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https://doi.org/10.1130/GES02812.1

13 figures; 1 set of supplemental files

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CITATION: Hollocher, K., Mundell Forgeng, H., Stack, K.M., Morgan, E., Denny, A., and Lott, E.A., 2025, Origin of big garnet amphibolites at Gore Mountain and other localities, Adirondack Mountains, New York State, USA: Whole-rock geochemical constraints: Geosphere, https://doi.org/10.1130 /GES02812.1

Science Editor: Christopher J. Spencer Associate Editor: Michael L. Williams

Received 19 July 2024 Revision received 3 January 2025 Accepted 13 January 2025

Published online 10 February 2025





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Origin of big garnet amphibolites at Gore Mountain and other localities, Adirondack Mountains, New York State, USA: Whole-rock geochemical constraints

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ABSTRACT

The Barton Mine garnet amphibolite orebody on Gore Mountain hosts garnet porphyroblasts routinely 15-30 cm across. The orebody was developed in the southern margin of a metamorphosed olivine gabbro pluton. Cumulate layering within the gabbro continues into the orebody in some places, through a transition zone 1–3 m thick. Though chemically similar for most elements, the orebody and transition zone are irregularly enriched in Li (x4) and depleted in Cs (x0.07) and Th (x0.15) relative to the gabbro. Though rare earth element patterns for elements heavier than Nd are similar, the average La,/Nd, ratio in gabbro is 1.45, but it gets as low as 0.94 in ore whole rock. Orebody wholerock δ¹⁸O values from previous workers range from ~6.8‰, typical for Adirondack olivine gabbro, to ~4.1‰. This indicates that the olivine gabbro south margin was hydrothermally altered and hydrated with meteoric water during emplacement in the upper crust. Ottawan Orogeny (ca. 1090-1040 Ma) granulite-facies metamorphism produced both the dry, fine-grained pyroxene granulite assemblages in the dry gabbro and the damp, coarse garnet amphibolite assemblages in the orebody. The non-ore-grade Warrensburg garnet amphibolite has been poorly studied compared to that at Barton Mine, but it is similar in having garnet porphyroblasts up to ~10 cm

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across and probable derivation from an olivine gabbro protolith. Compared to a nearby, compositionally similar olivine gabbro, Warrensburg amphibolite is enriched in Li (\times 1.4) and Cs (\times 6, opposite to the trend at Barton Mine) and depleted in Th (\times 0.6). La_n/Nd_n ratios in the amphibolite are also slightly lower than in the gabbro. Though the apparent chemical changes compared to nearby gabbros are different than those at Barton Mine, we infer that they also took place during low-temperature hydrothermal alteration. The geochemistry of the Ruby Mountain garnet deposit is even less well studied than the Warrensburg deposit. It was derived from an anorthositic troctolite precursor, rather than olivine gabbro.

INTRODUCTION

The Adirondack region is part of the extensive middle Proterozoic Grenville geologic province in eastern and southeastern North America (Fig. 1). The Adirondack region is an eastward peninsular extension of the exposed Grenville orogenic belt, surrounded by Paleozoic sedimentary rocks. The geologic history of the Adirondacks is complex and involved several generations of volcanic arc development, arc-continent and continentcontinent collisions, and metamorphism, with igneous emplacement ages of ca. 1426–1024 Ma (e.g., Heumann et al., 2006; McLelland et al., 2010). The Grenville orogenic episode culminated with the Ottawan (ca. 1090–1020 Ma) continent-continent collision between Rodinia and Amazonia, with resulting regional metamorphic grades of amphibolite to granulite facies for rocks now exposed in the Adirondack Highlands (Bohlen et al., 1985; Mezger et al., 1991; Spear and Markussen, 1997; Storm and Spear, 2002, 2005; Peck and Valley, 2004; Ream and Dunn, 2008).

One of the products of Ottawan metamorphism was amphibolite containing especially large almandine-rich garnets. The Barton Mine locality on Gore Mountain is well known for having garnet porphyroblasts of large size, with some exceeding 30 cm (up to 90 or 100 cm; Levin, 1950; Luther, 1976; McLelland and Selleck, 2011). Big garnet amphibolites also occur as smaller bodies in numerous other localities in the eastern Adirondacks (Krieger, 1937; Levin, 1950; Bartholomé, 1960; McLelland et al., 2011, stop 1). Here, we examined the geochemistry of rocks from three garnet localities, with emphasis on the Barton Mine site, to gain insight into the processes that produced these remarkable rocks.

DESCRIPTIONS OF THE GARNET LOCALITIES

Barton Mine Locality

The Barton Mine pit on the north flank of Gore Mountain, North River, New York, USA, was active



Figure 1. Generalized geologic map of the Adirondacks and southern Canadian part of the Grenville Province, with large anorthosite bodies shown. Locations of Figures 2 and 4 are indicated. Geology is adapted from Ludden and Hynes (2000).

from 1878 to 1983 (Fig. 2; Kelly and Darling, 2002) and produced garnet abrasive material for sandpaper, grinding and polishing, sand blasting, water jet cutting, and other uses. It is now a summer tourist attraction as the Gore Mountain Gem and Mineral Shop. The geology has been discussed at length by many others (e.g., Levin, 1950; Bartholomé, 1960; Luther, 1976; Sharga, 1986; Weakliem, 1984), so here we summarize the information. The most abundant rocks surrounding the Barton Mine and many other garnet orebodies (Fig. 2A) are metamorphosed syenite, anorthosite, granite, and gabbro. The exact age relations of these rock bodies are not always clear, but most belong to the anorthosite-mangeritecharnockite-granite (AMCG) suite that is abundantly exposed in the Adirondack Highlands. The AMCG suite also includes coeval gabbro and olivine gabbro. These rocks have emplacement ages of ca. 1165-1145 Ma (McLelland et al., 2010; Valentino et al., 2019) and were magmas produced following: (1) collision of a volcanic arc with composite Laurentia (Shawinigan orogeny, 1180-1165 Ma) and (2) foundering of the subducted slab and possibly delamination of subarc lithosphere with production

of postcollision AMCG suite magmas from upwelling asthenospheric mantle (Hamilton et al., 2004; Heumann et al., 2006; Chiarenzelli et al., 2010; Regan et al., 2011; Valentino et al., 2019). The gabbros are generally tholeiitic and are somewhat enriched in light rare earth elements (LREEs) and other incompatible elements (Olson, 1992; Regan et al., 2011).

The Barton Mine garnet orebody (Fig. 2B) forms a zone ~100 m wide and 1500 m long (Luther, 1976) between metamorphosed pyroxene syenite to the south and metamorphosed layered olivine gabbro to the north. This gabbro body contains anorthosite xenoliths, and so it is interpreted to have intruded the adjacent anorthosite (Luther, 1976; Sharga, 1986). Luther (1976) and Sharga (1986) described in detail a fault at the orebody's southern contact with pyroxene syenite. The fault has evidence of both ductile (high-temperature minerals, foliation, isoclinal folds) and brittle deformation (slickensides, microbreccias, low-temperature phyllosilicates). These observations indicate that there was movement along this surface multiple times under different conditions. The fault is not mapped much beyond the mine pit, and its offset is unknown.

The gabbro-orebody contact is transitional over 1–3 m. The garnet ore was derived from the gabbro, as indicated by cumulate layering in the gabbro that can be traced without interruption or strong deflection through the transition zone into the garnet ore (Luther, 1976; still visible in pit 1), and by very similar gabbro and orebody compositions. The gabbro that was parental to the garnet ore has not been dated to our knowledge, but it is probably similar in age to other 1154 \pm 6 Ma AMCG suite gabbros of nearly identical lithology and composition (McLelland et al., 2004, 2011). The pyroxene syenite south of the southern contact has been dated at 1154 \pm 17 Ma (Hamilton et al., 2004).

The Barton Mine garnet orebody metamorphism has been dated by a number of workers using different chronometers: hornblende-garnet Sm-Nd (1059 \pm 19 Ma-Basu et al., 1989; 1051 \pm 4 Ma-Mezger et al., 1992), garnet Lu-Hf (1046.6 \pm 6.1 Ma-Connelly, 2006), and zircon U-Pb (1055 \pm 2 Ma-Scherer et al., 2000; 1053.9 \pm 5.4 Ma-Shinevar et al., 2021). These yielded a weighted mean Ottawan age for garnet growth of ca. 1054 \pm 2 Ma. This age is consistent with a granitic pegmatite



Figure 2. Geologic map of the North River–Barton Mine area. (A) Smaller scale map, adapted from Krieger (1937) in most of the area. Geology inside the dashed line was adapted from Sharga (1986, fig. 3). (B) Detailed geologic map of the Barton Mine excavation, showing sample traverse locations, geology adapted from Luther (1976, plate 1), with pit boundary cliff locations from Goldblum and Hill (1992).

