Paulingite: variations in composition

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Abstract

Paulingite, originally found at Rock Island Dam near Wenatchee, Washington, is now known from three more localities, (1) near Riggins, Idaho, (2) Chase Creek, north of Falkland, British Columbia, and (3) Three Mile Creek, northwest of Ritter, Oregon. In all four localities paulingite forms early in the zeolite sequences and is associated with a phillipsite phase.

Averaged electron probe microanalyses of the paulingites give the following cell contents (Z = 16): Rock Island Dam, Washington, $Ca_{1.88}Ba_{0.18}K_{4.44}Na_{0.95}[Al_{9.82}Si_{32.21}O_{84}]\cdot44H_2O$; Chase Creek, British Columbia, $Ca_{2.32}Mg_{0.11}Sr_{0.09}Ba_{0.81}K_{3.55}Na_{0.53}[Al_{10.71}Si_{31.23}O_{84}]\cdot xH_2O$; Riggins, Idaho, $Ca_{2.41}Mg_{0.04}Sr_{0.02}Ba_{0.32}K_{4.68}Na_{0.42}[Al_{10.80}Si_{31.22}O_{84}]\cdot xH_2O$; and Ritter, Oregon, $Ca_{3.70}Ba_{0.10}K_{2.67}Na_{0.86}[Al_{10.78}Si_{31.21}O_{84}]\cdot34H_2O$. These compositions can be expressed by the general formula $(K_2, Ca, Na_2, Ba)_5[Al_{10}Si_{32}O_{84}]\cdot34-44H_2O$.

The early formation in the crystallization sequence and the high water content suggest that paulingite forms from relatively dilute pore fluids.

Introduction

Paulingite was first described by Kamb and Oke (1960) from boulders dredged from the channel of the Columbia River at Rock Island Dam near Wenatchee, Washington, where it is associated with clinoptilolite, phillipsite, calcite, and pyrite. It occurs as dodecahedra and has a very large unit cell with $a = 35.10$Å.

Until recently Rock Island Dam was the only known locality for paulingite. Three new localities have now been found in the Pacific Northwest. The purpose of this paper is to report the locations and mineralogy of these occurrences, and to characterize the compositional range of paulingite and its associated minerals.

Paulingite localities

Rock Island Dam, Washington

Material analyzed for this paper was collected from rip-rap boulders along the Columbia River on the east side of the dam. Vesicular basalt boulders, weighing up to three tons, were dredged from the river channel during the construction of Rock Island Dam. The paulingite-bearing rock has never been seen *in situ*.

Rounding of some of these boulders suggests that the rock may have been transported from some other locality upstream, although similar zeolite-bearing rock has not been found along the river either above or below the dam. Zeolites are not found in the extensive basalt flows around the dam site. Construction of the Second Powerhouse at the dam has now been completed, and information regarding the sub-surface of the powerhouse site, which covers the western half of the river channel, is available from core drilling and geologic mapping. Mr. Tracy Lyman, Geotechnical Engineer of the project, reports that several flows of vesicular basalt exist in and below the foundation. These vesicles are either empty or have calcite, opal, and iron oxide fillings or coatings. No zeolites have been recognized in these basalts.

Paulingite crystals from this locality range from

light yellow to colorless and commonly are 0.2 to 0.8 mm in diameter, although a very few reach 3 mm. The dodecahedron is the common form, but small cube and trapezohedral modifications are present. The minerals crystallized in the following order: offretite overgrown by erionite (Wise and Tschernich, 1976) or erionite alone, paulingite, phillipsite covered with a reddish-golden clay, followed by clinoptilolite, very rarely chabazite, and lastly pyrite and calcite.

Riggins, Idaho

Paulingite is believed to have been collected from the area near the junction of Papoose Creek and Squaw Creek, west of Riggins, Idaho. The specimens were collected by A. D. Ptacek during field work but he is not sure of the exact locality of his samples. The area near the junction of Papoose and Squaw Creeks consists of over 2300 feet of basalt belonging to the Columbia River Group. The upper flows are massive and conspicuously non-porphyritic, while the lower unit consists of eight flows ranging from 50 to 150 feet thick with vesicular upper portions. The lower flows are characterized by large plagioclase phenocrysts, and vesicles containing zeolites, calcite, and chalcedony or opal (Ptacek, 1965).

The paulingite-bearing samples are red vesicular basalt with 5 to 25 mm laboradorite phenocrysts and small altered pyroxene crystals set in glass altered dark red. Vesicles ranging from 2 to 20 mm are lined with yellow-gray montmorillonite, which is richly covered with small, 0.2 to 0.5 mm, colorless to light yellow, transparent dodecahedra of paulingite. Phillipsite, forming small white crystals, is the only other zeolite present.

