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GEOLOGY OF NATURAL ZEOLITES AND ZEOLITIC ROCKS

Azuma Iijima

Geological Institute, Faculty of Science, University of Tokyo,
7-3-1 Hongo, Tokyo 113, Japan

ABSTRACT

Present status, particularly development in the latest decade, of the geology of natural zeolites and zeolitic rocks has been overviewed. Emphases are focused on the classification of genetical occurrences and the synthesis deduced from the nature.

INTRODUCTION

Nearly two centuries have passed since zeolite was discovered and named by Cronstedt in 1756. Collection and mineralogical description of pretty, coarse crystals were the primary studies of zeolites for a long time till early this century. It is a great monument that the concept of zeolite facies was established by Eskola in 1936 as the lowest grade of the metamorphic facies. The concept was greatly developed by Coombs in New Zealand, having further been visualized by Iijima, Seki and Utada in Japan. Researches on zeolites in alkaline, saline lake deposits by Hay, Gude and Sheppard in USA made our eyes open to the zeolite formation at or near the Earth's surface. From deep-sea sediments zeolites were already reported by Murray and Renard in 1891. The Deep Sea Drilling Project (1968–1975) by the Glomar Challenger cruises shed light on the deep-sea zeolites. Our knowledge on natural zeolites and zeolitic rocks has rapidly expanded during the latest two decades. The growth of study on natural zeolites has been and will be stimulated by increasing needs of them as a potential natural resource, instead of synthetic zeolites, particularly in Africa, East and West Europe, Japan, USA and USSR. A recent result is summarized in "Natural zeolites: occurrence, properties and use" [1].

This paper has been prepared for an overview of geology of natural zeolites and zeolitic rocks in the world. A brief note on zeolite mineralogy is followed by classification of genetic types of occurrence and a geological synthesis on zeolite formation. Readers can refer to Coombs[2], Hay [3, 4], Iijima and Utada [5, 6], Iijima [7], Kossovskaya [8], Sheppard [9], Surdam and Sheppard [10], Gottardi and Obradovic [11], Sersale [12], Kastner and Stonecipher [13] and their references.

Table 1. Composition of natural zeolites and composition of host igneous rocks.

| Species | R | Dominant cation | Host rock | | | |
|----------------|-----------|-----------------|-----------|---|---|---|
| Gismondine | 0.50-0.57 | Ca | U | B | | |
| Phillipsite | 0.52-0.77 | Ca, Na, or K | U | B | I | A |
| Thomsonite | 0.50-0.52 | Ca | U | B | | |
| Gonnardite | 0.52-0.58 | Na | U | B | | |
| Ashcroftine | 0.55 | K | U | | | |
| Mesolite | 0.60 | Ca, or Na | U | B | I | |
| Scolecite | 0.60 | Ca | U | B | | |
| Natrolite | 0.60 | Na | U | B | I | |
| Cowlesite | 0.60 | Ca | | B | | |
| Edingtonite | 0.60 | Ba | | | | |
| Garronite | 0.63 | Ca | | B | I | |
| Analcime | 0.63-0.74 | Na | U | B | I | A |
| Chabazite | 0.63-0.80 | Ca, or Na | U | B | I | A |
| Gmelinite | 0.67 | Ca, or Na | | B | | |
| Levyne | 0.67 | Ca | | B | | |
| Laumontite | 0.66-0.71 | Ca | U | B | I | A |
| Wairakite | 0.67 | Ca | | B | I | A |
| Faujasite | 0.71 | Na | U | B | | |
| Offretite | 0.72 | Ca, or Mg | | B | | |
| Harmotome | 0.73 | Ba | | B | | |
| Mazzite | 0.73 | Na | | B | | |
| Stilbite | 0.72-0.78 | Ca, or Na | | B | I | A |
| Heulandite | 0.73-0.80 | Ca | | B | I | A |
| Erionite | 0.74-0.79 | Ca, Na, or K | | B | I | A |
| Yugawaralite | 0.75 | Ca | | B | I | A |
| Brewsterite | 0.75 | Sr | | | | |
| Epistilbite | 0.75 | Ca | | B | I | A |
| Barrerite | 0.77 | Na | | | | A |
| Stellerite | 0.78 | Ca | | | | |
| Paulingite | 0.78 | K | | B | | |
| Dachiardite | 0.78-0.86 | Ca, or Na | | B | | A |
| Clinoptilolite | 0.80-0.85 | Ca, Na, or K | | B | I | A |
| Mordenite | 0.81-0.85 | Ca, or Na | | B | I | A |
| Ferrierite | 0.85 | Mg, or K | | B | I | A |

R = Si: (Si+Al+Fe).

U: ultrabasic rock, B: basic rock, I: intermediate rock, and A: acidic rock.

NATURAL ZEOLITES

Zeolites are a group of basic, hydrous aluminosilicate minerals. The name was created by Cronstedt in 1756 from the Greek ζεω and λιθος which mean 'boiling stone' [14]. They possess an open aluminosilicate framework structure containing channels filled with water molecules and cations. The water molecules are easily dehydrated by heating and rehydrated in the air without significant changes of the framework. The cations are usually exchangeable at low temperature below 100°C.

