

Duration of regional kyanite-staurolite grade metamorphism during the Acadian Orogeny: Preliminary results of diffusion modeling of garnet zoning in the Wissahickon Schist, SE Pennsylvania

Howell Bosbyshell (hbosbyshell@wcupa.edu)

and Melissa A. Murdock

Department of Earth and Space Sciences, West Chester University
750 South Church Street, West Chester, PA 19383 USA

ABSTRACT

We estimate the duration of maximum temperatures in amphibolite grade rocks of the Wissahickon Schist in the Central Appalachian Piedmont by modelling diffusive modification of an inferred step function in core/overgrowth compositional zoning in garnet. Published Arrhenius parameters describing major element diffusion in Grt are not consistent, Ca and Mn diffusivities can vary by more than an order of magnitude. We compare results obtained from the parameters determined numerically by Carlson (2006) with those based on a statistical analysis of published experimental results by Chu and Ague (2015).

In the Wissahickon, Silurian-aged, low-pressure, And-Sil facies series assemblages (M1) are overprinted by Devonian-aged (Acadian), moderate-pressure, Ky- and St-bearing assemblages (M2). M1 assemblages are best developed near Silurian intrusions while the M2 overprint is regional in extent. Peak metamorphism during M2 is estimated at ~600 °C and 700 MPa. X-ray maps and profiles of Grt from two locations, B-22 and Ge-06-33, ~20 km apart, reveal similar Ca zoning patterns: a low-Ca core surrounded by a high-Ca overgrowth, with a diffusively modified boundary of ~50 µm. Mn zoning differs between samples. In Ge-06-33, a relatively unzoned core gives way to bell-shaped growth zoning, a profile not amenable to diffusion modeling. In B-22, growth zoning preserved within a 500 µm core is surrounded by a homogeneous, lower Mn overgrowth. This pattern enables identification of a diffusively modified core/overgrowth boundary ~150 µm wide.

The duration of max T (600 °C) required to reproduce Ca zoning is the same in both samples: ~16 Ma using Chu & Ague's (2015) parameters vs. ~2 Ma using Carlson's (2006). The time required to reproduce Mn zoning is <1 Ma and ~2 Ma, respectively. The preservation of growth-zoning in Mn at the sub-500 µm scale is consistent with the short duration of max T obtained from both sets of Mn and Carlson's (2015) Ca parameters. This short duration regional metamorphism requires a transient heat source that is, at present, unidentified.

