

Uranium- and thorium-rich vesuvianite from the Seward Peninsula, Alaska

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Abstract

Vesuvianite rich in U, Th, and REE occurs in a syenite and nepheline syenite in southeastern Seward Peninsula, Alaska. The vesuvianite occurs as large (up to 1.5 cm) tabular crystals; in thin section it is brownish-yellow and commonly zoned with an isotropic (metamict) core and an anisotropic (non-metamict) rim. The chemical composition can be approximated by the formula $(\text{Ca,Na,L a,Ce,Pr,Nd,U,Th})_{18.1}(\text{Al,Ti,Fe,Mn,Mg})_{12.9}\text{Si}_{18}(\text{O,OH,F})_{76}$. UO_2 content ranges from 0.39 (non-metamict) to 0.84 weight percent (metamict), and ThO_2 ranges from 0.72 (non-metamict) to 2.70 weight percent. Coexisting allanite has UO_2 and ThO_2 contents that range from 0.29 to 0.40 and 0.77 to 1.30 weight percents, respectively. The vesuvianite probably formed by metasomatic activity prior to intrusion of subsilicic alkaline dikes.

Introduction

Vesuvianite occurs in a variety of environments, principally in metamorphosed limestone but also in veins associated with mafic and ultramafic rocks and in nepheline syenite and other alkalic rocks. Inoue and Miyashiro (1951) have shown that compositional variations of vesuvianite are related to its occurrence. The mineral generally does not contain appreciable amounts of uranium and thorium nor is it metamict. To our knowledge, the only previously-reported occurrence of U- and Th-rich vesuvianite contained 1.00 weight percent U_3O_8 and 0.53 weight percent ThO_2 and occurred in a nepheline syenite in the USSR (Kononova, 1960). We report a recent finding of a U- and Th-rich metamict vesuvianite in syenite and nepheline syenite from the southeastern Seward Peninsula, Alaska (Fig. 1). The mineral was earlier reported to be allanite (Miller *et al.*, 1976), but more detailed study has shown that it is vesuvianite; locally, allanite is abundant and in hand specimen is indistinguishable from vesuvianite. The identification of vesuvianite is based on optical properties,

chemical composition, and the powder X-ray diffraction pattern of a heated sample.

Geologic setting and petrography

The vesuvianite-bearing syenite occurs in the center of the Kachauik pluton, which is a large composite body of monzonite, syenite, and granodiorite of mid-Cretaceous age (Miller and Bunker, 1976). The pluton occupies an upland region west of the Darby Mountains and has an outcrop area of about 530 km². A N40°E-trending alkaline dike swarm consisting of pulaskite and pseudoleucite porphyry cuts much of the north half of the pluton.

Vesuvianite occurs in syenite boulders scattered along a ridge crest over an area approximately 1.3 by 0.4 km in the north-central part of the Kachauik pluton (Fig. 1). Extensive frost action has reduced most outcrops to rubble and talus. Due to the absence of outcrop, the relation of the vesuvianite-bearing syenite to the remaining syenite and monzonite of the pluton is uncertain. Vesuvianite-bearing syenite occurs as discrete boulders, although thin-section study indicates some gradation into adjacent vesuvianite-