Twenty-three types of framework have been known in natural zeolites [14] and thirty-four species are listed in Table 1. Gottardi [14] emphasizes that the ratio $R=Si:(Si+Al+Fe)$ of a zeolite, which represents the percentage of the tetrahedra occupied by Si, is an important chemical parameter with respect to the Order-Disorder relation in zeolites; zeolites are classified into "basic" with $0.50 < R < 0.625$, "intermediate" with $0.625 < R < 0.75$, and "acidic" with $0.75 < R$. These three classes seem to be closely related to the chemical composition of host rocks including zeolites as shown in Table 1. Zeolites in undersaturated, alkali rocks largely belong to "basic", whereas those in oversaturated, acidic rocks are "intermediate" to "acidic". Zeolites often show a wide compositional variation even in the same species [14, 15]; in particular, phillipsite [16, 17], chabazite [18, 19], clinoptilolite-heulandite [20, 21, 22, 23], erionite [24], ferrierite [25], and analcime [26, 27, 28]. The variation reflects various factors, which act on the zeolite formation, such as P-T conditions, chemistry of original material and pore water, and others as discussed later.

GENETIC TYPES OF OCCURRENCE OF ZEOLITES

Zeolites form at present or formed in the past in various sediment or rocks under varying physical and chemical environments. Genetic classification of occurrence has been attempted by some workers; e.g., Hay [3, 4], Iijima and Utada [6], Iijima [7], Sheppard [9], Gottardi and Obradovic [11] and Mumpton [29]. Much work in the field and laboratory has explicitly proved that temperature is an important factor to control zeolite formation [30-35]. Another significant factor is the chemistry of pore water in which zeolites precipitate [3, 10, 13, 36, 37]. As a result of the geothermal or chemical gradient, zeolites commonly occur in a vertically or laterally zonal arrangement which is usually mappable as zeolite zones. Therefore, temperature and nature of pore water should be emphasized as the criteria to classify the genetic types of occurrence. In addition, zeolite species formed are influenced by the original material such as acidic or basic volcanic glass, clay and etc. Nine genetic types are classified as shown in Table 2. More than two types frequently overlap one another to make a complex type. It is sometimes difficult to distinguish a specific type of occurrence from the shallow-burial diagenesis, percolating groundwater, low-temperature hydrothermal and contact metamorphism without regional mapping of zeolite zones.

Magmatic Primary Zeolites. Analcimes that are considered as a primary mineral of late formation occur in some alkali rocks. The distinction between primary and secondary analcimes, however, is not easy when the analcime occurs as interstitial grains [38]. In plutonic rocks such as teschenite, essexite, and syenite, analcimes sometimes occur as a main constituent with or without nepheline. Analcime occurs as small globules in inclusions of analcime trachybasalt in the phonolite of Traprain Law. The globules originate probably in a magmatic emulsion formed by the separation of a water-rich magma into two immiscible liquids [39]. In volcanic rock analcime is known as a primary constituent in some basalts, where typically it is restricted to the groundmass [38].

Table 2. Genetic types of occurrence of zeolites.

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- A. *Zeolites form at elevated temperature, the zones being primarily caused by geothermal gradient.*
1. Magmatic primary zeolites
 2. Contact metamorphism
 3. Hydrothermal
 4. Burial diagenesis (or metamorphism)
- B. *Zeolites form at or near the surface condition, the zones being principally caused by chemical gradient.*
5. Percolating groundwater
 6. Weathering
 7. Alkaline, saline lake deposits
- C. *Zeolites form at low temperature, any zones being not recognized.*
8. Marine environment
- D. *Zeolites form in impact craters.*
9. Impact crater
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Contact Metamorphism. Zeolite is widespread in contact aureoles of the vulcanoplutonic complexes which intruded into a thick sequence of porous tephra, volcanoclastic sediments or feldspathic sandstone filled with pore water. Good examples are reported from the Tanzawa Mountains [31], the Misaka Mountains [40], the Motojuku area [41] and some other areas [32] in the Green Tuff region of Japan, where Neogene basic to acidic tephra and volcanoclastic sediments with a thickness of some kilometers accumulated in marine basins.

Metamorphic minerals appear to make a concentric pattern around intrusive bodies. In andesitic tephra and andesitic sandstones of the Tanzawa Mountains, five metamorphic zones are distinguished toward a quartz-diorite mass [31]; 1) stilbite-(clinoptilolite)-vermiculite, 2) laumontite-mixed layer-chlorite, 3) pumpellyite-prehnite-chlorite, 4) actinolite greenschist, and 5) amphibolite. Heulandite, mordenite and analcime are rarely found in the zone 1. Wairakite and yugawaralite occur commonly in the high-temperature part of the zone 2. Seki et al. [31] insisted that the lowest-grade metamorphism of the zeolite facies can be divided into the high solid pressure type characterized by stilbite and/or heulandite and the low solid pressure type characterized by mordenite. However, heulandite and stilbite form at the low solid pressure in andesitic tephra of the Motojuku area [41].