Metamorphism in the Wissahickon Schist

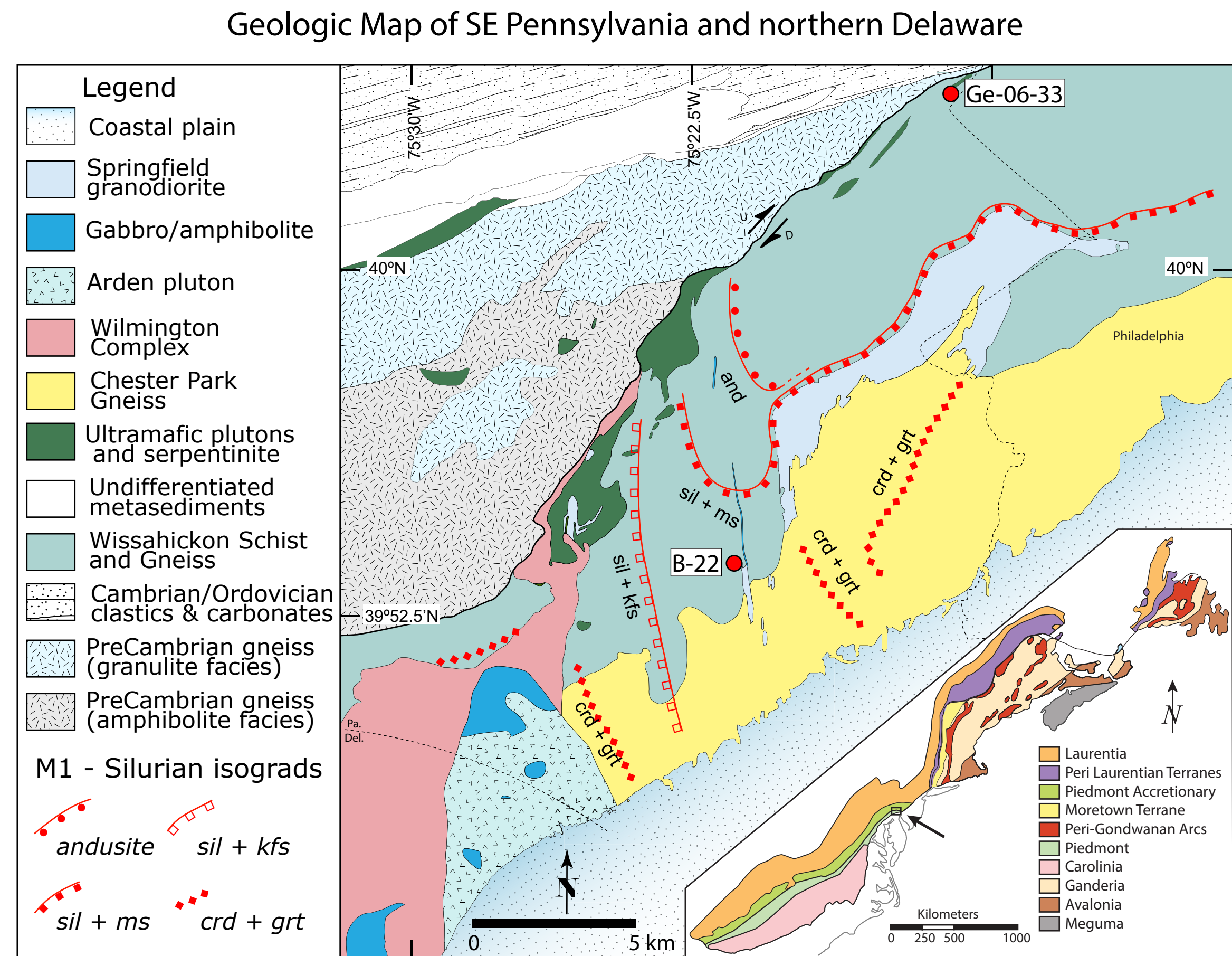


Figure 1. This study focuses on the Wissahickon Schist in Philadelphia and Delaware counties of SE Pennsylvania. The Wissahickon is pelitic to psammitic schist that is interlayered with three to more than ten meters thick amphibolites. Wissahickon sediments were likely deposited in a back-arc setting based on amphibolite geochemistry and an intrusive relationship with magmatic arc rocks of the Wilmington Complex (Bosbyshell et al., 2014). The Wissahickon Schist and adjacent Chester Park Gneiss contain a non-Laurentian sourced detrital zircon population (Bosbyshell et al., 2015) and may be correlative with the Moretown Terrane in New England (inset map, after Hibbard et al., 2006 and MacDonald et al., 2014). Sample locations B-22 and Ge-06-33 are indicated.

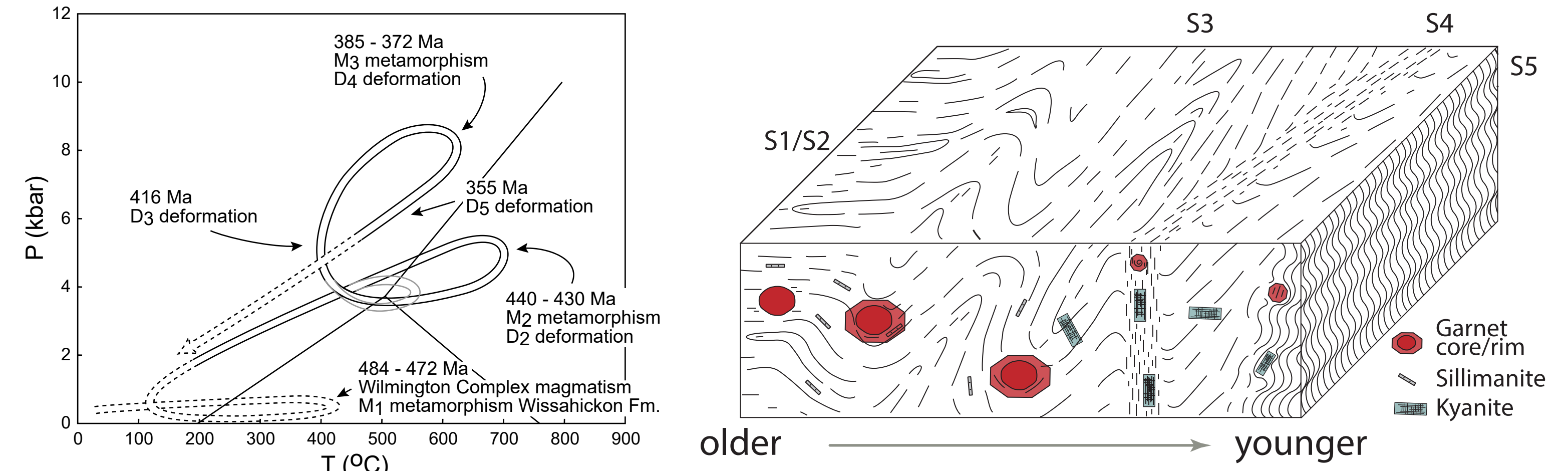


Figure 2. (Left) Schematic "Philadelphia pretzel" pressure-temperature-deformation-time path. Ages are *in situ* U-Th-total Pb EPMA monazite results (Bosbyshell, 2001; 2004). (Right) Schematic representation of the sequence of deformation and metamorphism in the Wissahickon Formation nearest the Wilmington Complex. Diagram is chronological from left to right. At left, S2 foliation and F2 isoclinal folds, early high T-low P mineral assemblage garnet and sillimanite. Center, F3 folds and S3 foliation; second generation garnet overgrowths and kyanite are younger than F3 folding. To right, S4 shear zone (Rosemont Shear Zone) synchronous with kyanite-grade metamorphism. At right end of diagram, shallowly dipping S5 crenulation. Modified from Bosbyshell (2004), Bosbyshell et al. (2014).

