

Geochemistry of Anthophyllite-Garnet-Talc Schists from the Little Pine Garnet Mine, North Carolina: Tectonic Implications for the Mars Hill Terrane and Grenville Basement

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Abstract
The Little Pine Garnet Mine (LPGM), located between the Mars Hill and Grenville basement terranes in the Western Blue Ridge province of the Appalachian Mountain Belt has outcrops of anthophyllite - gedrite - biotite - chlorite ± staurolite ± garnet schists (group I), garnet - hornblende - biotite - quartz - plagioclase gneisses (group II), and talc - gedrite - chlorite - garnet - ilmenite ± anthophyllite ± staurolite schists (group III), interbedded with quartzofeldspathic biotite gneisses. These mineral assemblages are indicative of protoliths enriched in Mg, but with significant amounts of Al, making them rather unusual. Geochemical analysis of these rocks reveals that groups I and II were mostly E-MORBs affected by hydrothermal alteration, whereas group III rocks were likely greywackes. None of the rocks analyzed have any subduction zone signatures characteristic of boninites or High Mg andesites. Isocon diagrams show that the LPGM groups I and II schists were depleted in Si, Ca, and Na, but enriched in Mg, Fe, Zr, La, and Ce relative to E-MORBs. Petrographic group I, containing fine-grained garnet, showed slight losses in Y and Yb, whereas petrographic group III with very coarse-grained garnet showed significant gains of these elements. These results suggest that the E-MORBs were affected by hydrothermal alteration on the seafloor, which in turn suggests the existence of a small ocean basin between the Mars Hill terrane and Laurentia.

Abbreviations:
Anth: anthophyllite; Alm: almandine; Ap: apatite; Bt: biotite; Chl: chlorite; Gd: gedrite; Gr: grossular; Gt: garnet; Ilm: ilmenite; Ms: muscovite; Plg: plagioclase; Prp: pyrope; Qz: quartz; Rt: rutile; Sill: sillimanite; Sps: spessartine; St: staurolite; Tc: talc; Tn: titanite; WBR: western Blue Ridge; Zrn: zircon

Introduction and Geologic Setting
Mapping by Thigpen and Hatcher (2017) places the LPGM (latitude: 35.770000, longitude: 82.622861), within the WBR in the Grenville basement close to its border with the Mars Hill terrane, and a few kilometers from the Haysville fault, which defines the boundary between the western and central blue ridge provinces (Fig. 1). According to Merschat (2009), the LPGM is located within the Taconic garnet zone close to the kyanite - in isograd (Fig. 2). The LPGM schists and gneisses are characterized by the assemblages: Anth - Gd - Bt - Chl - St - Rt - Ilm - Qz - Plg - Gt (fine - grained) - Sill ± Ms (group I), Qz - Hb - Grt - Bt - Plg - Ilm - Sill (group II), and Tc - Gd - Ilm ± Gt (very coarse grained; Fig. 3) - Chl ± Anth ± Bt ± Plg ± Qz ± Rt (group III; Table 1) indicating that it belongs to the sillimanite rather than the garnet zone. The abundance of Anth, Gd, and Tc coupled with the presence of significant amounts of Bt, Gt, St, and Qz suggest that the protolith of these rocks may be an adakite, a boninite, or a high Mg andesite, all of which are characteristic of subduction zone settings. Alternatively, the LPGM rocks' protolith may have been an altered basalt or peridotite, typical of ophiolitic fragments, indicative of a different tectonic setting. To understand the origin of the Little Pine Garnet Mine a geochemical analysis with emphasis on immobile element concentrations is necessary. This study focuses on the chemical signatures of the three different petrographic groups comprising Little Pine Garnet Mine in order to determine its protolith and tectonic setting, and, therefore better understand the history of the Western Blue Ridge Province.



Table 1: Mineral assemblages for analyzed samples

| Group | Sample # | Mineral Assemblage |
|-------|----------|---|
| I | LP-1 | Anth - Gd - Chl - Bt - St - Rt - Ilm - Qz - Plg - Sill - Ttn |
| | LP-7 | Gd - Anth - Bt - Ms - St - Chl - Rt - Ilm - Qz - Gt - Sill - Ttn - Ap |
| II | LP-10 | Hb - Gt - Bt - Qz - Plg - Rt - Ilm - Sill - Ap |
| | LP-12 | Gd - Anth - Gt - Tc - Chl - Bt - St - Qz - Rt - Ilm |
| III | LP-13/30 | Tc - Chl - Gd - Gt - Ilm - Qz - Bt - Ms - Ttn |

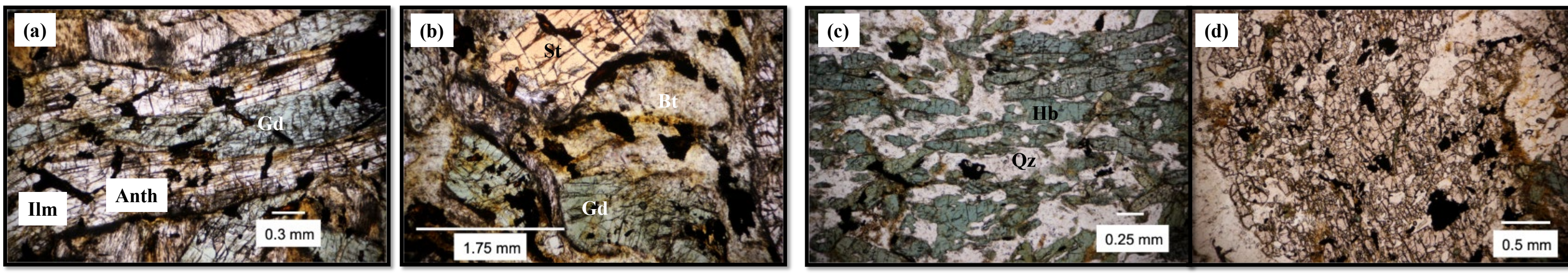


Figure 4: Photomicrographs of LPGM samples (a) Gd and Anth, LP-1, PPL; (b) St, Gd & Bt, LP-1, PPL; (c) Hb + Qz + Ilm, LP-10, PPL; (d) Garnet porphyroblast, LP-10, PPL; (e) Fibrous sillimanite with Qz, Gd, and Bt, LP-10; (f) Gt - Chl - Tc, LP-12; XPL.