The effect of chemical composition of host rocks to zeolite assemblages is explicitly documented in the western Misaka Mountains [40], where Late Miocene granitic complex intrudes basaltic and rhyodacitic tephra which were alternately laid in the Miocene marine basin. The alteration zones and mineral assemblages are shown in Figure 1. On the one hand, clinoptilolite, mordenite, analcime, heulandite, laumontite and albite appear in each of the same zones of both acidic and basic tephra; on the other hand, phillipsite, stilbite, mesolite, thomsonite, epistilbite, yugawaralite and wairakite are found only in vesicles and vugs in basalts.

Hydrothermal. Zeolites precipitate extensively from alkaline to weakly acid hot water in active geothermal areas; e.g., Wairakei, New

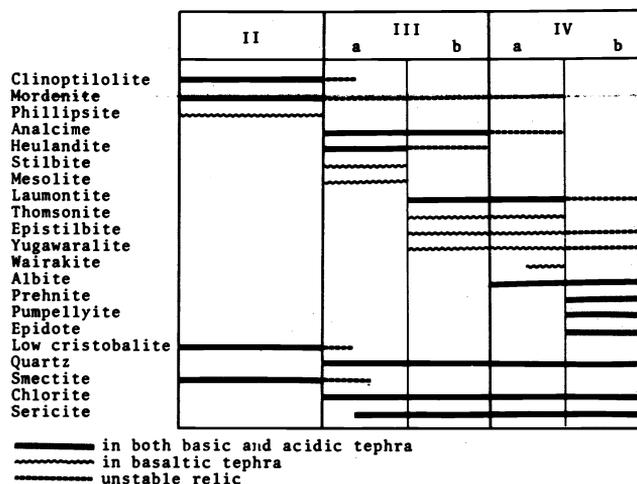


Figure 1. Zeolite zones in Neogene acidic and basic tephra in contact aureole in the western Misaka Mountains, central Japan. The zoning is referred to Burial Diagenesis. Slightly modified [40].

Zealand [42, 43], Yellowstone Park, Wyoming [33], Iceland [34], and Onikobe in Japan [44]. The zeolite assemblage and zone are principally controlled by temperature and chemical composition of host rocks and subordinately by permeability, composition of geothermal fluids, and age of geothermal area and host rocks.

In Quaternary basaltic flows and hyaloclastic rocks of Iceland, zeolite zones are principally resulted from geothermal gradient in the low-geothermal areas where the top 1 km-depth is less than 150°C. Four zeolite zones are commonly discriminated; 1) chabazite-thomsonite, 2) mesolite-scolecite, 3) stilbite, and 4) laumontite. By contrast, zeolites do not make any clear zone in the high-geothermal areas where the top 1 km-depth is more than 200°C [34].

Zeolite zones in the Tertiary basalts of eastern Iceland [45] and Northern Ireland [46] are similar to those in the Quaternary basalts in the low-geothermal areas of Iceland besides the occurrence of a zone of Na zeolites, analcime and natrolite, beneath the top chabazite-thomsonite zone. They are considered to have formed by geothermal gradient.

In acidic tephra of geothermal areas, zeolite assemblages are not different from those in basalts in the deep, high-temperature zones but quite distinct in the shallow, low-temperature zones. Four zones are vertically arranged in Onikobe [44]; 1) mordenite, 2) laumontite, 3) laumontite-wairakite, and 4) wairakite. Yugawaralite and analcime are common in the laumontite zone. In Yellowstone Park [33] analcime or heulandite zone intervenes between the top clinoptilolite-mordenite and the laumontite zones. The content of water molecules in the zeolites decreases with increasing temperature.

Submarine hydrothermal activities produce a peculiar alteration pattern. Analcime and mordenite occur in a zone surrounding the hydrothermal clay zones which enclose the Miocene Kuroko polysulfides ore deposits in Odate [47] and Nishiaizu [48] in the Green Tuff region of Tohoku, Japan. The analcime and mordenite formed by reaction of dacitic glass with the Na-rich hydrothermal water which migrated from the clay zones into porous vitric tuff. The clinoptilolite-mordenite zone superimposes on the hydrothermal alteration zones. Ferrierite is locally associated with mordenite and clinoptilolite [49].

lake deposits of the San Simon valley in Arizona by Loew in 1875 [74] and from ferruginous clay of Duingen in Germany by von Seebach in 1862 [11].

Modern saline lakes are restricted in the semiarid tracts of the Earth; e.g., in the rift valley of East Africa and Israel and in the Basin and Range province of the western United States. The Quaternary and Neogene saline lake deposits which contain zeolites are also widespread in the western United States [3, 4, 10, 36, 74 - 76] and in East Africa [3, 10, 68-70]. The Paleogene deposit is the well-known Green River Formation of Wyoming, Utah and Colorado [3, 28, 77-80].