The Papoose Creek area has been searched by several mineral collectors, yet the paulingite-bearing flow remains to be found. Red vesicular basalt is abundant in the area, and cavities are lined with small transparent crystals of heulandite, chabazite, analcime, and thomsonite.

Chase Creek, British Columbia

Paulingite was found in rounded vesicular basalt fragments in Chase Creek near the junction of Charcoal Creek, north of Falkland, British Columbia. Specimens of a very fine-grained, black, olivine basalt consist of microphenocrysts of augite and olivine set in a groundmass of plagioclase microlites and glass. Common vesicles, ranging from 3 to 30 mm across, are lined with a characteristic gray-white montmorillonite. A brown weathered zone penetrates the fragments up to 4 cm.

The source of the paulingite rock is not readily apparent. Volcanic rocks belonging to the Kamloops Group are found in the general area. Outcrops along the east side of the creek are massive, non-vesicular basalts without zeolites, while far to the west Mt. Martin is formed of steep basaltic cliffs covered with thick vegetation. Rock similar in appearance to the zeolitic rock has been found in glacial deposits in the area, but these do not contain zeolites. It is likely that the zeolitic rock was glacially deposited and reworked by the stream, and the original source was probably somewhat distant.

Erionite is the most abundant zeolite in the rock, forming attractive colorless to golden-yellow hexagonal prisms up to 0.5 mm long and 0.1 mm in diameter. Paulingite, ranging from bright orange and shades of yellow to colorless, is found as small (0.1 mm) dodecahedra on erionite prisms and as large (0.8 mm) crystals lining vesicles. It is also associated with 0.5 mm cream-colored, elongated harmotome crystals and small aggregates of colorless heulandite. The complete sequence of crystallization can be seen in a single vesicle, where the clay lining is followed by erionite, paulingite, harmotome, heulandite, and lastly clay aggregates (Fig. 1).
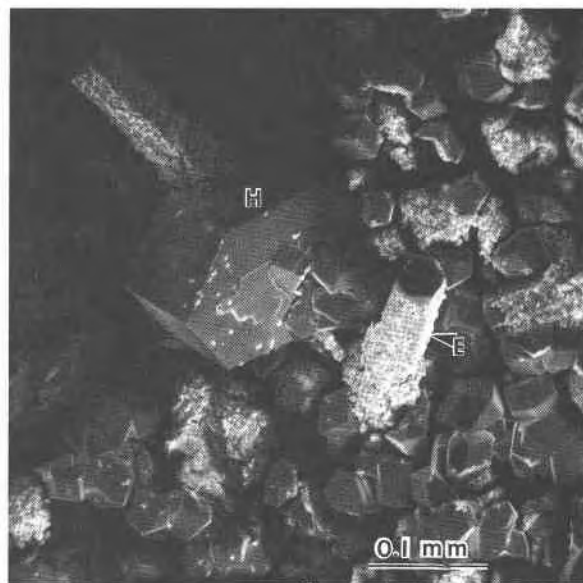

Fig. 1. Scanning electron micrograph of paulingite from Chase Creek north of Falkland, British Columbia. The associated minerals are erionite (E) partially coated with clay and heulandite (H). The crystallization sequence is erionite, paulingite and heulandite.

Ritter, Oregon

Paulingite occurs abundantly, lining vesicles of a brown-gray olivine basalt, belonging to the Columbia River Group near Three Mile Creek, northwest of Ritter, Grant County, Oregon. This is the first locality where paulingite has been found *in situ*. The paulingite-bearing basalt flow averages 2 meters in thickness and can be traced for over one kilometer to where it is truncated by a northwest trending fault toward the north and is buried in a flat field in the south. The basalt consists primarily of phenocrysts of laboradorite with a groundmass of augite, olivine, and magnetite, and contains numerous vesicles from 2 mm to 4 cm in diameter.

The vesicles in some of the rock appear barren, but close examination shows the cavities to be richly lined with very small, 0.1 to 0.5 mm, light yellow to colorless, transparent dodecahedra of paulingite. Small trapezohedron modifications are commonly seen on the dominant dodecahedron. Smectitic clay first lined the vesicles and was followed by paulingite. In some vesicles clay continued to form during the paulingite crystallization and partly engulfs the zeolite, but nowhere completely covers it. In some rocks the clay-paulingite crystallization is followed by other zeolites in the order: heulandite, Ca-phillipsite, and lastly chabazite (Fig. 2). Because of the small size of the paulingite and its early formation, it is not obvious in specimens containing large amounts of other zeolites.

