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Chabazite in spodumene-bearing Alpine-type fissure veins from Hiddenite, North Carolina, USA

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Abstract Alpine-type fissure vein mineralization in the Hiddenite area of western North Carolina, USA consists mostly of quartz, but locally contains Cr-bearing beryl (emerald) or Cr-bearing spodumene (hiddenite). These gem minerals occur in mineral-lined cavities and may be accompanied by euhedral crystals of quartz, calcite, muscovite, rutile, albite, pyrite, siderite and dolomite. Chabazite-Ca occurs as a late stage phase in spodumenebearing veins, but is absent in emerald-bearing veins. Chabazite-Ca occurs as simple penetrating twins of pseudocubic rhombohedra and as the lens-shaped variety, phacolite. Chabazite-Ca from Hiddenite contains minor amounts of Na, Mg, Fe and K. Phacolitic chabazite-Ca shows Fe-enriched but Mg-depleted cores relative to the rims. Chemical zoning is absent in rhombohedral chabazite. The Hiddenite chabazite apparently precipitated under low temperature $(< 250^{\circ}$ C) and low pressure $(< 2$ kbar) conditions during the waning stages of crystallization of an alkaline hydrothermal fluid.

Introduction

Within the immediate vicinity of the town of Hiddenite, North Carolina (latitude 35.90N, longitude 81.09W) are quartz veins which host gem- and specimen-grade Crbearing beryl and Cr-bearing spodumene, better known in

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the gem trade as emerald and hiddenite, respectively. According to Wise and Anderson [\(2006](#page-7-0)), both gem minerals occur as part of an assemblage that formed from hydrothermal fluids. The Hiddenite area is particularly interesting because emeralds are extremely rare in North America and their association with Cr-bearing spodumene is not known from other worldwide emerald deposits. The unusual geochemical features of the deposits, (e.g., presence of Li, Be and Cr in a non-pegmatitic environment) has led to an ongoing investigation into the origin of the gem deposits (Wise and Anderson [2006](#page-7-0)). Previous studies of the Hiddenite deposits consisted mainly of descriptions of the various mineral species present in quartz veins (Davidson [1927;](#page-6-0) Palache et al. [1930](#page-6-0); Sinkankas [1976;](#page-6-0) Brown and Wilson [2001](#page-6-0)). More recently, additional mineral species including graphite, monazite-(Ce) and molybdenite have been recognized (Wise and Anderson [2006](#page-7-0)). During the present study of quartz veins from the North American Emerald Mine (NAEM) property (part of the former Rist Emerald mine), chabazite was found as part of a late stage assemblage. Subsequent to this discovery, examination of spodumene samples that reside in the mineral collection of the National Museum of Natural History, Smithsonian Institution, revealed the presence of chabazite crystals from the Adams property (formerly the Warren Farm), the site of the original discovery of hiddenite. To the best of the author's knowledge, chabazite has never been reported previously from the Adams property, and was only recently described by Wise and Anderson ([2006\)](#page-7-0) from the NAEM property. Furthermore, the occurrence of chabazite with spodumene in a fissure vein setting has not been described elsewhere in the world. The present paper reports on this rare and unusual association and discusses the conditions in which chabazite is stable with spodumene.

Geology

The Hiddenite deposits are located in the intensely deformed and metamorphosed Inner Piedmont Belt of western North Carolina (Fig. 1). This area is nearly 100 km wide and extends approximately 700 km southwest of the Sauratown Mountain window from North Carolina to Alabama. The Inner Piedmont Belt is bounded on the west by the northeast-trending Brevard Fault Zone which separates the Inner Piedmont Belt from the Blue Ridge, and is bounded on the east by the Carolina Piedmont Suture which separates it from the Carolina Terrane. The Inner Piedmont Belt consists of sillimanite-grade rocks that include 500 to 750 Ma old gneisses, migmatites and schists that have been intruded by numerous deep- and shallowlevel granitic to gabbroic plutons.