Objectives
 > Investigate chemical patterns for petrographic groups I, II, and III
 > Identify protolith(s) and tectonic setting of LPGM schists & gneisses
 > Refine tectonic history of the WBR Provinces based on LPGM protolith

Analytical Techniques
Six samples from the Little Pine Garnet Mine were analyzed for major and trace elements using an Agilent 5110 VDV inductively coupled plasma atomic emission spectrometer (ICP-AES). Preparation for major element analysis consisted of fusion of rock powders with 1:2 lithium metaborate: lithium tetraborate flux and dissolution in 1:7 H₂SO₄. Trace element analysis preparation consisted of fusion of rock powders with 1:2 lithium metaborate: lithium tetraborate flux and dissolution in reagent grade 5% HCl (e.g. Cremer and Schlocker, 1976; Delijska et al., 1988).

Results
 • All rocks have SiO₂ values characteristic of ultrabasic to basic rocks.
 • Group II gneisses are characterized by higher SiO₂, CaO, Na₂O, K₂O, Rb, Nd ± Sr compared to groups I & II (Tables 2 & 3).
 • Group III schists have unusually high Fe₂O₃ (> 18 wt%), and the highest contents of Hf, Y, Yb, and Zr (Tables 2 & 3).
 • All samples display concave upward REE patterns (Fig. 5a)
 • None of the samples plot in the adakite or boninite fields of Martin (1986) or Shervais (1982) (Figs. 5b & 6c)

Table 2: Major element oxides (weight %) of LPGM samples arranged by group

| | Petrographic Group I | | Petrographic Group II | | Petrographic Group III | | |
|--------------------------------|----------------------|-----------|-----------------------|----------|------------------------|----------|--|
| | LP-1 | LP-7 | LP-10 | LP-12 | LP-13 | LP-30 | |
| SiO ₂ | 47.8185 | 35.0385 | 52.4193 | 38.127 | 30.76785 | 37.0194 | |
| TiO ₂ | 1.1869 | 3.7018 | 2.0086 | 2.2161 | 1.4027 | 4.067 | |
| Al ₂ O ₃ | 11.907 | 17.6715 | 14.0805 | 16.39575 | 20.06235 | 17.97825 | |
| Fe ₂ O ₃ | 11.44949 | 17.26001 | 15.50899 | 20.42613 | 25.81496 | 18.65367 | |
| MnO | 0.0774 | 0.09675 | 0.2709 | 0.16125 | 0.4128 | 0.16125 | |
| MgO | 11.75138 | 15.82933 | 4.71724 | 13.26309 | 14.56697 | 15.99543 | |
| CaO | 1.3475 | 0.998875 | 4.44125 | 1.11375 | 1.47125 | 5.54125 | |
| Na ₂ O | 0.62054 | 0.816145 | 1.531115 | 0.98477 | 0.12141 | 0.83638 | |
| K ₂ O | 0.14272 | 0.603 | 1.75473 | 0.13266 | 0.04221 | 0.10854 | |
| P ₂ O ₅ | 0.2291 | 0.561393 | 0.240555 | 0.41238 | 0.309285 | 0.584205 | |
| LOI | 3.441 | 3.49 | 0.29 | 2.05 | 5.33 | 2.98 | |
| Total | 93.524 | 96.065303 | 97.26318 | 95.28288 | 100.3018 | 103.9254 | |

Table 3: Trace element concentrations (ppm) of LPGM samples. b.d. = below detection limit.

| | Petrographic Group I | | Petrographic Group II | | Petrographic Group III | | |
|----|----------------------|--------|-----------------------|--------|------------------------|--------|--|
| | LP-1 | LP-7 | LP-10 | LP-12 | LP-13 | LP-30 | |
| Ba | 37 | 74.46 | 476.96 | 594.2 | 30.69 | 22.28 | |
| Ce | 80.785 | 71.89 | 73.89 | 54.86 | 51.94 | 68.535 | |
| Cr | 62.69 | 34.48 | 746.94 | 164.11 | 50.27 | 40.2 | |
| Cu | 231.47 | 36.76 | 31.13 | 59.45 | 160.45 | b.d. | |
| Dy | 2.18 | 2.87 | 9.64 | 3.4 | 19.42 | 9.98 | |
| Er | 1.99 | 8.83 | 5.22 | 1.03 | 9.31 | 18.13 | |
| Eu | 2.62 | 2.085 | 2.45 | 1.98 | 1.89 | 2.34 | |
| Gd | 9.25 | 11.66 | 11.35 | 6.3 | 17.04 | 13.26 | |
| Hf | 4.63 | 1.65 | b.d. | 2.82 | 13.69 | 2.72 | |
| La | 57.2 | 61.12 | 59.52 | 60.21 | 49.51 | 47.8 | |
| Lu | 2.81 | 1.71 | 1.6 | 0.56 | 3.06 | 2.2 | |
| Nb | 10.37 | 27.66 | 14.2 | 10.07 | 10.22 | 30.71 | |
| Nd | 18.09 | 21.77 | 34.96 | 30.81 | 23 | 23.43 | |
| Ni | 86.47 | 70.34 | 33.48 | 62.58 | 58.55 | 86.75 | |
| Pr | b.d. | b.d. | 14.74 | 4.86 | 4.52 | b.d. | |
| Rb | 5.55 | 17.39 | 68.71 | 18.57 | 0.15 | 2.57 | |
| Sr | 24.31 | 23.79 | 41.46 | 14.81 | 84.91 | 39.54 | |
| Sm | 2.82 | 6.44 | 6.45 | 3.99 | 5.53 | 6.05 | |
| Mg | 14.6 | 15.34 | 3.37 | 588.69 | 7.25 | 14.68 | |
| Tm | b.d. | b.d. | b.d. | b.d. | 0.76 | b.d. | |
| Th | 1.4 | 1.71 | 1.49 | 0.8 | 2.57 | 1.85 | |
| V | 240.22 | 295.68 | 356.25 | 146.04 | 214.14 | 354.91 | |
| Y | 22.34 | 24.53 | 49.67 | 18.45 | 146.09 | 84.59 | |
| Yb | 3.49 | 4.24 | 5.54 | 2.06 | 12.17 | 10.95 | |
| Zn | 108.37 | 216.22 | 160.55 | 168.99 | 113.31 | 103.64 | |
| Zr | 311.29 | 316.95 | 124.65 | 215.75 | 598.94 | 333.52 | |