In acidic tuffs of alkaline, saline lake deposits, diagenetic minerals occur in lateral zones contrasted with the vertical zones due to burial diagenesis. A typical occurrence is seen in the Late Pleistocene Tecopa Lake Beds in southern California [36]. Rhyolitic glass shards remain unaltered in the flood plain and lake margin facies in which fresh-water prevails. They alter to phillipsite, clinoptilolite and erionite associated with some chabazite and mordenite in the saline water facies. Small amounts of analcime may replace the precursor zeolites. K-feldspar occurs in the supersaline facies of the lake center, is commonly associated with saline minerals like trona, and replaces the precursor zeolites. The content of analcimes in alkaline, saline lake deposits tends to increase with age [3, 4]. Analcimes do not make a clear zone in the Late Pleistocene Tecopa Lake Beds, but occur in a zone between the zeolite and the K-feldspar zones in the Pliocene Big Sandy Formation, and are the principal zeolites in the Eocene Green River Formation. Authigenic albite that replaces analcime is only found in the Green River Formation which was buried at the maximum depth of approximately 2 km [28].

The lateral zones of the diagenetic facies, viz. fresh silicic glass/zeolites/analcime/K-feldspar are undoubtedly caused by a chemical gradient of pore water within the alkaline, saline lake deposits. Consequently, this type is often said as the closed-system groundwater type [9, 10]. The hydrology and geochemistry of alkaline, saline lake deposits are reviewed by Surdam and Sheppard [10].

Ca-clinoptilolite and (Si-rich heulandite) with little erionite replace silicic vitric tuffs in the Eocene Wagon Bed Formation in Wyoming [81]. These zeolites alter to K-feldspar in the lake center. No phillipsite and chabazite and little analcime are recognized in the saline lake deposit. Boles and Surdam [81] consider that the lake was not highly alkaline with a pH less than 9.

Marine sediments. Zeolite from deep-sea sediments was recorded by Murray and Renard in 1891 [82]. Much work has been done since then, but the Deep Sea Drilling Project (1968-1975) and the International Phase of Ocean Drilling (1976-) shed light upon the whole deep-sea zeolites, of which overview was made by Hay [4], Iijima [7] and Kastner and Stonecipher [13].

K-zeolites such as phillipsite and clinoptilolite are dominant. Harmotome is commonly associated with phillipsite. Analcime is much less common than the K-zeolites and occurs usually in basaltic sediments. Other zeolites including chabazite, erionite, laumontite, gmelinite, natrolite, and thomsonite are very rare in basic volcanics. A little amount of laumontite was found in Upper Miocene to Cretaceous, terrigenous and volcanic sediments of the D.S.D.P. cores at Site 323 in the Bellingshausen Abyssal Plain off Antarctica 83. However, its authigenesis seems not to be evident.

Phillipsite is common in post-Miocene brown clay, vitric siliceous and calcareous oozes, and basic volcanic sediments in the slow sedimentation areas of the Pacific and Indian Oceans [7, 13, 84]. The field of stability of phillipsite seems to be restricted, because the crystal faces are corroded not only by circulating sea water in the surficial bottom sediments within a depth of about 1–2 m but also by pore water in the sediments below about 4 m [84]. The pore water in phillipsite-rich sediments poses a lower silica and higher potassium environment. The origin of deep-sea phillipsite is probably related with basaltic glass, considering the common association with palagonite and basaltic glass fragments [4, 7, 13] and from a high Ti/Al ratio of phillipsite-containing sediments [85]. The moderately higher content of silica in the deep-sea phillipsite suggests the contribution of biogenic silica [19]. Deep-sea phillipsite occurs exceptionally in acidic vitric tuff at Site 205 [86].

Clinoptilolite is common in Paleogene and Cretaceous calcareous sediments and terrigenous clay in the Atlantic Ocean and the Pacific Margin, though it is not uncommon in post-Miocene brown clay and other sediments in the Pacific and Indian Oceans. Clinoptilolite crystals are not corroded. The pore water in clinoptilolite-rich sediments suggests a higher silica environment [7]. Clinoptilolites are mostly originated from acidic glass in vitric tuffs and vitric sediments due to burial diagenesis particularly in the rapid sedimentation areas adjacent to continents and island arcs [7]. In the slow sedimentation areas where phillipsite may occur, clinoptilolites probably form by reaction of basaltic glass with pore water rich in dissolved silica of a biogenic or weathering origin [4, 7, 13, 87]. Also, X-ray amorphous clay and smectite may be the original material of some clinoptilolite [4, 13, 87].

The decrease in the amount of phillipsite in the Paleogene and Cretaceous sediments is interpreted that composition of host sediments, particularly volcanic material, changes from basaltic to andesitic [88]; that phillipsite may alter to either K-feldspar or analcime [7]; and that phillipsite may be replaced by clinoptilolite or sepiolite [13, 87]. However, these interpretations are still not entirely proved.

Impact Crater. Zeolites are discovered in suevite and lake sediment of the Nördlinger Ries impact crater in Bavaria, West Germany [89, 90]. Glass in suevite alters to analcime and smectite, while microcavities of suevite are filled by analcime, clinoptilolite, phillipsite, erionite and harmotome. Zeolites are common in the upper suevite sequence, in which analcime and clinoptilolite occur in bituminous, dolomitic shale and sandy sediments with some altered suevite.