B-22

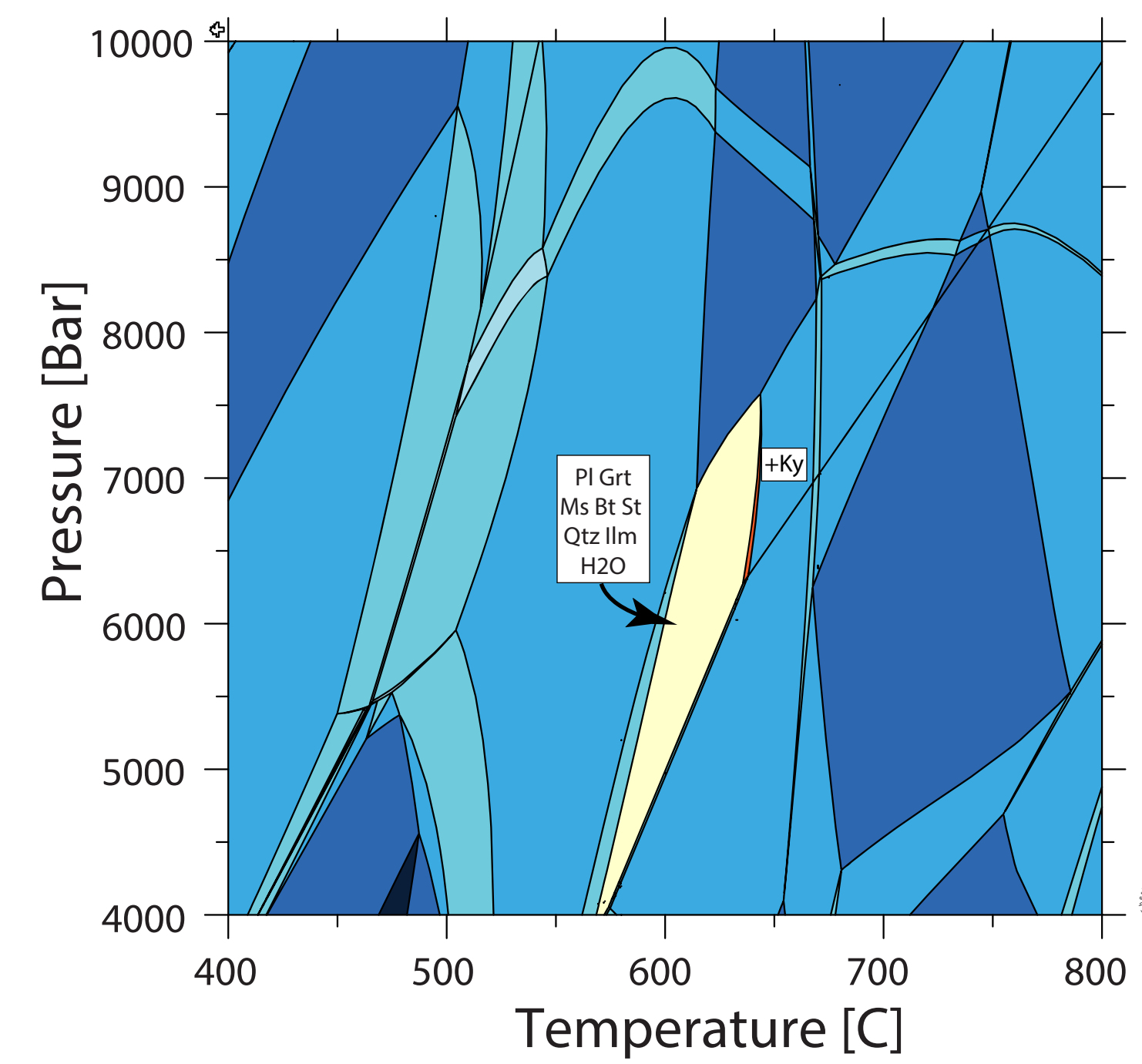
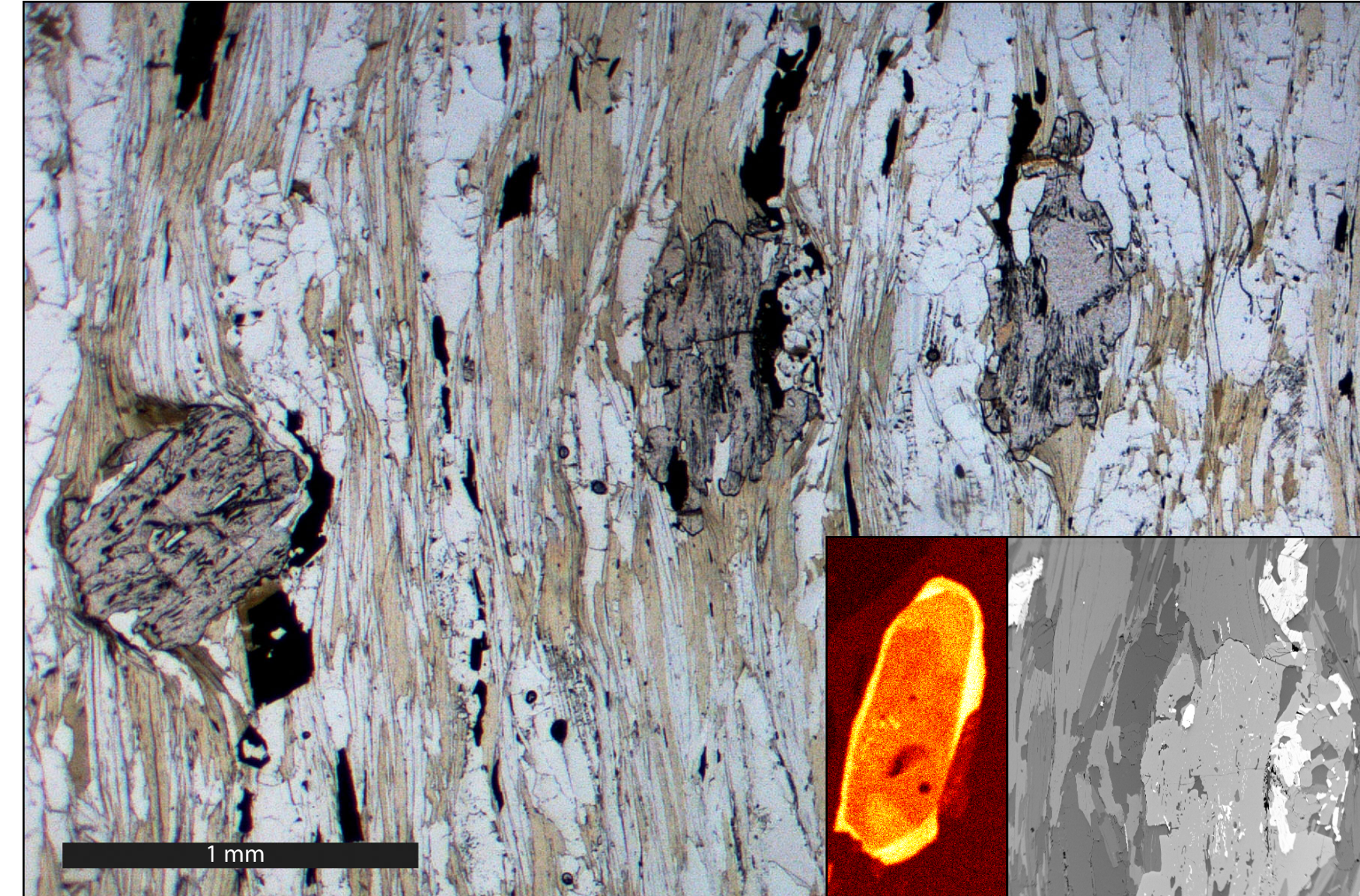


