ion incorporated by the glass counterbalances electrostatically the dissolving cation.

The processes above can be evaluated so that a glass structure being close to that of Zahariassen is transformed into a glass of polymer structure

of Hess. This is amorphous both from the optical and from the X-ray points of view, but probably represents a lower energy level, in so far as it means a step towards the devitrification crystallization state. This corresponds also to the Ostwald's "step rule", i. e. "the transition of the unstable forms into stable ones takes often place through an intermediary state, i. e. through a phase which can be reached by the least energy loss".

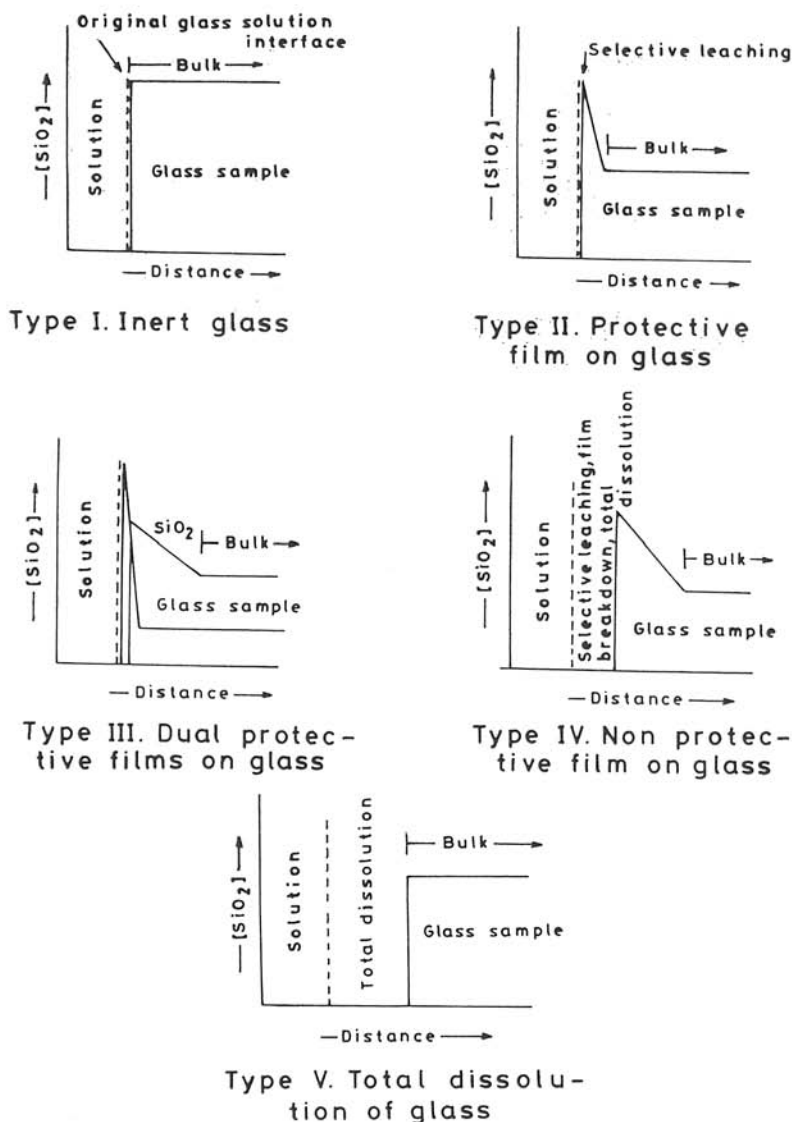


Fig. 3. Five characteristic types of hydration of glass surfaces. Modified after Hench-Clark, 1978.

2. The loose but strong silicate network, its isovolumetric character developed during palagonitization means that the original surface of the pyroclastic glass grain preserved since the selective dissolution took place from the internal part of the glass. All these are in harmony with the statement of H e n c h — C l a r k (1978). They assigned the dissolution of silicate glasses to five types (Fig. 3). In the first type the dissolution is negligible, in the fourth and fifth the surface are eroded with or without selective dissolution. Palagonitization corresponds to the second and third type where the original surface remains intact due to the formation of the selectively dissolved protective layer. The acidic volcanic glasses are characterized by the fourth dissolution type, where the surface-erosion continuously destructs the constant surface from which the inward acting devitrification as well as the formation of upgrown crystals at the external surface of the grains (to be discussed) could start.