GEOLOGICAL SYNTHESIS ON NATURAL ZEOLITE FORMATION

Source and Distribution of Zeolite. Natural zeolites occur as an alteration product of glass of a volcanic or impact origin, amorphous clay, and aluminosilica gel. They replace crystalline materials such as nepheline, plagioclase, precursor zeolite, and smectite. Also, they precipitate in cavities and veins from hot or cold solution. However, fine-grained glass fragments are the most important raw material of natural zeolites for almost all types of occurrence, because of their high reactivity and similar chemical composition to certain zeolites. In fact, zeolite-rich rocks composed of one or some species of

zeolite are largely derived from altered vitric tuffs, in which the content of zeolite is sometimes over 90 percent of the rock. Clinoptilolites in deep-sea sediments and marine strata are often interpreted as originating in clay material owing to the negative evidence that 'volcanic glass can't be seen'. However, this evidence does not necessarily deny the origin of volcanic glass, because altered, very fine-grained, vitric fragments in zeolitic clays and claystones are usually impossible to be identified under the microscope, as Kossovskaya [8] pointed out.

The distribution of zeolitic rocks is usually very closely related to the site of volcanism. Zeolites of the hydrothermal, contact metamorphism, burial diagenesis, and percolating groundwater origins are commonly widespread in the younger orogenic belts and hot spots where thick deposition and contemporaneous volcanism occurred: viz., in the Circum-Pacific region including New Zealand, Japan, Korea, Sakhalin, Kamchatka, Alaska, western United States, Chile, and other potential areas; in the Tethys region including Spain, France, Italy, Switzerland, Yugoslavia, Bulgaria, Roumania, Hungary, Turkey, north Iran, South Russian Basin, Ural Basin and Central Asia; and in Hawaii and Iceland. Clinoptilolites in acidic vitric tuffs and vitric sediments interbedded with the deep-sea deposits in the rapid sedimentation areas adjacent to continents and island arcs seem to be caused by burial diagenesis [7, 91]. Volcanism as well as semi-arid climate are stressed by Surdam and Sheppard [10] in terms of the geological situations of the alkaline, saline lake deposits which contain abundant zeolite. The rift valley in East Africa and the Basin and Range Province in western United States fulfill the condition.

Most if not all known zeolite ore deposits are derived from vitric tuffs: e.g., clinoptilolites of Itaya in Japan [92], Hector in California [93], Northeast Rhodopes in Bulgaria [94], the Tokay in Hungary [95], and Dzegvi and Khekordzula in Georgia and Ay-dag in Azerbaydzhan [96]; mordenites of Itado and Shiroishi in Japan [92]; and chabazites of Bowie in Arizona [74], and Campania in Italy [11, 12].

Zeolitization of Volcanic Glass. Much work on zeolitization of volcanic glass has been done both in the field and laboratory. Hydration of glass is often considered to be the preliminary stage of zeolitization [97]. The rate of hydration is represented by a simple equation, $S^2 = CT$ where S is thickness of hydrated rind on glass, T is years, and C is a constant relating to temperature and composition of glass and pore water [98, 99]. However, a complicated chemical reaction concurs with the hydration and active migration of such components as Na, K, Ca, Mg, silica and even alumina occurs between glass and pore water [47, 64, 100]. On the one hand, the leached alkalis increase pH and alkalinity of pore water, accelerating dissolution of glass: on the other hand, silica and alumina released from the glass are utilized for constructing zeolite frameworks. In the Teels Marsh and Lake Magadi, volcanic glass is dissolved to form an aluminosilica gel which changes to phillipsite in water of pH over 9, while such gel is not found in water of pH 8-9 in which clinoptilolite forms [10].

The rate of zeolitization is represented by a function with multi-variables such as time, temperature, composition of glass, and composition and flow rate of pore water. Zeolites may grow very fast in high temperature geothermal fluids, considering the results of hydrothermal experiments. Even in pure water, chabazite, phillipsite and analcime are synthesized from basaltic glass at 200°C for 5 days while mordenite and analcime are produced from rhyolitic glass at 250°C for

