

BARRERITE AND OTHER ZEOLITES FROM KUIIU AND KUPREANOF ISLANDS, ALASKA

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ABSTRACT

Barrerite, considered to be the rarest zeolite of the stilbite group, is abundant in the basalt of the Kuiiu–Etolin Formation on Kuiiu and Kupreanof islands in southeastern Alaska. Several other sodium-rich zeolites are present in the tidal belt, including previously unreported monoclinic sodian stilbite and sodian epistilbite.

Keywords: zeolites, barrerite, stilbite, epistilbite, heulandite, cation exchange, Kuiiu Island, Kupreanof island, Alaska.

SOMMAIRE

La barrerite, considérée jusqu'à présent comme le membre le plus rare du groupe de la stilbite, est une zéolite abondante dans les basaltes de la formation Kuiiu–Etolin sur les îles de Kuiiu et Kupreanof, dans l'Alaska sud-orientale. Plusieurs zéolites sodiques sont présentes dans la zone à marée, entre autres stilbite sodique monoclinique et épistilbite sodique.

Mots-clés: zéolites, barrerite, stilbite, épistilbite, heulandite, échange cationique, île de Kuiiu, île de Kupreanof, Alaska.

INTRODUCTION

Barrerite is the sodium-rich member of the stilbite group of zeolites. The members of this group, stilbite $\text{NaCa}_4(\text{Al}_9\text{Si}_{27}\text{O}_{72})\cdot 30\text{H}_2\text{O}$, stellerite $\text{Ca}_4(\text{Al}_8\text{Si}_{28}\text{O}_{72})\cdot 28\text{H}_2\text{O}$, and barrerite $\text{Na}_8(\text{Al}_8\text{Si}_{28}\text{O}_{72})\cdot 26\text{H}_2\text{O}$, share the same topology in their aluminosilicate networks (Gottardi & Galli 1985). As a consequence, they share the same structural type, *i.e.*, STI according to the nomenclature of the International Zeolite Association (Meier & Olson 1992). The International Mineralogical Association classifies them as three different mineral species (Fleischer & Mandarino 1995), and indeed they can be easily differentiated by chemical analysis and X-ray diffraction.

The only occurrence of barrerite reported to date is at Capo Pula, Sardinia, Italy (Passaglia & Pongiluppi 1974, 1975). Barrerite crystals from the type locality present a cation ratio $M/(M+D)$ of 0.87 (here, M stands for monovalent cations, and D , for divalent cations), compared with a value of 0.20 in the "ideal" formula of

stilbite (Gottardi & Galli 1985). Nonetheless, the cation content of stilbite can vary over a large range, and Na-rich stilbite is not uncommon. Samples with a $M/(M+D)$ value of 0.65 (Harada & Tomita 1967), 0.68, 0.73 (Passaglia *et al.* 1978), 0.75 (Slaughter 1970), 0.77 and 0.82 (Birch 1989) have been reported. All these specimens exhibit the $C2/m$ space group of stilbite, and not the $Amma$ space group of barrerite (Galli & Alberti 1975), with the possible exception of the most Na-rich sample, from Phillip Island, Victoria, Australia, for which no crystallographic data are available (Birch 1989).

All samples of Na-rich stilbite reported in the literature have been found at seaside localities, as has barrerite in its type locality. Passaglia *et al.* (1978) have suggested that barrerite first crystallized in the presence of large amounts of calcium, thus with a stilbite-like composition, and that later ion-exchange by sea water increased the sodium content, eventually altering the stilbite to barrerite. This hypothesis seems to have been disproved by the results of sodium exchange of stellerite, the calcian end-member with the stilbite topology

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and a *Fm* space group (Passaglia & Sacerdoti 1982). Sodium-exchanged stellerite has the same composition as barrerite, but retains the *Fm* symmetry. This result suggests that the peculiar pattern of occupancy of cation sites, which is responsible for the *Amm* space group of barrerite (Galli & Alberti 1975), is difficult to attain by exchange of a calcium-rich zeolite. An alternative mechanism of formation of barrerite is by direct crystallization in the presence of sea water percolating through a volcanic horizon.

The present report describes barrerite from a locality in southeastern Alaska. Characterizations allow the mineral to be classified as barrerite, and the finding is discussed in connection with the mineralogy of other zeolites found in the area, in order to give new information related to the genesis of barrerite.

EXPERIMENTAL

The mineral specimens were collected by one of the authors (Z.G.) on the eastern coast of Kuiu Island (Sitka Borough, Alaska) and the southwestern coast of Kupreanof Island (Wrangell-Petersburg Borough). Both islands, separated by the narrow and shallow Rocky Pass, feature wide areas of pillow basalt, having the characteristic texture of lavas solidified under water or ice. Zeolite-containing vugs have been exposed in the tidal area. Inland outcrops are less easily accessible and have only been explored along creeks: Irish Creek on Kupreanof Island and Mud Creek on Kuiu Island.

The area of the Rocky Pass, from which specimens were collected, can be divided into four main geological regions (Fig. 1), each being homogeneous for the nature and composition of the specimens: 1) Quaternary and Tertiary basalts [QTb in Brew *et al.* (1984), from which all geological abbreviations are taken, unless otherwise stated] in the tidal area of Kuiu Island, 2) Quaternary and Tertiary basalts (QTb) and volcanoclastic rocks (QTC) inland on Kuiu and Kupreanof islands, 3) Quaternary and Tertiary rhyolites (QTr) in the tidal area of the islets at the southern inlet of Rocky Pass, and 4) Triassic basaltic breccia [TRV in Muffler (1967), TRhh in Brew *et al.* (1984)] in the tidal area of Kuiu Island near the northern inlet of Rocky Pass.

