Zeolites from Etsumi, Ogi Town, Sado Island, Niigata Prefecture, Japan

By

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Abstract   Phillipsite, analcime, chabazite, gmelinite, calcite, and smectite are found in vesicles and fissures of basaltic hyaloclastite, pillow and ordinary lavas at the locality. The first and second form monominerallic aggregates, respectively, or aggregates of two.   The third and fourth simulate a single crystal composed of their epitaxial intergrowth.   The anhydrous empirical formulae of the first to fourth zeolites are, respectively, $Na_{8.62}K_{5.54}Ca_{0.79}Al_{15.97}Si_{32.09}O_{96}$, $Na_{14.86}Al_{15.75}Si_{32.48}O_{96}$, $Na_{11.93}K_{3.17}Ca_{0.13}$ $Al_{15.14}Si_{32.80}O_{96}$, and $Na_{13.07}K_{2.16}Ca_{0.24}Al_{15.37}Si_{32.55}O_{96}$, where all are normalized to O=96. Phillipsite and chabazite are low in CaO content, especially the latter is one of the most siliceous low Ca chabazite.   Gmelinite is high in K_2O content, extending the known compositional range.   The vesicles and the deformed ones are resided by calcite, phillipsite, analcime and smectite, whereas the fissures have phillipsite, analcime, chabazite-gmelinite intergrowth and smectite therein.   Some of fissures cut vesicles. Above association means that more watery zeolites with looser structures appeared later within a single rock.   All the described zeolites have Si/Al about 2, which corresponds to the point between SiO_2 saturation and undersaturation states in zeolites. Those with above 2 are able to co-exist with silica minerals, whereas those with below 2 are not.

Introduction

During the survey of mineral constituents of basaltic pillow lava and the accompanying members exposed in Ogi Peninsula situated in the southwestern end of Sado Island, Niigata Prefecture (Fig. 1), a few zeolite assemblages are found.   The occurrence of analcime and natrolite in the basalt has been already reported by Yamakawa and Chihara (1968).   The visually realized species in vesicles or veinlets include calcite, analcime, phillipsite, phacolite-type chabazite, and smectite.   The X-ray powder study revealed the chabazite to be actually epitaxial intergrowth of chabazite and gmelinite.   The subsequent microprobe analyses informed the analcime to be high in SiO_2, the phillipsite and chabazite to be low in CaO, and the gmelinite to be rather high in K_2O content.

A comparative study of the present phillipsite with its available analyses informs it to be involved within the compositional field of the mineral in deep sea sediments (Sheppard et al., 1970).   The chemical composition of chabazite is
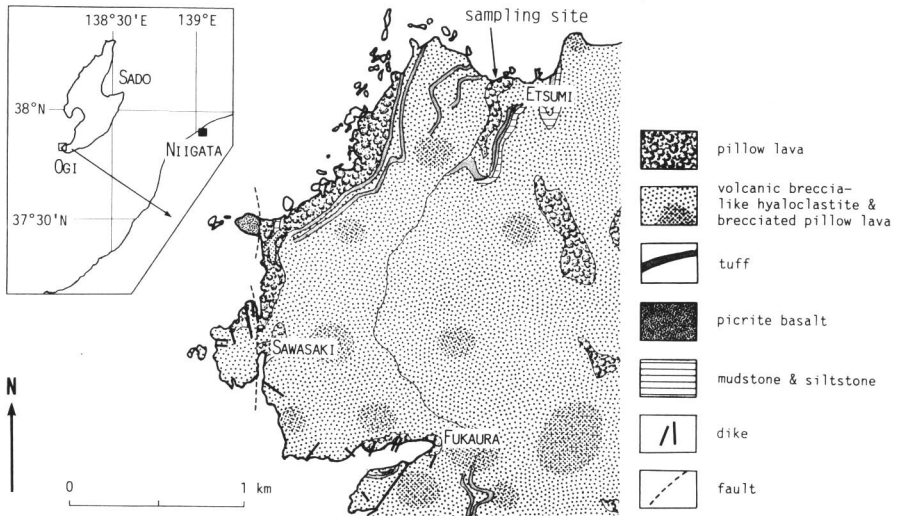
Fig. 1. Index and geological maps of the locality (after Research Group of the Ogi Basalts, 1977).

characterized by its very low CaO content, corresponding to those called under the variety name herschelite. The present material is compositionally characterized by its extremely low CaO content and less Al_2O_3 nature as compared with the original herschelite from Sicily (Passaglia, 1970). The compositional characteristics of intergrown gmelinite is represented by the higher K_2O content.