Figure 3. (Left) Photomicrograph of sample B-22 illustrates the complex metamorphic and deformational history represented schematically in Fig. 2. A small inclusion-free core is visible in the garnet crystals to the left and right (the plane of the thin section apparently does not pass through the core of the center garnet). The dominant foliation wraps around cores, but inclusion trails in garnet overgrowth are parallel to the external foliation. Younger deformation rotated the garnet at left so that inclusions are no longer parallel to external foliation. Multistage growth is also evident in monazite: cores give a Silurian age (~430 Ma) while syn-tectonic, high-U rims yield early Devonian ages (405 - 415 Ma; Bosbyshell et al., 2016). Monazite with high-U rims are included in garnet overgrowths. (Right) B-22 contains the assemblage Ms + Bt + Grt + Pl + Qtz; sillimanite is present as inclusions in garnet. (Right) Theriak-Domino mineral assemblage diagram shows stability field (yellow) of assemblage without kyanite; ky + st coexist only in the small field in orange. Thus, peak metamorphic conditions in the Devonian are estimated at ~600 °C and 650 - 700 MPa. Grt-Bt and GASP thermobarometry on near-by rock yielded results of 600 ± 50 °C and 750 ± 100 MPa (Bosbyshell 2001).

Ge-06-33

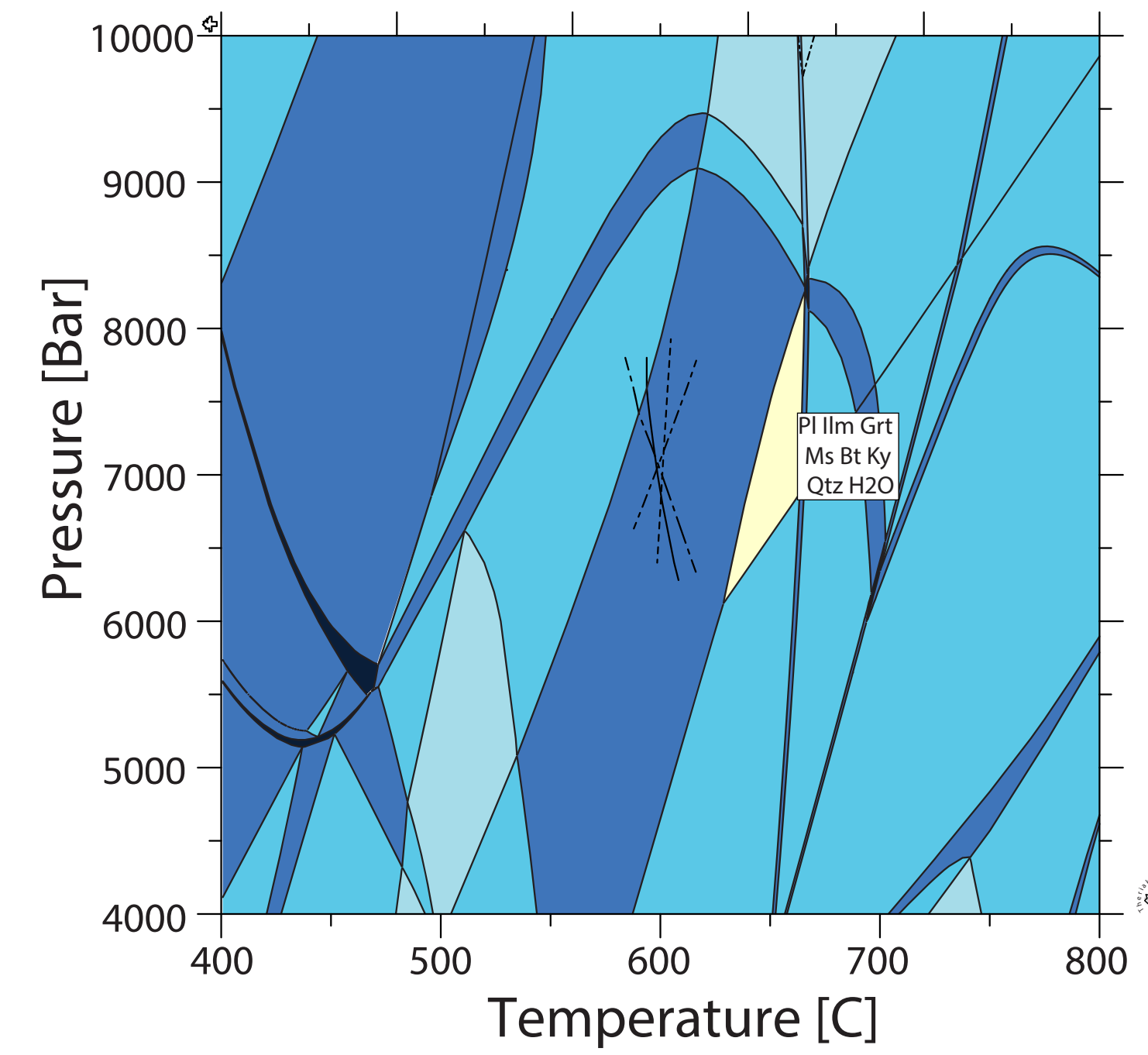
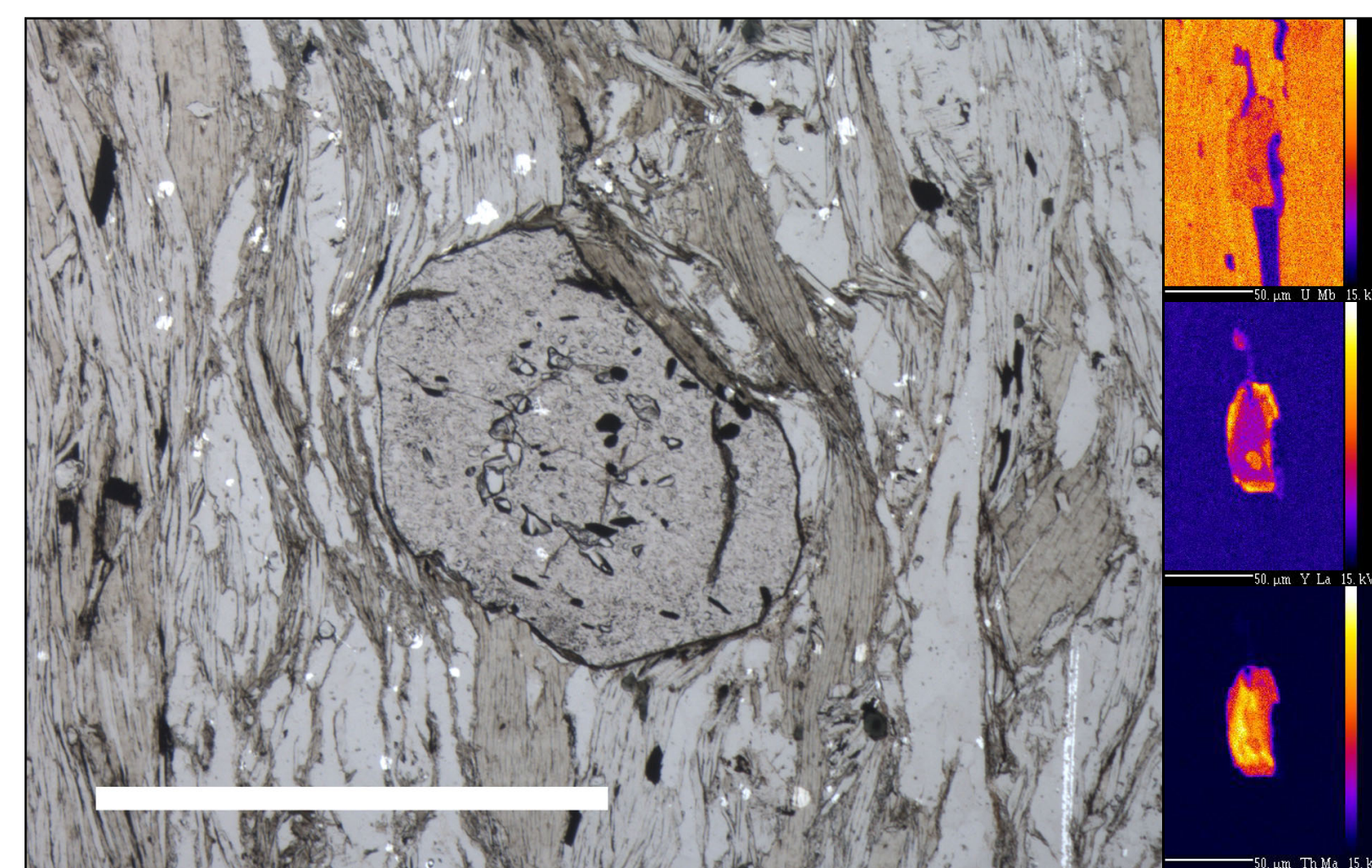