40–60 days [101]. The experiments are accelerated by adding a little amount of NaOH or KOH [35, 101]. Basaltic ash laid on the Surtsey from November 1963 to April 1964, is altered to zeolite, perhaps chabazite, by heated sea water of below 100°C after 7 years [102]. Phillipsite is associated with fresh glass and gel in rhyolitic vitric ash of 600 y.b.p. in the Teels Marsh, an alkaline, saline playa-lake of Nevada. Abundant chabazite and phillipsite were formed by percolating groundwater in alkali-trachytic glass fragments of the Neapolitan Yellow Tuff of $1-1.2 \times 10^4$ y.b.p.; the zeolitization is estimated to have continued for $4-5 \times 10^3$ years though it is now inactive [103]. Not only phillipsite and chabazite but also analcime occur in basanite tuff of Koko Crater of 3.5×10^4 y.b.p. by reaction of sideromelane with percolating groundwater [4]. Phillipsite crystals grow up to 45 μm for 1.5×10^5 years in deep-sea sediments of the Indian Ocean [104]: the rate of growth is correlative to the slow rate of sedimentation which is 0.5–0.8 mm/ 10^3 years [105]. Approximately 10^6 to 10^7 years are necessary for rhyolitic or dacitic glass in marine sediments to change to clinoptilolite and mordenite due to the present-day burial diagenesis which are influenced by geothermal gradient and the rate of burial and sedimentation [7, 30, 51]. The rate of zeolitization is proportional to the content of silica in glass under the same physicochemical conditions it is significantly accelerated by increasing temperature and increasing pH, alkalinity and salinity of pore water.

Formation of Zeolite Species. Formation of zeolite species is influenced by various factors. Chemical composition of original material of the zeolite and composition of host rocks primarily control zeolite species particularly at low temperature. Zeolites in alkali rocks are of "basic" species excepting analcime and faujasite, while those in acidic rocks are "acidic" and "intermediate" ones (Table 1). Even

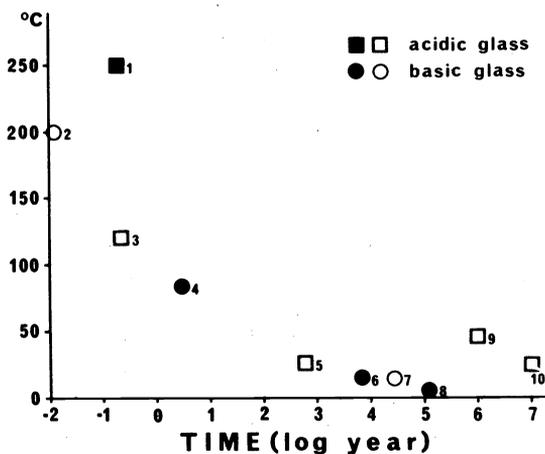


Figure 2. Rate of zeolitization of volcanic glass in various occurrences. Solid symbols represent analcime. 1) mordenite-analcime and 2) chabazite-phillipsite-analcime by hydrothermal synthesis in pure water [101]; 3) mordenite by hydrothermal synthesis in weakly alkaline geothermal fluid in the Shikabe geothermal well [109]; 4) chabazite on the Surtsey [102]; 5) phillipsite in the Teels Marsh [10], 6) phillipsite-chabazite in the Neapolitan Yellow Tuff [103]; 7) phillipsite-chabazite-analcime in the Koko Crater Tuff [4]; 8) phillipsite in the Indian Ocean [104]; 9) clinoptilolite in the Niigata oilfield [30]; and 10) clinoptilolite at Site 439 [51].

Burial Diagenesis. The concept of burial metamorphism was established by Coombs [50] based on the study of the Triassic geosynclinal deposits in New Zealand. Zeolitic burial diagenesis is defined that zeolites form progressively within a thick sequence of strata with increasing burial depth [3, 4, 5, 7]. It has been best documented in the Tertiary and Cretaceous geosynclinal basins of Japan, where marine and fresh-water sequences are commonly interbedded with acidic vitric tuffs and volcanoclastic beds [7, 30, 51-53]. Two zeolitic reaction series are recognized in acidic tuffs and volcanoclastic sediments: one is alkali zeolite reaction series, acidic volcanic glass + $H_2O \rightarrow$ alkali clinoptilolite + mordenite + low cristobalite \rightarrow analcime + quartz + $H_2O \rightarrow$ albite + H_2O ; and the other is calcic zeolite reaction series, alkali clinoptilolite \rightarrow heulandite + quartz \rightarrow laumontite + quartz. In acidic tuffs the alkali zeolite reaction series is practical to set up

because it occurs more commonly than the calcic zeolite reaction series. As a result, four diagenetic zones are constructed; namely, Zone I is a zeolite-free zone characterized by glass shards which alter partially or sometimes wholly to smectite and opal; Zone II is a zone characterized by clinoptilolite, mordenite or both which originate from acidic glass; Zone III is a zone characterized by analcime replacing the precursor zeolites, which often coexist as relic; and Zone IV is a zone characterized by albite replacing analcime. Plagioclase in tuffs and sandstones usually changes to albite, too.

The zeolite zones are widespread and mappable. Boundaries of each zone is rather gradational. The zoning is primarily controlled by geothermal gradient. In the Niigata, Akita and Tenpoku oilfields of Japan, the present-day zeolitic burial diagenesis is certainly proceeding in the Quaternary and Neogene marine strata. Five drillholes, penetrating the strata, show that the top of Zone III (analcime) occurs at $84^\circ-91^\circ C$ in a depth range between 1700 and 3500 m; and that the top of Zone IV (albite) is at $120^\circ-124^\circ C$ in a depth range between 2500 and 4500 m [30, 51]. The wide depth ranges, compared with the restricted temperature ranges, suggest that PH_2O and the difference between P total and PH_2O do not practically influence the reaction temperature in those depths. The good correlation of the zeolite zones with the degree of coalification [54-58] supports the progress of temperature-dependent reactions during the burial diagenesis. The transition of Zone I/II occurs at $25^\circ-60^\circ C$ in the depth range between 635 and 1900 m. The change of acidic glass to zeolite is probably influenced by composition of pore water, time and temperature.