The antecedence relations of spaces as the sites of zeolite formation are given by the order of vesicles, deformed vesicles, and fissures or veinlets. Here, vesicles are defined as spherulitic spaces without any notable projection from the walls, which are at any points concave. Deformed vesicles are elongated voids in which the walls lack any concave portions. Fissures are further elongated voids where any tabular and long lasting natures of them begin to emerge. Veinlet is a tabular space completely or partially filled with minerals with flat walls and long lasting nature beyond the order of the dimension of hand specimen.

All the analyzed zeolites have the ratio Si : Al close to 2. This value is considered to be implicative as the boundary point to indicate the degree of SiO_2 saturation, namely zeolites with larger ratio than this (i.e., more siliceous) are able to co-exist with silica minerals, whereas those with smaller value than 2 are not.

The present description is for the chemical compositions and characteristics of zeolites, leading to the decision of the order of formation, which is well conformable with their crystal structures admitting the involvement of higher contents of water due to their looser nature.

Occurrence

Ogi peninsula of Sado Island is geologically occupied by piles of basaltic lavas, hyaloclastites, dikes and picritic sills as the products of submarine volcanism of the middle Miocene age in connection with the opening of Japan Sea (Fig. 1). At Etsumi, Ogi Town, located near the western end of the peninsula, the pile composed of five members is observed. The member embodying zeolites here studied are from the middle member composed of pillow lavas, mafic and felsic tuffs, hyaloclastite and intercalated mudstone, among which hyaloclastites is most prolific of zeolites but the number of visually identified species are rather few, phillipsite, analcime and phacolite-type chabazite besides calcite and smectite. The studied materials are all found in voids therein. As to the description of voids, two morphological terms, vesicles and fissures, as defined in the previous section, are here incorporated. The simple usage of term "void or voids" is to include both of them.

All the voids are internally coated by thin white smectite films occasionally coated by very minute asterisks of dark brown matter and the existence seems to be distanced by zeolites. Vesicles are from a to a few millimeters across. The lodging members are here introduced in the order of formation supposed from the degree of deformation of vesicles that the earlier the more ideally spherulitic.

Macroscopically, the basalt is notably altered into light to dark green grey rock with abundant vesicles occasionally accompanied by fissures of larger dimension and veinlets of far larger dimension. The walls of vesicles and fissures are covered with white film of smectite in most cases. Though the groundmass is altered, many plagioclase phenocrysts retains the primary form, even in some cases where the larger grains are externally pseudomorphed by less lustrous white smectite. Some plagioclase grains form aggregates embodying light green grains of clinopyroxene of submillimeter size. The X-ray powder studies inform that the alteration products are dominantly occupied by saponite. But, unless confused, the term smectite will be used in place of saponite.

Under the microscope, the groundmass consists of plethora of apparently unaltered laths of plagioclase forming a trachytic texture. The interstitial matter is completely altered to form a dark to light brown aggregates of smectite involving very minute spherules of chlorite. Phenocrysts of plagioclase and clinopyroxene are unaltered in most of them. Now, the visual observation of calcite and zeolites will follow.

Calcite is exclusively found in less deformed vesicles. It forms radially grown tapering hexagonal prisms of a few millimeter long or complete filling material, whereby turbid. The more developed crystal forms the more clear the whole aggregate, and partially turbid and partially clear aggregates are extant. Phillipsite forms a millimeter order radial aggregates of inward-tapering pseudotetrago-

nal prisms with sharp tops or a single grain composed of short prismatic eightling. These lodge in vesicles or distorted ones. In more deformed vesicles the wall is directly coated by minute phillipsite aggregates which larger grains of trapezohedral crystals of analcime overly. The same relation is seen on walls of fissures as well. Some other fissure walls are covered exclusively by phillipsites, or exclusively by analcime, or by two where phillipsite overlies analcime without exception. Both of them have good clarity but in all cases analcime is superior to phillipsite in clarity enabling the visual discrimination together with the morphology. Some fissures are dwelled by phacolite-type chabazite crystals up to a few millimeters across. It has a rather turbid surface though internally clear. According to the X-ray powder study and the subsequent microprobe analyses, the crystals consist of chabazite host and gmelinite as guest.