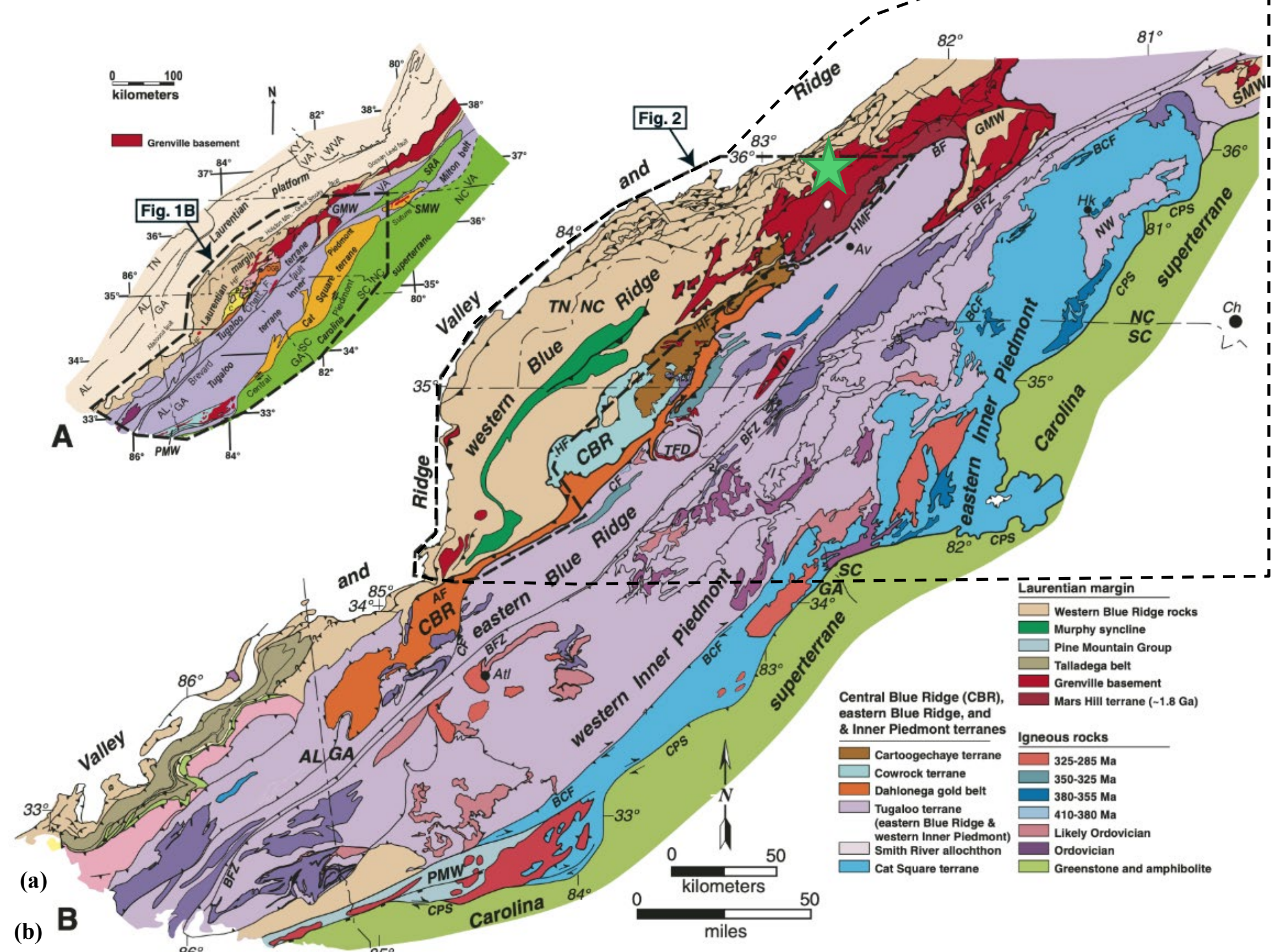


Figure 1: A) & B) Geological maps of part of the Southern Appalachians showing the Blue Ridge & Inner Piedmont terranes and their tectonic boundaries. CBR: Central Blue Ridge; HMF: Holland Mountain Fault; BFZ: Brevard Fault zone; GMW: Grand Father Mountain Window. From Thigpen & Hatcher (2017). Green star: LPGM location.