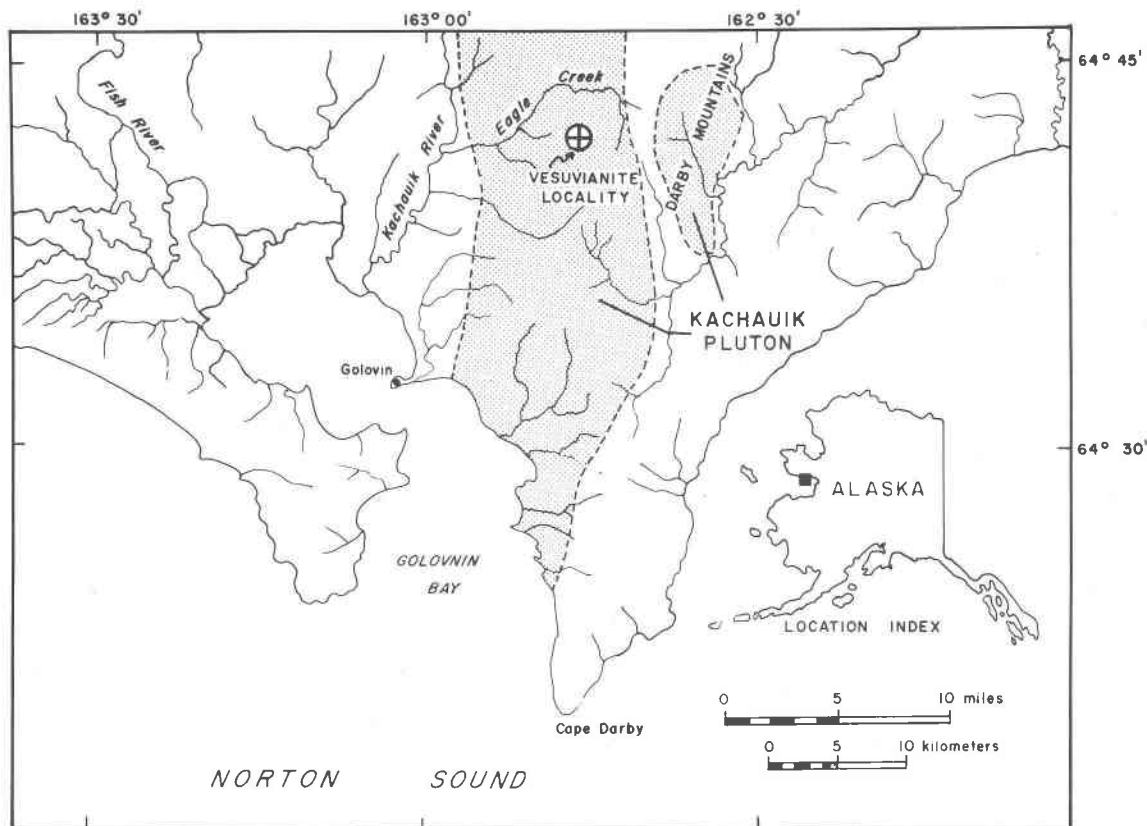


Fig. 1. Index map showing the location of uranium- and thorium-rich vesuvianite-bearing nepheline syenite (stipple pattern).

free syenite and monzonite. These boulders occur within 250 m of a pulaskite dike which is approximately 10 m wide and over 3 km long and strikes $N40^{\circ}E$. Although the absence of outcrops makes determination of attitudes difficult, the vesuvianite-bearing syenite boulders also appear to occur discontinuously along a $N40^{\circ}E$ trend.

The monzonite and syenite are porphyritic; phenocryst minerals, set in a medium-grained groundmass, are perthitic potassium feldspar, hornblende, and clinopyroxene. Groundmass minerals are dominantly potassium feldspar and subordinate plagioclase (An_{30-45}); quartz ranges up to 5 volume percent. Biotite is rare, and melanite garnet is locally present in border phases. Nepheline is rare except in and near vesuvianite-bearing syenite. Ubiquitous sphene, apatite, zircon, and sporadically distributed magnetite and allanite are accessory minerals. Alignment of potassium feldspar phenocrysts imparts a trachytoid texture.

The vesuvianite-bearing syenite contains perthitic potassium feldspar and either nepheline or plagioclase (An_{30}), but not both in the same specimen.

Plagioclase is unaltered or sericitized, and in some samples nepheline is altered to cancrinite. Mafic minerals are vesuvianite, hornblende, and lesser amounts of green clinopyroxene; biotite is present in minor amounts, generally as a replacement of hornblende. Zircon, sphene, and apatite are the most common accessory minerals; zircon occurs as large euhedra as much as 10 mm across and locally constitutes 2 to 3 percent of the rock. Melanite garnet and allanite are less common, although allanite does occur locally in amounts of a few percent. The vesuvianite-bearing syenite is medium- to coarse-grained and porphyritic, commonly with a trachytoid alignment of potassium feldspar phenocrysts.

Individual blocks of the vesuvianite-bearing syenite are highly radioactive; a hand-held scintillometer yielded a counting rate up to 8000 counts per second (total counts). Delayed neutron and gamma-ray spectrometric analyses were obtained on rock samples showing the highest radioactivity and containing an estimated 30–50 volume percent vesuvianite. Uranium in the samples reaches a maximum of 1545 ppm as compared to a maximum of over 9000 ppm

thorium (Table 1). Semiquantitative spectrographic analysis of the same samples indicates a rare-earth element (REE) content of over 2 weight percent, principally consisting of La, Ce, Pr, Nd, Sm, Gd, and Y (Miller *et al.*, 1976).