The composition of the crystals was determined by electron-probe micro-analysis (Cambridge Stereoscan 260, 20 kV, 135 pA) using as references specimens of stilbite from Cape Sharp, Nova Scotia, barrerite from Capo Pula, Sardinia, and stellerite from the Rössing mine, Namibia. Partial dehydration under the electron beam generally prevents a reliable measurement of zeolitic water by electron-probe micro-analysis. The amount of water was determined by thermogravimetry (TG, Stanton Redcroft ST-780 thermobalance, heating rate 20°C min⁻¹ in static air, weight loss measured after a 2 hr isotherm at 800°C). Powder X-ray diffraction (XRD) data were recorded using a CGR Theta-60 diffractometer (monochromatic CuK α radiation). Orthorhombic and monoclinic phases

were identified using the method of Passaglia *et al.* (1978), based on the analysis of the diffraction profile of the peaks 204 and 040 (indices of the pseudo-orthorhombic *F2/m* cell, in the case of stilbite). According to this method, a sharp 204 peak corresponds to orthorhombic samples (pattern *a*), a broad peak corresponds to stilbite having a low β (lower than approximately 90.30°) (pattern *b*), two distinct 204 and 040 peaks are characteristic of normal stilbite with $\beta \approx 90.75^\circ$ (pattern *c*), and a broad band centered around 23.8° 2 θ is typical of heterogeneous samples (pattern *d*). Identification of other zeolite phases (mordenite, laumontite, epistilbite, clinoptilolite, chabazite, and members of the heulandite and natrolite groups) was confirmed by their characteristic XRD patterns.

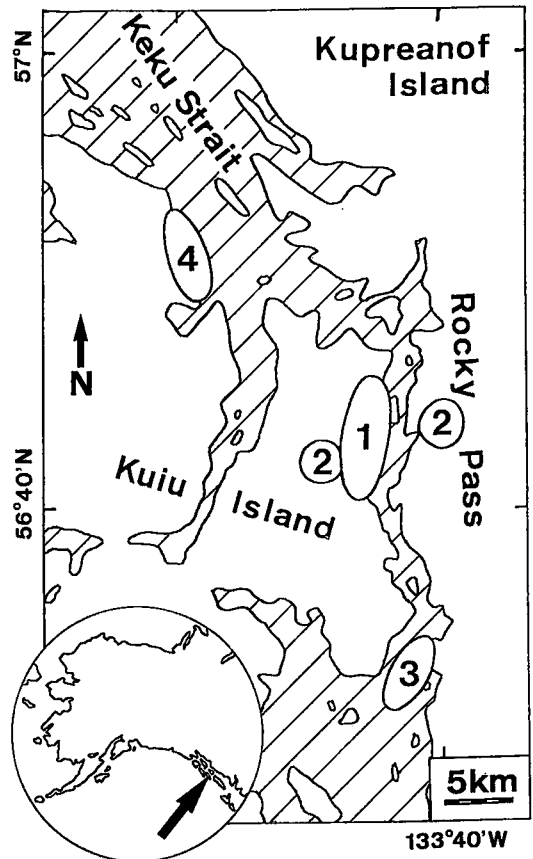


Fig. 1. Map of zeolite findings in the Rocky Pass area. The Kuiu-Etolin Tertiary and Quaternary volcanic suite consists of (1) tidal-area basalts, (2) inland basalts and volcanoclastic rocks, and (3) tidal-area rhyolites. (4) Tidal-area Hound Island Triassic breccias.

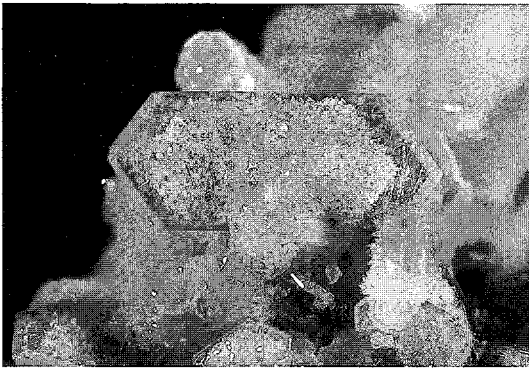


Fig. 2. Barrerite and dendritic quartz from the eastern coast of Kuiu Island (sample 1). Length of the main barrerite crystal is 18 mm.

BARRERITE AND STILBITE FROM ROCKY PASS

Crystals having the classical morphology of stilbite are the most common in the Quaternary and Tertiary basalts of the Kuiu–Etolin volcanic belt, which constitute region (1). The specimens feature the (010)(110) (001) tabular habit flattened on (010) typical of composite crystals of stilbite (indices of pseudo-orthorhombic cell of stilbite, Gottardi & Galli 1985). Zeolite crystals are in some cases as developed in 010 as in 001 direction. The thickest crystals may present small (100) facets. Aggregates of sheaf-like crystals are locally observed.

Zeolite crystals up to several centimeters in length, accompanied by microcrystalline quartz in characteristic stalactite-like dendritic aggregates, line vugs as wide as several decimeters. Zeolite crystals and quartz aggregates overgrow one another (Fig. 2), probably as the result of several sequences of alternating crystallization. Less commonly, stilbite-like crystals are overgrown by large crystals of calcite. Some samples having the typical morphology of stilbite have been collected on Kuiu Island in the bed of Mud Creek, from its mouth in the Kuiu–Etolin basalts (region 1) to about 500 m upstream and 5 m higher than the current upper tide limit, in an area of volcanoclastic deposits connected to the Kuiu–Etolin belt (region 2). Calcite is generally associated with the specimens from Mud Creek.