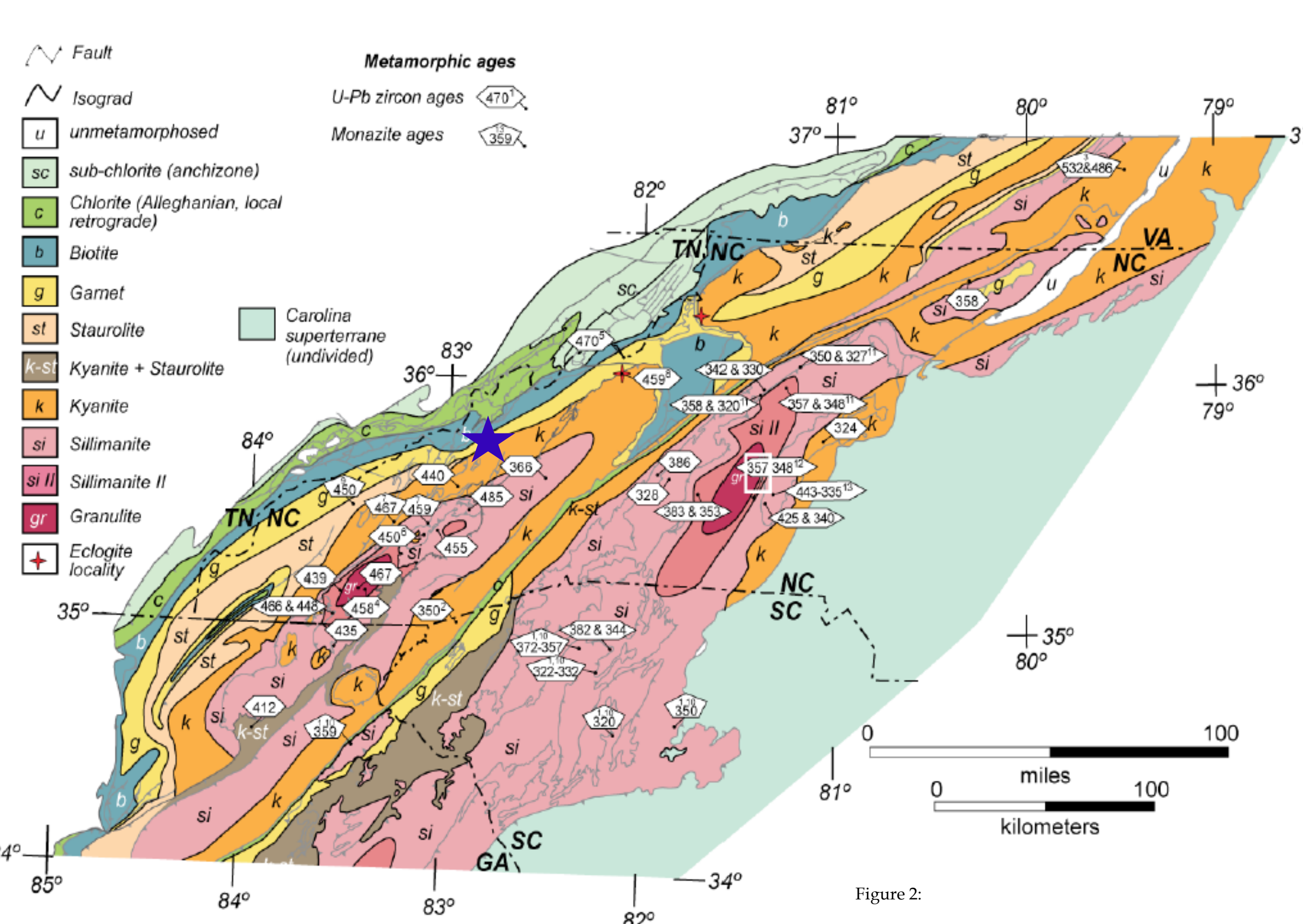


Figure 2: Metamorphic map of part of the Southern Appalachians outlined by dashed frame in Fig. 1 showing the distribution of the Taconic isograds, as well as U-Pb zircon and Th-Pb monazite ages. From Merschat (2009). Location of the LPGM indicated with a blue star.

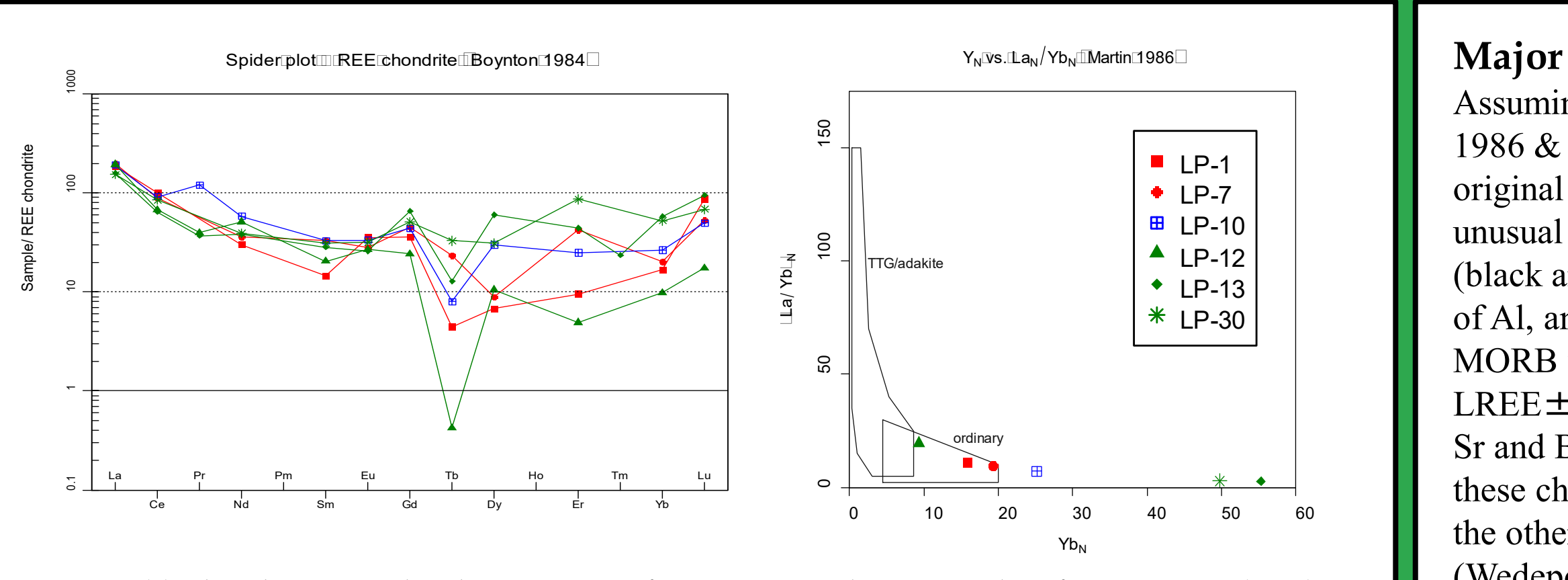


Figure 5: (a) Chondrite normalized REE patterns for LPGM samples using values from Boynton (1984) showing E-MORB like patterns; (b) Plot of normalized Yb vs. La/Yb normalized ratios after Martin (1986).

Tectonic Setting of Protoliths
Based on their major element compositions and their REE patterns, all LPGM protoliths were likely basalts except LP-10 which was most likely a greywacke. The tectonic setting of LPGM protoliths was investigated following the method of Pearce (2014). On the Nb/Yb vs Th/Yb plot of Pearce (2014), almost all samples fall in the MORB/OIB array, closest to E-MORBs (Fig. 6a). LPGM samples then plot in the E-MORB tholeiitic field on the Nb/Yb vs. TiO₂/Yb diagram (Fig. 6b). This is further supported by all samples plotting in the MORB/OIB fields of Shervais (1982) (Fig. 6c), and the lack of an arc signature on N-MORB normalized spider plots (Fig. 7). All LPGM samples also plot in the field of oceanic islands on the discriminant diagram of Hollocher et al. (2012) (Fig. 7b). Because LP-10 is rich in Ca and Fe and plots close to the other samples on the same discriminant diagrams, its clastic protolith was likely derived from E-MORBs.