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Hollocher et al. | Gore Mountain garnet

that cuts the orebody having a zircon U-Pb age of 1045 \pm 7.5 Ma (McLelland and Selleck, 2011). This pegmatite and similar-age granites elsewhere in the Adirondacks have been interpreted to be related to 1050–1025 Ma decompression melting during unroofing and uplift of the region late in the Ottawan orogenic episode (Lyon Mountain Granite and pegmatites; Scherer et al., 2000; Bickford et al., 2008; McLelland and Selleck, 2011; Wong et al., 2012; Chiarenzelli et al., 2019).

Olivine gabbro on the north flank of Barton Mine has assemblages and textures indicative of fluidabsent granulite-facies metamorphism, containing the typical but texturally complex assemblage plagioclase-clinopyroxene-orthopyroxene-garnetbrown hornblende-Fe-Ti oxide-olivine-red-brown biotite-spinel. This and similar gabbro bodies in the Adirondacks were scarcely deformed during Ottawan granulite-facies metamorphism, as indicated by common preservation of relict igneous cumulate textures defined by layering, and by subhedral blocky plagioclase and interstitial pyroxene (Levin, 1950; Luther, 1976; McLelland and Selleck, 2011). Cumulus plagioclase, olivine, and Fe-Ti oxides have been highly modified by fluid-absent, diffusion-controlled metamorphic reactions that formed corona (concentric shell) textures (Bartholomé, 1960; Whitney, 1972; McLelland and Whitney, 1980; Johnson and Carlson, 1990). Though the corona sequence varies considerably, olivine is characteristically surrounded by layers in the sequence: olivine, orthopyroxene (Opx), clinopyroxene (Cpx) ± plagioclase, garnet ± plagioclase, and garnet. Around Fe-Ti oxide grains, the corona sequence is typically: ilmenite-red-brown biotite ± spinel-brown hornblende ± spinel-garnet. Blocky plagioclase between the coronas is green in outcrop (Fig. 3A) and in thin section because of abundant, minute green spinel inclusions, which precipitated from excess Mg, Fe, and Al during the corona-forming reactions. In contrast, the garnet amphibolite orebody is completely recrystallized and has been somewhat deformed with a faint foliation generally oriented E-W and dipping ~45° to the north, and lineations ranging from steeply plunging to roughly horizontal within the foliation plane (Goldblum and Hill, 1992).

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Figure 3. Field photos of typical sampled lithologies. (A) Corona gabbro from the north margin of Barton Mine pit 1, showing greenish plagioclase. Garnet grains in pinkish areas are ~0.1 mm across. (B) Garnet ore, Barton Mine pit 1, in which the largest garnet porphyroblasts are ~14 cm across. (C) Warrensburg garnet amphibolite, where largest garnet porphyroblasts are ~9 cm across. (D) Garnet ore from Ruby Mountain, upper pit, where largest garnet porphyroblasts are ~3 cm across.

In the Barton Mine corona gabbro, garnet typically occurs as equant $50-100 \ \mu m$ grains. Through the 1–3-m-thick transition zone, hornblende becomes more abundant and coarser, and it changes color from brown to brownish-green. Most or all Cpx and Fe-Ti oxides and most Opx are replaced by hornblende. Biotite changes color from red-brown to brown and becomes somewhat less abundant, and plagioclase becomes colorless as it has recrystallized and lost all spinel inclusions. Garnet grains become larger in size across the transition zone while remaining almost constant in modal abundance and composition (approximately Al₄₇Py₄₀Gr₁₂Sp₁; Levin, 1950; Luther, 1976; Sharga and Sclar, 1987). Major-element whole-rock compositions do not change for most elements across the transition zone, within analytical and mineral mode uncertainties. H_2O content increases from ~0.6% in the gabbro and 0.8% in the transition zone to 1.1% in the orebody. Fe^{3+}/Fe_{total} increases in the same sequence: 0.08, 0.13, and 0.16 (Shand, 1945; Levin, 1950; Bartholomé, 1960; Luther, 1976).

The amphibolite matrix surrounding garnet porphyroblasts in the orebody has grains typically 1–5 mm across and is made of hornblende, plagioclase, minor biotite, and Opx, and traces of apatite, ilmenite, and pyrrhotite. Cpx is rare, though it can be abundant in other big garnet amphibolites in the Adirondacks (e.g., McLelland et al., 2011, stop 1, based on our own samples). Matrix amphibolite minerals are typically inhomogeneous. Hornblende grains tend to have slightly browner (Ti-richer) cores and greener rims. Individual plagioclase grains can have small amounts of irregular zoning, and internal composition boundaries (not twin planes) can be sharp enough to yield Becke lines. This texture suggests dissolution and reprecipitation during orebody deformation, not exsolution or two coexisting plagioclase phases on either side of a miscibility gap. Garnet porphyroblasts in the orebody are somewhat zoned, particularly near their rims, where they tend to be more Ca-rich and Mg-poor. Garnet margins are also commonly surrounded by calcic plagioclasehornblende–Opx \pm biotite symplectites 0.5–5 mm thick, visible in outcrop, that probably represent a late metamorphic garnet-consuming decompression reaction (McLelland and Selleck, 2011; Shinevar et al., 2021). Garnet porphyroblasts are commonly surrounded by black hornblendite rims <1–4 cm thick (Fig. 3B), particularly in the central and western parts of the orebody. Garnet porphyroblasts are commonly associated with coarse strain shadows adjacent to garnet or hornblendite rims that can contain 1–3 cm grains of euhedral to subhedral plagioclase, Opx, hornblende, and biotite, but coarse, irregular patches are also common away from garnet porphyroblasts (Shaub, 1949; Luther, 1976; McLelland and Selleck, 2011).

Warrensburg Locality

Located ~30 km southeast of the Barton Mine site, the most accessible Warrensburg big garnet amphibolite outcrops (Fig. 4) are at the intersection of East Schroon River Road and Wall Street near Highway I-87, ~2 km east-northeast of the town of Warrensburg, New York (McLelland and Selleck, 2011). Lacking in the commercial attraction of the Barton Mine body, this occurrence has received



Figure 4. Geologic map of the Warrensburg area, showing sample locations. There is no single large-scale map that covers this area, so the geology was adapted from five sources: SE corner, Fisher (1985); SW corner, Miller (1923); NW corner, Miller (1914); NE corner, Dicken et al. (2008); and for the E-W-oriented gabbro body from which corona gabbro samples were taken, not shown on other maps, Thompson et al. (1990).

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much less attention in the literature. We will discuss only the 70-m-long exposure on the east side of Wall Street, and a gabbro exposure 2 km to its south.

The Warrensburg garnet amphibolite is much like the Barton Mine orebody (Fig. 3C), but garnet porphyroblasts are generally smaller (up to 10 cm) and less abundant (3%-5% of the rock), and many lack or have only partial hornblendite rims. The commonly slightly elongate garnet porphyroblasts are associated with coarse strain shadows that, along with faint streaking in the finer-grained garnet-free matrix, define a steeply plunging lineation. The strain shadows contain anhedral to euhedral plagioclase, Opx, hornblende, and biotite, and these and garnet are set in a finer-grained (1-5 mm) matrix of hornblende, plagioclase, biotite, Opx, ilmenite, and pyrrhotite, ± Cpx. This amphibolite matrix contains more biotite than that at Barton Mine (~3% vs. ~1%), more ilmenite (~1% vs. ~0.1%), and more pyrrhotite (~0.2% vs. <0.1%). At the north end of the Warrensburg exposure, the garnet amphibolite is in contact with felsic rocks. The contact is a sharp, smooth, curved surface coated with biotite. Immediately north of the contact, there is a tonalitic pegmatite ~1 m thick. The pegmatite grades northward into migmatitic white tonalitic gneiss ~5 m thick, which grades into white granitic gneiss ~6 m thick and then into pink granitic gneiss. None of these rocks has been dated, to our knowledge. Within a few meters of the contact, garnet grains in the amphibolite become smaller and less abundant. Half a meter from the contact, garnet vanishes, biotite becomes somewhat more abundant, and the amphibolite becomes finer grained.

The Warrensburg garnet amphibolite is inferred to have formed from a gabbro body like that at Barton Mine (McLelland and Selleck, 2011), but gabbro–garnet amphibolite contacts are not exposed, so this relationship is hypothetical. Corona gabbro is found ~2 km south along a road cut next to the northbound Exit 23 ramp of Highway I-87 (Fig. 4). Like that at Barton Mine, the Warrensburg gabbro has green plagioclase and minor olivine in the centers of some coronas. In the outcrop, there is

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also a garnet-rich and Fe-Ti oxide–rich rock in sharp contact with the gabbro, which we interpreted to be a premetamorphic ferrogabbro dike.