Chemical composition

In order to make comparisons of analyses of all known paulingites, we analyzed several crystals from Rock Island Dam as well as those from the new localities. Paulingite and associated zeolite phases were analyzed with an electron microprobe. Crystals or groups of crystals were embedded in epoxy, ground to expose the center of the crystal, and coated with approximately 200Å of carbon. An accelerating voltage of 15 kV was used for all elements, and the sample current was 10 nA. Common silicate standards were used, and emission data were reduced with a slightly modified version of the computer program EMPADR 7 (Rucklidge and Gasparrini, 1969). In order to overcome some difficulties in analyzing zeolites by EMX methods, large beam diameters (at least 20 μm) were used. To minimize the ion migration effect, the counting rates for alkalis were projected to time zero.
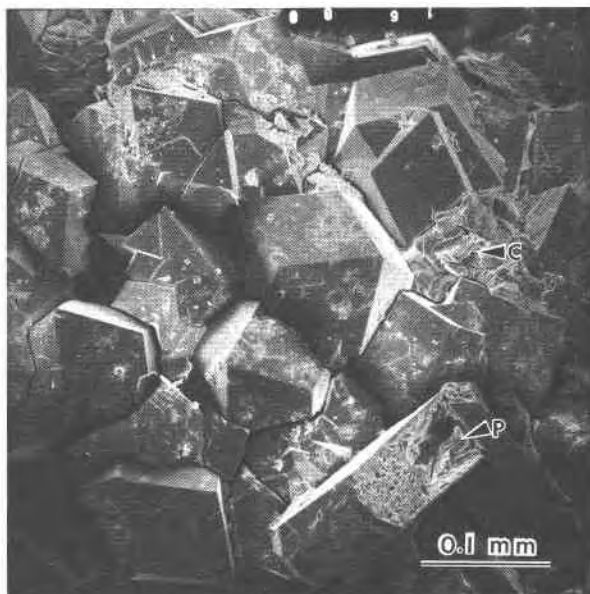

Fig. 2. Scanning electron micrograph of paulingite from Ritter, Oregon, showing the dodecahedral crystal form. The associated phillipsite (P) has been deeply etched. The crystallization sequence is clay (C), paulingite, and phillipsite.

Averaged analyses from all four localities are given in Table 1. The cell contents of the associated zeolites are listed in Table 2.

The range of compositions of the paulingite framework from each of the four localities is relatively narrow. Si/Al is 3.28 in the Rock Island Dam crystals, but consistently near 2.90 in those from the three new localities. The exchangeable cation content exhibits a wider range but all are similar with high amounts of K and Ba.

Water determination on micro-samples of zeolites has been a problem. EMX analyses of the framework and the exchangeable cations, expressed as oxides, commonly sum only to 80 or 90%. The remainder is due to water, but all zeolites dehydrate to some extent in the vacuum of the microprobe. In most instances the "water by difference" is substantially less than the water content in the zeolite equilibrated with some standard humidity at atmospheric pressure.

The relatively large number of crystals available from the Ritter locality make accurate density and H_2O content determinations possible. A 45 mg sample of hand picked crystals, cleaned of clay by ultrasonic scrubbing, was weighed in the powder basket of a Berman balance, using toluene as the immersion liquid. The mean density of this sample is 2.085(5) g/cm^3, and is markedly lower than the

Table 1. Averaged electron probe analyses, cell contents, and physical properties of paulingites

	Rock Island Dam Washington	Chase Creek British Columbia	Riggins Idaho	Ritter Oregon
	Electron probe analyses			
	average of 5	average of 10	average of 4	average of 4
SiO_2	63.53	61.99	61.13	62.65
Al_2O_3	16.43	18.04	17.95	18.36
Fe_2O_3	0.16	0.18	0.04	0.08
MgO	0.02	0.14	0.05	0
CaO	3.46	4.30	4.41	6.94
SrO	0	0.32	0.07	0
BaO	0.90	4.11	1.58	0.50
Na_2O	0.97	0.54	0.43	0.89
K_2O	6.87	5.53	7.19	3.57
	92.34	95.15	92.85	92.99
	Cell contents with 84 oxygens			
Si	32.21	31.23	31.22	31.21
Al	9.82	10.71	10.80	10.78
Fe	.06	.07	.02	.03
Mg	0	.11	.04	0
Ca	1.88	2.32	2.41	3.70
Sr	0	.09	.02	0
Ba	.18	.81	.32	.10
Na	.95	.53	.42	.86
K	4.44	3.55	4.68	2.27
% error †	-3.7	-0.4	-1.3	-0.7
	Refractive index and cell edge			
n	1.473(1)*	1.484(1)	1.480(1)	1.484(1)
a (Å)	35.093(2)**	35.049(7)	35.059(4)	35.088(6)

the cell edge was refined from X-ray powder data standardized with synthetic CaF_2 (a = 5.459 Å).