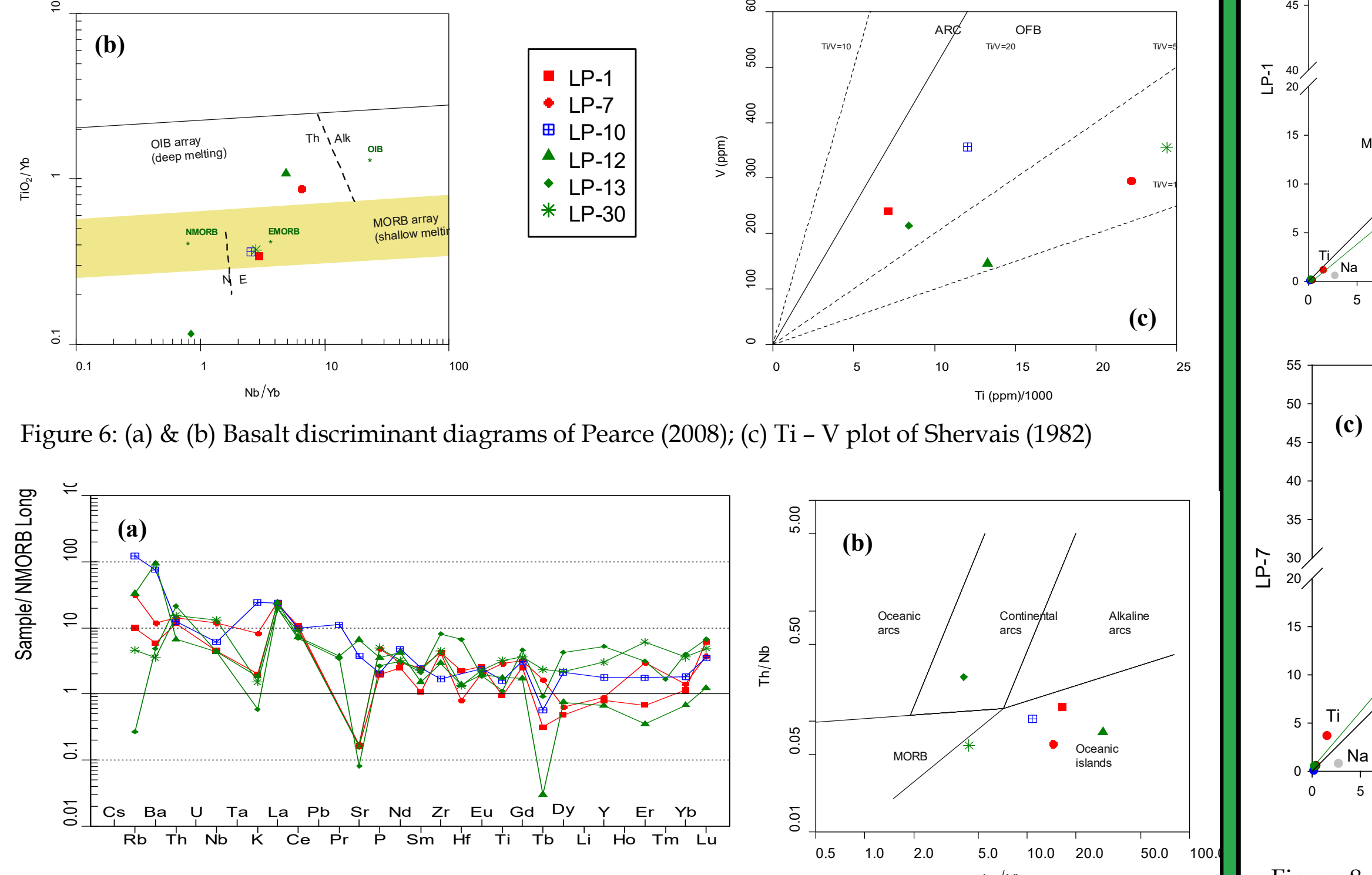


Figure 6: (a) & (b) Basalt discriminant diagrams of Pearce (2008); (c) Ti - V plot of Shervais (1982).

Major and Trace Element Mobility
Assuming that Groups I & III LPGM samples represent metamorphosed E-MORBs, isocon diagrams (Gresens, 1967; Grant, 1986 & 2005) can be used to investigate how much deviation there is between the composition of these rocks and their original protoliths. This is needed to understand the processes that may have contributed to these rocks developing their unusual compositions. Comparison using isocon diagrams was carried out on the basis of constant mass and constant Al₂O₃ (black and green lines, respectively, Figs. 8-10). The proximity of both lines on most plots attests to the relative immobility of Al, and suggests that changes to E-MORB chemistry involved minimal changes in volume. Compared to average E-MORB values (Gale et al., 2013), Groups I and III LPGM samples both showed gains of Mg, Fe²⁺, Zn, Zr, Hf, and LREE ± Ti, and losses of Ca, Si, Na, Cr, and Ni. V, Nb, Th and Sr remained almost unchanged (Figs. 8 & 10; Table 4). Sr and Ba registered significant losses for all samples except LP-12 which showed significant gains (Table 4). In addition to these changes, Group III LPGM schists show large gains in HREE, Sc, and Y; elements typically concentrated in garnet. On the other hand, Group II LPGM show enrichment for all major and trace elements relative to average greywackes (Wedepohl, 1995), except for Si, Na, K, Lu, Th, and Zr (Fig. 9, Table 4). The enrichment of Mg, Fe²⁺ and Zn, and depletion of Ca, Na, and Si ± Sr ± Ba are consistent with hydrothermal alteration at T = 200 - 300°C and water : rock ratios of 5 - 125 (Seyfried & Bischoff, 1981; Seyfried and Mottl, 1982; Seyfried, 1987). The apparent enrichment of most elements in LP-10 relative to average greywacke is likely reflective of the siliciclastic protolith of LP-10 being more mafic than average greywacke. The unusually high contents of HREE, Sc, and Y in Group III schists may be an artefact of the coarse-grained nature of garnet in these talc schists, and the difficulty of analyzing representative aliquots of these rocks. The large variation in composition, and relative loss or gain of some elements among samples from the same petrographic group (e.g. LP-13 vs. LP-30, or enrichment of Sr and Ba in LP-12) are likely caused by variations in the extent of hydrothermal alteration (or water : rock ratio), where extensively altered samples tend to be most depleted in SiO₂, and enriched in the relatively immobile elements like Zr, Hf, Y, and Yb. It should be noted that despite the enrichment in LREE, Ti, Yb, and Nb in some LPGM samples relative to E-MORB, the REE and spider plot patterns and the locations of these samples on the discriminant diagrams used in this work are unlikely to be affected given the relatively small changes in the ratios of the elements used.