The bedrock geology of the Hiddenite area consists of Precambrian migmatitic schists and gneisses that are crosscut by an extensive set of steeply dipping, NE trending quartz veins. The schists are interlayered with discontinuous lenses of calc-silicate rocks consisting of calcite, grossular, diopside, titanite and quartz. The area is locally intruded by the medium-grained leucocratic Rocky Face Granite. Prolonged weathering of the migmatitic bedrock has resulted in the formation of a thick red lateritic saprolite horizon. Quartz veins may be identified near the surface in the upper part of the saprolitic zone and followed downward through the saprolite into the unweathered bedrock.

Fig. 1 General geologic map of the major tectonic units of the southern Appalachians showing the location of the Hiddenite emerald and spodumene deposits

Details of the geology and mineralogy of the quartz veins were provided by Palache et al. ([1930\)](#page-6-0), Brown and Wilson ([2001\)](#page-6-0) and most recently by Wise and Anderson ([2006\)](#page-7-0). Sinkankas [\(1976](#page-6-0)) noticed a remarkable similarity in the structure and mineral assemblage of the Hiddenite quartz veins to the Alpine-type fissure veins found in the Swiss Alps. Classic Alpine-type fissure veins are mineralized infillings of brittle tensional fractures that develop in relatively competent rock-units during regional deformation and strain-related metamorphism. The fissure minerals which form in cavities result from the chemical leaching of surrounding rock by hydrothermal solutions and subsequent precipitation of low temperature minerals into localized open fractures. Minerals which are typical of Alpine-type veins include quartz, fluorite, calcite, adularia, chlorite, titanite anatase, rutile and brookite (Graeser [1998](#page-6-0)).

The quartz veins sampled in this study are from the same part of the NAEM property studied by Wise and Anderson [\(2006\)](#page-7-0) and from the Adams property which lies approximately 3.2 km southwest of the NAEM property. All of the known Hiddenite emerald occurrences occur within the same migmatitic schist and gneiss unit. The Hiddenite quartz veins are typically 1 to 10 cm wide, but may reach widths of up to 1.5 m. Some quartz veins are characterized by rare-element mineralization in the form of Cr-bearing beryl (variety emerald) and Cr-bearing spodumene (variety hiddenite) which occur in voids within the veins. The beryl and spodumene are accompanied by quartz, carbonates (calcite, siderite and dolomite), sulfides (pyrite and pyrrho-

tite), rutile, graphite, muscovite and a clinochlore-like phase (Wise and Anderson [2006](#page-7-0)), although minor differences in accessory mineralogy between the vein types have been observed. Beryl and spodumene appear to be almost mutually exclusive, occurring only rarely together within an individual cavity. The origin of the gem-bearing veins has been debated over the past 75 years. Derivation of the emeralds, and presumably the hiddenite from a pegmatite source was favored by Palache et al. ([1930\)](#page-6-0) and Brown and Wilson [\(2001](#page-6-0)). Crystallization from hydrothermal fluids, however was proposed by Sterrett ([1908](#page-7-0)), Sinkankas [\(1976](#page-6-0), [1981\)](#page-6-0) and Tacker [\(1999](#page-7-0)) and later confirmed by Wise and Anderson ([2006\)](#page-7-0).

At the Adams and NAEM properties, chabazite occurs only in quartz veins that carry Cr-bearing spodumene and is always one of the last minerals to form (Fig. 2). Veins consist mainly of massive white quartz which locally develops cavities that contain euhedral crystals that protrude inward from the roof and walls. The cavities that contain hiddenite are relatively simple in their mineralogical makeup consisting mostly of quartz, muscovite, spodumene, calcite, rutile and pyrite. Euhedral quartz crystals are typically 1 to 2 cm in length, although crystals as long as 15 cm have also been recovered and generally exhibit the prismatic Tessin habit characterized by steep rhombohedral faces and a tapered termination. At the NAEM locality pale purple quartz sometimes occurs as small clusters or radiating aggregates of pale purple crystals, 0.3 to 0.5 cm long, typically forming on the terminations of colorless quartz prisms to form pale purple scepters. Muscovite ranges from silver- to bronze-colored crystals at the NAEM locality, but may sometimes display deep green cores or rims. Muscovite is conspicuously absent in the veins hosting chabazite at the Adams property. The carbonate mineralogy is dominated by rhombohedral

