Hydrothermal Formation of Unakite in the Blue Ridge Mountains, Virginia: A Geochemical Analysis

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GEOL394: Senior Thesis II

May 5th, 2017

Background

Unakite is a rare, altered granitoid consisting chiefly of epidote, orthoclase feldspar, and quartz. It was described in 1874 by F. H. Bradley and given the name unakite for its location in the Unaka Mountain Range, North Carolina. Unakite has gone largely unstudied for the past one hundred years despite being a globally occurring rock-type present in Fennoscandia and the Indian subcontinent, as well as the Blue Ridge Mountains of Virginia. This work elucidates some of the complications associated with unakite, epidote minerals, and the associated interactions between them.

Hydrothermal alteration is certainly at play here, with the epidote exhibiting sparry vugs (a low temperature hydrothermal texture) and chemical signatures being exchanged between rock types during variations in their alteration. Determination of the differences between these chemical signals, and how they relate to the spatial field relations is crucial for understanding the chemical, physical, and lithologic parameters in the formation of this rare but beautiful stone.

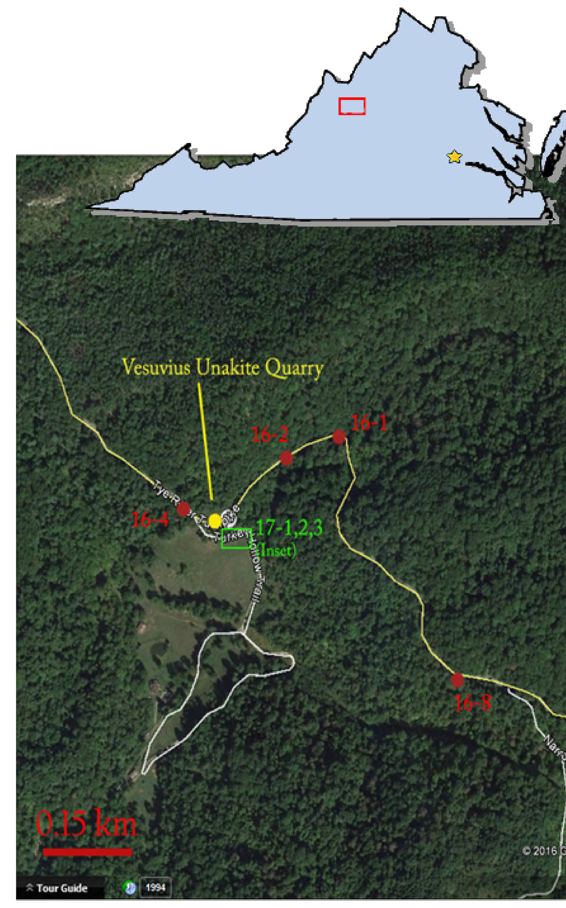
Unakite is found in the hydrometamorphically-altered granites and granodiorites of its localities. In Virginia, the prevalent theory is that the alteration of the charnockite is believed to have come from the hydrothermal fluid of the Catoctin basalt flows (Phalen 1904, Cloos c. 1930), a neoproterozoic lava flow that overlies the charnockite basement rock (Bailey 2013). The unakite itself is believed to have formed by the replacement of plagioclase and ferromagnesian minerals with epidote, leaving the quartz and potassium feldspar relatively untouched (Bradley 1874, Phalen 1904, Watson & Cline 1916). The unakite is absent any of the ferromagnesian minerals of the charnockite, including biotite, pyroxene, and hornblende (Watson 1904).