The calcic zeolite reaction series roughly concurs in the analcime zone, though laumontite can coexist with albite in Zone IV. Therefore, Zone III is sometimes subdivided into IIIa (analcime-heulandite) and IIIb (analcime-laumontite) [7, 51]. Heulandite and laumontite are common in andesitic and basaltic volcanoclastic rocks; e.g. the Triassic deposits of New Zealand [50, 59] and the Paleogene flysch of the North Helvetic [60, 61] and the northern Apennine [11]. Shallower zeolite zones are missing due to denudation in the Triassic of New Zealand. The reaction heulandite \rightarrow laumontite is influenced by not only temperature but also PH_2O , PCO_2 and the activities of silica and cations in pore water [59, 62]. The reaction occurs in Miocene dacitic tuff at $120^\circ C$ at the depth of 4310 m of the MITI-Masugata Hole in the Niigata oilfield, where the present-day burial diagenesis is in progress.

Phillipsite, chabazite and erionite seem not to occur in acidic vitric tuffs in marine or fresh-water deposits by burial diagenesis.

Percolating groundwater. Zeolites precipitate from groundwater percolating through a sequence of porous pyroclastic material rich in reactive glass. Consequently, they are often said as the open-system groundwater type [4, 9]. This type of zeolitization was established by Hay in the John Day Formation in Oregon [63]. Most spectacular example would be Late Pleistocene palagonite tuffs on Oahu Island, Hawaii [64, 65]. Many small tuff cones of nephelinite and basanite ash-fall deposits demonstrate a characteristic alteration pattern. The surface of tuff cones are covered with subtropical soil, which is followed by a carapace of fresh tuffs or slightly-altered, opal-cemented tuffs with a thickness of 12-18 m. Below the carapace with a sharp contact, orange to brown zeolitic palagonite tuffs constitute the main part of the tuff cones. The upper zone of the palagonite tuffs is dense, cemented with phillipsite, chabazite and Mg calcite, while the lower zone of it is rather porous and characterized by analcime partially replacing the precursor zeolites and partially cementing pores. On the foot of the southeast wall of Kahauloa Crater, below the analcimic tuffs are the subpalgonite tuffs which overlie slightly-altered, opal-cemented tuffs. This alteration pattern is interpreted as suggesting the chemical gradient produced by reaction of percolating groundwater with sideromelane particles. The pH and the concentrations of dissolved ions increase as the groundwater percolates through porous sideromelane tuffs, until zeolites precipitate in interstitial pores. A 12-18 meter-thick column of sideromelane ash is needed to form zeolitic palgonite tuffs. It is remarkable that palagonitization is hardly proceeding in sideromelane tuffs below the groundwater table so that zeolites do not form.

In rhyolitic vitric tuffs of the John Day Formation, a 200 meter-thick column is necessary for percolating groundwater to gain salinity sufficient to precipitate clinoptilolite [63]. How thick it is as compared with 12-18 m in ultrabasic tuffs on Oahu! Below the clinoptilolite zone with a thickness of 700 m, analcime formed by reaction of the clinoptilolite with alkaline pore water, making the analcime zone. The vertical arrangement, viz., fresh glass/c clinoptilolite/analcime, is the same as that formed by burial diagenesis in acidic vitric tuffs. The sharp boundary between fresh glass and clinoptilolite zones is characteristic in the open-system groundwater type and the radiometric age of authigenic minerals is a useful tool for the specification [4].

Zeolitized vitric tuffs of the Quaternary alkali rocks in southern Italy, e.g., chabazite and phillipsite in alkali-trachytic tuffs in Campania and the Neapolitan Yellow Tuff of Campi Flegrei, are considered to form percolating groundwater [11, 12].

Weathering. Zeolites are formed by chemical weathering in alkali soils and land surfaces in semi-arid tracts. Recent to Pleistocene examples are reported from the San Joaquin valley of California [66], Ruzizi in Burundi [67] and the Olduvai gorge in Tanzania [3, 68-70]. Regional Mesozoic analcimolites interbedded with redbed facies in Utah [71], Congo Basin [72] and Central Sahara [73] were probably formed by weathering of non-tuffaceous fluvial claystones on flood plains soon after deposition [4]. It is remarkable that analcime and illite are formed by reaction of smectite with the Na-HCO₃-CO₂ soil water in alkali soils. Hay [4] wrote a nice review and nothing adds to it.