Fig. 2 Generalized paragenetic sequences for spodumene-bearing cavity mineralization in the A) NAEM and B) Adams properties

crystals of calcite although dolomite may sometimes be present. Silver-gray, prismatic crystals of rutile are found attached to the vein walls, included in quartz and calcite or perched on quartz, calcite and muscovite. Crystals of Crbearing spodumene, up to 7 cm long, occur attached to the cavity walls or loose in the red saprolitic clay of weathered pockets. The most valued crystals are emerald green in color; but most crystals show pronounced color zonation with dark emerald-green tips and grading to yellowishgreen along the length of the crystal. They are usually etched and commonly covered by thin layers of a dark to light green clinochlore-like mineral. Late-stage mineralization of the pocket includes the formation of sulfides and graphite in addition to chabazite. Pyrite is the dominant sulfide mineral present and forms 1 mm wide cubooctahedrons which crystallize on quartz, calcite and muscovite. Other sulfides of note include rare molybdenite and pyrrhotite. Graphite crystals, 1 mm in diameter, occur in, and on the surfaces of calcite, muscovite and chabazite. Schorl and zircon were rarely observed in some hiddenitebearing cavities.

Chabazite is rare in the quartz veins and represents the only zeolite mineral found to date in the Hiddenite deposits. Chabazite is typically found growing on the surfaces of quartz, calcite and muscovite, but very rarely on Cr-bearing spodumene. All chabazite collected from the NAEM property displays pseudocubic rhombohedral crystals that form transparent and colorless penetration twins (Fig. [3](#page-3-0)). Most crystals are 0.5 to 0.7 mm in diameter and rarely exceed 1 mm in length. At the Adams property, chabazite has been found only as pale yellow to honey-yellow colored crystals that show complex twinning to form the lens-shaped variety known as phacolite. This habit results from multiple penetration twins rotated 60º on the c-axis (Akizuki and Konno [1987\)](#page-6-0). Crystals may show color zonation with yellow cores and colorless rims. The largest crystals found measure only 2.5 mm in length; most are typically ≤ 1 mm long.

Compositional characteristics

X-ray powder diffraction data were obtained from finely ground chabazite that was attached to a glass fiber and mounted on a Rigaku D/MAX-RAPID microdiffractometer system operating at 50 kV and 40 mA using M_0K_α radiation (λ =0.7093Å). The X-ray beam was focused on the sample using a 0.3 mm collimator for an exposure time of 10 min. Samples were identified as chabazite using the search-match routine of the JADE program. The X-ray diffraction patterns of the two samples show a small shift in peak position and slightly different peak intensities (Fig. [4](#page-3-0)). Unit-cell parameters obtained from refinement of the powder

Fig. 3 Back-scattered SEM photographs of A) rhombohedral chabazite (Cbz) showing penetration twinning with pyrite (Py) and B) phacolitic chabazite on calcite (Cal)

Fig. 4 Comparison of X-ray diffraction patterns of rhombohedral and phacolitic chabazite from Hiddenite, North Carolina

data in the space group R -3 m, were $a = 9.400(7)$ Å, α = 94.36(3)° and V = 822.9(6) Å³ for the NAEM chabazite and $a = 9.395(7)$ Å, $\alpha = 94.36(3)$ ° and V = 821.8(6) Å³ for the Adams chabazite. The unit-cell data suggest only a modest difference in the structure of the two chabazite samples.

Ten colorless and five yellow chabazite crystals were selected from samples that were collected in the Hiddenite area and obtained from the Mineralogy collection of the National Museum of Natural History, Smithsonian Institution for use in the current study. Quantitative chemical analyses of chabazite were obtained using a JEOL Model JXA-8900R electron microprobe in the wavelengthdispersion mode. Operating conditions were: 15kV and 15 nA using a defocused beam diameter of 10μm to minimize alkali loss. Counting time for background and peak determinations were 5-10 s and 15-40 s, respectively. Natural mineral standards used for analyses were microcline (Si, Al, K), anorthoclase (Na), hornblende (Fe, Mg, Ti), and apatite (Ca). The structural formula for chabazite was calculated on the basis of 24 oxygens. Chabazite is slightly unstable under the electron beam and tends to suffer alkali loss thus resulting in poor analyses. The balance error function of Passaglia ([1970\)](#page-6-0) expressed by the following equation:

$$
E\% = 100 \times \frac{(A1 + Fe^{3+}) - (Li + Na + K) - 2(Mg + Ca + Sr + Ba)}{(Li + Na + K) - 2(Mg + Ca + Sr + Ba)}
$$

is a widely accepted criterion for evaluating analyses of zeolites. The calculated $E%$ value should be <10% and preferably <5% for an acceptable analysis (Coombs et al. [1998;](#page-6-0) Coombs et al. [2005](#page-6-0)).