† error = [(Al+Fe)-Σcharge Ca,Sr,Ba,Mg,Na,K]/(Al+Fe)

* Kamb and Oke (1960), ** Gordon, Swanson, and Kamb (1966)

2.24 g/cm³ calculated by Kamb and Oke (1961). In order to verify that the difference is related to the number of water molecules within the cell, a 20 mg sample was step heated to 600° C, above which the sample became non-crystalline.

The Ritter paulingite contains 18.5% H_2O. The water loss upon heating is rapid and continuous. More than half the water was driven off by 150° C, and the remainder was driven off by 450° C. With this water content the calculated density is 2.098 g/cm³. This value yields 34.80 H_2O molecules per 84 framework oxygens, which compares with the 44.06 observed in the Rock Island Dam paulingite (Gordon *et al.*, 1966). There is little reason to suspect that the Rock Island Dam paulingite water content is in error. Because many of the H_2O molecules occur as hydration spheres around exchangeable cations, the Rock Island Dam paulingite would be expected to have more H_2O, because it has more large cations than that from Ritter (see Table 1).

With the variations in Table 1 and the water contents discussed above the general composition of paulingite can be expressed by the formula $(K_2, Ca, Na_2, Ba)_5[Al_{10}Si_{32}O_{84}]\cdot34$–$44\ H_2O$.

Origin

Paulingite is such a rare and unusual zeolite that it is worth searching for various chemical factors that might account for its formation. In considering the compositions of the solutions from which paulingite crystallizes, it is first instructive to compare the Si/Al ratios and exchangeable cation content of the associated zeolites (Table 2). The exchangeable cations incorporated into zeolites to some measure reflect the chemistry of these solutions. The zeolite compositions in Table 2 show a fairly wide variation from locality to locality. The Rock Island Dam and Riggins zeolites are K-rich, while the Chase Creek minerals are relatively Ba-rich and the Ritter ones are Ca-rich. This demonstrates that these cations alone do not control the formation of the paulingite framework.

The Si/Al content of the framework of these zeolites varies within a narrow range with the exception of the phillipsite and chabazite from Ritter. If the Si/Al ratio of a zeolite is largely controlled by the pH of the solution from which it forms (Mariner and Surdam, 1970), then this variable is also not controlling the nucleation of these particular frameworks.

Because the compositions and crystallization sequences of paulingite-bearing assemblages are similar to those with faujasite (Wise, 1982), there may

Table 2. Comparison of the formulas of paulingite and associated zeolites. All zeolite formulas have been normalized to 84 oxygens for comparative purposes, and have been listed in their order of crystallization.

	Si	Al	Mg	Ca	Sr	Ba	Na	K
ROCK ISLAND DAM, WASHINGTON								
erionite/offretite	31.57	10.41	.79	2.29	--	--	.63	3.66
paulingite	32.21	9.82	--	1.88	--	.18	.95	4.44
phillipsite	31.21	10.91	--	1.96	--	.09	2.93	3.37
clinoptilolite	33.83	8.51	.48	2.00	--	--	.88	1.33
CHASE CREEK, BRITISH COLUMBIA								
erionite	31.50	10.79	1.47	2.08	.09	.07	.05	2.12
paulingite	31.23	10.71	.11	2.32	.09	.81	.53	3.55
harmotome	31.20	10.82	.09	.75	.08	3.08	.39	2.27
heulandite	33.03	8.97	1.32	2.14	.15	.11	.18	1.31
RIGGINS, IDAHO								
paulingite	31.22	10.80	.04	2.41	.02	.32	.42	4.68
phillipsite	31.33	10.70	.03	1.76	.04	.59	.75	4.99
RITTER, OREGON								
paulingite	31.21	10.78	--	3.70	--	.10	.86	2.77
phillipsite	27.09	15.03	--	5.49	--	--	.39	3.14
chabazite	27.70	14.35	--	6.62	.18	--	--	.04

be similarities in origin as well. Breck (1974, p. 340) suggests some zeolite frameworks form around hydrated or partially hydrated alkali and alkaline earth cations, which act somewhat like a template. Such zeolites have high water molecule to cation ratios; paulingite and faujasite may be good examples. It was suggested (Wise, 1982) that relatively dilute solutions (low salinity) are most likely to provide such templates for minerals like faujasite.

Gordon *et al.* (1966) located cations in paulingite in two kinds of positions, (1) in 8-fold coordination with water molecules inside large cages and (2) bonded to the framework and presumably also to several water molecules. The implication is that paulingite, because of its early appearance in the zeolite sequences, crystallizes when pore solutions are most dilute. It is also interesting to note that the Si/Al ratio of faujasite and associated phillipsite, commonly between 2.6 and 2.1 (Wise, 1982), is lower than the 3.1 to 2.9 of paulingite and associated phillipsite. This appears to reflect the alkaline nature of the faujasite-bearing host rocks, while paulingite occurs in sub-alkaline rocks, like those of the Columbia River Group.

Acknowledgments

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