The occurrences of stilbite-like crystals are much scarcer in the altered rhyolites of the Kuiu–Etolin belt (region 3) and in the Triassic basaltic breccia of the Hound Island Formation (region 4), where other zeolites predominate.

The results of the micro-analysis of stilbite-like crystals are given in Table 1. The composition of the samples collected in the tidal area (samples 1–3 from region 1; samples 7 and 8 from region 3, and sample 9 from region 4) is quite constant, independently of

the age of the host rock. The average composition is $\text{Na}_{4.2}\text{K}_{1.5}\text{Ca}_{0.9}\text{Mg}_{0.1}(\text{Al}_{7.8}\text{Si}_{28.2}\text{O}_{72}) \cdot 25.7 \text{H}_2\text{O}$, with a $M/(M + D)$ value of 0.85. The composition of barrerite from the type locality at Capo Pula is $\text{Na}_{5.45}\text{K}_{1.06}\text{Ca}_{0.84}\text{Mg}_{0.17}(\text{Al}_{8.19}\text{Si}_{27.72}\text{Fe}_{0.01}\text{O}_{72}) \cdot 25.78 \text{H}_2\text{O}$ (Passaglia & Pongiluppi 1974), and the $M/(M + D)$ value is 0.87. The $M/(M + D)$ value of the most Na- and K-rich zeolite of the stilbite group having $C2/m$ as its space group is 0.75 (Slaughter 1970). Therefore, the stilbite-group zeolites from the tidal area of Rocky Pass are compositionally to be considered barrerite. Note that even crystals nearly completely embedded in calcite overgrowths feature this alkali-rich composition.

The samples collected along Mud Creek (region 2) display a significant change of composition as a function of the distance from the seaside. Sample 3, composed of centimeter-size crystals from a calcite-filled vein from the tidal area at the mouth of the creek, has the composition of barrerite. Samples 4 and 5 correspond to different parts of one specimen, collected near the limit of the highest tide. The composition of the sample varies, with the cation ratio $M/(M + D)$ ranging from 0.60 to 0.70, still within the compositional limits of sodium-rich stilbite (Passaglia *et al.* 1978). Sample 6, collected nearly 5 m above the highest tide limit, is extremely Ca-rich, with a $M/(M + D)$ value of 0.13, which suggests that it should be classified as stilbite poor in monovalent cations, not far from the compositional limits of stellerite.

The samples from the Kuiu–Etolin basalts of the tidal area, exemplified by samples 1 and 2, give the XRD pattern of the orthorhombic zeolites of the stilbite

TABLE 1. CHEMICAL COMPOSITION OF STILBITE AND BARRERITE SAMPLES FROM THE ROCKY PASS AREA, ALASKA

	1	2	3	4	5	6	7	8	9
electron probe									
SiO ₂	59.95	59.50	59.28	60.59	60.56	60.32	59.89	58.32	59.97
Al ₂ O ₃	14.46	14.03	15.13	14.63	14.07	14.11	13.95	15.54	14.20
MgO	0.00	0.26	0.20	0.19	0.00	0.09	0.16	0.16	0.20
CaO	2.23	1.84	1.99	3.25	4.00	6.92	1.69	1.59	1.93
Na ₂ O	4.53	4.28	4.46	3.15	2.41	0.37	4.81	4.93	4.36
K ₂ O	2.89	2.74	2.67	2.29	1.42	0.32	2.39	3.04	2.66
H ₂ O	15.94	17.35	16.27	15.90	17.54	17.87	16.91	16.42	16.68
thermal gravimetry									
H ₂ O	16.35	16.22	n. a.	n. a.	n. a.	18.58	16.47	16.60	n. a.
formulae									
Si	28.05	28.18	27.68	28.04	28.27	28.23	28.26	27.41	28.16
Al	7.95	7.82	8.32	7.96	7.73	7.77	7.74	8.59	7.84
Mg	0.00	0.18	0.14	0.13	0.00	0.06	0.11	0.11	0.14
Ca	1.12	0.93	0.99	1.61	2.00	3.47	0.86	0.80	0.97
Na	4.11	3.92	3.95	2.82	2.18	0.34	4.39	4.49	3.96
K	1.73	1.66	1.59	1.35	0.85	0.19	1.56	1.82	1.60
H ₂ O	25.5	25.6	25.4	24.5	27.3	29.1	25.9	26.0	26.1
E%	-1.6	+0.3	+6.7	+4.1	+10.0	+2.4	-1.9	+5.7	+0.8

The proportion of oxides is given in weight %. Cation proportions are calculated on the basis of 72 atoms of oxygen. Samples: 1, 2: barrerite from the eastern coast of Kuiu Island; 3: stilbite from the mouth of Mud Creek, Kuiu Island; 4 to 6: stilbite from the bed and banks of Mud Creek; at an increasing distance from the sea; 7–8: stilbite from islets along the southwestern coast of Kupreanof Island; 9: stilbite from the northeastern coast of Kuiu Island, north of Kadake Bay. The evaluation of H₂O content by electron-probe micro-analysis is affected by partial dehydration under the electron beam. The more reliable thermogravimetric values have been used for formula calculations where available. A low charge-balance error, E% = 100|(Al) - (Na + K) - 2(Mg + Na)| / ((Na + K) + 2(Mg + Na)), is a condition for a reliable determination of a zeolite's composition (Gottardi & Galli 1985).