Devitrification

The rock glass is a super-cooled material, the structure of which is analogous to the melt phase. In relation with the super-cooled silicate melt T a m m a n stated the crystallization is determined by two conditions: the nucleation and the linear growth, respectively. Having studied the conditions of nucleation K l e b e r made distinction between the *homogeneous* crystallization, when within the melt phase crystal germ may elsewhere develop, and the *heterogeneous* crystallization, which is bound to a phase boundary. The activation conditions of the latter are much more favourable. In case of devitrification, where the activation energy is extremely high due to the high viscosity, the chances of heterogeneous crystallization exceed by orders of magnitude those of the homogeneous one.

These facts verify that both the natural and the experimental devitrification of sideromelane may proceed solely by heterogeneous crystallization. In case of natural conditions this surface may be vesicular bubble-surface, fissure traversing glassy groundmass of the volcanic rocks and in case of pyroclastics the surface of the grains itself.

Based on the X-ray diffractometric records, the predominant crystal phase is plagioclase in the experiment of 550 °C. Having studied the morphological change of feldspars as a function of ΔT , K i r k p a t r i c found the relationship below:

$\Delta T/^{\circ}\text{C}$	Morphological character
~ 50	tabular
~ 100	skeletal
~ 200	dendritic
~ 450	spherulitic

Observations on palagonite as well as on the samples after the experiments agree with the statement above, that is the radial-fibrous texture consisting of acicular crystals penetrating from the surface inward (Fig. 4) (being the crystal either feldspar or zeolite), is an inverse spherulitic crystallization. At

the phase boundary, that is at the internal surface of grain, the growth of the crystal germs laying close to each other and being of stable state, can take place only in one direction, towards the internal part of the palagonitized sample. As against this centripetal crystallization, the real, that is centrifugally oriented spherulite formation may proceed in case of vesicular texture.

The loosened, fractured silicate network prepared by palagonitization serves as a basis to the crystallization of devitrification character, its chemically leached composition is insufficient to form the crystals. The crystals growing inwards are built up partly by capturing the actions mobilized during hydration and flowing by centrifugal dissolution. This abundant ion supply favours the rapid devitrification which has been observed in the thin sections of the samples after experiment.

The acicular plagioclase crystals developed during devitrification are of somewhat diverging texture under higher magnifications (Fig. 6). The migration of the ions mobilized by dissolution in the deeper horizons of the grains near the surface of it may take place only in the interstices between the plagioclase crystals.

This is why in the interstices the microprobe analyses showed decrease of sodium and increase of iron and titanium concentrations (Figs. 7 and 8). The accumulation of titanium in form of dark silicate grains solely in the fissures between plagioclases is verified by the on-line profile analyses (Figs. 9 and 10). Thus, during palagonitization only the cations get the pore space which surpassed the filter of devitrification crystallization. This kind of interpretation of the lithological process explains the observations on natural and experimental samples, that due to palagonitization and to the simultaneous devitrification the concentration of an element determined by microprobe does not change monotonously as it could be concluded from the dissolution process.

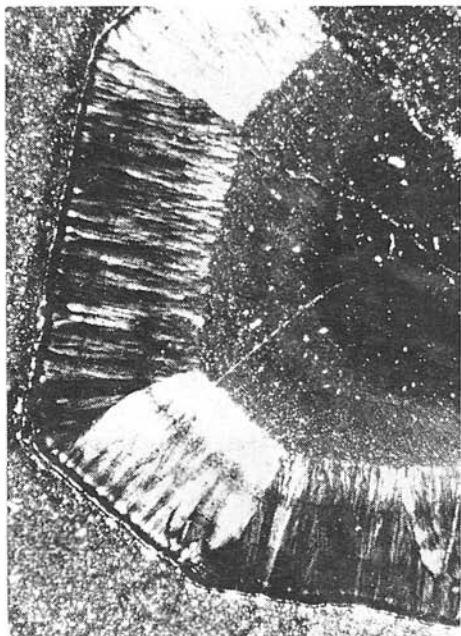


Fig. 4. Reverse-oriented, spherulitic devitrification of basalt glass at $T = 60^{\circ}\text{C}$, $P_{\text{H}_2\text{O}} = 1.0$ kbar, and $\tau = 168$ hours.