Ruby Mountain Locality

Ruby Mountain (Fig. 2) has been an active Barton Group (formerly Barton International) garnet mine since 1983. The orebody is a severely deformed and metamorphosed, garnet-rich gneissic anorthositic troctolite (Fig. 3D). The ore rock is inhomogeneous and has been cut by numerous garnet-rich and Fe-Ti oxide-rich metamorphosed ferrogabbroic dikes. Garnet porphyroblasts are commonly 3-5 cm across in the gneiss, and they commonly have plagioclase-rich rims or occur in coarse, nebulous leucocratic patches. The garnet orebody is not associated with olivine gabbro or another distinct precursor or protolith (Miller, 1912; Krieger, 1937; Levin, 1950; Novillo and Sclar, 1982; R.R. Rapple, Barton International, 2007, personal commun.). However, the orebody is underlain by a strongly deformed, non-olivine-bearing metagabbro unit (Weakliem, 1984), which has smaller garnet grains than the gneiss and is not ore grade.

Although the Ruby Mountain orebody is distinct from most garnet ore at Barton Mine and Warrensburg, garnet-rich leucocratic gneiss similar to that at Ruby Mountain occurs at the eastern end of the Barton Mine orebody, near its contact with anorthosite (Fig. 2; "white" or "light" ore: Novillo, 1981; Novillo and Sclar, 1982; Weakliem, 1984). The Ruby Mountain orebody is also lithologically similar to that exposed at Hooper Mine (Fig. 2), another local garnet orebody that was mined from 1894 to 1904 (Krieger, 1937).

SAMPLES AND ANALYTICAL METHODS

Samples were collected for petrographic and geochemical purposes from outcrops excavated in the past 120 yr, and so they were quite fresh.

At Barton Mine, only grab samples were available in pit 1 (Fig. 2B), which is preserved as an historical site, but access was granted to parts of pits 4 and 9, where collection traverses were made across the gabbro-garnet orebody transition zone, and some grab samples were also collected. All highwalls more than a few meters high were off limits to collecting for safety reasons, so no samples or close examination of lithologic variations came from most of those areas. At Warrensburg, a sampling traverse was made along the Wall Street garnet amphibolite outcrop, and another, shorter traverse was made along the I-87 northbound Exit 23 ramp where corona gabbro and a ferrogabbro dike are exposed. At Ruby Mountain, an active mine, only grab samples were available as all highwalls were off limits.

Relatively fine-grained samples (garnet grains <25 mm) weighing 2-40 kg depending on grain size were crushed for analysis. For Barton Mine, wholerock compositions of coarser garnet amphibolite were calculated from analyzed separates of bulk garnet (with any inclusions), hornblendite rims on garnet, and amphibolite matrix, combined in the weight proportions 11:15:74, respectively, typical of the "dark" ore (Levin, 1950). At the Warrensburg outcrop, few fine-grained garnet amphibolites were available. Instead, mostly amphibolite matrix samples were collected and analyzed. Two whole-rock compositions were calculated from two samples, with analyzed separates of matrix amphibolite and extracted coarse garnet-Opx-plagioclase-hornblende-biotite segregations (Fig. 3C), combined in weight proportions 10:1, respectively (our estimate), yielding ~4.5% garnet in the resulting whole rock. For Ruby Mountain, three whole-rock samples were crushed and analyzed. Sample crushing and analysis were done using methods described in Hollocher et al. (2007). Data can be found in Tables S1, S2, and S3.1 In addition, 149 polished thin sections were made for petrographic examination and microbeam analysis. Microbeam analyses were done as described in Hollocher et al. (2015, not shown but mentioned in the Thermodynamic Modeling section).

¹Supplemental Material. Excel file: Tables S1–S3; PDF file: Tables S4–S5, Figures S1–S5: annotated outcrop photographs, and Figures S6–S14: explanation of thermodynamic calculations and thermodynamic results. Please visit https://doi.org/10.1130/GEOS.S.28200308 to access the supplemental material; contact editing@geosociety.org with any questions.

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Major Elements

Figure 5 shows major-element graphs of samples analyzed in this and other studies. Corona gabbro samples from Barton Mine define linear composition trends, suggesting the dominant influence was the proportion of cumulus olivine + pyroxene versus plagioclase, with little or no titanomagnetite control. Five gabbro samples are anomalously MgO-rich, which include grab and outcrop samples from pits 1, 4, and 9, but these samples were collected more or less at random because there was little obvious difference in field appearance. The lack of similar MgO-rich, Al₂O₃-poor garnet amphibolite samples probably resulted from our own inadvertent sampling bias against amphibolites with little or no garnet, which likely would have had MgO-rich compositions. We did not encounter garnet-poor rocks in the four transition zone traverses.

Figure 5A shows that data for some composite whole-rock and matrix samples are displaced toward higher MgO and/or higher Al₂O₃ compared to the gabbro trend by ~0.5-1 wt%. That could have been caused by less cumulus titanomagnetite or Cpx, though the lack of similar displacement toward lower TiO₂ in Figure 5B indicates that less Cpx accumulation was more likely. Figure 5C shows that all amphibolite composite whole-rock and most matrix samples have ~0.5-1 wt% higher CaO and/or 1-2 wt% higher MgO than the Mg-poorer gabbros. This may have been caused by more Cpx accumulation, in apparent contradiction to what can be inferred from Figure 5A, suggesting that other processes were involved in producing these CaO-rich and/or MgO-rich garnet amphibolite compositions (e.g., hydrothermal alteration).

Warrensburg samples were clearly derived from a more evolved (fractionally crystallized) magma than those at Barton Mine, as indicated by their lower MgO and higher TiO₂ contents, and their lower Mg# of $0.53 \pm 0.01 2\sigma$ (molar Mg/[Mg + Fe_{total}]) for composite whole rocks, compared to the Barton Mine value of $0.63 \pm 0.02 2\sigma$. The Warrensburg garnet amphibolites have somewhat lower Al₂O₃ and TiO₂ contents than the nearby gabbros,



Figure 5. Graphs for some major elements: (A) Al₂O₃ vs. MgO, (B) Al₂O₃ vs. TiO₂, and (C) CaO vs. MgO. Arrows show directions of composition change caused by crystal accumulation, with arrow lengths proportional to accumulation of the same mass of each phase. Small colored circles are Barton Mine analyses from other workers (Buddington, 1939; Shand, 1945; Levin, 1950; Bartholomé, 1960; Luther, 1976; Olson, 1992; Shinevar et al., 2021). Small black dots are anorthosite-mangerite-charnockite-granite suite gabbros and leucogabbros from elsewhere in the Adirondacks (Olson, 1992; Seifert et al., 2010; Regan et al., 2011). Cpx-clinopyroxene; Ol-olivine; Opx-orthopyroxene; Plag-plagioclase; TiMt-titanomagnetite.

but similar CaO and MgO contents. Figures 5A–5C suggest the dominant control for Warrensburg rock compositions was the relative proportion of cumulus plagioclase versus mafic minerals including titanomagnetite.

Data for gabbros and gabbroic anorthosites from elsewhere in the Adirondacks (not Barton

Mine or Warrensburg) are shown in Figure 5 as tiny black dots. These indicate that more evolved gabbro compositions like those in Warrensburg are common in the Adirondacks, but more primitive compositions like those at Barton Mine are less common. In particular, the MgO-rich gabbro compositions at Barton Mine seem to be rare elsewhere.

Samples from Ruby Mountain have higher CaO and Al₂O₃ than all other samples, except for CaO in the Warrensburg ferrogabbro dike. They also have relatively low concentrations of MgO and TiO₂. These compositional differences compared to the Warrensburg and Barton Mine samples are expected, considering the inferred anorthositic troctolite protolith for Ruby Mountain ore. However, data from gabbros and gabbroic anorthosites elsewhere in the Adirondacks do not plot with the Ruby Mountain samples in Figure 5A, and few do in Figure 5C. Anorthositic rocks having Al₂O₃ contents of ~21% like the Ruby Mountain samples typically have much less than 6% MgO. Volume norms calculated for the three analyzed Ruby Mountain samples (not shown) indicate that the protolith was troctolitic rather than gabbroic, which may be unusual for other AMCG suite mafic rocks in the Adirondacks.

Lanthanides

Figure 6 shows rare earth element (REE) diagrams for samples from the three localities. Figure 6A shows that the average REE pattern for Gore Mountain corona gabbros lies below most individual samples from the garnet amphibolite orebody. As noted in the Major Elements section, five of the 15 gabbro samples have >12% MgO, and these also have lower concentrations of REEs and other incompatible trace elements like Ta and Zr. If those five gabbros were excluded, the average pattern would be almost coincident with the garnet amphibolite average from Nd to Lu. For La, Ce, and Pr, there is a concave-down curvature in normalized REE values for amphibolites, whereas gabbros have straight, negative slopes across the LREEs. Models combining different cumulus mineral modes (not shown) indicate that this La-Ce-Pr curvature did not result from different cumulus mineral or trapped liquid modes, so it must have had another cause. Figure 6B shows that the gabbro Eu anomaly size varies inversely with Sm concentration, probably the result of differing proportions of cumulus plagioclase and trapped intracumulus liquid.