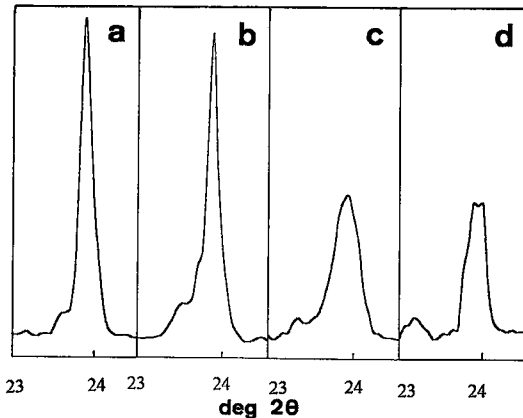


FIG. 3. X-ray-diffraction profiles in the range 23–24.50° (2θ , $\text{CuK}\alpha$) for (a) sample 1, orthorhombic sodian barrerite from Kuiu Island, tidal area, (b) orthorhombic sodian barrerite from Capo Pula, Sardinia, (c) sample 3, monoclinic sodian stilbite from Kuiu Island, tidal area, and (d) sample 6, monoclinic calcian stilbite from inland Kuiu Island.

group, as indicated by the sharp 204 diffraction peak (type-*a* pattern). Two zeolites of the stilbite family, barrerite and stellerite, share the orthorhombic symmetry. The low Ca content of the samples from Rocky Pass is sufficient to discard any attribution to stellerite, $\text{Ca}_4(\text{Al}_8\text{Si}_{28}\text{O}_7) \cdot 26\text{H}_2\text{O}$. The diffraction profile of the 204 peak for sample 1 is shown in Figure 3, along with the 204 peak of a sample of barrerite from the type locality (courtesy of A. Alberti). The diffraction pattern of sample 1 can be indexed on the *Amma* cell of barrerite from the type locality (a 13.643, b 13.200, c 17.842 Å; Galli & Alberti 1975), with the square mean error σ equal to 0.0041. The orthorhombic symmetry is characteristic of all samples from the quartz-rich amygdals on the eastern coast of Kuiu Island.

The specimens from the rhyolites of southwestern Kupreanof (samples 7 and 8), show a broad 204 peak. The type-*b* pattern corresponds to a monoclinic stilbite with low β , although the samples have the same composition as orthorhombic barrerite. Some heterogeneity of the sample possibly contributes to the broadening of the 204 peak (pattern *d* of Passaglia *et al.* 1978).

The samples from the mouth and bed of Mud Creek (samples 3 and from 4 to 6, respectively) feature the same type-*b* diffraction pattern, independent of their composition, and cover the complete range from Na-rich (sample 3) to Ca-rich (sample 6). The 204 peaks of the samples 3 and 6 are presented in Figure 3.

We herein suggest that a stilbite-group zeolite should be considered as barrerite if it has both orthorhombic

symmetry and a composition rich in monovalent cations. As a consequence, the samples from the quartz-rich vugs of the eastern coast of Kuiu Island (1 and 2) are henceforth considered as barrerite, and the samples from Mud Creek (3 to 6) and from the rhyolites of the southern mouth of Rocky Pass (7 and 8), as stilbite. In Figure 4, the composition of samples of barrerite and stilbite from the Rocky Pass area is compared with literature data on the composition of the zeolites of the stilbite group.

The thermogravimetric (TG) patterns of the sodium-rich samples, regardless of their symmetry, closely resemble the pattern of barrerite from the type locality (Gottardi & Galli 1985). The calcium-rich samples from inland Kuiu Island show a stilbite-type TG pattern. As typical examples, the differential thermogravimetric (DTG) curves of samples 1 and 6 are shown in Figure 5. The data reported in Table 1 indicate that the water content, as evaluated by the weight loss, is a function of the cation content. In good agreement with the literature data (Gottardi & Galli 1985), the number of water molecules per unit cell ranges from 25–26, for the Na-rich barrerite or stilbite samples, to 29 for the Ca-rich stilbite.

OTHER ZEOLITES FROM KUIU AND KUPREANOF ISLANDS

Samples from the Kuiu–Etolin basalts, tidal area

Barrerite and microcrystalline quartz in dendritic aggregates are the main secondary minerals in this region. They nearly always coexist, and no clear genetic sequence can be found. Laumontite is also common in the same vugs, usually clearly formed after barrerite and quartz. Barrerite is more rarely associated with large crystals of calcite, which occupy the central parts of the geodes.

Other zeolites are less common. Aggregates of flat needles of mordenite are associated with quartz crystals, usually larger than those of the aggregates of stalactitic quartz accompanying barrerite. Centimeter-size crystals of heulandite are also found in vugs occupied by calcite crystals. More rare is scolecite (the Ca-rich member of the natrolite group), which occurs in characteristic radial aggregates several centimeters across.