Figure 4. A similar multistage history is evident in sample Ge-06-33, which comes from the contact between the Wissahickon Schist and a small body of granodioritic gneiss. The age of the igneous protolith is uncertain, but a larger intrusion of similar composition, the Springfield Granodiorite (Fig. 1), yielded a U-Pb zircon age of 427 ± 3 Ma (Bosbyshell et al. 2005). This is the same as the age of the high-Y, low-Th monazite core shown above, 428 ± 4.5 Ma (Bosbyshell, et al., 2016). Bosbyshell et al. (2016) concluded that the monazite core and the garnet core likely formed during a period of contact metamorphism related to the granodiorite intrusion. Regional metamorphism is thought to be Devonian, based on the ~380 Ma age of monazite in this and other Wissahickon Schist samples (Bosbyshell, 2008, Bosbyshell et al., 2016). (Right) Theriak-Domino mineral assemblage diagram. Garnet isopleths from the central portion of the overgrowth intersect at approximately 600 °C and 700 GPa, but the position of the stability field of the observed mineral assemblage indicates that maximum temperature exceeded 600 °C.

Diffusion modeling

Assuming f_{O_2} is nearly that of the graphite- O_2 buffer (Chakraborty and Ganguly, 1991; Carlson, 2006; Chu and Ague, 2015), the diffusivity (D) of cation i , is given by:

$$\ln D_i = \ln D_{O,i} + k_i(a_o - a_{O,Alm}) - \frac{Q_i + PV_i}{RT}$$

where

D_o = pre-exponential term

Q = activation energy

V = activation volume

k = compositional coefficient

i refers to the cation

$a_{O,Alm}$ = unit cell dimension of Alm

$$a_O = X_{Alm}a_{O,Alm} \cdot X_{Prp}a_{O,Prp} \cdot X_{Sps}a_{O,Sps} \cdot X_{Grs}a_{O,Grs}$$

Numerous workers have carried out experiments to constrain these parameters. Carlson (2006) derived a set of parameters based on numerical simulation of natural diffusion profiles. Chu and Ague (2015) presented a set derived from a statistical analysis of published experimental values. Here we model Ca and Mn zoning profiles across a core-overgrowth boundary in garnet and compare results obtained using the two sets of parameters.