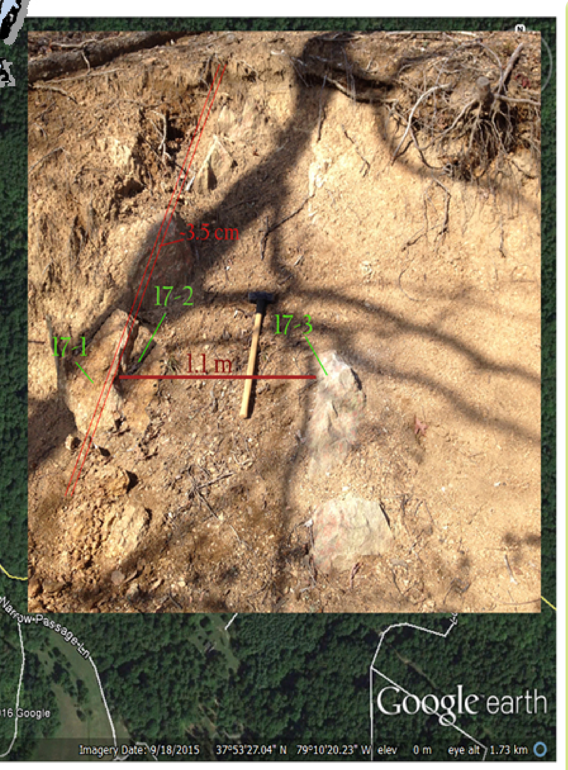
Hypotheses

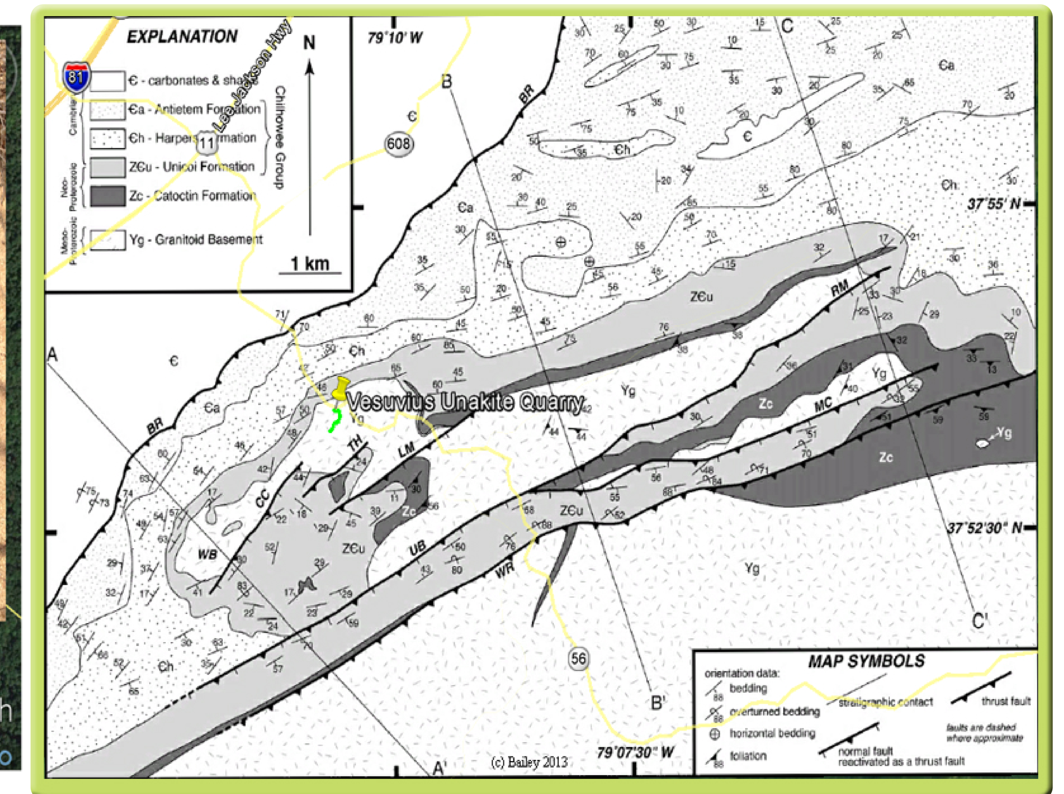
1.) Concentrations of (fluid mobile) LILEs and REEs will increase with distance from the alteration contact between the charnockite and the unakite.

2.) The chemical composition of the epidote is the same in the Catoctin, the unakite, and the charnockite.

Field Location







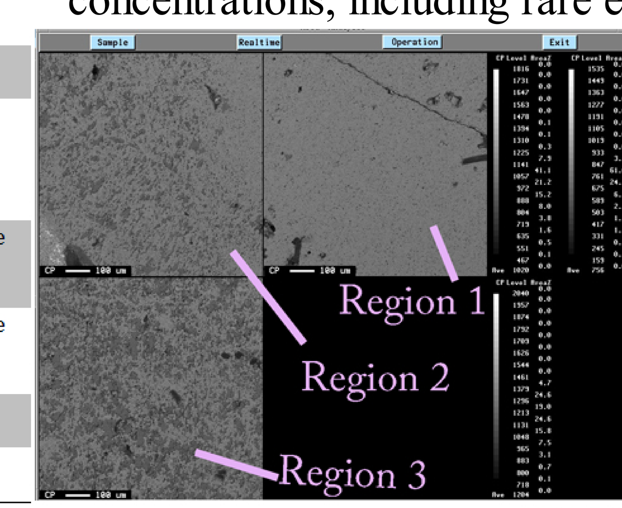
The field location for this study was a defunct unakite quarry nestled in the bend of a state route approximately two kilometers southeast of Vesuvius, Virginia. The quarry now sits on the property of a former geologist named Gary Ochsenbein whose driveway contains an exposed contact in an outcrop of unakite that demonstrates visceral spatial relations and something of the scale to which this unakite alteration took place. The contact itself (inset above) is an alteration zone several centimeters in width which continues lengthwise into the ground, both above and below the outcrop in a planar, almost tabular, fashion.