Mordenite is very sodium-rich, with a composition $\text{Na}_{5.3}\text{K}_{1.5}\text{Ca}_{0.5}\text{Mg}_{0.1}(\text{Al}_{7.7}\text{Si}_{40.3}\text{O}_{96}) \cdot n\text{H}_2\text{O}$. The composition of the mordenite from the tidal area is quite constant, whereas the composition of heulandite varies greatly. Electron-microprobe analysis indicates heulandite compositions ranging from $\text{Na}_{2.1}\text{K}_{2.8}\text{Ca}_{2.0}(\text{Al}_{8.4}\text{Si}_{27.6}\text{O}_{72}) \cdot n\text{H}_2\text{O}$ to $\text{Na}_{0.7}\text{K}_{1.0}\text{Ca}_{3.3}(\text{Al}_{8.6}\text{Si}_{27.4}\text{O}_{72}) \cdot n\text{H}_2\text{O}$ within the same crystal. The composition of scolecite is $\text{Na}_{0.3}\text{Ca}_{8.3}(\text{Al}_{16.2}\text{Si}_{23.8}\text{O}_{80}) \cdot n\text{H}_2\text{O}$, commonly encountered for this species.

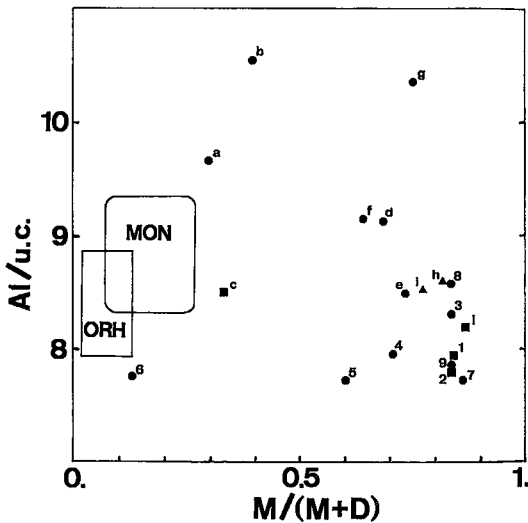


FIG. 4. Content of aluminum and monovalent cations in zeolites of the stilbite group. Proportion of Al per 36 tetrahedra versus $(\text{Na} + \text{K})/(\text{Na} + \text{K} + \text{Mg} + \text{Ca})$ atomic ratio. Monoclinic (●), orthorhombic (■), and undetermined (▲) symmetries. Samples from the Rocky Pass area are numbered from 1 to 9, as in Table 1. ORH: usual compositional field of stellerite [15 samples from Passaglia *et al.* (1978)], MON: usual compositional field of stilbite [28 samples from Passaglia *et al.* (1978)], *a* to *e*: samples 48, 49, 15, 44, and 21, in this order, from Passaglia *et al.* (1978), *f*: stilbite from Onigajo, Mié Prefecture, Japan (Harada & Tomita 1967), *g*: stilbite from Nova Scotia (Slaughter 1970), *h* and *i*: samples from Phillip Island, Victoria, Australia (Birch 1989), and *l*: barrerite from Capo Pula, Sardinia, Italy (Galli & Alberti 1975).

Samples from Kuiu–Etolin basalts and volcanoclastic rocks, inland

Stilbite crystals were collected inland on Kuiu Island (*vide supra*). Mordenite-containing pebbles were found along Irish Creek on Kupreanof Island. Mordenite is present as fibrous woolly aggregates in amygdules or as isolated, 50- μm -long flat needles in sponge-like chalcedony pebbles, formed by 10- μm spindle-shaped aggregates of quartz fibers. The composition of mordenite in both occurrences is $\text{Na}_{2.8}\text{K}_{0.5}\text{Ca}_{1.7}\text{Mg}_{0.3}(\text{Al}_{7.3}\text{Si}_{40.7}\text{O}_{96})\cdot n\text{H}_2\text{O}$, significantly more Ca-rich than the samples from the tidal area. Pebbles formed of aggregated Na,K-feldspar crystals 10 μm across were found in the creeks of both Kuiu and Kupreanof. The surface of the feldspar crystals is pitted and weathered, and cavities of the pebbles are filled by microcrystalline kaolinite.

Samples from the Kuiu–Etolin rhyolites, tidal area

The most common zeolite from the islets along the southwestern coast of Kupreanof Island is epistilbite.

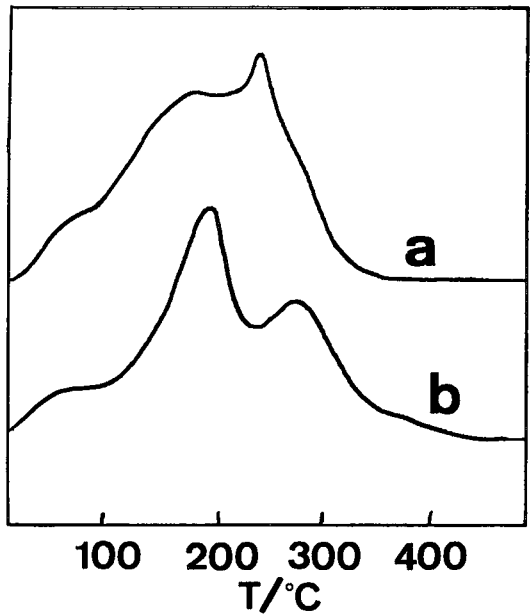


FIG. 5. Differential thermogravimetry curves: (a) sample 1, sodian barrerite from Kuiu Island, tidal area; (b) sample 6, calcian stilbite from inland Kuiu Island. Total loss in weight is 16.8% for sample 1 (curve a), and 18.5% for sample 6 (curve b).

Well-formed crystals can be found in geodes several centimeters in size, accompanied by microcrystalline fibrous quartz, massive cleavable calcite and, more rarely, microcrystalline biotite. Heulandite locally accompanies epistilbite in millimeter-size crystals, or is present in separate vugs as radial aggregates. Laumontite and apophyllite are common. Sodian stilbite and cottony mordenite are less common occurrences, whereas chabazite is rare.

