2023 AGeS-Grad Award Application

Project Title:
Can Sm-Nd garnet geochronology on rodingites hosted in serpentinite constrain the timing of serpentinization in the northern Appalachian Mountains?

Indicate the primary geochronology method you will use:
Lu-Hf, Sm-Nd, Rb-Sr, Pb-Pb

If you intend to work with two AGeS labs, indicate the secondary geochronology method you will use:

Indicate the primary broad research area you will focus on:
Tectonics

Indicate the secondary broad research area you will focus on:
Petrology and Geochemistry

State the geoscience question or hypothesis that this project will address:
Can Sm-Nd garnet geochronology on metasomatized mafic rocks (rodingite) hosted in serpentinite constrain the timing of serpentinization in the northern Appalachian Mountains? I hypothesize that garnet in rodingite from Belvidere Mountain in northern Vermont formed during one of three tectonic events related to the early tectonic evolution of the Appalachian Mountains. 1. If the garnets in rodingite formed during ocean-floor serpentinization, then the Sm-Nd garnet ages are hypothesized to be coeval with the age of the Iapetus Ocean (> 600 Ma [1 and references therein]). 2. If the garnets in rodingite formed during subduction-zone serpentinization, then the Sm-Nd garnet ages are hypothesized to be coeval with the timing of Ordovician subduction-zone metamorphism during the Taconic Orogeny (~500-470 Ma, [2]). 3. If garnets in rodingite did not form during serpentinization or were recrystallized during subsequent metamorphic events, then the Sm-Nd garnet ages are hypothesized to reflect post-serpentinization alteration, likely associated with Taconic Orogeny terrane obduction or the Devonian Acadian Orogeny (~450-350 Ma [2]).

Discuss the importance of the proposed study:
Serpentinization--the hydration of ferromagnesian minerals--is a key process that affects the rheology, composition, and evolution of the Earth's upper mantle (e.g., 3; 4). In subduction zones, serpentinite recycles water and volatiles into the mantle, which can trigger arc volcanism and deep-focus earthquakes (5; 6, and references therein). Serpentinites also host economically important metals (e.g., nickel, chromium, and platinum) and minerals (e.g., talc and chrysotile) (6). Despite their tectonic and societal importance, determining the timing of serpentinite formation is hindered by the paucity of minerals produced during serpentinization that can be dated using radiometric techniques (see 7). However, calcium-rich, alkaline fluids released during serpentinization can also metasomatically alter nearby rocks, producing rodingites, which are calc-silicate rocks typically composed of grossular garnet, epidote, and chlorite (8). Garnet Sm-Nd

geochronology was recently used to date eclogite facies metamorphism and garnet recrystallization for subducted meta-rodingites (9). However, no study to date has used garnet Sm-Nd geochronology to determine the timing of serpentinization. Serpentinite-hosted garnet-rich rodingite zones occur at Belvidere Mountain in the northern Vermont Appalachian Mountains (Fig.1A, B, C) (10). The serpentinized ultramafic rocks at Belvidere Mountain are part of the suture zone for the Ordovician Taconic Orogeny. Although serpentinites occur throughout this major orogenic suture, the timing and environment of serpentinization is not well understood. The serpentinites may represent ocean-floor serpentinites that were obducted to the Laurentian margin as fragmented ophiolites, or they may represent supra-subduction zone serpentinites that formed in the mantle-wedge of the Taconic subduction complex (c.f., 11, 12). Determining the timing of Taconic serpentinization using garnet Sm-Nd geochronology would provide a timeframe that could be temporally linked to tectonic events, improving tectonic models for serpentinization during the Taconic Orogeny. This study aims to demonstrate that Sm-Nd garnet geochronology can be used to determine the timing of serpentinization in places where serpentinites host garnet-rodingite zones.

Briefly explain the relevance of your project to NSF-EAR science goals, which are aimed at ''improving the understanding of the structure, composition, and evolution of the Earth, the life it supports, and the processes that govern the formulation and behavior of the Earth's materials''; NSF-GEO Website:
The process of serpentinization influences the structure and composition of the Earth's upper mantle, especially at plate boundaries. Serpentinites host critical materials used by industry, but they can also leech dangerous elements (e.g., arsenic) into groundwater (13, 14). This study will test the hypothesis that Sm-Nd geochronology on rodingite zones can be used to infer the timing of serpentinite formation. The results will improve our understanding of the serpentinization process.