Warrensburg gabbro REE patterns (Fig. 6C) are similar in shape to those of Barton Mine, and both



Figure 6. (A) Barton Mine rare earth element (REE) patterns. (B) Barton Mine Eu anomaly $(Eu_n/[Sm_n \times Gd_n]^{0.5})$ showing negative correlation with Sm_n. (C) Warrensburg REE patterns. (D) Warrensburg Eu anomaly showing negative correlation with Sm_n. (E) Ruby Mountain REE patterns, compared with Barton Mine gabbro and garnet amphibolite averages. Chondrite normalizing values are from McDonough and Sun (1995).

have the same La_n/Yb_n ratios (average 3.2 at both localities). However, the Warrensburg samples have ~2.5 times higher REE concentrations and no Eu anomalies, consistent with their origin as cumulates from more fractionally crystallized magmas. Warrensburg amphibolites have somewhat higher REE concentrations than the nearby gabbros. Some of the garnet amphibolite patterns have the same concave-down curvature for La, Ce, and Pr as is seen in Barton Mine samples, but to a lesser extent. Warrensburg gabbros have an inverse relationship between Eu anomalies and Sm like those at Barton Mine (Fig. 6D), though the relationship is less distinct, in part perhaps because there are fewer samples.

Ruby Mountain middle REE (MREE) and heavy REE (HREE) patterns (Fig. 6E) have shapes similar to those of Barton Mine gabbros and amphibolites, with somewhat lower average concentrations. These samples also have concave-down curvatures toward the lightest REE, similar to some garnet amphibolites at Barton Mine and Warrensburg. However, it is difficult to infer the cause of this curvature because there is no known parental

rock–garnet ore relationship at Ruby Mountain (Miller, 1912; Krieger, 1937; Levin, 1950; Novillo and Sclar, 1982; R.R. Rapple, Barton International, 2007, personal commun.).

Multi-Element Comparison

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Figure 7 shows rock compositions for most of the analyzed elements normalized to average corona gabbro at Barton Mine (Fig. 7A) and Warrensburg (Fig. 7B). Although the older literature has noted almost identical major-element compositions for Barton Mine garnet amphibolite ore and its parental gabbro (except for higher H_2O and Fe³⁺/Fe_{total} in the amphibolites; Levin, 1950; Bartholomé, 1960; Luther, 1976), there are some substantial trace-element differences. As seen in Figure 7A, Barton Mine garnet amphibolite matrix samples are enriched in Li compared to the corona gabbro 2σ range, and they are depleted in Rb, Cs, Pb, Th, and U. Though the uncertainty is greater for some elements, the same elements are also enriched or depleted in composite whole-rock compositions. These gabbro-orebody differences are unlikely to have been the result of differences in crystal fractionation, crystal accumulation, or proportion of cumulate trapped liquid because all of the listed elements are incompatible to highly incompatible in basalt systems, and so they should have behaved similarly (Bacon and Druitt, 1988; Blundy et al., 1998; Brenan et al., 1998).

It is necessary to interpret Figure 7B somewhat differently than Figure 7A. Recall that the Warrensburg gabbro is exposed ~2 km south of the garnet amphibolite outcrop, so the amphibolite is unlikely to have been derived from gabbro of the exact same composition. However, by analogy with Barton Mine and similar corona gabbro-big garnet amphibolite associations elsewhere in the Adirondacks (McLelland and Selleck, 2011), such amphibolites are observed or inferred to have been derived from precursor olivine gabbro. Major- and trace-element concentrations for both the Warrensburg gabbro and garnet amphibolite are quite similar for most elements, so here we use that gabbro as a reasonable proxy for the garnet amphibolite protolith.

In the Warrensburg garnet amphibolite matrix and composite whole-rock analyses, Zr, Nb, Sm, and Gd to Lu (Fig. 7B; also Y, Nd, Hf, Ta) all have similar enrichment factors compared to the nearby gabbro, $1.27 \pm 0.11 2\sigma$. These incompatible elements are generally thought to be resistant to mobility during most metamorphic and alteration processes



Figure 7. Concentrations of the most analyzed elements, normalized to average corona gabbro at each locality (excluded are Si, C, Y, Sb, Hf, Ta, and half of the lanthanides). (A) Barton Mine: The corona gabbro average excludes the five samples having MgO > 12%. Ruby Mountain samples are normalized to the same corona gabbro for comparison purposes. (B) Warrensburg: The corona gabbro average does not include the metamorphosed ferrogabbro dike (sample W100). The Warrensburg amphibolite matrix average excludes samples W121A and W121B, which were collected adjacent to a pegmatite and have somewhat anomalous compositions. Error bars are 2o.

Hollocher et al. | Gore Mountain garnet

(e.g., Winchester and Floyd, 1977; Greenough et al., 1990; Hastie et al., 2007; John et al., 2008), are not among elements already known to have anomalous concentrations at Warrensburg or Barton Mine (Li, Rb, Cs, La–Pr, Pb, Th, U), and are not important constituents in likely liquidus phases like TiO_2 in titanomagnetite. Thus, the similar enrichment of these elements in the garnet amphibolite relative to the nearby gabbro indicates that they were likely uniformly enriched in the amphibolite protolith by crystal fractionation or larger cumulus trapped liquid fraction.

Incompatible elements with enrichment factors outside of the range of 1.27 ± 0.11 include Cs, enriched by a factor of ~6, and Pb, enriched by a factor of ~1.6 (Fig. 7B). Th is depleted by a factor of ~0.6. Enrichment factors for the two whole-rock composite samples are somewhat different, but in the same directions. Taken together, these incompatible element concentration differences between Warrensburg garnet amphibolite and gabbro likely indicate that they differ by more than their degree of fractional crystallization or cumulus trapped liquid fraction.

Ruby Mountain samples (Fig. 7A) also seem to be somewhat enriched in Li and depleted in Cs and LREEs and other elements compared to Barton Mine gabbro. Although it is possible that these elements differ from Barton Mine gabbro for the same reasons that the garnet amphibolite does, such a determination is impossible to make without a distinct body of parental material for comparison. The elements that are depleted at Ruby Mountain relative to Barton Mine gabbro tend to be incompatible to highly incompatible, which may indicate that the ore rock protolith was a plagioclase-rich adcumulate, containing little trapped liquid that would have carried the highest incompatible element concentrations.

Trace-Element X-Y Diagrams

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Figure 8A shows that the Barton Mine gabbro samples along with many transition zone samples have ~1 ppm Th and ~3 ppm Li. Some transition zone samples plot at lower Th concentrations, and



Figure 8. Composition changes between parental corona gabbro, transition zone, and garnet amphibolite ore for some elements that differ considerably between gabbro and ore rock. (A) Li vs. Th; (B) Li vs. Cs; (C) Li vs. La,/Ce,. Broad gray arrows show apparent composition change paths. Small black arrows show calculated fractional crystallization composition path for average Warrensburg corona gabbro, where the arrow tip represents crystal fractionation sufficient to increase incompatible element concentrations by a factor of 1.27 (see text).

garnet amphibolite whole-rock and matrix samples mostly have ~0.03–0.4 ppm Th and ~15 ppm Li. Figure 8B shows that the gabbros have ~0.2 ppm Cs, which decreases through the transition zone, with the garnet amphibolites and matrix having ~0.01–0.05 ppm Cs. Though the changes in La_n/Ce_n ratios

are small, Figure 8C shows that the compositional pattern, decreasing in general from gabbro through the transition zone to amphibolite, is similar to that seen for Th and Cs. The wide variability in compositions observed across the gabbro-transition zone-garnet amphibolite sequence suggests that

GEOSPHERE

Hollocher et al. | Gore Mountain garnet

the process of composition change was more effective in some rock volumes than in others; that is to say, it was channelized.

Figure 8 shows considerable overlap in Warrensburg gabbro and garnet amphibolite compositions. Student's time (*t*)-tests (unpaired, unequal variance, two-tailed) were performed on the samples to determine if the gabbros (n = 7) and garnet amphibolites (n = 17: matrix samples + two whole-rock composites, does not double count matrix from the composites) were statistically different. For Li, Cs, Th, and La_n/Ce_n values, the probabilities that the datasets are from the same population are 0.02, <0.01, <0.01, and <0.01, respectively. The same tests comparing Warrensburg gabbro with the two garnet amphibolite whole-rock compositions alone are 0.2, 0.2, 0.4, and 0.3, respectively. We conclude that the two datasets are not of the same population.