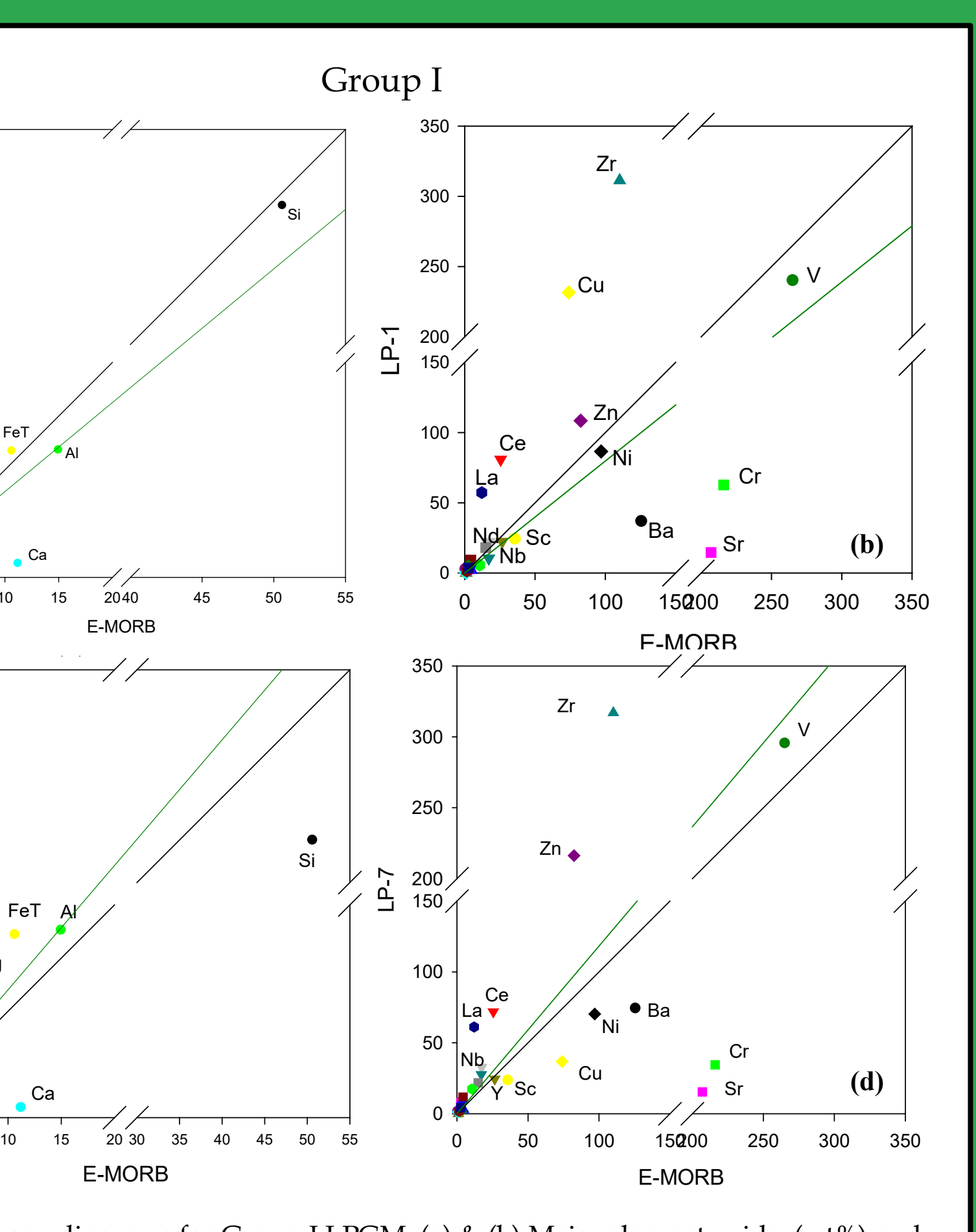


Figure 8: Isocon diagrams for Group I LPGM. (a) & (b) Major element oxide (wt%) and trace element (ppm) values for LP-1; (c) & (d) Major element oxide (wt%) and trace element values for LP-7 compared to average E-MORB of Gale et al. (2013). Note that only the elements of the relevant oxides are labeled on (a) & (c).

Table 4: Average % change in Gp I & III LPGM samples relative to average E-MORB, and Gp II samples relative to average greywackes.

| | Group I | Group III | Group II* |
|--------------------------------|---------|-----------|-----------|
| SiO ₂ | -16.20 | -30.20 | -15.32 |
| TiO ₂ | 59.76 | 67.45 | 178.97 |
| Al ₂ O ₃ | -1.01 | 21.46 | 4.30 |
| Fe ₂ O ₃ | 37.02 | 103.99 | 162.86 |
| MnO | -47.23 | 48.55 | 170.30 |
| MgO | 95.86 | 98.22 | 105.10 |
| CaO | -89.52 | -75.77 | 70.82 |
| Na ₂ O | -73.59 | -76.19 | -48.96 |
| K ₂ O | -5.11 | -76.02 | -12.26 |
| P ₂ O ₅ | 61.99 | 78.40 | 85.04 |
| Ba | -55.59 | 71.89 | 11.96 |
| Cr | 199.13 | 129.02 | 27.40 |
| Ce | -77.51 | -60.71 | 66.98 |
| Cu | 81.24 | 48.58 | 29.71 |
| Dy | -45.35 | 136.65 | 183.53 |
| Er | 96.73 | 245.09 | 137.27 |
| Eu | 82.36 | 60.47 | 104.17 |
| Ga | 58.38 | 41.81 | 73.50 |
| Gd | 145.42 | 186.38 | 183.75 |
| Hf | 23.62 | 223.03 | |
| La | 392.18 | 336.83 | 75.06 |
| Lu | 494.74 | 410.53 | -99.57 |
| Nb | 11.39 | -0.41 | 69.05 |
| Nd | 34.12 | 73.26 | 39.84 |
| Ni | -19.17 | -28.56 | 39.50 |
| Rb | 8.62 | -32.80 | -4.57 |
| Sc | -32.63 | 30.03 | 159.13 |
| Sm | 24.46 | 39.52 | 40.22 |
| Sr | -92.77 | -1.67 | 67.35 |
| Th | 13.75 | 27.29 | -83.44 |
| V | 1.11 | -10.05 | 263.52 |
| Y | -11.90 | 212.19 | 91.04 |
| Yb | 49.23 | 224.07 | 163.81 |
| Zn | 96.96 | 56.12 | 111.25 |
| Zr | 185.30 | 247.63 | -58.73 |