Vesuvianite

Description and powder X-ray diffraction pattern

The vesuvianite occurs as euhedral tabular crystals as long as 1.5 cm. These crystals may constitute up to 50 volume percent of individual syenite boulders. On weathered surfaces vesuvianite is altered to an unidentified bright orange material. In hand specimen the vesuvianite is black, in thin section it is brownish-yellow with anastomosing fractures. Both isotropic (metamict) and anisotropic (non-metamict) vesuvianite are present in the same thin section. Zoning of vesuvianite crystals is common; inner parts are generally isotropic, have low relief, and are darker-colored than the anisotropic, higher relief, lighter-colored rims. Contacts between zones are abrupt and irregular, and some grains show more than two zones. The anisotropic material is uniaxial negative, nonpleochroic with low birefringence. Vesuvianite contains inclusions of all other major minerals in its host rock and is one of the last minerals to have crystallized. Relict ragged grains of allanite are commonly enclosed in vesuvianite.

Because of the metamict character of most of the vesuvianite crystals, it was not possible to obtain a powder X-ray diffraction pattern of the material in its natural state. Following the method of Kononova (1960), we heated the vesuvianite to a temperature of 800°C for 1 hour. The diffraction pattern obtained from the annealed material is compared to the more

Table 1. Uranium and thorium analyses in parts per million (ppm) of selected samples of vesuvianite-bearing syenite, Kachauik pluton, Alaska

Sample No.	U ppm* (CV)	U ppm**	Th ppm* (CV)	Th ppm**
76 AMm 112	1107 (1)	1000	6619 (2)	5700
76 AEr 23	1162 (1)	1050	7692 (1)	6400
76 AMm 112B	1486 (1)	--	9240 (1)	--
76 AEr 23B	1545 (1)	1500	8408 (2)	7000
77 AMm 62	1411 (3)	--	9355 (5)	--

*Delayed neutron determination. CV = Coefficient of variation = one standard deviation, expressed as percentage of concentration. Analysts: A. J. Bartel and R. J. Vinnola.

**Gamma-ray spectrometric analysis. Analysts: C. M. Bunker and C. A. Bush.

--not determined

Table 2. Interplanar spacing of Alaskan vesuvianite, USSR vesuvianite, and JCPDS vesuvianite 22-533

Alaskan I/I ₁	d(Å)	U.S.S.R. I/I ₁	d(Å)	JCPDS 22-533 I/I ₁	d(Å)
40	3.29			30	3.25
50	3.018	40	3.01	60	2.948
100	2.803	100	2.77	100	2.759
80	2.646	80	2.61	80	2.599
30	2.513	60	2.48	60	2.465
		10	2.39	10	2.354
10	2.187			50	2.128
10	1.935			30	1.892
				50	1.767
10	1.704			30	1.682
		40	1.677	50	1.666
70	1.658	70	1.647	80	1.625
10	1.585	10	1.590	40	1.562

Alaskan vesuvianite (sample 77 AMm 70) heated at 800°C for 1 hour. U.S.S.R. vesuvianite is analysis no. 1 from Kononova (1960).

intense lines of the JCPDS vesuvianite pattern 22-533 and to Kononova's analysis No. 1 (Table 2). The Alaskan vesuvianite pattern is generally comparable to the JCPDS pattern, although the interplanar spacings of the Alaskan vesuvianite are invariably larger than those of the JCPDS pattern, as are those of Kononova's sample. The differences in interplanar spacings are probably related to differences in chemical composition of the Alaskan and USSR vesuvianites relative to the more standard chemical composition.

Chemical composition

The chemical composition of the Alaskan vesuvianite was determined with an ARL EMX-SM electron microprobe, and representative analyses of a zoned crystal are given in Table 3; each analysis is an average of 5 spots. Standards were as follows: U metal for uranium; natural thorite for Th; synthetic glass for REE; and natural and synthetic pyroxenes for all other elements. Characteristic X-ray lines measured were; $UM\beta$, $ThM\alpha$, $REEL\alpha$, and $K\alpha$ for the remainder of the elements. The $LaL\beta$ peak overlaps with the $PrL\alpha$ peak, and thus in analyses for Pr the X-ray intensity obtained at the $PrL\alpha$ wavelength setting must be corrected for the $LaL\beta$ contribution. According to Åmli and Griffin (1975), this correction is approximately 12.7 percent. Although this correction is substantial and critical for many analyses of Pr, it is insignificant at the concentration levels of Pr in the vesuvianite. Uranium values were checked with a