The increase in Li concentrations from gabbro to garnet amphibolite at Warrensburg (averages 28-38 ppm, respectively, a ratio of 1.36) is reasonably consistent with fractional crystallization sufficient to have increased incompatible element concentrations by a factor of $\sim 1.27 \pm 0.11$ above that in average corona gabbro (Fig. 8A), or a similar increase in trapped liquid volume in the protolith gabbroic cumulate. Both of these processes should also increase Th concentrations, but Th in the garnet amphibolite (~0.9 ppm) is lower than Th in the gabbro (~1.5 ppm), i.e., not in the same direction as predicted for fractional crystallization or increased trapped liquid. Cs concentrations are higher in the amphibolite by a factor of ~6 (~3.6 ppm; Fig. 8B) relative to the gabbro (~0.6 ppm). In Figure 8C, the small decrease in La₂/Ce₂ ratios in the amphibolites is inconsistent with crystal fractionation or trapped liquid fraction models (Fig. 8A).

Traverses

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Figure 9 shows four traverses across Barton Mine exposures of the garnet amphibolite transition zone. See Figures S1–S4 for annotated field photographs. The left-most samples in each traverse are corona gabbro, so all of them plot within the 2σ range of all Barton Mine gabbros. The right-most



Figure 9. Rock compositions along traverses from the parental corona gabbro, through the transition zone, and into the garnet orebody in Barton Mine pits 4 (A, B) and 9 (C, D). The traverses all start in fresh or partly recrystallized corona gabbro that retains green plagioclase and garnet grains \ll 1 mm across. Traverses extend through the transition zone to garnet amphibolite with garnet porphyroblasts ≥ 2 cm across (garnet ore). Samples were taken from oblique sections through the transition zones. Limited exposure and restricted access above some of the outcrops made the exact position of each sample within the transition zones uncertain, except along the line of traverse. Averages with uncertainty bars (2σ) are for all Barton Mine corona gabbro and garnet amphibolite whole rock and amphibolite matrix that are superimposed on the error bars are from the same pits as the traverses. Field composite photographs of traverse outcrops are in Figures S1–S4 (see text footnote 1). Note that the pit 9, traverse 1 samples (C) were collected in the reverse direction from that shown here.

samples in each traverse are in the garnet amphibolite orebody, so most of those plot within the 2σ range of whole-rock and matrix samples from Barton Mine. Figure 9A shows the first transition zone sample having a composition within the 2σ gabbro range, but the next two have much lower

Cs and Th contents. The right-most orebody sample has higher Li and lower Cs and Th contents than the gabbros. Figure 9B shows the three transition zone samples to be within the range of the gabbros, whereas the orebody sample has Li and Cs concentrations outside of that range (barely so for Li). In Figure 9C, Li and Th concentrations vary more or less within the gabbro range, but Cs for transition zone and orebody samples is below that range. In Figure 9D, most transition zone Li concentrations are within the gabbro range, but the orebody sample is much higher. Cs and Th concentrations vary, with some concentrations being much lower than the gabbro range, as is the orebody sample for Cs. The transition zones are not just partially hydrated versions of the gabbro; they have also experienced composition modification.

Figure 10 shows the sample traverse for Warrensburg, showing Li, Cs, and Th as in Figure 9. See Figure S5 for an annotated field photograph. The garnet amphibolite contact is exposed against tonalitic pegmatite and granitoid gneisses at 19 m. Blue horizontal lines and 20 uncertainty bands represent the seven corona gabbro samples from 2 km south, approximating the garnet amphibolite parental rock. The garnet amphibolite sample Li concentrations tend to be only slightly higher than ~1.27 times the gabbro average, and so this may not be significant, as discussed in the Multi-Element Comparison section. In contrast, Cs has ~6 times higher concentrations than the gabbro, and Th concentrations are generally lower, i.e., the reverse of what additional crystal fractionation or greater amounts of trapped liquid in the amphibolite protolith should have produced.

There is a thin pegmatite, typically ~10 cm thick, at ~29 m along the traverse. Amphibolite samples W121A and W121B were taken ~0.5–5 cm and ~7 cm south of this pegmatite, respectively, and are particularly enriched in Cs (also K and Rb, not shown), possibly from fluids from the adjacent pegmatite or for some other reason (Fig. 11A). Sample W121C, taken ~15 cm from the small pegmatite contact, has an unremarkable composition, as do the two amphibolite samples immediately adjacent to the meter-thick pegmatite at the northern contact.

Warrensburg Felsic Rocks

North of the Warrensburg garnet amphibolite contact (Fig. 10), there are, in sequence, white tonalitic pegmatite, white tonalitic gneiss, white



Figure 10. Sample traverse along the Warrensburg Wall Street outcrop, showing Li, Cs, and Th concentrations. The nearby corona gabbro is included for comparison (average does not include the ferrogabbro dike). Notable samples are labeled with their sample numbers. A field composite photograph of the outcrop is given in Figure S5 (see text footnote 1).

granitic gneiss, and pink granitic gneiss. The two tonalitic gneiss samples nearest to the contact have Li concentrations similar to the gabbros and somewhat lower than most amphibolites, but the five granitic rocks farther from the contact have substantially lower Li concentrations. The felsic rocks generally have higher Cs concentrations than the gabbros but similar to or slightly lower Cs values than the amphibolites. The two tonalitic gneisses have Th concentrations at the high end of the range for Warrensburg gabbro, and higher Th values than all amphibolites, but the five granitic gneisses have higher Th concentrations than any other samples. The two pegmatites have compositions guite different from one another and from the felsic gneisses.

Figure 11A shows that the five K₂O-rich granitic gneisses plot together, and the tonalitic gneisses and two pegmatites plot at lower K₂O and higher CaO concentrations, as expected for tonalites. The prominent compositional differences suggest that the tonalitic rocks were restites following granitic liquid escape as a contact metamorphic effect of gabbro intrusion. Figure 11B shows that four of the five granitic gneisses have high REE concentrations and similar LREE-enriched patterns with negative Eu anomalies. Sample W133 is also granitic, but it has an unusual V-shaped pattern. Tonalitic gneiss sample W128 has a V-shaped pattern similar to W133, but at one tenth the REE concentrations and with a large positive Eu anomaly. Tonalite W127 has LREE concentrations almost identical to W128 but

Hollocher et al. | Gore Mountain garnet



Figure 11. Compositions of Warrensburg felsic gneiss and pegmatites compared to garnet amphibolite and corona gabbro. (A) CaO vs. K₂O diagram, with arrows showing hypothetical processes causing rock composition changes (see text). (B) Rare earth element (REE) diagram. Rocks with patterns above the garnet amphibolite matrix average are granitic; those below are tonalitic. REE normalizing factors are from McDonough and Sun (1995).

much lower HREE concentrations. The two tonalitic pegmatites have less unusual patterns, but they have low REE concentrations and prominent positive Eu anomalies that also suggest melt escape to yield a plagioclase-rich restite.

Oxygen Isotopes

scienceworld.org/gsa/geosphere/article-pdf/doi/10.1130/GES02812.1/7112555/ges02812.pdf

Figure 12 shows δ¹⁸O values (relative to Vienna standard mean ocean water) values from other workers for Barton Mine orebody mineral separates, calculated whole-rock values from those separates, and separates from the Willsboro wollastonite orebody and several other localities in the region. The Willsboro orebody (Fig. 1) largely contains wollastonite, grossular-andradite garnet, and diopside, and it occurs on the north margin of a large anorthosite intrusion (Valley and O'Neil, 1982; Valley, 1985; Clechenko and Valley, 2003). Wollastonite, garnet, and diopside from this site have variable but commonly low δ^{18} O values (7‰ to -1.3‰) compared to the presumed protoliths of marble (20‰-30‰) and minor mafic igneous layers in the orebody (4‰-10‰). Thin marble layers within the orebody also have low δ^{18} O values (4‰-6‰) that overlap Willsboro wollastonite and garnet.

The Willsboro orebody has been interpreted to have originally formed from largely carbonate rocks in a shallow (<10 km) crustal hydrothermal system, driven by heat from the adjacent Westport Dome anorthosite body (AMCG suite; Whitney and Olmstead, 1998). Large volumes of meteoric water circulated through the system, changing rock compositions and dramatically lowering δ¹⁸O values. Clechenko and Valley (2003) reported evidence for growth of euhedral, chemically and isotopically zoned grossular-andradite garnet in apparent former open cavities, supporting the idea of shallow depths. The altered rock and surrounding region were later metamorphosed to granulite facies during the Ottawan orogenic episode.