The composition of the epistilbite varies in different parts of the same sample. It ranges from $\text{Na}_{0.9}\text{K}_{0.3}\text{Ca}_{2.5}\text{Ba}_{0.1}(\text{Al}_{5.6}\text{Si}_{18.4}\text{O}_{48})\cdot n\text{H}_2\text{O}$ to $\text{Na}_{2.2}\text{K}_{0.9}\text{Ca}_{1.3}\text{Ba}_{0.1}(\text{Al}_{5.9}\text{Si}_{18.1}\text{O}_{48})\cdot n\text{H}_2\text{O}$. Thermogravimetric data indicate that on average, *n*, the number of water molecules per cell, is 14.8. The more Na-rich compositions correspond to the lowest content of divalent cations ever reported for epistilbite (Galli & Rinaldi 1974).

Heulandite crystals have compositions ranging from $\text{Na}_{3.6}\text{K}_{3.3}\text{Ca}_{0.6}(\text{Al}_{8.4}\text{Si}_{27.6}\text{O}_{72})\cdot n\text{H}_2\text{O}$ to $\text{Na}_{3.6}\text{K}_{3.1}\text{Ca}_{1.4}(\text{Al}_{9.0}\text{Si}_{27.0}\text{O}_{72})\cdot n\text{H}_2\text{O}$. The distinction between heulandite and clinoptilolite, two zeolites presenting the same network topology, has been a subject of debate. Some of the proposed criteria of differentiation are

based on composition. Mason & Sand (1960) defined clinoptilolite as a zeolite of the heulandite group with $(\text{Na} + \text{K}) > \text{Ca}$. Boles (1972) proposed to apply the name *clinoptilolite* to zeolite samples of the heulandite group with $\text{Si}/\text{Al} > 4$. The samples from the Kuiu-Etolin rhyolites, which present $(\text{Na} + \text{K}) > 4.8 \text{ Ca}$ and $\text{Si}/\text{Al} < 3.3$, could be alternatively considered as clinoptilolite or heulandite, according to which of these definitions is preferred. A more reliable criterion of distinction between heulandite and clinoptilolite is provided by their behavior under thermal treatment. Mumpton (1960) proposed to define as clinoptilolite all samples of the heulandite group whose X-ray-diffraction pattern is not modified by a thermal treatment at 450°C overnight. Boles (1972) and Alietti (1972) investigated the phases formed when heulandite is heated; they showed that heulandite samples undergo phase transitions that are not encountered by clinoptilolite samples. Samples from region 3 of this study, after overnight heating at 450°C, present a room-temperature X-ray-diffraction pattern including the initial phase and the phases B (Mumpton 1960) and I (Alietti 1972, Boles 1972), and correspond to type-2 heulandite of Alietti (1972).

Mordenite fibers have a fairly narrow range of composition, from $\text{Na}_{5.4}\text{K}_{1.4}\text{Mg}_{0.3}(\text{Al}_{7.6}\text{Si}_{40.4}\text{O}_{96}) \cdot n\text{H}_2\text{O}$ to $\text{Na}_{6.0}\text{K}_{1.1}\text{Ca}_{0.2}(\text{Al}_{8.3}\text{Si}_{39.7}\text{O}_{96}) \cdot n\text{H}_2\text{O}$. Chabazite also is rich in monovalent cations, with a composition $\text{Na}_{1.9}\text{K}_{1.3}(\text{Al}_{3.5}\text{Si}_{8.5}\text{O}_{24}) \cdot n\text{H}_2\text{O}$.

Samples from the Hound Island Triassic breccias, tidal area

The most common zeolite in this area is scolecite; it occurs in classical radial aggregates of white crystals with a near-ideal composition, $\text{Na}_{1.4}\text{Ca}_{6.9}(\text{Al}_{16.1}\text{Si}_{23.9}\text{O}_{80}) \cdot n\text{H}_2\text{O}$. Well-crystallized laumontite and heulandite also are common, whereas barrerite is very rare. Scolecite and heulandite are invariably associated with calcite having a fibrous or tabular habit. Zeolite areas are not far from, but do not correspond to, fluorite-rich areas.

DISCUSSION

The symmetry of the various zeolites of the stilbite group is strictly related to the number of cations per unit cell (Galli & Alberti 1975). The deviation of stilbite from the orthorhombic symmetry of stellerite is attributed to the uneven occupancy of the C2 sites by Na⁺ cations. In the ideal structure of barrerite, the higher occupancy of the C2 sites compensates for this cause of the lowering of symmetry (Passaglia *et al.* 1978, Quartieri & Vezzalini 1987).

No such easy correlation between composition and symmetry can be found in the samples from the Rocky Pass trap: orthorhombic and monoclinic specimens share the same field of cation content (Table 1). This

result can be accounted for if the data of Passaglia & Sacerdoti (1982) are taken into account. These authors prepared a sample having the composition of barrerite, but with the space group *Fm3m* (and not *Am3m*), by sodium exchange of a specimen of stellerite. As yet, no cation-exchange method has led to the preparation of a sample having the typical symmetry of natural barrerite. On the basis of these data, the barrerite and sodian stilbite of Rocky Pass do not appear to have formed in the same way. Barrerite, the orthorhombic phase whose occurrence is restricted to the tidal area, probably formed by crystallization in the presence of seawater, whereas the monoclinic stilbite, having a composition that varies as a function of the distance from the seaside, likely crystallized in the calcian form and later equilibrated with solutions of diverse cation content. The presence of orthorhombic and monoclinic zeolites of the same composition and the same framework topology as stilbite clearly indicates that precise crystallographic data are a necessary criterion to identify barrerite.