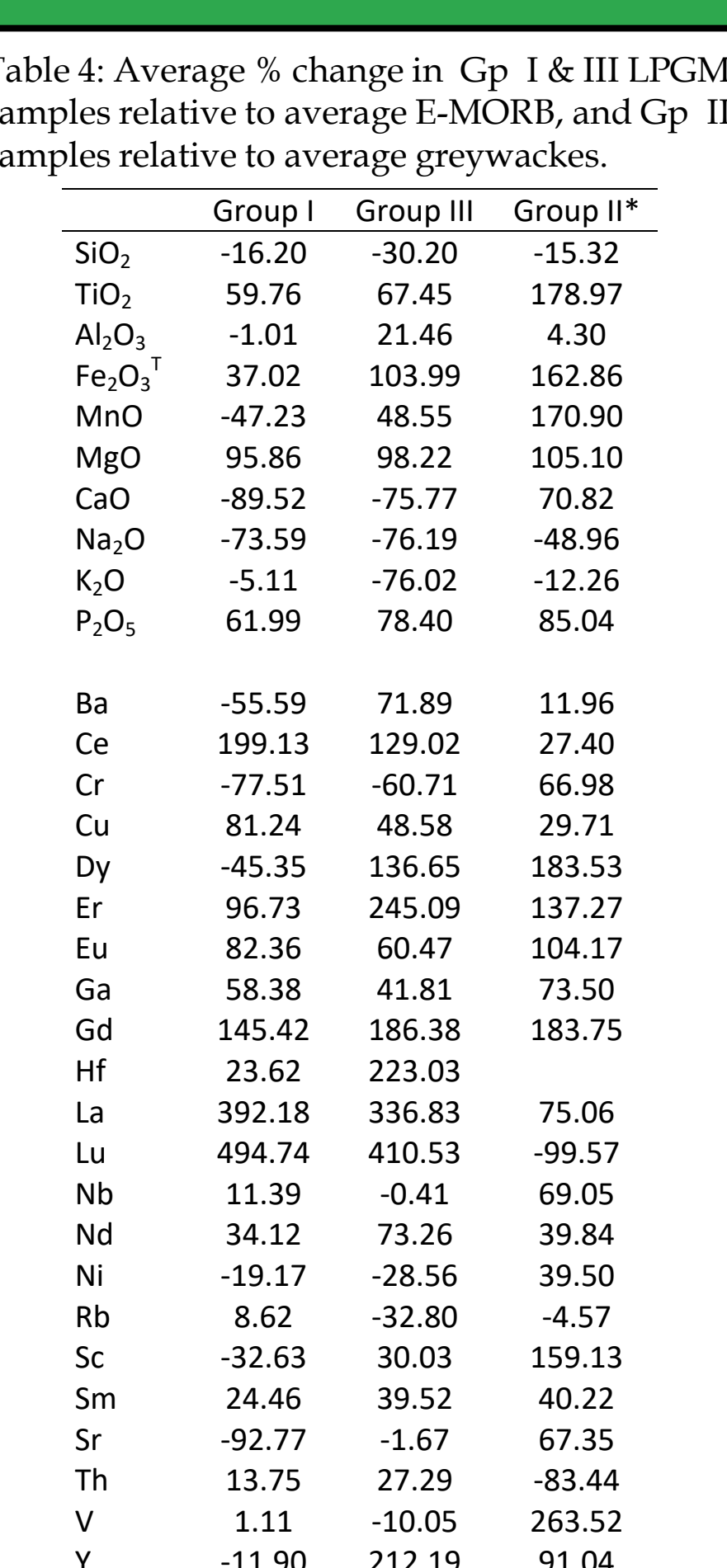


Figure 9: Isocon diagrams for Group II LPGM. (a), (c) & (e) Major element oxide (wt%) and trace element values (ppm) for LP-10; (b), (d) & (f) trace element values (ppm) for LP-12, LP-13, and LP-30, respectively, compared to average greywacke of Wedepohl (1995). Note that only the elements of the relevant oxides are labeled on (a), (c) & (e). Note that Zr (very large gain) for LP-13 and LP-30 and Sr and Ba (very large gains) for LP-12 are not shown as they plot outside the limits of the diagram (Table 4).

Conclusions
 > The LPGM schists and gneisses were metamorphosed under amphibolite facies conditions corresponding to the 1st sillimanite isograd at 580 - 620°C, 5 - 6 kbar (Felix, 2012).
 > LPGM samples have no geochemical signatures characteristic of subduction zones, such as those of boninites or adakites.
 > The protolith of Groups I and III LPGM schists was an E-MORB, likely emplaced on land as an ophiolitic fragment during the Grenvillian orogeny? Group II gneisses were likely greywackes.
 > Isocon diagrams show that LPGM protoliths were likely affected by hydrothermal alteration on the seafloor at T < 300°C and W/R < 125.
 > Within the WBR terrane, the Grenville basement of Laurentia must have been separated from the Mars Hill terrane by a small ocean basin in which the E-MORB protoliths of the LPGM schists formed.