Some calculated Barton Mine garnet amphibolite whole-rock δ^{18} O values (Fig. 12) are consistent with corona gabbros in the Adirondacks ($\delta^{18}O$ = 6.8‰ ± 0.6‰; Valley et al., 1994, p. 197), and presumably also with the corona gabbro at Barton Mine. To our knowledge, the only oxygen isotope data for the Barton Mine gabbro is a plagioclase δ^{18} O value of 8.2% from Taylor (1969). Assuming a typical plagioclase versus mafic mineral δ^{18} O difference of 1.4‰ (calculated from Kohn and Valley, 1998) and 50% plagioclase in the gabbro, the Barton Mine gabbro whole-rock δ^{18} O value can be estimated to be ~7.4‰, at the upper 2σ range of other AMCG suite gabbros in the Adirondacks (Fig. 12). Analyzed Barton Mine garnet amphibolite phases have a range of δ^{18} O values, and calculated amphibolite whole rocks have δ^{18} O values up to ~3‰ lower than the Adirondack olivine gabbro average. We interpret this to indicate premetamorphic hydrothermal alteration of the Barton Mine orebody protolith with meteoric water that lowered the δ^{18} O values, coincident with shallow gabbro intrusion and cooling. This inferred alteration is analogous to that seen in the Willsboro and similar orebodies, but much less extreme.

There are several possible alternatives to the low-pressure hydrothermal alteration hypothesis, of which we describe two. One possibility is contamination of the orebody protolith gabbroic magma with rock having δ^{18} O values substantially lower than the 6.8‰ ± 0.6‰ value found in AMCG suite gabbros (Valley et al., 1994, p. 197). A review of the oxygen isotope analyses of several workers (Taylor, 1969; Jiang et al., 1988; Lancaster et al., 2009; and others listed in Fig. 12, along with some whole-rock values estimated by us) and simple mixing models show that no rock types were available for assimilation that could have lowered gabbro ore protolith δ^{18} O values by even a few per



Figure 12. Mineral separate and whole-rock δ¹⁸O values for rocks in the Adirondacks and Quebec, Canada. The meteoric water approximate upper limit is from Bindeman (2008). Data for the Barton Mine are from Kohn and Valley (1998), from which we calculated 24 whole-rock compositions using the following mineral modes for hornblende, plagioclase, orthopyroxene (Opx), garnet, clinopyroxene (Cpx), and biotite: 0.28, 0.55, 0.04, 0.11, 0.01, and 0.01, respectively, for their felsic equigranular ore: 0.61, 0.20, 0.06, 0.11, 0.01, and 0.01 for their mafic equigranular ore (from which the Barton Mine dark ore average was also calculated): 0.7, 0.24, 0.06, 0, 0, and 0 for their mafic coronate ore (amphibolite matrix); and 0.52, 0.08, 0.01, 0.38, 0, and 0.01 for their <5% plagioclase ores (hornblendite rim + garnet). Phase δ^{18} O averages were used in cases where not every phase was analyzed in each whole-rock category. Average Adirondack olivine gabbro and 20 uncertainty range are from Valley et al. (1994, p. 197). Willsboro orebody data are from Valley and O'Neil (1982), Valley (1985), Kohn and Valley (1998), and Clechenko and Valley (2003). Data from elsewhere are from Valley (1985, marble, anorthosite, amphibolite), Kohn and Valley (1998, Lewis wollastonite mine), and Kretz (2001, Quebec marble). Analyzed Barton Mine garnet samples are almandine; all others are grossular-andradite. VSMOW-Vienna standard mean ocean water.

mil without large changes in major-element concentrations. Because such large gabbro-orebody major-element differences are not seen, magmatic assimilation of local rock can be discounted as a likely process for lowering δ^{18} O values.

A second possibility is that the Barton Mine garnet amphibolite protolith was altered by early, relatively low-temperature H_2O -rich fluid released by nearby dehydrating rocks. Most lithologies now surrounding the orebody and gabbro are metamorphosed AMCG suite syenites, anorthosites, and granites (Fig. 2), which are relatively dry at present (minor hornblende and/or biotite), and probably were also relatively dry at the time of emplacement (Hamilton et al., 2004; McLelland et al., 2010, 2011; Regan et al., 2011). The most H_2O -rich protoliths available in the Adirondacks were likely pelites, and schists and migmatites derived from them are exposed to the north of Barton Mine (Fig. 2; Krieger, 1937). Migmatitic pelites analyzed by Lancaster et al. (2009) have δ^{18} O values of ~12‰-16‰ (our whole-rock estimates). Dehydration and fluid escape tend to raise residual rock δ^{18} O values, but only by up to ~1‰ (Sharp, 2017, section 12.2.2). H₂Orich fluid from such pelitic rocks would likely have been close to equilibrium with the source rock, so at 300 °C, it would have had δ^{18} O values of ~7‰ (calculated using the optimized equations of Vho et al., 2019). However, such H₂O-rich fluid hydrating the orebody protolith would have raised its $\delta^{18}O$ values above the 6.8% ± 0.6% typical of AMCG suite olivine gabbro, not lowered them as seen in Figure 12, because of the way in which oxygen isotopes partition between fluid and rock ($\delta^{18}O$ in fluid is lower). A metamorphic fluid source, therefore, also seems to be an unlikely mechanism for having lowered δ^{18} O values in the Barton Mine garnet amphibolite protolith.

THERMODYNAMIC MODELING

We did extensive thermodynamic modeling of the rocks discussed here, with emphasis on understanding the conditions of garnet growth. These calculations were done using different versions of Perple-X (Connolly, 2009) and Theriak–Domino (de Capitani and Petrakakis, 2010), and different mafic rock thermodynamic databases. Starting compositions were derived either from whole-rock analyses or by combining mineral analyses. In general, the results were inconsistent in terms of model versus actual phase compositions and modes, so we are not able to present specific metamorphic pressure or temperature estimates and do not discuss these results here in detail (see Supplemental Text S1; Figs S6–S14). However, some aspects of the results tangentially contribute to our concepts of garnet amphibolite ore formation and is discussed in the next section.

DISCUSSION

Barton Mine Garnet Ore

There seems to be a consensus in the literature that the Barton Mine garnet amphibolite and similar rocks elsewhere in the region formed as a result of aqueous fluid infiltration during high-grade metamorphism (Buddington, 1939; Bartholomé, 1960; Luther, 1976; Sharga, 1986; Goldblum and Hill, 1992; McLelland and Selleck, 2011; Kelly, 2016). The proposed fluid source has generally been either decompression-induced dehydration of nearby rocks during Ottawan unroofing and uplift, or fluids released from crystallizing Ottawan magmas produced by decompression melting. However, the geochemistry we present and the oxygen isotopic results of others, combined with thermodynamic results, instead support the idea that gabbro margin hydrothermal alteration was an early process, decoupled from much later development of the garnet amphibolite high-grade metamorphic assemblages.

Ottawan metamorphism in the Adirondack Highlands has generally been estimated to have

occurred at pressures of 6.5–9 kbar and temperatures of 650–850 °C (Bohlen et al., 1985; Mezger et al., 1991; Spear and Markussen, 1997; Storm and Spear, 2002, 2005; Peck and Valley, 2004; Ream and Dunn, 2008). Conditions for garnet amphibolite formation at Barton Mine specifically have been estimated at 6–8 kbar and 700–800 °C (Luther, 1978; Sharga, 1986; Darling et al., 1997), similar to Ottawan prograde metamorphism elsewhere in the Adirondacks. Shinevar et al. (2021) estimated that garnet amphibolite formation took place at ~950 °C and 9–10 kbar, i.e., 150–250 °C hotter and 1–4 kbar higher pressure than most other estimates.

Though our own thermodynamic calculations (Supplemental Text S1) have been inconclusive in some respects, they do indicate that a 700-900 °C and 8-11 kbar range is plausible for formation of the orebody hornblende-plagioclase-Opx-garnet assemblage, provided H₂O contents of the model rocks do not much exceed the stoichiometric amount needed to form hornblende in proportions currently found in the orebody (1-1.4 wt% H₂O, depending on bulk composition). This constraint precludes an H₂O-rich fluid phase over our entire 6-12 kbar and 700-900 °C modeling range (Supplemental Text S1; Figs. S6-S9). Shinevar et al. (2021) estimated that 1% H₂O would have been sufficient to produce plausible model assemblages, consistent with our results of 1%-1.4%, but less than the model 3% H₂O and resulting large melt fraction of Ferrero et al. (2021). H₂O fluid saturation in our models yielded calculated melt fractions of ~20% by volume at 800 °C and 8 kbar, and ~29% at 900 °C (Supplemental Text S1; Fig. S10), which would likely have resulted in melt escape (Vigneresse et al., 1996; Sparks et al., 2019) or segregation as tonalitic veins during deformation. Melt escape would have dramatically changed garnet ore compositions compared to the parental gabbro, rather than the relatively subtle changes we observed, and tonalitic veins in the orebody are not seen. Melt escape might also have disrupted orebody deformation structures (Goldblum and Hill, 1992). Our calculations at H₂O saturation also indicate no stable garnet-plagioclase assemblages in the range of 700-900 °C and 6-12 kbar, contrary to observed phase relations. Reducing

 H_2O activity by dilution with CO_2 (e.g., molar $CO_2/[CO_2 + H_2O] = 0.02-0.23$) does not much change the pressure-temperature (*P*-*T*) range of hornblende-plagioclase-Opx-garnet assemblages (Supplemental Text S1; Figs. S11–S14).