Sampling

From west to east, charnockite can be seen beginning bearing epidote, the quintessential unakite mineral, at this contact, grading into unakite within a little more than a meter. From this contact area, three samples were collected: one of charnockite to the left, and one each of charnockite and unakite to the right. Four more samples were collected from the nearby area in order to obtain epidote-bearing Catoctin, unweathered charnockites, and epidosite.

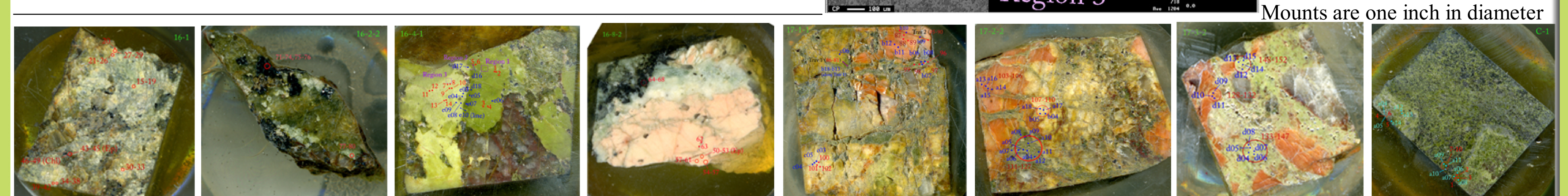
Sample No.	Rock Type	Comments
16-1	Weathered Charnockite	Weathered
16-2-2	Charnockite	Minor Alteration (Uralization)
16-4-1	Epidosite	"High-Grade Unakite"
16-8-2	Charnockite	Megacrystic K-spar (Vesuvius Megaporphyry type locality); Minor Alteration (Uralization)
17-1-1	Charnockite	Heavily Weathered, "Low-Grade Unakite"; **Left of Contact**
17-2-2	Charnockite	Heavily Weathered, "Low-Grade Unakite"; **Right of Contact**
17-3-2	Unakite	Sparry Vugs, **Right of Contact**
C-1	Catoctin	Greenschist Facies,with Epidote

EPMA and LA-ICP-MS techniques were applied to the samples to quantify major and trace element concentrations, including rare earth elements (REE).

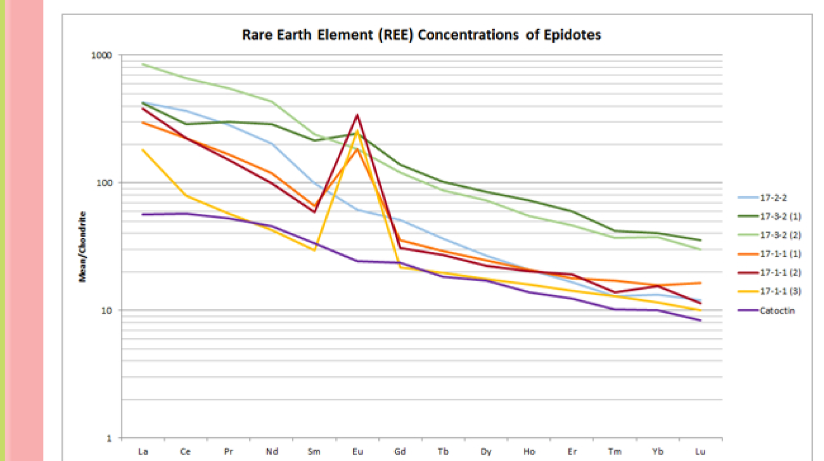


Backscatter electron (BSE) image of 16-4-1. Albitization (darker phase) is variable across a single sample. This albitization is macroscopically visible as dark and light epidotes in sample 16-4-1 below.