Proposed work. Concisely state your research plan and how it will answer the question or test the hypothesis outlined above:
To test the hypothesis that Sm-Nd garnet geochronology can be used to determine the timing of serpentinization, garnets from rodingite at Belvidere Mountain in northern Vermont will be dated. The resulting ages will be interpreted with reference to previously dated tectonic events (e.g., Precambrian Iapetus Ocean formation; Ordovician Taconic Orogeny-blueschist facies metamorphism; Silurian-Devonian regional retrograde metamorphism). Linking the age of serpentinization at Belvidere Mountain with major Appalachian tectonic events will also help constrain the serpentinization environment (e.g., rodingite formation during Iapetus Ocean formation or rodingite formation during mantle wedge serpentinization). To help interpret the Sm-Nd data, electron probe microscopy, Raman spectroscopy, XRF, ICPMS, and pseudosection modeling will be used to constrain the rodingite petrogenesis (funded separately from this proposal). Field work and sample collection were completed in August 2022. Petrographic and electron microprobe analyses identified three generations of chemically and texturally distinct garnets in the rodingite (Fig 1. D). Disseminated round garnets (~200 μm; 75% grossular, 15% almandine, 8% andradite; #3 on Fig. 1D) are the most common, comprise ~70% of the matrix, and are parallel to the dominant foliation. Veins of garnetite (1-5 mm wide; 79% grossular, 11%

almandine, 8% andradite; #2 on Fig. 1D) crosscut the disseminated garnets. Massive aggregates of anhedral garnets (>.5 cm, 82% grossular, 15% andradite, 2% almandine; #1 on Fig.1D) are also crosscut by garnetite veins. In Fall 2023, Sm-Nd analyses will be conducted on the matrix, vein, and massive garnets from the rodingite. Garnet veins and massive garnets will be separated from the matrix garnets and analyzed using the methods described by Haws et al., 2021 (9). The analyses will be conducted at Boston College under the supervision of Professor Ethan Baxter, whose research group previously dated garnets in meta-rodingite that recrystallized at eclogite facies conditions (9). The rocks at Belvidere Mountain are key candidates for this study because they preserve mineral assemblages and structures from the Ordovician Taconic Orogeny and do not exhibit strong post-Taconic (i.e., post-serpentinization) retrograde metamorphism compared to other areas in the Appalachian Mountains (12), thus increasing the likelihood that the garnet ages reflect serpentinization and not subsequent metamorphism.

Enter brief timeline:

Summer 2022- Conducted field work. Fall 2022- Presented and discussed proposed garnet rodingite project with Professor Ethan Baxter. Conducted petrographic and electron microprobe analyses of the rodingite. Whole-rock geochemical analyses conducted. Spring 2023- Begin sample preparation at Syracuse University. Continue electron microprobe and Raman analyses. Summer/Fall 2023- Visit Boston College and conduct analyses. Spring 2024- Interpret results and write a manuscript for publication.

References cited in proposal:

(1) Robert, B., Domeier, M., and Jakob, J., 2021, On the origins of the Iapetus Ocean: Earth-Science Reviews, v. 221.; (2) Laird, J., Lanphere, M.A., and Albee, A.L., 1984, Distribution of Ordovician and Devonian metamorphism in mafic and pelitic schists from northern Vermont: American Journal of Science, v. 284.; (3) Moody, J.B., 1976, Serpentinization: a review: Lithos, v. 9.; (4) Deschamps, F., Godard, M., Guillot, S., and Hattori, K., 2013, Geochemistry of subduction zone serpentinites: A review: Lithos, v. 178.; (5) Meade, C., and Jeanloz, R., 1991, Deep-Focus Earthquakes and Recycling of Water into the Earth's Mantle: Science, v. 252.; (6) Guillot, S., and Hattori, K., 2013, Serpentinites: Essential roles in geodynamics, arc volcanism, sustainable development, and the origin of life: Elements, v. 9.; (7) Cooperdock, E.H.G., and Stockli, D.F., 2016, Unraveling alteration histories in serpentinites and associated ultramafic rocks with magnetite (U-Th)/He geochronology: Geology, v. 44.; (8) Bach, W., and Klein, F., 2009, The petrology of seafloor rodingites: Insights from geochemical reaction path modeling: Lithos, v. 112.; (9) Haws, A.A., Starr, P.G., Dragovic, B., Scambelluri, M., Belmonte, D., Caddick, M.J., Broadwell, K.S., Ague, J.J., and Baxter, E.F., 2021, Meta-rodingite dikes as recorders of subduction zone metamorphism and serpentinite dehydration: Voltri Ophiolite, Italy: Chemical Geology, v. 565.; (10) Allen, F., Buseck, P., 1988, XRD, FTIR, and TEM studies of optically anisotropic grossular garnets: American Mineralogist, v. 73.; (11) Stanley, R.S., and Ratcliffe, N.M., 1985, Tectonic synthesis of the Taconian orogeny in western New England (USA): Geological Society of America Bulletin, v. 96.; (12) Boutier, A., Vitale Brovarone, A., Martinez, I., Sissmann, O., and Mana, S., 2021, High-pressure serpentinization and abiotic methane formation in metaperidotite from the Appalachian subduction, northern Vermont: Lithos, v. 396-397.; (13) Ryan, P.C., Kim, J., Wall, A.J.,