It seems likely that there were small amounts of silicate liquid present during garnet growth and formation of coarse patches and strain shadows because tonalitic inclusions have been found inside garnet porphyroblasts in the orebody (Darling et al., 1997; Ferrero et al., 2021), and in similar rocks elsewhere in the region (Charles et al., 1998). These authors interpreted the melt inclusions to have been trapped during garnet growth. Grain boundary liquid would have greatly enhanced diffusion of chemical components required for garnet growth and formation of the coarse-grained strain shadows, compared to solid-state diffusion for the fine-grained, dry, adjacent gabbro body. Coarse patches and strain shadows around garnet porphyroblasts may also have been melt accumulation zones, which allowed grain coarsening from faster diffusion through additional intragranular melt and protection from deformation by the adjacent garnet crystals. Grain boundary tonalitic melt was presumably resorbed into orebody solid phases during cooling. We speculate that the amphibolite matrix to garnet is relatively fine grained because moderate deformation (Sharga, 1986; Goldblum and Hill, 1992) caused continued grain-size reduction during garnet growth.

Another problem we see in the formation of garnet amphibolite with high-pressure, high-temperature H_2O -rich Ottawan fluids is the range of oxygen isotope ratios in the Barton Mine orebody. High-temperature fluids released from pelitic rocks or crystallizing granitic magmas, for example, would also have tended to raise $\delta^{18}O$ values in the altered orebody protolith in the same way, as discussed in the Oxygen lsotopes section, for low-temperature fluids, not lowered them as seen in the measured values (Fig. 12).

We interpret the oxygen isotope evidence to indicate that heated meteoric water altered the Barton Mine gabbro pluton during its emplacement at shallow crustal levels, hydrating it and modifying its chemical and oxygen isotopic composition. Greater composition changes took place within and adjacent to the most effective fluid pathways. Such channelized hydrothermal alteration of shallowly emplaced gabbros is common (e.g., Taylor, 1974; Ito and Anderson, 1983; Fehlhaber and Bird, 1991) and can yield similar 2‰–4‰ reductions in whole-rock δ^{18} O values if the circulating water was meteoric. Changes in δ^{18} O values can also be restricted to pluton margins or other rheological discontinuities (Crowley and Giletti, 1983; Fehlhaber and Bird, 1991). It is unknown if meteoric water access to the gabbro was related to the fault on the south side of the Barton Mine orebody.

Low-pressure hydrothermal fluids should have easily transported relatively soluble elements like Li and Cs (Fig. 8), and possibly Ca and/or Mg (Fig. 5C). In contrast, REE and Th are commonly considered to be "immobile" elements that are not prone to movement during most forms of chemical alteration (e.g., Greenough et al., 1990; Hastie et al., 2007; John et al., 2008), yet we see evidence that these elements were mobile (Figs. 6A and 8). Ague (2017) surveyed a wide range of regional metamorphic and subduction zone hydrothermal vein environments and found that LREEs, Th, and other immobile elements can be mobilized in some circumstances. Mobility was found to correlate more strongly with changing phase relations than with metamorphic P-T conditions. Nisbet et al. (2019) found that Th in particular could be mobilized relatively efficiently in somewhat acidic, sulfate-bearing waters at temperatures of 175-250 °C, with Th concentrations exceeding 1 ppm in fluids in some experiments. Grønlie and Torsvik (1989) and Mutasingwa (2017) described oxidized, Th- and REE-rich hydrothermal veins on the island of Yttrøy, Trondheimsfjord, Norway, in which Th and LREEs have clearly been mobilized and concentrated. These veins also contain barite, suggesting sulfate-bearing hydrothermal solutions.

Warrensburg Garnet Amphibolite

The north end of the Warrensburg garnet amphibolite is in sharp contact with felsic rocks and was

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interpreted to be a fault by McLelland and Selleck (2011). However, we interpret the contact to be a metamorphosed chilled margin based on the decrease in grain size within ~50 cm of the contact, and the change in mineralogy within ~1 m of the contact (smaller and decreasing numbers of garnets, garnet absent within 50 cm of the contact, more biotite near the contact). The grain-size difference suggests rapid cooling, and obvious chilled margins on gabbro bodies are known to have survived Ottawan metamorphism in some places in the Adirondacks (Olson, 1992; McLelland and Selleck, 2011, stop 5; Hollocher, 2014, figs. 25.1E, 25.1F, and 25.19). The mineralogy change suggests that the marginal rock had a somewhat different composition than that found a few meters farther south along the outcrop. This difference could have been caused by a difference in composition between the chilled margin gabbroic magma and the possibly cumulate pluton interior, by contamination with assimilated adjacent felsic rock, or by later exchange of fluids with adjacent rocks.

Although a contact with its presumed parental gabbro is not exposed, we suspect the Warrensburg garnet amphibolite was derived from olivine gabbro very similar to that sampled 2 km to the south. If correct, then Figures 8 and 10 indicate probable Cs gain and Th loss, as compared to the gabbro. Li has slightly higher concentrations than the gabbro by an amount consistent with crystal fractionation or more trapped cumulus liquid, like the MREEs, HREEs, Zr, Nb, and several other elements, so there is no change for Li that we can confidently ascribe to alteration processes.

We note that changes in garnet amphibolite trace-element compositions at Barton Mine (Li enrichment, Cs depletion, Th depletion) and in Warrensburg (Li no significant change, Cs enrichment, Th depletion) are different compared to their nearby gabbros. Both sites have reductions in La, Ce, and Pr as compared to Nd, though this change is less at Warrensburg (Figs. 6A, 6B, and 8C). We speculate that these differences resulted from differences in the hydrothermal waters at the two locations, possibly having had different pH, metal concentrations, ligands and ligand concentrations (e.g., sulfate), temperatures, and water/rock ratios.

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Warrensburg Felsic Rocks

We attempted to model tonalitic gneiss and pegmatite trace-element concentrations (not shown) using the average of the four most similar granitic gneisses (W129–W131 and W134) as the starting composition. Simple equilibrium and fractional melting trace-element models that best reproduced the REE patterns of tonalitic rocks seen in Figure 11B required melt extraction along with formation of improbably large proportions of garnet (several weight percent), though the four granitic gneisses presently have almost none. The calculated model restites following melt extraction had even more garnet, though the maximum found in the tonalitic rocks is only 1.7% by volume (sample W128).

To better constrain melting assemblages and modes, we used the same average granitic gneiss composition for melting calculations using MELTS Excel (Gualda and Ghiorso, 2015) and Theriak-Domino (de Capitani and Petrakakis, 2010). For these models, we added Mn to Fe, and we removed C as calcite and P as apatite to simplify calculations, and we converted 10%-30% of Fe²⁺ to Fe³⁺. Models were run at 2, 4, and 6 kbar with 1%–4% H₂O (not shown). In all cases, model melt compositions were substantially more Na-rich than the rather K-rich granitic gneisses because the granitic system eutectics and minima were always on the Na-rich side of the granitic gneiss starting composition. Extraction of such melts drives model restites toward even more K-rich granitoids, not tonalites. The origin of the range of felsic rocks near the exposed garnet amphibolite contact must have involved processes more complex than simple partial melting and melt extraction, and understanding them will require further work.

Ruby Mountain

Ore rock at the Ruby Mountain site is inferred to have been derived from an anorthositic troctolite protolith. Unlike at Barton Mine or even Warrensburg, the Ruby Mountain orebody has no likely protolith distinct from the orebody itself. We suspect that this orebody may have originally been hydrated by processes unknown, possibly hydrothermal water, that permitted formation of small melt phase volumes during later Ottawan metamorphism that enhanced diffusion and allowed large garnet porphyroblasts to grow.

Why Such Big Garnets?

Why are garnet porphyroblasts so large at Barton Mine, Warrensburg, and many other Adirondack garnet amphibolite localities, but not at others? Although we have not made a detailed comparison, it is clear from a review of available data that many Adirondack mafic rocks are too Mg- or Ca-rich to have formed much or any garnet under Ottawan metamorphic conditions. Many rocks that were in the right composition range to grow Ottawan garnet do have substantial volume fractions of garnet, like the gabbroic Barton Mine ore protolith and many other AMCG suite gabbros. These rocks, however, were relatively dry at the time of Ottawan metamorphism, and their garnet grains are tiny. We suggest large garnet porphyroblasts formed in rocks (1) that had the right initial composition (relatively evolved gabbros), (2) that were hydrated prior to Ottawan metamorphism (permitting minor melting), and (3) that followed P-T paths that entered the melt stability field first and then entered the garnet stability field. The presence of minor grain-boundary melt as the rocks entered the garnet stability field would have suppressed additional garnet nucleation because fast diffusion through the liquid would have reduced overstepping of the garnet-forming reactions (Carlson, 2002). A few large garnets could have grown in the altered, damp rocks, in contrast to large numbers of tiny garnets growing in adjacent dry but otherwise compositionally similar gabbro. Although Luther (1976) also proposed limited nucleation as the cause of few but large garnet crystals in Barton Mine amphibolite ore, growth progressed in his model in the presence of H₂O-rich fluid, which we think could not have been present because it would have caused excessive melting. Shinevar et al. (2021) concurred with the limited nucleation hypothesis but suggested that either fluids or

melt could have been sufficient to increase diffusivity. We also note that Goldblum and Hill (1992) proposed an alternative grain-coarsening mechanism, where tiny garnet crystals from peak Ottawan metamorphism became many fewer and grew much larger during an influx of high-temperature, H₂O-rich fluid, deformation, and retrogression from pyroxene granulite- to amphibolite-facies assemblages.