Representative analyses of chabazite from Hiddenite are listed in Table [1.](#page-4-0) The balance error function for the Hiddenite chabazite ranged from -13.2 to 8.6, but only those $\leq 10\%$ are reported in this study. The composition of the chabazite from both Hiddenite localities is chabazite-Ca with Ca>(Na+K) and plots along the Ca-K join towards chabazite-K of the Na-K-Ca ternary diagram (Fig. [5](#page-4-0)). In general, the chabazite exhibits Si/Al ratios of 2.37 to 3.32 and contains variable amounts of Ca and K, but with low Na and moderate amounts of Mg. The K content varies from 2.00 to 3.76 wt.% K₂O. Na content from 0.04 to 0.23 wt.% Na₂O and Mg content varies from 0.00 to 1.48 wt.% MgO. Samples were checked for the presence of Sr and Ba, but none was detected.

The analyses of phacolitic chabazite from the Adams property indicate slightly higher Si/Al ratios (2.37 to 3.32) than found in the rhombohedral chabazite of the NAEM site (2.42 to 2.83). The Adams property chabazite has similar K contents but slightly less Ca than chabazite from the NAEM property (Table [1](#page-4-0)). The Mg content of the

Table 1 Average representative electron microprobe analyses of chabazite from the Hiddenite spodumene-quartz veins

	NAEM1	NAEM ₂	NAEM3	NAEM4	NAEM ₅	ADAMS1	ADAMS2	ADAMS3	ADAMS4	ADAMS5
SiO ₂	52.03	52.16	53.53	52.51	52.15	51.61	54.39	56.51	53.59	56.97
TiO ₂	0.00	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.01
Al_2O_3	17.55	17.65	17.43	17.25	16.73	17.00	17.19	16.98	17.03	15.73
Fe ₂ O ₃	0.02	0.02	0.01	0.00	0.02	0.47	0.18	0.18	0.25	0.04
CaO	7.88	7.83	7.61	8.20	8.15	6.63	7.01	6.69	6.98	5.92
MgO	0.32	0.24	0.49	0.16	0.18	0.67	0.74	1.00	0.73	1.33
Na ₂ O	0.16	0.06	0.08	0.09	0.06	0.15	0.15	0.17	0.17	0.09
K_2O	2.15	2.62	3.18	3.00	2.49	2.85	2.86	2.77	3.14	2.63
Total	80.11	80.58	82.34	81.22	79.79	79.38	82.53	84.30	81.90	82.72
Si^{4+}	8.578	8.573	8.628	8.599	8.658	8.607	8.705	8.813	8.671	9.001
Ti^{4+}	0.000	0.000	0.001	0.001	0.001	0.000	0.001	0.001	0.001	0.001
Al^{3+}	3.412	3.418	3.312	3.329	3.275	3.344	3.243	3.125	3.249	2.930
$Fe3+$	0.002	0.002	0.002	0.000	0.002	0.060	0.021	0.022	0.030	0.005
Ca^{2+}	1.393	1.379	1.315	1.438	1.450	1.186	1.202	1.121	1.211	1.002
Mg ²	0.078	0.059	0.118	0.038	0.044	0.165	0.175	0.230	0.175	0.312
Na^+	0.050	0.019	0.025	0.028	0.018	0.049	0.046	0.051	0.053	0.029
\mbox{K}^+	0.452	0.550	0.655	0.628	0.528	0.607	0.584	0.552	0.648	0.531
Total	13.965	14.000	14.056	14.061	13.976	14.018	13.977	13.915	14.038	13.811
$E\%^a$	-0.9	-0.6	-6.5	-7.7	-7.2	1.3	-3.5	-4.7	-5.6	-7.9
Si/Al	2.52	2.51	2.61	2.58	2.64	2.59	2.69	2.83	2.67	3.08