and others, 2011, Ultramafic-derived arsenic in a fractured bedrock aquifer: Applied Geochemistry, v. 26.; (14) Brigham, J.M., Baldwin, S.L., 2022, Petrogenesis of arsenic and platinum-group minerals from a partially serpentinized dunite in East Dover, Vermont, USA. GSA Bulletin.

Available funds. Please explain if you currently have any funds available for the proposed geochronology work. Is your project unlikely to occur without AGeS support? If you require more money than AGeS can support, then where will those additional funds come from? Additional funds are not required:
Field work and preliminary analyses (XRF, microprobe, Raman) were supported by a grant from Syracuse University and by my advisor's funding. I do not currently have funding for the Sm-Nd garnet analyses. The geochronology portion of this project is dependent upon funding from AGeS. If this proposal is not fully funded by AGeS, then I intend to revise and resubmit or seek funding elsewhere.

Budget Table
List in order of priority and be sure to total up each column of budgeted item costs. If you intend to work with two AGeS labs, each budget item listed should indicate which lab it relates to.

	Budget Item	**Total Amount Budgeted**	**Amount Requested AGeS Program** (maximum of $10,000)
1.	Garnet Sm-Nd Analyses at Boston College	$3,000	$3,000
2.	Food while staying in Boston	$1,800	$1,800
3.	Mileage	$1,343	$1,343
4.	Parking at Boston College	$350	$350
5.			
6.			
7.			
8.			
	TOTALS:	**$6,493**	**$6,493**

Budget justification for funds requested from the AGeS program:
Budgets may include funds for travel to and from the AGeS lab where you propose to work, food and lodging while visiting the lab, analytical and training fees, equipment or consumables required for analysis, and sample preparation fees (including mineral separation accomplished at another facility if necessary). Requested budgets may not exceed $10,000 per proposal. AGeS awards do not go directly to the students nor to their institutions. Travel is generally reimbursed, although we also work with students for airfare purchased in advance, etc. to ease your financial burden. Lab and other processing costs are invoiced directly to ASU upon analysis completion. Awardees can spend up to

their award amounts in analytical and other costs until the date specified in their award documents (typically within one year of the award).

The cost of producing a 5-point isochron at Boston College, including training and consumables required for analysis, is $1,000 per garnet sample. This project will analyze 3 garnets (each textural garnet type: matrix, vein, and massive) to constrain the rodingite petrogenesis ($3,000 total). I will stay with family in the Boston area, 12 miles from the college. After discussing project goals with Professor Ethan Baxter, a timeline of approximately 3 months was recommended. I will be appointed as a visiting scholar during this time at Boston College. For food, I am requesting $1,800 ($20 per day for 90 days). For mileage, I am requesting $400 for travel from Syracuse to Boston and return (612 miles, 65.5 cents per mile). In addition, I request $943 to cover the commute to and from Boston College (24 miles per day, 20 days per month for 3 months, 65.5 cents per mile). Finally, I request $350 for a parking pass at Boston College. The total amount requested from AGeS-grad is $6,493.