Figure 13 illustrates our garnet growth concept using three hypothetical P-T paths for dry or damp gabbro. Path 1 entered the garnet stability field at relatively low temperature. Garnets nucleated and started to grow soon after crossing into the garnet

stability field. Nucleation continued along the path because of short solid-state diffusion length scales in both dry and damp rocks below the solidus, though some grain coarsening would have taken place, particularly if melt became stable at the highest temperatures. Along path 2, garnet also nucleated soon after the rock crossed into the garnet stability field. Just like for path 1, both dry and damp rocks were limited to slow solid-state diffusion, so garnet nucleation and slow growth resulted in many small garnet crystals. Along path 3, melt was already present in damp but not dry rocks when they entered the garnet stability field. Damp rocks nucleated garnet soon after entering



Figure 13. Schematic Ottawan Orogeny metamorphic pressure-temperature (P-T) paths (black arrows) relating to garnet nucleation and growth for identical gabbroic compositions like those at the Barton Mine. Garnet nucleates (black circles) soon after entering the garnet stability field in all cases. Details of garnet nucleation and growth depend on rock H₂O content controlling the stability of silicate melt (see text). This phase diagram is used schematically here, but it is based on a calculated phase diagram for the Barton Mine orebody (Fig. S6A [see text footnote 1]). Black arrows are hypothetical P-T paths that dry gabbro and damp orebody rocks may have followed. Light-gray circles and half circles represent dry compositions having $\sim 0.6\%$ H₂O, which is insufficient for stable melt in this *P-T* range. Dark-gray circles and half circles represent damp compositions having ~1.4% H₂O, which is sufficient to produce stable silicate melt at high temperature.

the garnet stability field, and fast diffusion through grain boundary liquid suppressed further nucleation, which allowed garnets to grow unusually large. In contrast, dry rocks following the same path but without melt continued to nucleate garnet, with little coarsening. To have preserved the large garnet porphyroblasts, we suggest that cooling initially followed a path more or less parallel to garnet isopleths (little pressure change), until the rocks were cool enough for melt to have vanished (resorbed into the assemblage solid solutions).

CONCLUSIONS

Big garnet amphibolites are among the more impressive mineralogical features of the Adirondacks. Many (all; McLelland and Selleck, 2011) are associated with metamorphosed post-Shawinigan olivine gabbro (1154 ± 6 Ma; McLelland et al., 2004, 2011) and are generally thought to have been derived from them by processes involving hydrothermal alteration, including those at Barton Mine and in Warrensburg. Garnet amphibolite formation has generally been estimated to have occurred in the pyroxene granulite facies, with which we concur, noting that pyroxene granulite assemblages are characteristic of rocks that were relatively dry. The Barton Mine orebody has large differences in the concentrations of certain trace elements in comparison to the adjacent parental gabbro. Among these are higher concentrations of Li and lower concentrations of Cs and Th in the orebody, La,/Nd, ratios reduced from ~1.45 in gabbro to as low as 0.94 in the garnet amphibolite, and orebody wholerock δ^{18} O values reduced from ~6.8‰ to as low as ~4.1‰ (Fig. 12).

Most authors have concluded that hydration

and garnet growth from former olivine gabbro occurred in the presence of Ottawan metamorphic fluids at high temperature and pressure. In our interpretation, hydration and chemical modification of the parental gabbro took place during post-Shawinigan magma emplacement at shallow depth with circulating meteoric water, rather than deep during late Ottawan metamorphism. Metamorphism to produce both regional granulite-facies

mineral assemblages and the big garnet amphibolites was simultaneous in our interpretation, rather than during decompression after peak Ottawan metamorphism (e.g., McLelland and Selleck, 2011; but see Shinevar et al., 2021, who also inferred simultaneous peak metamorphism and garnet amphibolite ore formation).

The amphibolite hosted only marginally more H_2O than was necessary to stabilize the typically 50–70 vol% hornblende in the garnet ore, with small amounts of melt, as suggested by tonalitic inclusions found inside garnet porphyroblasts. The presence of melt is also implied by the high diffusion rates necessary to grow large garnet porphyroblasts and centimeter-scale euhedral and subhedral hornblende, Opx, and plagioclase in coarse patches and strain shadows.

Less is known about the garnet amphibolite in Warrensburg. The whole-rock and amphibolite matrix data we report indicate that it was plausibly derived from an olivine gabbro protolith that was similar to the gabbro exposed 2 km south. The northern end of the amphibolite outcrop near its contact with felsic rocks is finer grained and lacks garnet, which we interpret to represent a metamorphosed chilled margin. Chilled margins can be found elsewhere in the Adirondacks around olivine gabbro plutons despite granulite-facies overprinting. The origin of the sequence of felsic rocks northward from the contact is not yet understood.

The enrichment of Li in the Barton Mine orebody by an average factor of ~4 suggests alteration by relatively Li-rich aqueous solutions. Lithium is found in small amounts in all subsurface waters, but high concentrations are generally restricted to arid intermontane basins such as the Atacama Desert (Chile), the Salton Sea in southern California (southwestern United States), and Clayton Valley in Nevada (southwestern United States; e.g., Bradley et al., 2013, and references therein). We speculate that Li enrichment of the big garnet ore rock protolith resulted from hydrothermal alteration by Li-rich groundwaters that presumably developed in an arid, post-Shawinigan landscape that existed when the AMCG suite magmas were emplaced. We note that Barton Mine whole-rock CI contents increase

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in the sequence from gabbro $(0.09\% \pm 0.05\% 1\sigma)$ to transition zone $(0.15\% \pm 0.02\% 1\sigma)$ and orebody (0.17% ± 0.04% 1σ; Buddington, 1939; Shand, 1945; Levin, 1950; Bartholomé, 1960; Luther, 1976), providing weak evidence that the hydrothermal solutions were chloride-bearing. The source of the high Cs concentrations seen in Warrensburg amphibolite is more speculative. Some modern arid salt lake waters can be relatively enriched in Cs (up to ~2000 ppm in brine: Tibet, China; Zheng and Liu, 2009). Alternatively, substantial Cs enrichment can occur in fine-grained, solid hydrothermal alteration products such as mixed-layer clays (up to ~100-240 ppm) by ion exchange with otherwise unremarkable waters (Mathurin et al., 2014). One or the other process may have produced the Csrich rocks that later recrystallized to become the Warrensburg garnet amphibolite.

There are many questions still to answer about these rocks. For example, do oxygen isotopes vary in parallel with variable Li, Cs, and Th concentrations? If so, this would strengthen the idea of meteoric hydrothermal waters and channelized flow. Paired oxygen isotope and trace-element analyses on single samples will be required to answer this question. One-hundred years of study is not enough to understand the origin of these complex rocks, and there is still much to learn.

ACKNOWLEDGMENTS

We would like to thank the Keck Geology Consortium for funding the 2007 summer research session for three undergraduate students (K.M. Stack, A. Denny, and E.A. Lott) and supporting travel to the 2008 Keck Research Symposium for initial presentation of our work. We also thank Bud Wobus, David Hirsch, and Darby Dyar for mentoring their then undergraduate students through thesis projects and Keck presentations. K.M. Stack's research contribution was carried out in part at the Jet Propulsion Laboratory, California Institute of Technology (Flintridge, California, USA), under a contract with the National Aeronautics and Space Administration. We thank Peter Robinson for giving K. Hollocher a big box of Barton Mine samples in the early 2000s, which was the start of this project. We thank Randy R. Rapple, then General Manager of Barton International, now chief executive officer of the Barton Group, who gave us a unique tour of the garnet oreprocessing facilities and access to the upper Ruby Mountain pit for sample collecting. We thank Bonnie Barton for giving us access to pits 4 and 9 for sample collection on two occasions, areas that are not usually open to the public. We thank William Peck and Timothy Grover for their helpful reviews of an earlier version of this manuscript and Janet Hollocher for reviewing a

later version. Union College provided support for major- and trace-element chemical analyses and summer research support for an additional undergraduate student (E. Morgan). The National Science Foundation supported instrumentation used for microbeam (grant MRI-0619578) and trace-element (grant DUE-9952410) analyses.

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