Thin section, $M = 35\times$, $+N$.

Uppgrown crystals

The ions mobilized by water diffusion, being displaced on the concentration slope and surpassing its surface, get the intersertal water phase, in which these remain dissolved or recrystallized in case of supersaturated solutions (Figs. 11 and 12). This crystallization depends on the local ionic concentration and the

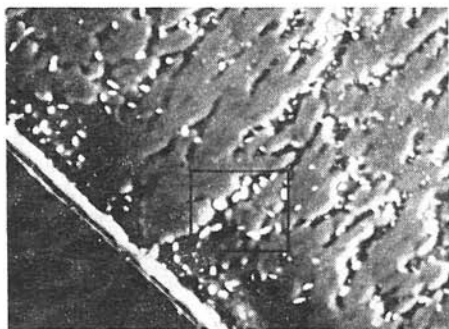


Fig. 5

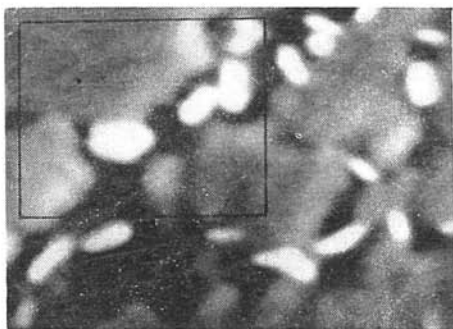


Fig. 6



Fig. 7



Fig. 8

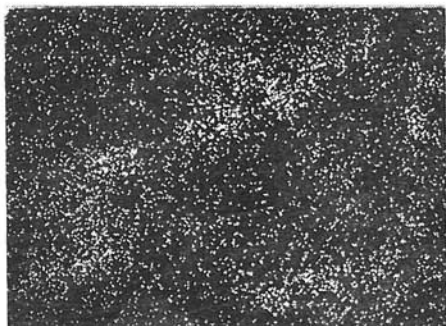


Fig. 9

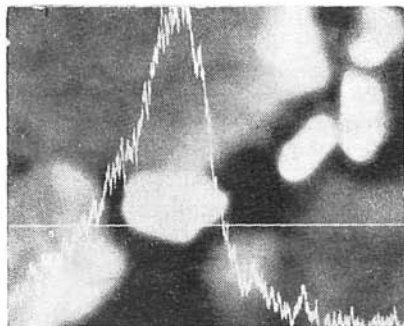


Fig. 10

Fig. 5. Devitrification of basalt glass bound to heterogeneous surface after the experiment of $T = 650^{\circ}\text{C}$, $P_{\text{H}_2\text{O}} = 2.0$ kbar and $\tau = 24$ hours. Surface section, microprobe composition picture. $M = 600\times$, in the frame see Fig. 6.

Fig. 6. Part of Fig. 5. $M = 2,800\times$, in the frame see Fig. 10.

Fig. 7. The Na-concentration, in Fig. 6.

Fig. 8. The Fe-concentration, in Fig. 6.

Fig. 9. The Ti-concentration, in Fig. 6.

Fig. 10. Part of Fig. 6 and the Ti-line profile, $M = 5,000\times$.