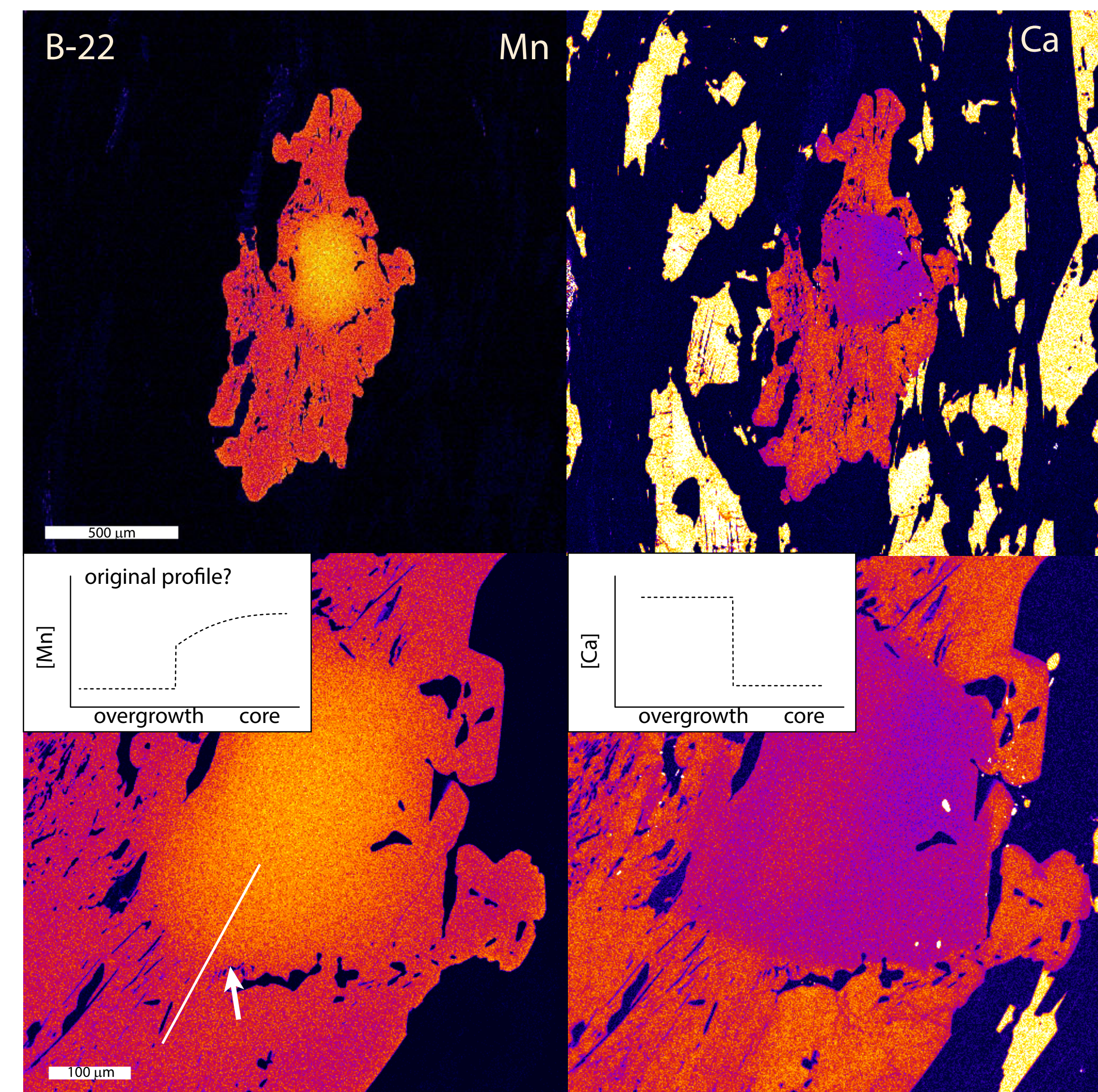


Figure 5. X-ray maps show the well defined core and overgrowth in garnet from both samples. In both B-22 (above) and Ge-06-33 (below), Ca maps indicate that the original core-rim boundary was an abrupt step. In B-22, the Mn map indicates Rayleigh fractionation controlled growth-zoning within the core while the core in Ge-06-33 appears homogeneous. The core-overgrowth boundary in both is somewhat diffuse, but arrows indicate where sharp boundaries are preserved, suggesting that a step was also present in the original Mn profile in garnet from both samples. Lines indicate the locations of the modeled transects.