Thus, the reconstructed order of formation is: smectite, calcite, phillipsite, analcime, and chabazite + gmelinite, if the shapes of voids are taken into consideration. Namely, vesicles are the products due to concentration of gaseous substances. The spherulitic form relates of the adaptability coming from semi-solid state of surrounding rock. While, the formation of fissure needs the contribution of contraction due to cooling and that a part of fissures cuts vesicles very clearly. But the rugged walls of fissures are indicative of the existence of viscosity of the country rocks. In case of development of veinlets, the long lasting flat walls means that the country rock was no longer possessive of viscosity but rigid liable to be fragmentary.

X-ray Powder Study

The X-ray power studies were made on phillipsite, analcime and chabazite-gmelinite intergrowth.

The pattern of radially aggregated phillipsite includes rather sharp peaks in the recorded chart. The cell parameters are: $a = 9.97$, $b = 14.23$, $c = 14.29$, $\beta = 90.2°$ in terms of the pseudoorthorhombic setting. That of the non-aggregated material is essentially same. These parameters enable the plots on the figures indicating the areas of phillipsite in deep sea deposits and in basalts forming radial aggregates using a and b for two axes (Fig. 2) and b and c for them (Fig. 3), originally drawn by GALLI and GHITTONI (1972). The points indicating the cell edge dimensions of the present phillipsite are both out of the two areas corresponding the sources, together with those of phillipsite from Maze located in the seashore just facing to Sado Island, where many zeolites occur in basalts and the associated pyroclastic rocks (HARADA et al., 1967).

The powder pattern of analcime is satisfactorily indexed on a cubic cell without any off-extinction rule diffraction, except $d = 3.80 \text{Å}$ indexed as (320) (GOTTARDI & GALLI, 1984). The careful examination has now proved it to be
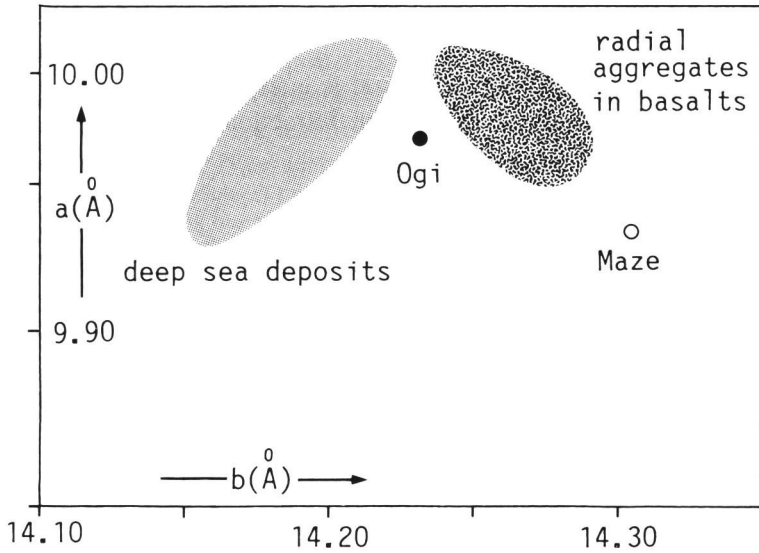
Fig. 2. Plot of the studied phillipsite in the diagram with *a* and *b*-dimensions for both axes (GALLI & GHITTONI, 1972). The original diagram is modified to make areas involving many plots.
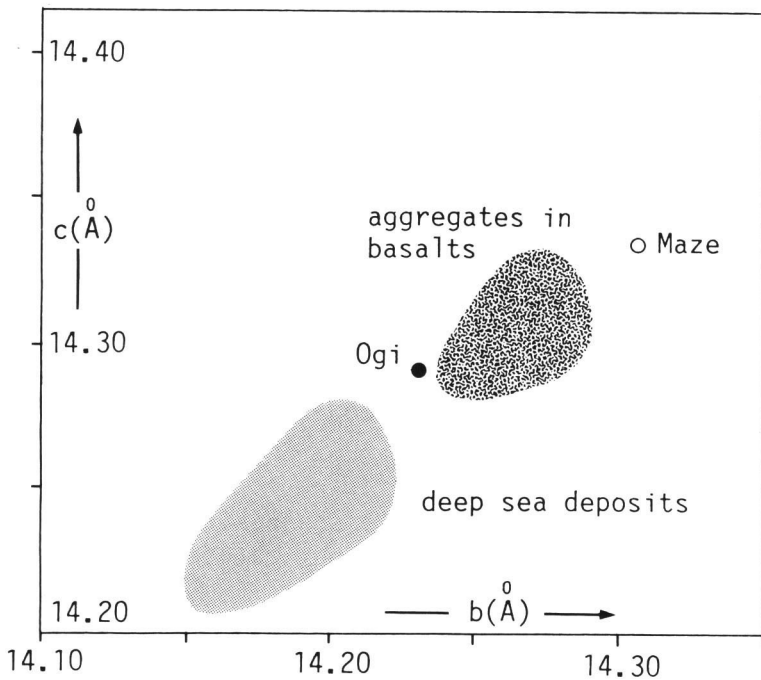

Fig. 3. Plot of the studied phillipsite in the diagram with *b* and *c*-dimensions for both axes (GALLI & GHITTONI, 1972). The same modification as in Fig. 2 is made.

due to Kβ of (400) and not to Kα. The calculated unit cell parameter is: $a =$ 13.725 Å.