Table 3. Chemical compositions and structural formulas of vesuvianite and allanite in nepheline syenite of the Kachauik pluton, Alaska

	Vesuvianite			Allanite
	Zone 1**	Zone 2	Zone 3	
SiO ₂	37.4	35.6	36.4	33.6
Al ₂ O ₃	11.3	11.8	12.0	15.7
TiO ₂	2.83	3.01	3.58	0.56
FeO*	8.83	8.72	7.87	15.9
MnO	0.25	0.25	0.21	0.22
MgO	1.58	1.50	1.49	0.21
CaO	29.4	31.0	32.1	13.4
Na ₂ O	0.37	0.38	0.38	0.04
La ₂ O ₃	1.40	1.16	0.78	5.84
Ce ₂ O ₃	3.11	2.06	1.23	10.0
Pr ₂ O ₃	0.48	0.32	0.20	1.52
Nd ₂ O ₃	1.07	0.65	0.42	1.70
ThO ₂	2.69	1.51	0.73	0.86
UO ₂	0.84	0.66	0.64	0.38
Total	101.55	98.62	98.03	99.93
	Cations per 72 oxygens			Cations per 12.5 oxygens
Si	18.474	17.901	18.049	3.111
Al	--	0.099	--	--
ΣZ	18.474	18.000	18.049	3.111
Al	6.579	6.894	7.013	1.713
Ti	1.051	1.138	1.335	0.039
Fe ²⁺	3.648	3.666	3.264	1.231
Mn	0.104	0.106	0.088	0.017
Mg	1.164	1.124	1.101	0.029
ΣY	12.546	12.928	12.801	3.029
La	0.255	0.216	0.143	0.199
Ce	0.562	0.380	0.223	0.339
Pr	0.086	0.058	0.036	0.051
Nd	0.189	0.117	0.074	0.056
Th	0.303	0.173	0.083	0.018
U	0.092	0.074	0.071	0.008
Na	0.353	0.372	0.366	0.007
Ca	15.560	16.701	17.053	1.329
ΣX	17.400	18.091	18.049	2.007

*Total iron as FeO

**Zone 1 is isotropic (metamict) core, Zone 2 is intermediate metamict zone of slightly higher relief than Zone 1, and Zone 3 is anisotropic (non-metamict) rim. Vesuvianite sample 77 AMm 70; allanite sample 77 AMm 62.

UO₂ standard, and differences obtained with U metal and UO₂ as a standard were ± 4 percent of the amount present. No standard check was available for the Th or REE. Matrix corrections were made by the procedure of Bence and Albee (1968) and the corrections factors of Albee and Ray (1970). There is no α -factor available for the UM β line, so the UM α α -factor was used in the correction. Judging from the mass absorption coefficients given by Heinrich (1966) for

UM α and UM β , any error introduced by using the UM α α -factor should be minimal.

Although the chemical formula of vesuvianite as proposed from a structural analysis by Warren and Modell (1931) can be written Ca₂₀Mg₄Al₈Si₁₈(O,OH,F)₇₆, vesuvianite analyses show considerable variation from this formula (Deer *et al.*, 1962, p. 116, 117). Machatschki (1932) proposed the alternate formula X₁₉Y₁₃Z₁₈(O,OH,F)₇₆ where X = Ca(Na,K,Mn), Y = (Al,Fe³⁺,Fe²⁺,Mg,Ti,Zn,Mn), and Z = Si, and analyses cited by Deer *et al.* (1962) fit this formula closer. Other proposed formulas (see Ito and Arem, 1970) are similar to Warren and Modell's original formula, but none agrees with all published analyses.

The Alaska vesuvianite formula was calculated anhydrous by Jackson *et al.*'s (1967) method. Total iron was calculated as Fe²⁺, although some Fe³⁺ is certainly present. The Alaskan vesuvianite differs from other reported vesuvianite analyses in its significant content of U, Th, and REE. All these elements have ionic radii comparable to Ca and have been assigned to the X group of elements substituting for Ca. For the Alaskan vesuvianite X is close to 18, Y to 13, and Z to 18. A similar formula was determined for the USSR U- and Th-bearing vesuvianite (Kononova, 1960).