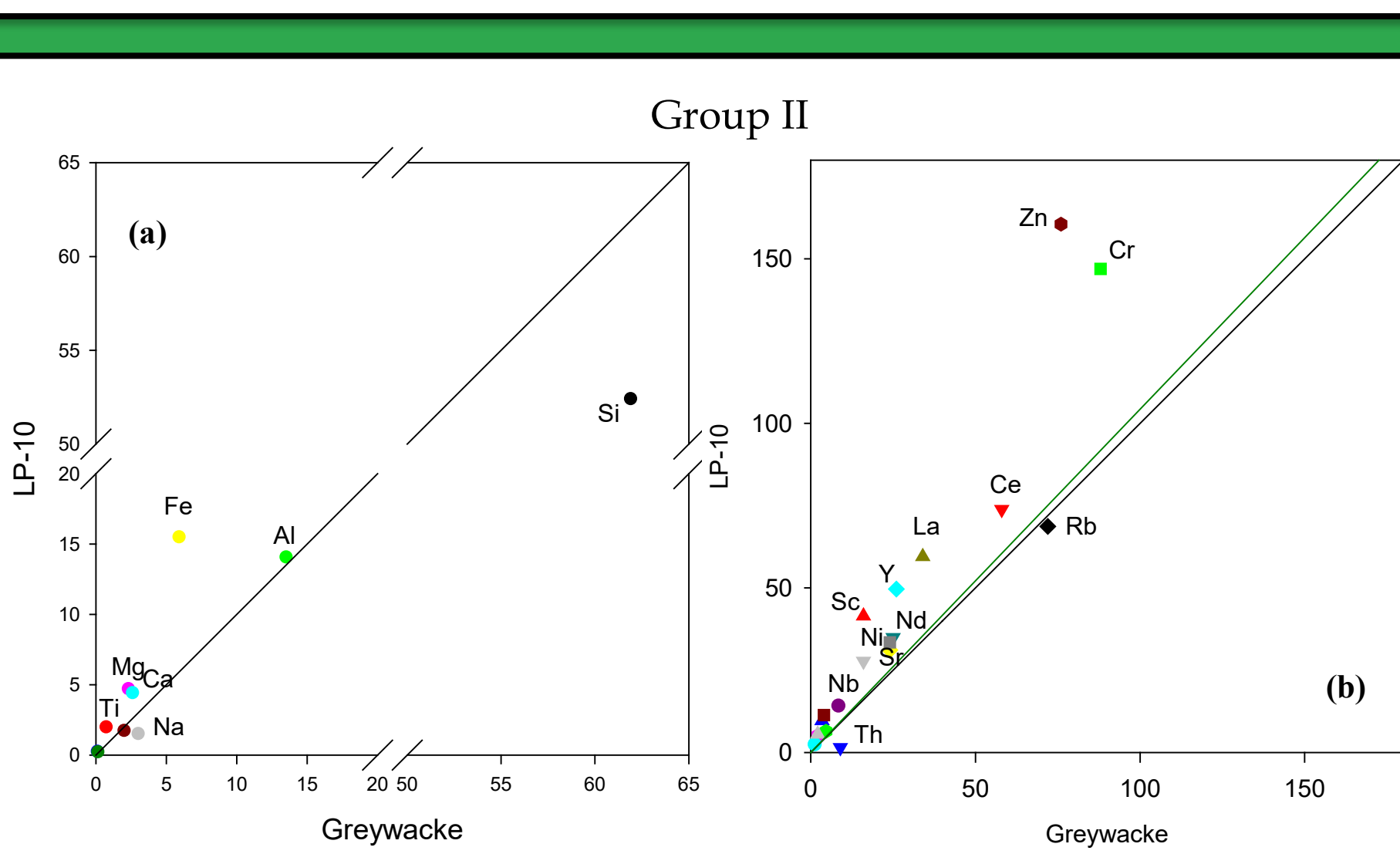


Figure 9: Isocon diagrams for LP-10 (Group II LPGM). (a) Major element oxides (in wt%) and (b) trace elements in ppm compared to average greywacke of Wedepohl (1995). Note that Zr (ost) and Sr and Ba (gained) are not shown as their values plot outside the diagram (Table 4).

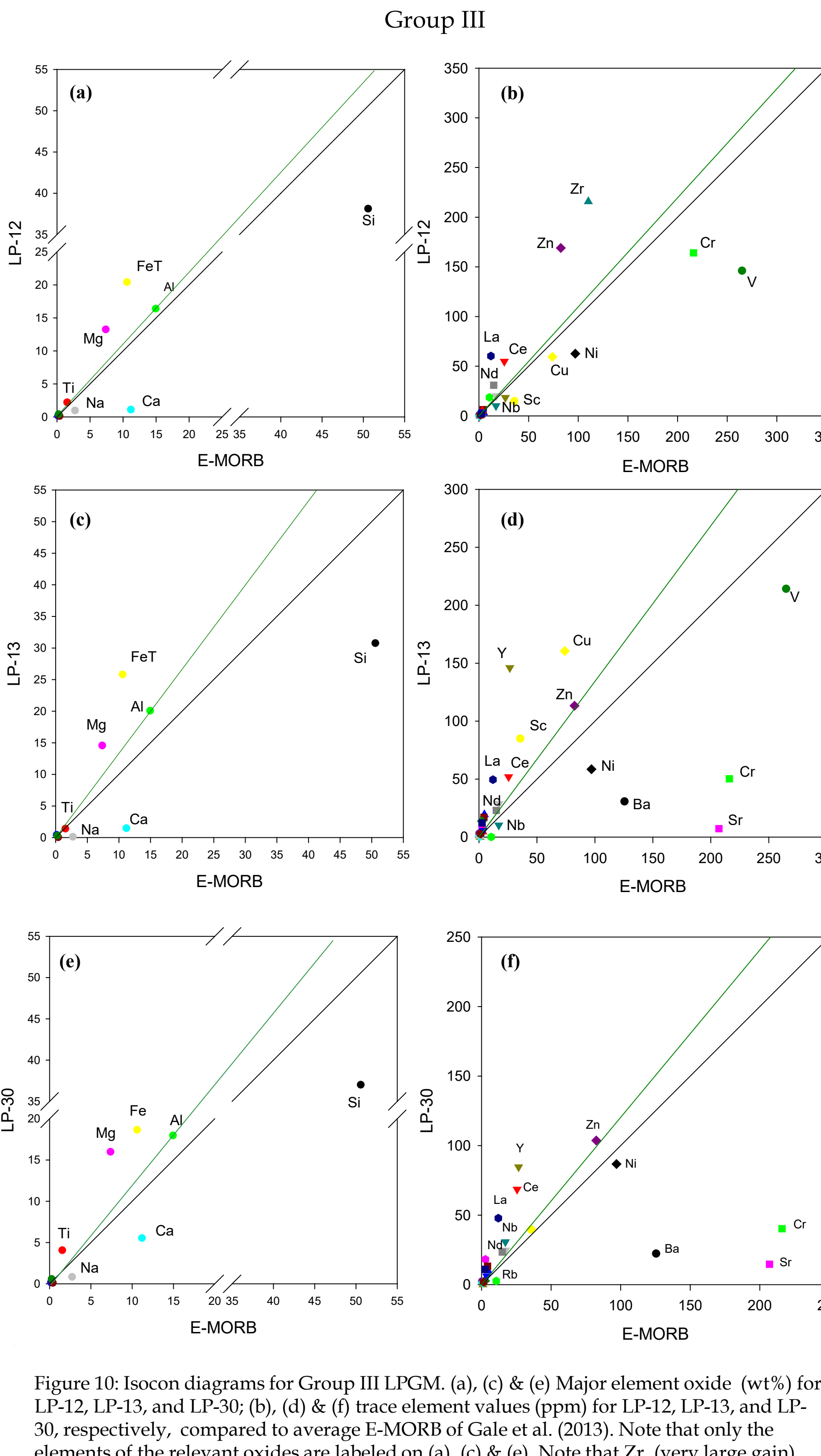


Figure 10: Isocon diagrams for Group III LPGM. (a), (c) & (e) Major element oxide (wt%) and trace element values (ppm) for LP-12, LP-13, and LP-30; (b), (d) & (f) trace element values (ppm) for LP-12, LP-13, and LP-30, respectively, compared to average E-MORB of Gale et al. (2013). Note that only the elements of the relevant oxides are labeled on (a), (c) & (e). Note that Zr (very large gain) for LP-13 and LP-30 and Sr and Ba (very large gains) for LP-12 are not shown as they plot outside the limits of the diagram (Table 4).