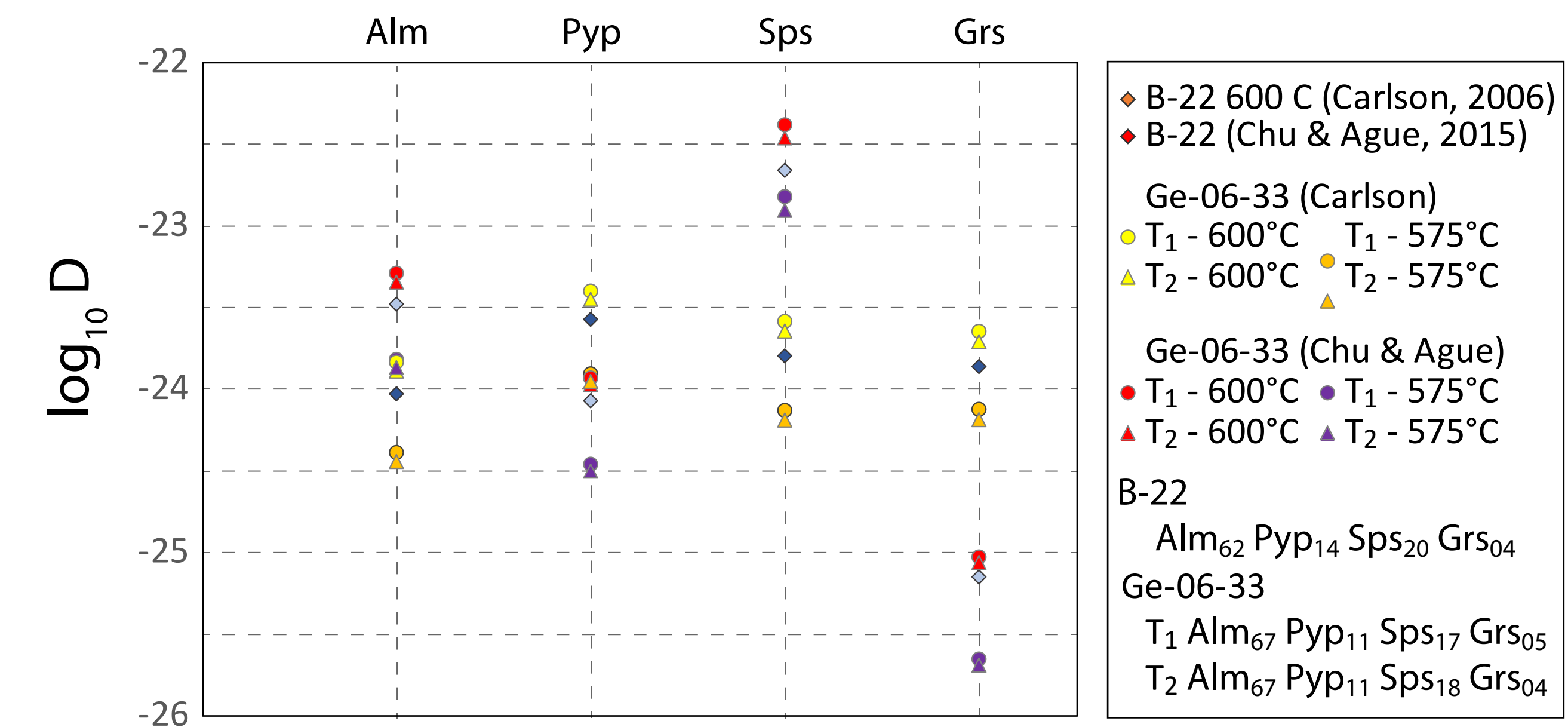
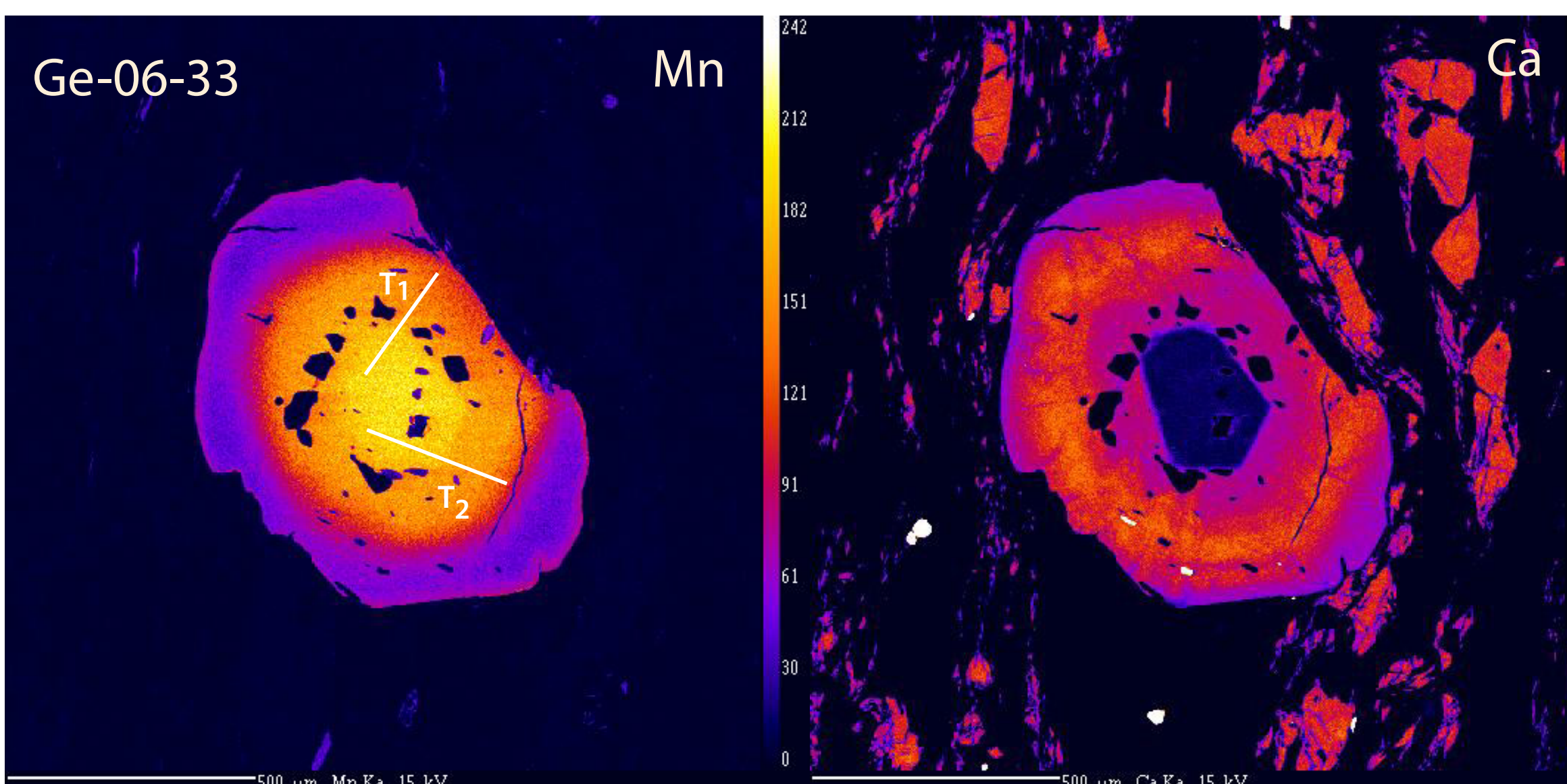
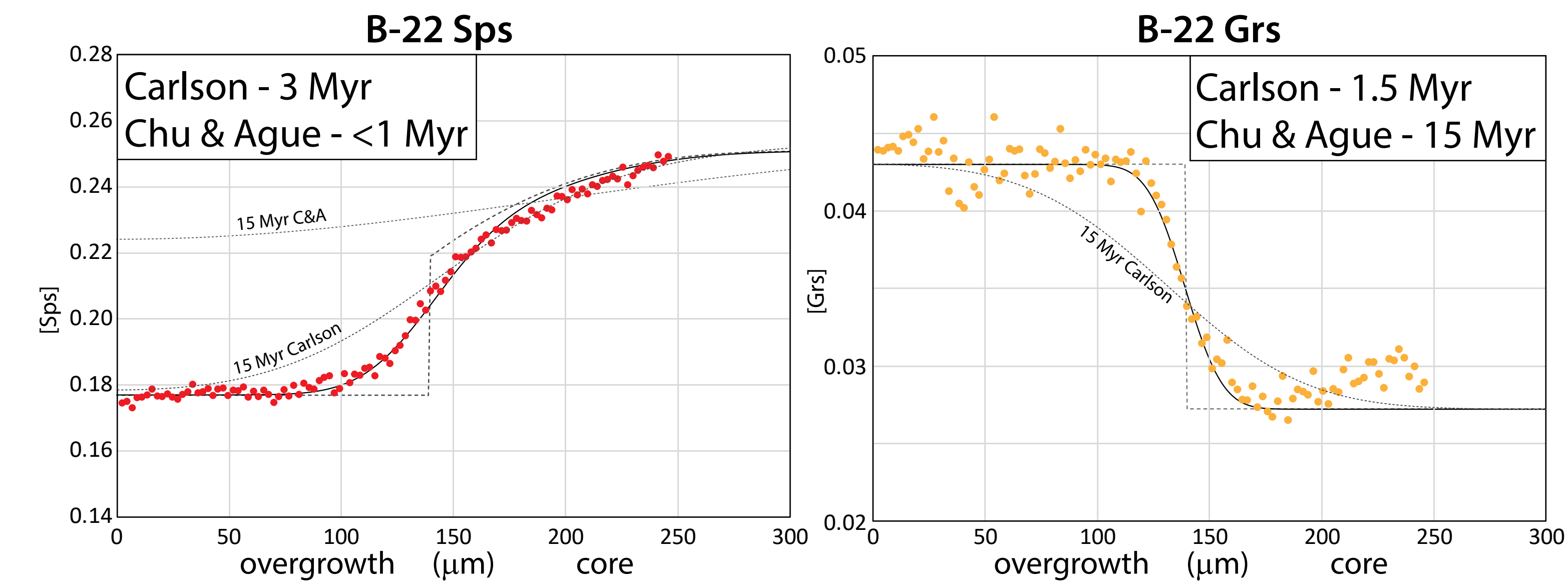