Except for the U, Th, and REE, the Alaskan vesuvianite is similar in composition to other vesuvianites. Inoue and Miyashiro (1951) reported that vesuvianites from nepheline syenites are characterized by higher contents of Al and Ti and lower contents of Ca and Mg than vesuvianites from metamorphosed calcareous rocks. They reported Al₂O₃ contents of approximately 18 and 19 weight percent for nepheline syenite vesuvianite; however, the Alaskan vesuvianite has only about 12 weight percent Al₂O₃. Similarly, the metamict vesuvianite reported by Kononova (1960) has an Al₂O₃ content of 14.5 weight percent.

The optical zonation of the vesuvianite shows a corresponding chemical zonation. The innermost metamict zone (zone 1, Table 3) is enriched in U, Th, REE, and Mg and depleted in Al, Ti, Fe, and Ca relative to the outer non-metamict zone (zone 3, Table 3). Additional U and Th analyses were made on several grains of vesuvianite in three samples. The metamict vesuvianite grains showed a range of 0.61 to 0.84 weight percent UO₂ and 1.38 to 2.70 weight percent ThO₂; non-metamict vesuvianite is lower in UO₂ and ThO₂, with approximately 0.40 weight percent UO₂ and 0.72 to 0.98 weight percent ThO₂. Spot analyses showed ThO₂ contents as high as 3.77

weight percent. The vesuvianite from the USSR contains 1.00 weight percent U_3O_8 (0.96 percent UO_2) and 0.53 percent ThO_2 .

Allanite

Allanite was also analyzed, and a representative analysis is given in Table 3. The mineral formula was calculated anhydrous on the basis of 12.5 oxygens. All iron was calculated as Fe^{2+} , although a small amount of the total iron is certainly Fe^{3+} , which would adjust the calculated formula. The allanite shows smaller amounts of UO_2 (0.29 to 0.40 weight percent) relative to the coexisting vesuvianite although ThO_2 contents are similar (0.77 to 1.30 weight percent). An optically zoned allanite shows Th zoning, the core having 0.77 weight percent, an intermediate zone 1.38 weight percent, and the rim 2.00 to 2.88 weight percent ThO_2 . These UO_2 and ThO_2 contents are relatively high for allanite but within the range reported by Frondel *et al.* (1967 p. 50).

Petrogenesis of the vesuvianite-bearing syenite

Although the exposures are poor and consequently interpretations are uncertain, the relation between the vesuvianite-bearing syenite and the surrounding syenite and monzonite of the Kachauik pluton appears to be gradational over a few centimeters. These observations suggest that the vesuvianite-bearing syenite is indeed a part of the enclosing syenite and monzonite and not a later intrusive phase.

Most of the vesuvianite-bearing syenite contains nepheline, whereas most of the surrounding monzonite and syenite are silica-saturated rocks with rare nepheline. Furthermore, nepheline and plagioclase are mutually exclusive in vesuvianite-bearing syenite, suggesting that nepheline may be a metasomatic product resulting from alkali-exchange reactions that converted plagioclase to perthite plus nepheline, as proposed by Rao and Murthy (1974). Textural evidence also suggests that the coarse vesuvianite was among the last minerals to form, since it contains abundant inclusions of all other minerals.

We therefore suggest that the vesuvianite and its host rocks of syenite and nepheline syenite were formed by metasomatic activity involving the introduction of alkali elements, U, Th, Zr, and REE into the syenite and monzonite of the Kachauik pluton. Chemical zonation of the vesuvianite grains suggests that the U, Th, and REE content of the metasomatic fluids decreased with time. Some allanite, which also occurs in the surrounding syenite and

monzonite, was probably a primary mineral; however, local concentrations of allanite suggest that much of it was also introduced. The thorium-rich rim on some allanite grains probably grew on primary grains during metasomatism.

The metasomatic fluids may be related to the alkaline pulaskite dikes which also contain nepheline and occur in the immediate area of the vesuvianite-bearing syenite. The dikes were emplaced along a persistent $N40^\circ E$ joint system in the syenite and monzonite. Since the occurrence of the vesuvianite-bearing syenite boulders also appear to trend roughly $N40^\circ E$, either the metasomatic fluids could have pervaded the syenite and monzonite along an incipient fracture system into which the pulaskite dikes were later emplaced, or the metasomatism may have occurred at the time of emplacement of the pulaskite dikes.

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