The pattern of phacolite-type crystal is interpreted to composed of chabazite and gmelinite as frequently seen. The diffractions characteristic to the latter

Table 1. Chemical analyses of phillipite (1), analcime (2), chabazite (3), and gmelinite (4). H_2O was measured on the intergrowths of chabazite and gmelinite. Anhydrous empirical formulae on basis of O=96. 1, $N_{8.62}K_{5.54}Ca_{0.79}Al_{15.97}Si_{32.09}O_{96}$; 2, $Na_{14.86}Al_{15.75}Si_{32.48}O_{96}$; 3, $Na_{11.93}K_{3.17}Ca_{0.13}Al_{15.14}Si_{32.80}O_{96}$; 4, $Na_{13.07}K_{2.16}Ca_{0.24}Al_{15.37}Si_{32.55}O_{96}$.

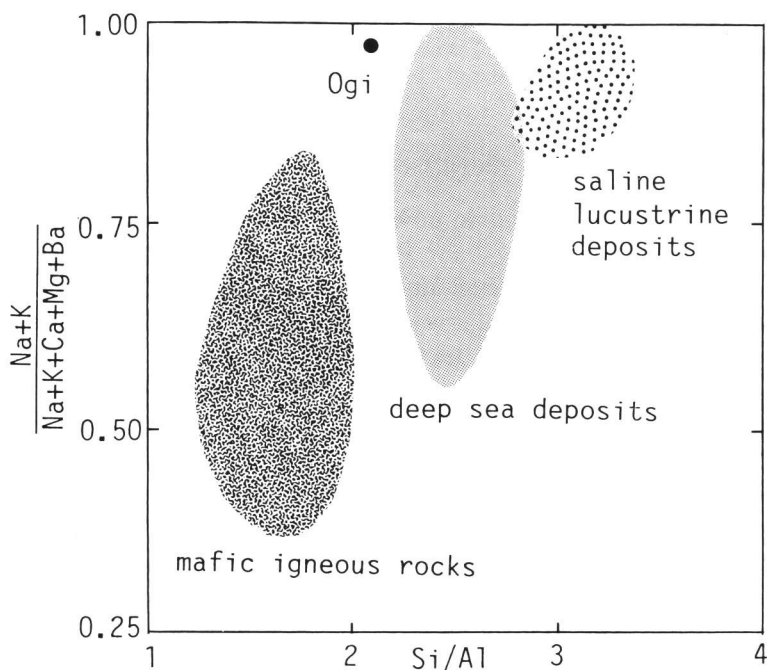| wt%	1	2	3	4
SiO_2	49.83	53.23	50.54	48.72
Al_2O_3	21.04	21.90	19.79	19.52
CaO	1.15	—	0.19	0.33
Na_2O	6.90	12.56	9.48	10.09
K_2O	6.75	—	3.83	2.53
Subtotal	85.67	87.69	83.83	81.19
H_2O	13.68	8.53	17.42	
Total	99.35	96.22		

Fig. 4. Plot of the studied phillipsite in the diagram $(Na+K)/(Na+K+Ca+Mg+Ba)$ (Sheppard et al., 1970). The same modification as in Fig. 2 is made.

have weaker intensity and this is ascribed to the difference in quantity, the former being dominant. The unit cell parameters of the chabazite are: $a = 13.801$ and $c = 15.114$ Å in terms of hexagonal setting. No discernible distortion was found in the chart. Those of gmelinite are less accurate owing to the existence of masking diffractions of chabazite. They are: $a = 13.80$ and $c = 10.05$ Å.

Chemical analyses

Chemical analyses were made by employing Link Systems energy dispersive X-ray spectrochemical instrument. Also, water contents of phillipsite, analcime, and intergrowth of chabazite and gmelinite were measured by Karl–Fischer method (Table 1).