Figure 6. Diffusivity is a function of composition and temperature. The graph above compares the diffusivities used in the calculations below. Garnet compositions are given at right.

Results



Conclusions

These results suggest that duration of maximum temperatures during the Acadian orogeny were short-lived, probably less than 5 Myr. The preservation of growth-zoning in Mn at the sub-500 µm scale is consistent with the short duration of max T obtained from both sets of Mn and Carlson's (2015) Ca parameters. This short duration regional metamorphism requires a transient heat source that is, at present, unidentified.

References

- Bosbyshell, H., 2001. Thermal evolution of a convergent orogen: Pressure-Temperature-Deformation-Time paths in the central Appalachian Piedmont of Pennsylvania and Delaware (Ph.D. thesis). Bryn Mawr, Pa, Bryn Mawr College, 233 p.
- Bosbyshell, H., 2004. Introduction to Day 2, in Blackmer, G.C. and Stogli, L., eds., Marginalia - Magmatic arcs and continental margins in Delaware and southeastern Pennsylvania: Guidebook, 68th Annual Field Conference of Pennsylvania Geologists, West Chester, PA, p. 82-88.
- Bosbyshell, H., 2008. Bedrock geologic map of a portion of the Philadelphia quadrangle, Montgomery and Philadelphia Counties, Pennsylvania: Pennsylvania Geological Survey, 4th series, Open-File Report OF-08-05, 21 p. (PDF).
- Bosbyshell, H., Albrecht, J. A., and Blackmer, G. C., 2005. A Silurian age for the Springfield Granodiorite: Tectonic and metamorphic implications for the central Appalachian piedmont. Geological Society of America Abstracts with Programs, v. 37, p. 65.
- Bosbyshell, H., Blackmer, G.C., Schend, W.S., and Stogli, L., 2014. Defining the West Grove Metamorphic Suite: Implications for tectonic interpretations of the central Appalachian piedmont. In P. de Wit, Ed., Field Trip Guide Northeastern Section of the Geological Society of America: Geological Society of America Field Guide, p. 17-33.
- Bosbyshell, H., Stogli, L., Blackmer, G.C., Schend, W.S., Mathur, R., and Valencia, V., 2015. The tectono-thermal evolution of the central Appalachian Orogen: Accretion of a peri-Gondwanan(?) Ordovician arc, in D.R. Brezinski, J.P. Haka, and R.A. Ort, Jr., Eds., Tripping from the Fall Line: Field Excursions for the GSA Annual Meeting, Baltimore, 2015: Geological Society of America Field Guide 40, p. 35. doi:10.1130/2015.004003.
- Bosbyshell, H., Stogli, L., and Blackmer, G.C., 2016. Monazite age constraints on the tectono-thermal evolution of the central Appalachian Piedmont. American Mineralogist, v. 101, p. 1820-1838.
- Carlson, W.D., 2006. Rates of Fe, Mg, Mn, and Ca diffusion in garnet: American Mineralogist, v. 91, p. 1-11.
- Chakraborty, S. and Ganguly, J., 1991. Cation diffusion in aluminosilicate garnets: Experimental determination in spinel-almandine diffusion couples, evaluation of effective binary diffusion coefficients, and applications: Contributions to Mineralogy and Petrology, v. 111, p. 74-86.
- Chu, X. and Ague, J.J., 2015. Analytical and experimental data on divalent cation diffusion kinetics in aluminosilicate garnets with application to timescales of peak Barrovian metamorphism, Scotland: Contributions to Mineralogy and Petrology, v. 170, p. 1-27.
- Hibbard, J.E., van Staal, C.R., Banks, D.W., and Williams, H., 2006. Lithotectonic map of the Appalachian orogen, Canada-United States of America. Geological Survey of Canada Map 2096A, scale 1:500,000.
- Meredith, F.A., Ryan, Davis, L., Conih, R.A., Crowley, J.L., and Karabinos, P., 2014. A newly identified Gondwanan terrane in the northern Appalachian Mountains: Implications for the Acadian orogeny and closure of the Iapetus Ocean. Geology, v. 42, p. 539-542. doi:10.1130/G35699.1.

Figure 7. Top, results for B-22 along the transect shown at left modeled at 600°C. Lower figures show results for Ge-06-33 along the two transects shown at left. At 600°C, the time required to reproduce the measured diffusional modification was < 0.5 Myr for all but Grs using the Chu and Ague parameters. These plots show the results at 575°C.