More examples of the effect of seawater on low-temperature hydrothermal processes can be derived from the distribution of zeolites of various compositions. According to their cation content and their location with respect to the present sea-level, the zeolites from the Rocky Pass trap can be classified in four groups: a) sodian zeolites found only in the tidal area, *e.g.*, barrerite, b) zeolites that are rich in monovalent cations in the tidal area and Ca-rich inland, *e.g.*, stilbite and mordenite, c) zeolites having a composition spanning from Ca-rich to monovalent-cation-rich for samples from the tidal area, *e.g.*, heulandite-clinoptilolite and epistilbite, and d) zeolites that are Ca-rich also where found in the tidal area, *e.g.*, scolecite and laumontite.

The distribution of zeolites of class *a* is similar to the distribution of gmelinite in the Antrim basalts, restricted to a narrow belt along the seashore, notwithstanding the presence of zeolites in a much larger area (Walker 1959). This distribution has been considered as evidence of direct implication of seawater in the crystallization of zeolite species. In the same way, barrerite is only present in the tidal area, whereas monoclinic stilbite and mordenite are distributed from the seashore to inland Kuiu Island. Moreover, the dendrites of microcrystalline quartz, which nearly always accompany barrerite in the Rocky Pass trap, are also restricted to the tidal area.

The cation content of the zeolites of class *b*, stilbite and mordenite, is correlated with distance from the sea; samples richer in alkali are found in the tidal area, and samples richer in Ca are found inland. A likely mechanism of formation of the sodium form of these zeolites is cation exchange between a seawater solution and a zeolite formed in the presence of different cations. Cation exchange at low temperature is easy, both for stilbite (Ames 1966) and mordenite (Ames 1961). Available data indicate an easy replacement of Ca by

Na in mordenite (Ames 1961). Stilbite seems to present a higher affinity for divalent cations (Ames 1966), but sodium-exchanged stilbite has been prepared (Passaglia 1980). Sodium exchange at low temperature under geological conditions has been well studied, even for silicates less easily exchangeable than most zeolites, *e.g.*, analcimization of leucite (Gupta & Fyfe 1975).

Class *c* includes specimens of heulandite and epistilbite with a heterogeneous composition, featuring alkaline and calcian parts in the same specimen, and in some cases, in the same crystal. The composition patterns are largely irregular, and their more probable genesis involves a partial exchange of cations at the surface and along cracks of the crystals.

Clinoptilolite is easily exchangeable, with some preference for Na over Ca in a large part of the isotherm (Ames 1964a, b). Clinoptilolite from the Kuiu–Etolin rhyolites is invariably alkali-rich. Heterogeneity of cation content is observed only in centimetric crystals sharing with calcite rare amygdules of the Kuiu–Etolin basalts. The interaction of tidal water and the Ca-rich environment can probably explain the nonequilibrium composition of the crystals.

No data are available in the literature on the exchange behavior of epistilbite. The usual composition of this zeolite covers a restricted Ca-rich range (Galli & Rinaldi 1974). In the absence of any indication about the crystallization of epistilbite in an alkaline environment, the heterogeneity of composition of the epistilbite samples can be tentatively attributed to a partial exchange of a calcian zeolite by seawater.

Class *d* includes calcian samples found in the tidal area, namely scolecite and laumontite. Scolecite is the calcian member of the natrolite group. Cation exchange within this group is possible only by the action of molten salts, and has never been performed by the action of aqueous solutions (Hey 1932). On the other hand, laumontite is only known in the calcium form. Both zeolites cannot be exchanged by seawater; their presence indicates that conditions were conducive to the formation of calcian zeolites in the Rocky Pass trap.

The modes of formation of scolecite and laumontite are quite different. Scolecite is abundant in the Triassic breccias of the Hound Island volcanic suite, locally much more Ca-rich than the Kuiu–Etolin basalt, as witnessed by the presence of abundant crystals of calcite in the amygdules. Barrerite is very rare, and no stilbite has been found in the Hound Island volcanic suite. Conversely, scolecite is rarely found in the recent basalts of the Kuiu–Etolin volcanic suite, and is not present in the barrerite-containing vugs. The marked differences in the distribution of zeolite species in the two areas suggest that they have been formed during separate events of crystallization. Also in this case, a better knowledge of the history of variations in sea level in the area could give useful information about the periods in which seawater was able to affect hydrothermal processes.

Laumontite can be found in any part of the Rocky Pass trap. It commonly accompanies, and generally overgrows, other zeolites, including barrerite. Its crystallization has clearly taken place under different conditions than those characterizing the formation of scolecite. Extremely mild hydrothermal conditions, at the limit of surface weathering, have been reported for the genesis of some occurrences of laumontite, as through the interaction of water from dissolved snow with plagioclase (Capdecemme 1952). Its position at the end of a genetic sequence and its ubiquitous distribution do not support any correlation with the conditions of formation of the other zeolites of the area.

The wide distribution of observed species and compositions is probably the final result of several independent events of secondary crystallization. A tentative genetic sequence can be drawn as follows: The conditions for the crystallization of calcian zeolites were established early in the area, as indicated by the presence in the tidal area of calcian scolecite, a high-temperature zeolite that is not easily exchanged. More easily exchangeable zeolites, like stilbite and mordenite, feature a composition richer in Na in the tidal area than inland, probably owing to the recent exchange by seawater of zeolites crystallized in the calcian form. In the case of epistilbite and heulandite, high variabilities in the composition of the samples suggest that slower cation-exchange processes are still taking place.