Provide the full URL (''http://...'') to the lab profile provided of the collaborating AGeS lab. Lab profiles may be viewed at https://www.colorado.edu/program/agesgeochronology/lab-partners/lab-partner-list:
https://www.colorado.edu/program/agesgeochronology/sites/default/files/attached-files/BC-CIG_LabProfile.pdf

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If you intend to work with two AGeS labs, provide the full URL to the lab profile of the second collaborating AGeS lab:

Geochronology Experience
List what geochronology experiences you already have. Be specific. Enter "None" if you have no geochronology experience at all. One goal of AGeS is to expand access to geochronology data and expertise, so if you have limited or no geochronology experience it can be advantageous for the broader impacts of your proposal.

#1

Technique Used:
None

Lab Used:

Type of Experience:

Duration of Experience:

Project Notes:

#2

Technique Used:
None

Lab Used:

Type of Experience:

Duration of Experience:

Project Notes:

#3

Technique Used:
None

Lab Used:

Type of Experience:

Duration of Experience:

Project Notes:

#4

Technique Used: None

Lab Used:

Type of Experience:

Duration of Experience:

Project Notes:

#5

Technique Used: None

Lab Used:

Type of Experience:

Duration of Experience:

Project Notes:

Geochronology Opportunities:

Explain what geochronology opportunities that you already have through your existing thesis research. Do you have local access to geochronology facilities and expertise? Does your advisor direct a geochronology lab? Does your advisor's research group regularly use the technique you propose to use in this project?

My advisor (Suzanne Baldwin) directs a noble gas lab at Syracuse University, and I assist with lab maintenance. Magnetite (U-Th)/ He has been used to date exhumation histories (not serpentinization timing) of altered ultramafic rocks (7), but the He line in our lab has been decommissioned. The serpentinite and rodingite samples that I am working with do not contain minerals applicable for analysis at the noble gas lab. Our research group has not used the Sm-Nd technique before.

New Collaborations and Improved Sense of Belonging.

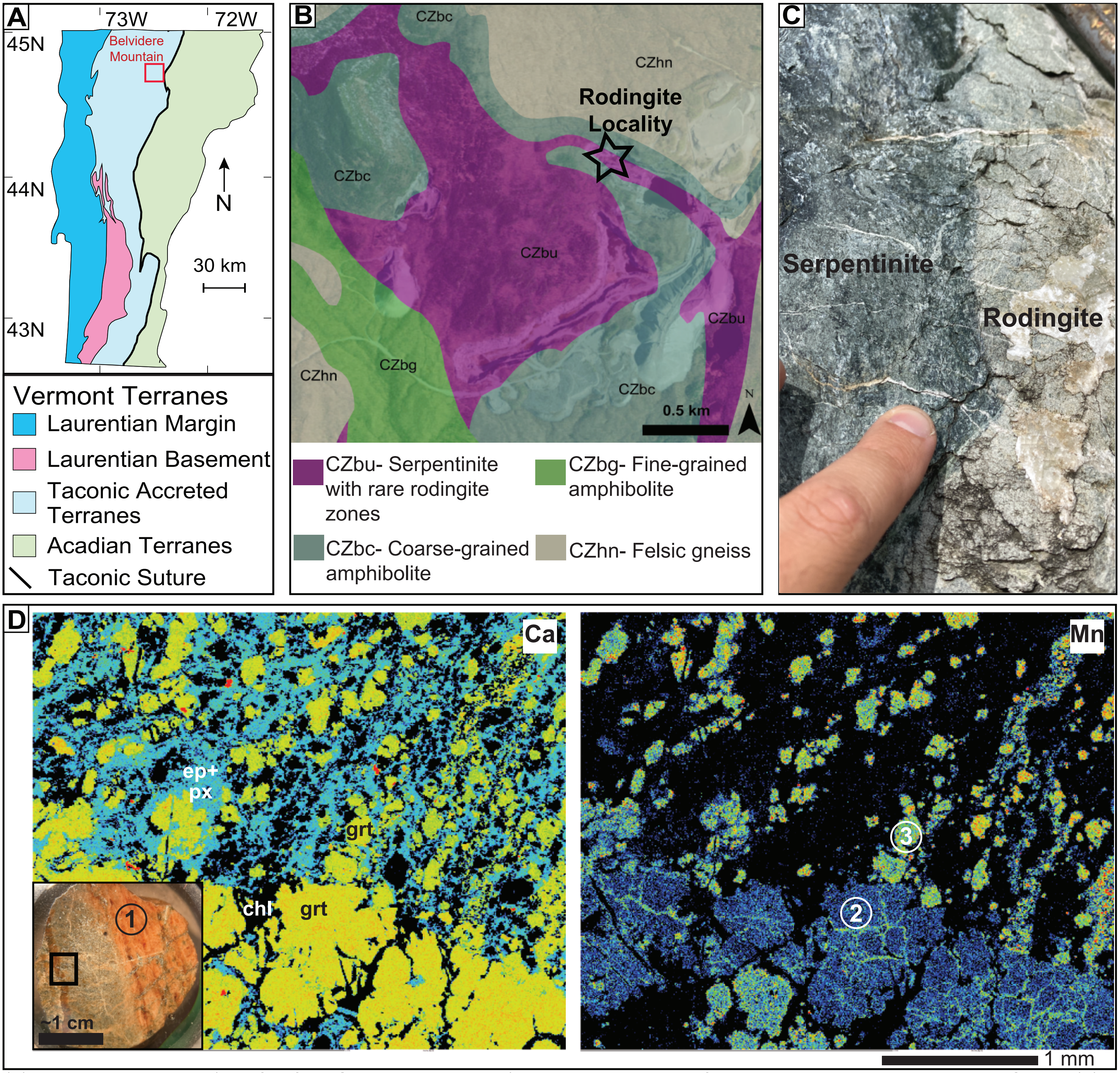
Explain the extent to which this project represents a new collaboration, new access to geochronology data or expertise, and/or an opportunity to strengthen your geoscience network. Are there ways in which your project and your experience address and support Belonging, Accessibility, Justice, Equity, Diversity and Inclusion (BAJEDI) values? Be specific. You may find it helpful to refer to the **AGeS inclusive community pages** as you write your response to this prompt.