The chemical analyses of phillipsite is characterized by the lower CaO content. The plotted point in the diagram with axes $(Na+K)/(Na+K+Ca+Mg+Ba)$ and Si/Al (SHEPPARD *et al.*, 1970) is excluded by the areas of mafic igneous rocks and of deep sea deposits (Fig. 4), denoting the compositional peculiarity of the studied phillipsite. Also, in the triangular diagram $Na-K-Ca$ $(Mg+Sr+Ba)$ in which the chemical compositions of phillipsite in basalts and in deep sea deposits are configured (GALLI & GHITTONI, 1972), the plot of the
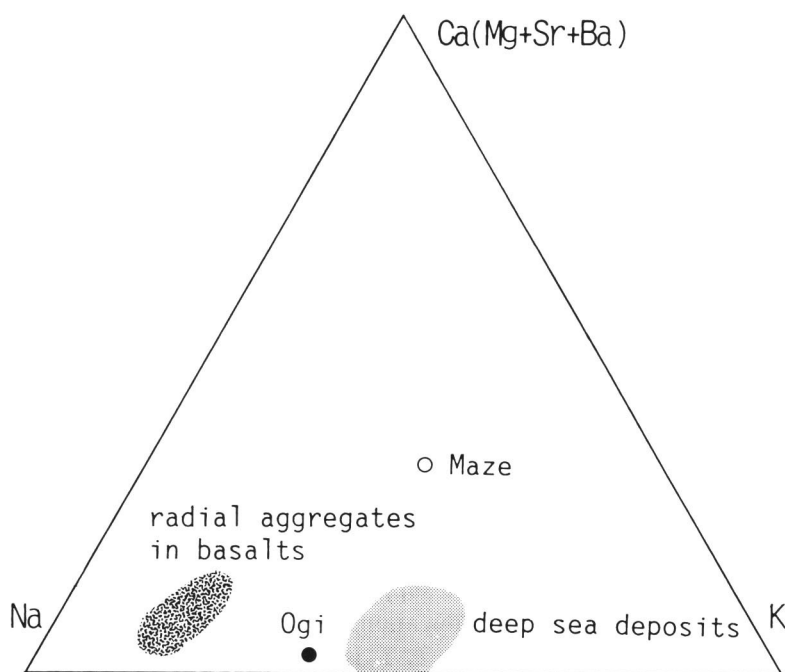
Fig. 5. Plot of the studied phillipsite in the triangular diagram of $Na-K-Ca(Mg+Sr+Ba)$ (GALLI & GHITTONI, 1972). The same modification as in Fig. 2 is made.

studied phillipsite is also excluded (Fig. 5), indicating the compositional peculiarity. Analcime is of slightly low Na_2O content, which links with SiO_2 excess nature. The low CaO content of chabazite is worthy of note. Therefore, the present chabazite is specified as chabazite–(Na, K) where Na > K, or herschelite. The present material has higher Si/Al ratio, in which is 2.16 as compared with 1.63 in herschelite from Sicily (PASSAGLIA, 1970). Later discussion will handle the importance of this difference. The chemical analyses of gmelinite has higher content of K_2O. Though our literature survey is not always complete, the figure seems to be highest among the available chemical analyses hitherto reported. It is worth mentioning that all of these zeolites are low in CaO content, despite the earlier appearance of calcite quite in the same manner in vesicles.

Si : Al Ratios of Zeolites Denoting the Degree of Silica Saturation

It is well-known fact that the ratio of total number of cations to Si in rock-forming mafic silicates is the measure to indicate the degree of silica saturation, i.e., if the ratio is larger than unity the silicate is to be undersaturated with silica as seen in olivines. The present statement is the proposal that Si/Al = 2 is the point to measure the degree of silica saturation in zeolites. The smaller Si/Al ratio is seen in thomsonite, gismondine, and amicite, where it is unity. While the larger ratio is found in mordenite in which the value approximates 6. If the associations of zeolites with silica minerals are critically examined, it is not difficult to find the boundary point at 2. Those with larger value than this are able to have association with silica minerals, whereas those with smaller value, such as fibrous zeolites, are not. Some zeolites have extensive variation range of chemical compositions involving this boundary, as given by chabazite. For example, chabazite from Vesuvio has Si : Al ratio 1.74 (DE GENNARO & FRANCO, 1976) and that from Grant County, Oregon found in silicic tuff has 3.87 (SHEPPARD & GUDE, 1970), the former being of occurrence in silica undersaturated condition. The present chabazite will be capable of co-existing with silica minerals, whereas the sicilian material will not, accounting for the compositional importance of the described chabazite.

Acknowledgments

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