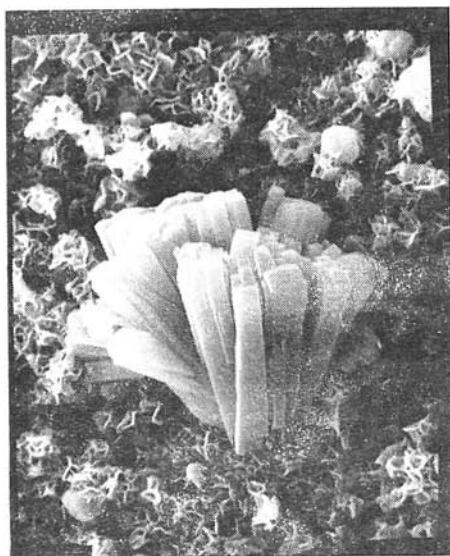


Fig. 11.

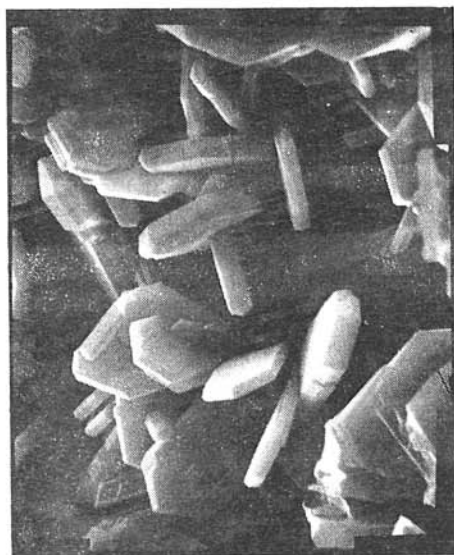


Fig. 12.

Fig. 11. Scanning electronmicroscopic image of upgrown clinoptilolite on the surface of basalt glass under $T = 250^{\circ}\text{C}$, $P_{\text{H}_2\text{O}} = 1.0$ kbar and $\tau = 48$ hours. $M = 3000\times$.

Fig. 12. Scanning electron microscopical image of upgrown phillipsite on the surface of basalt glass under $T = 250^{\circ}\text{C}$, $P_{\text{H}_2\text{O}} = 1.0$ kbar and $\tau = 48$ hours. $M = 2200\times$.

quantity of the upgrown crystals varies between the total absence (Furnes, 1984) and the predominant amounts (Hay—Iijima, 1968). In addition to the crystallization from the solution it is also possible that the ions migrated to the surface do not leave the grain surface, but migrate by means of surface diffusion and get the crystal germs capturing them. Parallel with this prograding process, the upgrown crystals may cement the originally loose sideromelane grains. This type of autigenic crystallization related to palagonitization was described by Sersale (1978) from the Lionato Tuffs near Rome, where thick phillipsite layer developed in the grains' surface.

Acknowledgements: I express my thanks to Dr. G. Nagy for the microprobe analyses carried out in the Laboratory for Geochemical Research of the Hungarian Academy of Sciences and to acad. prof. Dr. B. Cambel and Dr. I. Holický for the scanning electron micrographs made in the Geological Institute of the Slovak Academy of Sciences.

REFERENCES

- AUGUSTITHIS, S. S. eds., 1983: Leaching and diffusion in rocks and their weathering. Theophrastus Publ., Athens.
- BONATTI, E., 1965: Palagonite, hyaloclastites and alteration of volcanic glass in the ocean. *Bull. volcanol. (Napoli)*, 28, pp. 251—269.
- BOULOS, E. N. — KREIDL, N. J., 1972: Water in glass: a review. *J. Can. ceram. Soc.*, 41, p. 83.
- DRURECHENSKI, A. V. — PETROV, V. A. — REZNIK, V. Yu., 1979: Spectral emittance of silica glasses at high temperatures. *High Temp. High Pressure*, 11, p. 425.