Barrerite, usually accompanied by arborescent quartz, is restricted to a limited area in the basalts of the tidal area. The peculiar distribution of its cations, not reproducible by ion exchange, suggests that it formed directly by crystallization in the presence of percolating seawater. Overgrowths of calcian laumontite on sodian zeolites of the tidal area indicate that Ca-rich mineralizing solutions have recently percolated through the shoreline basalts, and that environments rich in monovalent and divalent cations have alternated many times in the trap.

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REFERENCES

- ALIETTI, A. (1972): Polymorphism and crystal-chemistry of heulandites and clinoptilolites. *Am. Mineral.* **57**, 1448-1462.
- AMES, L.L., JR. (1961): Cation sieve properties of the open zeolites chabazite, mordenite, erionite and clinoptilolite. *Am. Mineral.* **46**, 1120-1131.

- _____ (1964a): Some zeolites equilibria with alkali metal cations. *Am. Mineral.* **49**, 127-145.
- _____ (1964b): Some zeolites equilibria with alkaline earth metal cations. *Am. Mineral.* **49**, 1099-1110.
- _____ (1966): Exchange of alkali metals cations on a natural stilbite. *Can. Mineral.* **8**, 582-592.
- BIRCH, W.D. (1989): Chemistry of Victorian zeolites. In *Zeolites of Victoria* (W.D. Birch, ed.). Mineralogical Society of Victoria, Melbourne, Australia (91-102).
- BOLES, J.R. (1972): Composition, optical properties, cell dimensions and thermal stability of some heulandite group zeolites. *Am. Mineral.* **57**, 1463-1493.
- BREW, D.A., OVENSHEINE, A.T., KARL, S.M. & HUNT, S.J. (1984): Preliminary reconnaissance geological map of the Petersburg and parts of the Port Alexander and Sumdum 1:250,000 quadrangles, southeastern Alaska. *U.S. Geol. Surv., Open-File Rep.* **84-405**.
- CAPDECOMME, L. (1952): Laumontite du Pla des Aveillans (Pyrénées-Orientales). *Bull. Soc. Hist. Nat. Toulouse* **87**, 299-304.
- FLEISCHER, M. & MANDARINO, J.A. (1995): *Glossary of Mineral Species 1995*. Mineralogical Record, Tucson, Arizona.
- GALLI, E. & ALBERTI, A. (1975): The crystal structure of barrerite. *Bull. Soc. fr. Minéral. Cristallogr.* **98**, 331-340.
- _____ & RINALDI, R. (1974): The crystal chemistry of epistilbites. *Am. Mineral.* **59**, 1055-1061.
- GOTTARDI, G. & GALLI, E. (1985): *Natural Zeolites*. Springer-Verlag, Berlin, Germany (284-300).
- GUPTA, A.K. & FYFE, W.S. (1975): Leucite survival: the alteration to analcime. *Can. Mineral.* **13**, 361-363.
- HARADA, K. & TOMITA, K. (1967): A sodian stilbite from Onigajo, Mié Prefecture, Japan, with some experimental studies concerning the conversion of stilbite to wairakite at low water vapor pressures. *Am. Mineral.* **52**, 1438-1450.
- HEY, M.H. (1932): Studies on the zeolites. III. Natrolite and metanatlolite. *Mineral. Mag.* **23**, 243-289.
- MASON, B. & SAND, L.B. (1960): Clinoptilolite from Patagonia. The relationship between clinoptilolite and heulandite. *Am. Mineral.* **45**, 341-350.
- MEIER, W.M. & OLSON, D.H. (1992): *Atlas of Zeolite Structure Types* (3rd ed.). Butterworth-Heinemann, London, U.K.
- MUFFLER, L.J.P. (1967): Stratigraphy of the Keku Islets and neighboring parts of Kuiu and Kupreanof islands, south-eastern Alaska. *U.S. Geol. Surv., Bull.* **1241-C**.
- MUMPTON, F.A. (1960): Clinoptilolite redefined. *Am. Mineral.* **45**, 351-369.
- PASSAGLIA, E. (1980): The heat behaviour of cation exchanged zeolites with the stilbite framework. *Tschermaks Mineral. Petrogr. Mitt.* **27**, 67-78.
- _____, GALLI, E., LEONI, L. & ROSSI, G. (1978): The crystal chemistry of stilbites and stellerites. *Bull. Minéral.* **101**, 368-375.
- _____ & PONGILUPPI, D. (1974): Sodian stellerite from Capo Pula, Sardegna. *Lithos* **7**, 69-73.
- _____ & _____ (1975): Barrerite, a new natural zeolite. *Mineral. Mag.* **40**, 208.
- _____ & SACERDOTI, M. (1982): Crystal structural refinement of Na-exchanged stellerite. *Bull. Minéral.* **105**, 338-342.
- QUARTIERI, S. & VEZZALINI, G. (1987): Crystal chemistry of stilbites: structure refinements of one normal and four chemically anomalous samples. *Zeolites* **7**, 163-170.
- SLAUGHTER, M. (1970): Crystal structure of stilbite. *Am. Mineral.* **55**, 387-397.
- WALKER, G.P.L. (1959): The amigdale minerals in the Tertiary lavas of Ireland. II. The distribution of gmelinite. *Mineral. Mag.* **32**, 202-217.

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