Mounts are one inch in diameter

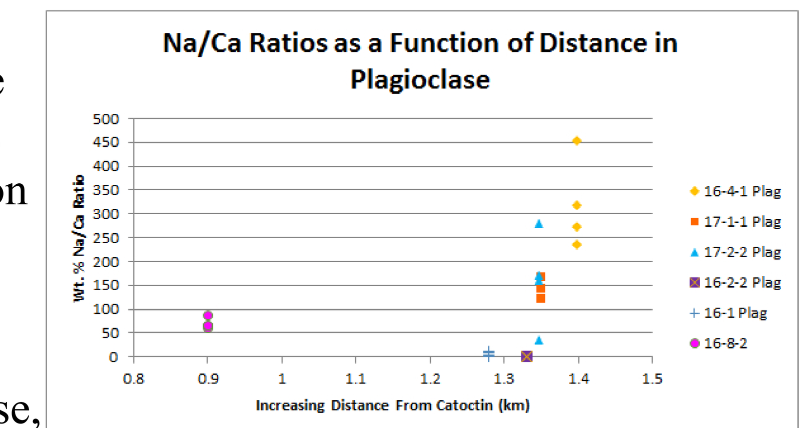


Analysis

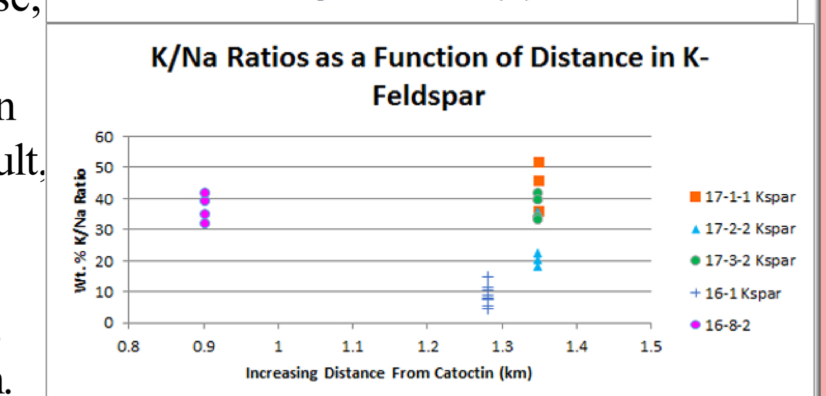


A positive europium anomaly is present only in the 17-1-1 sample. Strangely enough, this sample is the furthest from the Catoctin, and lies on the left of the contact shown in the field map. Catoctin epidote shows relative LREE depletion.

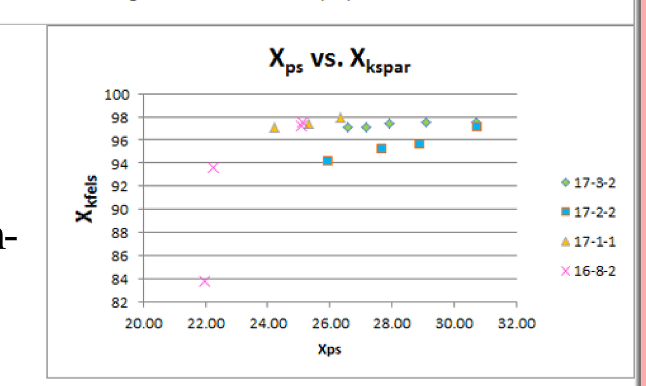
Albitization of Plagioclase



As distance increases from the Catoctin, plagioclase becomes increasingly Na-rich, the reason for the different greens visible in sample 16-4-1. Epidote requires calcium to form and the closest source is plagioclase, which will readily accept the sodium from alkali feldspars in exchange for its loss. As a result, the alkali feldspars become enriched in potassium, the plagioclase becomes albitized, and the epidotes still need iron.



The pistacite component (Xps) is a measure of the iron concentration of the epidotes. Xps in nature rarely exceeds 33%. The epidotes increase their iron content to near that limit here, as the K-spars become potassium enriched.



Conclusions

1. LILE concentrations in the epidotes increased with distance from the Catoctin, but for REE the story is a bit more complicated. Sample 17-1-1 is the only sample that exhibits a (+) europium anomaly but all epidotes are LREE enriched realtive to the Catoctin. Additionally, sample 16-8-1 is *unweathered* charnockite but lies closer to the Catoctin than the unakite. The spatial relationships behind unakite formation may be much more complicated than originally assumed.

2. Epidotes in samples closer to unakite have higher iron ratios than others, suggesting that epidote formation is controlled by host rock bulk composition, but also considerably by alteration fluid composition.

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