- FREER, R., 1981: Diffusion in silicate minerals and glasses. *Contr. Mineral. Petrology* (Berlin — New York), 76, pp. 440—454.
- FURNES, H., 1974: Volume relations between palagonite and authigenic minerals in hyaloclastite and its bearing on the rate of palagonitization. *Bull. volcanol.* (Napoli), 38, pp. 173—186.
- FURNES, H., 1968: Element mobility during palagonitization of a subglacial hyaloclastite in Iceland. *Chem. Geol.* (Amsterdam), 22, pp. 249—264.
- FURNES, H., 1980: Chemical changes during palagonitization of an alkaline olivine basaltic hyaloclastite. Santa Maria Azores. *Neu Jb. Mineral., Abh., Mh.* (Stuttgart), 138, pp. 14—30.
- FURNES, H., 1984: Chemical changes during progressive subaerial palagonitization of a subglacial olivine tholeiite hyaloclastite: a microprobe study. *Chem. Geol.* (Amsterdam), 43, pp. 271—285.
- GREENWALD, J. E. — EXARHOS, G. J., 1978: Vibrational studies of metal cation reduction at oxide glass surfaces. *J. N. Cryst. Sol.*, 28, p. 259.
- HARDING, F. L., 1972: Dependence of melt oxygen activity and water retention on composition of amber glass. *J. Amer. ceram. Soc.* (Easton), 55, p. 368.
- HAY, R. T. — IJIMA, A., 1968: Petrology of palagonite tuffs of Koko Craters, Oahu, Hawaii. *Contr. Mineral. Petrology* (Berlin — New York), 17, pp. 141—154.
- HENCH, L. L. — CLARK, D. E., 1978: Physical chemistry of glass surfaces. *N. J. Cryst. Sol.*, 28, p. 83.
- HESS, P. C., 1971: Polymer model of silicate melts. *Geochim. cosmochim. Acta* (London), 35, p. 289.
- HONNOREZ, J., 1972: La palagonitisation, l'alteration sousmarine du verre volcanique basique de Palagonie (Sicile). *Vulkaninstitut Immanuel Friedlander 9*, Birkhauser, V. Basel, p. 131.
- HOPPE, H. J., 1941: Untersuchungen an Palagonittuffen und über ihre Bildungsbedingungen. *Chem. d. Erde*, 13, pp. 484—514.
- HUANN JIH LO, 1978: Composition and origin of analcime in taiwanite, a glassy basaltic rock in the eastern coast range, Taiwan. See: Sand, A. B. — Mumpton, F. A., pp. 303—307.
- KLEBER, W., 1962: Keimbildung und Kristallisationswachstum in Gläsern. *Silikat-Technik*, 13, p. 5.
- PESTY, L., 1980: Optische Untersuchung der Wasserdiffusion in ursprünglichen und künstlichen vulkanischen Gläsern, unter hohen PT Bedingungen. 26. Congress Geologique Internat., Paris, Resumes, I, p. 73.
- PESTY, L., 1982: A víz szerepe a kőzetüvegék kristályosodási folyamataiban (Kandidátusi értekezés). Role of water in crystallization processes of rock glasses (C. Sc. thesis).
- PESTY, L., 1983: Experimental investigation of water diffusion in silicate rock glasses at elevated p-t conditions. In: Leaching and diffusion in rock and their weathering products. Ed.: Augustithis, S. S., Theophrastus Publ. Athens, pp. 93—112.
- SAND, A. B. — MUMPTON, F. A., 1978: Natural zeolites, occurrence, use. Pergamon, Amsterdam.
- SERSALE, R., 1978: Occurrences and uses of zeolites in Italy. See: Sand, A. B. — Mumpton, F. A., p. 285.
- STOKES, K. R., 1971: Further investigations into the nature of the materials chlophaeite and palagonite. *Mineral. Mag.* (London), pp. 205—214.
- STORREY, W. C., 1975: The solubility of H₂O in silicate melts. *Prog. Exper. Petrol.*, 3, p. 265.
- TAMANN, G., 1903: Kristallisieren und Schmelzen. Leipzig, Verlag J. Ambrosius Barth.
- WALTERSHAUSEN, W. S., 1853: Über die vulkanischen Gesteine in Sizilien und Island und ihre submarine Umbildung. Göttingen.
- ZAHARIASSEN, W. H. 1932: The atomic arrangement in glass. *J. Amer. Chem. Soc.*, 54, p. 3841.

Manuscript received February 1, 1985

The author is responsible for language correctness and content.