Reported data represents the average of 5 analyses per grain. Structural formula calculated on the basis of 24 oxygens. Total iron as $Fe₂O₃$ a E% balance error function of Passaglia [\(1970](#page-6-0))

Adams chabazite is consistently higher than the NAEM chabazite. The Adams phacolitic chabazite is also chemically zoned with respect to $Fe₂O₃$ and MgO unlike the rhombohedral chabazite from the NAEM property, which shows no chemical zonation and is essentially devoid of Fe. Analyses that correspond to the yellow core of the phacolitic chabazite show $Fe₂O₃$ contents of 0.44 to 2.17 wt.%. Rim compositions are significantly lower in Fe at 0.03 to 0.06 wt.% Fe₂O₃. By comparison MgO values are

Fig. 5 Compositions of Hiddenite chabazite plotted on the chabazite group Na-K-Ca ternary diagram (Coombs et al. [1998\)](#page-6-0). a NAEM property (open circles). b Adams property (open diamonds)

highest in the rim $(0.44 \text{ to } 1.46 \text{ wt.})$ and decrease gradually to core $(0.63 \text{ to } 0.68 \text{ wt\%}).$

Genetic implications

Conditions of chabazite formation

The observed mineral associations of the spodumenebearing cavities show that chabazite was one of the last minerals to precipitate from the mineralizing fluid. Chabazite-Ca formed after the crystallization of spodumene, quartz and pyrite and may have been contemporaneous with the growth of calcite. The formation of chabazite known from volcanic rocks and sedimentary environments is influenced by a number of factors including: chemical composition of the starting material; chemical activities of $CO₂$, H₂O and SiO₂; alkalinity of the fluid; Si/Al ratio; and temperature and pressure (Hay [1978](#page-6-0); Passaglia and Vezzalini [1985](#page-6-0); Barth-Wirsching and Höller [1989\)](#page-6-0). In most cases, decomposition of a basaltic glass precursor favors chabazite formation, although rhyolitic glasses may produce chabazite-K in the presence of K-rich fluids. Thermodynamic modeling of a suite of zeolites found in hydrothermal environments shows that chabazite is unstable at temperatures >150 °C (Chipera

and Apps [2001](#page-6-0)). In mafic volcanic rocks chabazite appears to be most stable at temperatures ≤ 100 °C. Chabazite has been recognized as part of the low temperature-low pressure mineral assemblage of some Alpine fissure-type veins (Weibel [1963;](#page-7-0) Graeser [1998](#page-6-0); Hrazdil [2001](#page-6-0); Bucher and Weisenberger [2006\)](#page-6-0) but in general this occurrence is uncommon. Köngisberger ([1901](#page-6-0)) estimated the crystallization temperature of chabazite at <130°C in quartz-orthoclase-calcite fissure veins from Aar, Switzerland. Chabazite from a fluorite-quartz assemblage in the Alpine fissures at Gibelsbach, Switzerland, was considered to have crystallized at temperatures <100 °C (Armbruster et al. [1996](#page-6-0)).

The conditions at which the Hiddenite chabazite crystallized were also likely at low temperatures and pressures. Preliminary fluid inclusion data of early generations of quartz crystals from the spatially associated emeraldbearing veins place the P-T conditions around 250ºC and 1 kbar (Lapointe et al. [2004;](#page-6-0) Alan Anderson, pers. comm. 2004). Since crystallization of chabazite occurred later than most quartz, we estimate that the temperatures of chabazite formation was probably <200ºC. This would be in general agreement with the range of crystallization temperatures (50 to 200ºC) determined by hydrothermal experiments and measured directly from geothermal areas (Kristmannsdóttir and Tómasson [1978;](#page-6-0) Cole and Ravinsky [1984;](#page-6-0) Höller and Wirsching [1988;](#page-6-0) Chipera and Apps [2001](#page-6-0)).

Crystallization of chabazite from the alteration of Carich feldspars was unlikely at Hiddenite as feldspar is generally absent in the hiddenite assemblage and, when present, is albitic in composition. Chabazite apparently precipitated from a fluid that was highly enriched in Ca, with high $CO₂$ fugacities as indicated by the Ca-rich nature of the chabazite, presence of abundant calcite, CO_2 -rich fluid inclusions (Lapointe et al. [2004\)](#page-6-0) and the absence of associated Na or K zeolites. This, plus the absence of kaolinitic clays suggests that the mineralizing fluid was alkaline prior to crystallization of chabazite. Leaching and mobilization of Ca, K, Cr, Fe, Mg and Ti from the schistose and calc-silicate wallrock is believed to be the main mechanism responsible for the fluid chemistry and subsequent mineralization of chabazite and associated minerals in the fissures.