Alkaline, saline lake deposits. Many zeolites form in alkaline, saline lake deposits of various ages from Recent to Upper Permian. The earliest records of sedimentary zeolites were indeed from the saline

Table 3. Geological synthesis and occurrence of natural zeolites. The indicated temperature is merely approximate.

| Type of occurrence | Temperature | Zeolite species |
|---|-------------|---|
| Deep-sea sediments | 4°–50°C | Ph, Cp, (An) |
| Earth's surface weathering | | Ph, Cp, Ch, Er, Mo, |
| Alkaline, saline lake | 20°–50°C | Gi, Fa, Go, Na, An, |
| Percolating groundwater (in basic tephra) | | (He) |
| Percolating groundwater (in acidic tephra) | 25°–100°C | Ph, Cp, Ch, Er, Mo, Fe, An, Th, Me, Sc, He, St, etc. except La, Wa, and Yu |
| Shallow burial diagenesis | | |
| Low-temperature hydrothermal | | |
| Deep burial diagenesis | | |
| Moderate-temperature hydro- thermal | >100°C | La, An |
| Low-grade metamorphism | | |
| High-temperature hydrothermal | >200°C | Wa, Yu, An |
| Magmatic primary | | An |

Ph: phillipsite, Cp: clinoptilolite, Ch: chabazite, Er: erionite, Mo: mordenite, Gi: gismondine, Fa: faujasite, Go: gonnardite, An: analcime, Na: natrolite, He: heulandite, Th: thomsonite, Me: mesolite, Sc: scolecite, St: stilbite, La: laumontite, Wa: wairakite, Yu: yugawaralite.

though they occur in various sediments and host rocks, phillipsite and chabazite cluster in the silica-poor variety with dominant Ca in ultra-basic and basic rocks, whereas they belong to the silica-rich variety with dominant alkalis in acidic tuffs in alkaline, saline lake deposits [16, 19].

Temperature is another important factor to control zeolite species as tabulated in Table 3. Zeolites formed in deep-sea sediments at low temperature are phillipsite and clinoptilolite, both of which contain dominant alkalis with $K > Na$, and possibly some analcime. Zeolites formed at or near the Earth's surface, viz., in alkali soils, in alkaline, saline lake deposits and in zeolitic tuffs altered by percolating groundwater, are phillipsite, chabazite, clinoptilolite, erionite, mordenite, natrolite, gismondine, faujasite, gonnardite, and analcime. Zeolites formed by deep burial and high-temperature hydrothermal alteration at a temperature over approximately 100°C are low-water, calcian zeolites such as laumontite, wairakite and yugawaralite besides analcime. In particular, wairakite and yugawaralite are frequently found in cores of geothermal wells at a temperature over 200°C. Analcimes in some igneous rocks are considered as the primary mineral of magma in later crystallization [38]. Zeolites formed by shallow burial and low-temperature hydrothermal alteration below about 100°C are thomsonite, ferrierite, heulandite, mesolite, scolecite and stilbite in addition to

those which occur at or near the surface. Analcimes occur in all over the temperature range from deep-sea sediments to magma. The Si:(Al+Fe) ratio in analcimes, varying from 1.7 to 2.9, is affected by various factors: it decreases with increasing temperature in synthetic analcimes [26], although it does not systematically change with increasing burial depth within the analcime zone of burial diagenesis [7, 106]; it is inherited from the precursor zeolites, viz., high-silica analcime replacing high-silica clinoptilolite and mordenite while low-silica one replacing low-silica phillipsite and chabazite [10, 75]. Analcime and wairakite constitute a solid solution [107], though detailed mineralogical study is a future problem [108].

Ageing, also, influences zeolite species. Natural zeolites occur in various rocks of varying geologic ages up to Late Precambrian time [3, 5, 7, 11]. The amount of zeolitic rocks in the Earth's crust seems to be fairly common in the Cenozoic and upper Mesozoic strata, while it

Table 4. Number of zeolite species in geologic time. Vein-fillings are excluded. See references [3, 5, 11, 13].

| Era | Number of zeolite species |
|-------------------|---------------------------|
| Cenozoic | 32 |
| Mesozoic | 7 |
| Late Paleozoic | 4 |
| Early Paleozoic | 2 |
| Late Precambrian | 1 |
| Early Precambrian | 0 |

becomes rather uncommon in the lower Mesozoic and Upper Paleozoic, scarce in the Lower Paleozoic, and negligible in the Precambrian. Moreover, the number of zeolite species found in strata of each geologic period tends to decrease rapidly with increasing age (Table 4). The ratio of analcime to all zeolites in alkaline, saline lake deposits increases with ascending age [3, 4]. These facts may be due to decomposition and substitution of many unstable zeolites by a few stable zeolites, like analcime and laumontite, which are eventually replaced by alkali feldspars and other minerals. The phenomenon seems to be interpreted as suggesting either ageing [3, 4] or deeper burial and so increasing temperature of older strata [6, 7].

Chemical composition of pore waters such as pH, alkalinity and the concentration and activities of chemical components essentially controls the formation of zeolites especially in saline lake deposits [10, 62]. Also, Kirov et al. [35] experimentally show that both geothermal and chemical gradients play important roles on the vertical zeolite zones during burial diagenesis. However, informations of interstitial water in a thick column of strata are very scarce and far from fully understood.

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