This project will be a new collaboration for myself, my advisor, and Ethan Baxter's Sm-Nd lab at Boston College. My experience as a first-generation college student has taught me the importance of inspiring young people of all backgrounds that they can pursue careers in science. I am a volunteer at the Southern Vermont Natural History Museum and, to promote scientific interest in young people, I will write a summary of my research to display alongside garnet samples from Belvidere Mountain.

Have you previously received an AGeS award? (Graduate students are eligible for one AGeS grant during each graduate degree.):

No.

Figure 1: Maps and Images Highlighting the Rodingite Locality at Belvidere Mountain in Lowell, Vermont, USA.



(A) Vermont terrane map (modified from Gonzalez et al., 2020) showing the location of Belvidere Mountain and the Taconic Suture. (B) Simplified bedrock geologic map (modified from Ratcliffe et al., 2011) draped over an aerial image showing the lithologies that comprise the Belvidere Mountain Complex. Rodingite is hosted in serpentinite (unit CZbu), and the locality sampled in this study is shown by the star. (C) Photograph showing the contact between serpentinite and rodingite. (D) Electron microprobe X-ray maps of the Belvidere rodingite showing calcium and manganese X-ray intensities. Warmer colors (red, yellow) indicate higher concentrations of Ca and Mn compared to cooler colors (blue, black). Major minerals are labeled in the Ca map (grt=garnet, yellow; ep+px=epidote and altered pyroxene, blue; chl=chlorite, black). Inset shows a photograph of the rodingite sample used for analysis with a box highlighting the mapped area. Numbers on inset photograph and Mn map indicate the three texturally and chemically distinct garnet types that will be dated (1=massive garnet [shown in inset photograph, not in X-ray maps]), 2=garnetite vein, 3=disseminated garnet). The Mn map highlights the compositional variation between vein garnets (#2, lower manganese) and disseminated garnets (#3, higher manganese).

References: Ratcliffe, N.M., Stanley, R.S., Gale, M.H., Thompson, P.J., and Walsh, G.J., 2011, Bedrock geologic map of Vermont: U.S. Geological Survey Scientific Investigations Map 3184.

Gonzalez, J.P., Baldwin, S.L., Thomas, J.B., Nachlas, W.O., and Fitzgerald, P.G., 2020, Evidence for ultrahigh-pressure metamorphism discovered in the Appalachian orogen: Geology, v. 48