Significance of habit distribution

Although there is little difference in the mineral assemblage between the spodumene-bearing veins of the Adams and NAEM properties, the habit of chabazite is distinctive for each locality. Several workers have recognized that development of chabazite habit was sensitive to changes in the growth conditions of its environment. Walker [\(1951\)](#page-7-0) suggested that the temperature of formation was the overriding factor responsible for variations in chabazite morphology based on his observations of chabazite crystallization in a series of lava flows in the Garron Plateau area, Ireland. Although Walker [\(1951](#page-7-0)) did not determine actual crystallization temperatures for the Garron chabazite, he concluded that chabazite with simple rhomobohedral habits, including those displaying penetration twins, crystallized at lower temperatures than phacolitic chabazite. According to Akizuki and Konno [\(1987](#page-6-0)), the phacolitic habit reflects a sudden change in the growth rate of chabazite. Under slow and constant growth rate, penetration twins predominate whereas a sudden increase in the growth rate due to changes in the chemical composition and Al-Si ordering causes the development of the phacolitic habit. Rapid crystallization in a Ca-rich solution, for example, appears to favor the development of the phacolitic habit over the rhombohedral form which requires slow growth rates (Akizuki et al. [1989](#page-6-0)). Experiments on the formation of chabazite conducted by Höller and Wirsching [\(1988\)](#page-6-0) demonstrated the effects of the alkali concentrations in the mineralizing fluid on chabazite morphology. In their experiments, high concentrations of Na caused the formation of rhombohedral chabazite while K-rich solutions resulted in the phacolitic habit. Passaglia ([1970\)](#page-6-0), Birch [\(1989\)](#page-6-0) and Graham et al. [\(2003](#page-6-0)) showed that there was no correlation between crystal morphology and chemical composition in natural samples; Na-rich chabazite can form rhombohera, phacolitic twins or flattened crystals. Based on the discussion above, the phacolitic chabazite from the Adams property probably crystallized under slightly different conditions (possibly higher temperatures, faster growth rates and higher concentration of K in solution) than the rhombohedral chabazite from the NAEM site.

Spodumene-chabazite association

The natural occurrence of zeolite minerals with spodumene is generally uncommon and develops mainly in granitic pegmatites as a result of the hydrothermal alteration of spodumene or eucryptite to form bikitaite (Hurlbut [1958](#page-6-0); Vidal and Goffé [1989\)](#page-7-0) or as the decomposition of associated pollucite to produce Cs-rich analcime (Černý [1972\)](#page-6-0). The association of spodumene and chabazite is extremely rare in granitic pegmatites and not known to occur at all in Alpine fissure-type veins. The only documented spodumene-chabazite association is from the Branchville pegmatite, Connecticut, where chabazite occurs as part of a late alteration assemblage within the albitespodumene zone of the pegmatite (Brush and Dana [1879](#page-6-0)). The chabazite occurs as crystals and irregular masses in rhodochrosite that resulted from the alteration of associated primary lithiophilite. Chabazite is known to occur at other pegmatite localities such as at Strzegom, Poland (Michell

1941; Janeczek 1985) and the Speranza vein near San Piero in Campo, Elba, Italy (Orlandi and Scortecci 1985) but none of these contain spodumene.

The estimated pressures and temperatures of crystallization for the Hiddenite deposits are well within the range of stability for bikitaite, yet spodumene appears as the stable Li phase (London 1984). The presence of Fe and Cr in the spodumene may be responsible for stabilizing it to lower temperatures and pressures and may also make it less susceptible to alteration to bikitaite (Brown 1971; Drysdale 1975; London 1984). In all probability, the crystallization of chabazite instead of bikitaite at Hiddenite may be due mainly to the removal of Li from the solution as a result of prior spodumene crystallization coupled with the overall Ca-rich nature of the hydrothermal fluid.

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