APPENDIX 1. ANALYTICAL METHODS

Whole rock analysis

The rocks (except R22517 and 10503) were analyzed under the direction of Ulrich Senff and Andrew Christy by the following methods at the Geoscience Australia (formerly the Australian Geological Survey Organisation or AGSO): (1) X-ray fluorescence (XRF) of 12-22 eutectic borate disks at a flux to sample ratio of about 6.5 to 1 – Na, Mg, Al, Si, P, S, K, Ca, Ti, Mn, Fe; (2) XRF of pressed rock powder pellets (10g weight, PVA binder) – Sc, V, Cr, Ni, Cu, Zn, As, Rb, Sr, Zr, Ba and F; (3) inductively coupled plasma mass spectrometry (ICP-MS) of nitric acid digestions of the borate disk – Ag, Be, Bi, Cd, Ce, Cs, Dy, Er, Eu, Ga, Gd, Ge, Hf, Ho, La, Lu, Mo, Nb, Nd, Pb, Pr, Sb, Sm, Sn, Ta, Tb,Th, U, Y, and Yb. The remaining constituents were measured at Analabs, Welshpool, Western Australia as follows: Li by ICP-MS; B by inductively coupled plasma optical (atomic) emission spectroscopy; Fe^{2+} by titration after digestion with HF/H_2SO_4 in an oxygen-free environment; and total C by Leco. Dissolution in HCl removed carbonate; the residue was dried and its C content determined by Leco. The difference between total C and insoluble C is reported as carbonate. H_2O^- is a moisture content determined by heating to 105 °C and measuring weight difference as H_2O^-, whereas H_2O^+ is calculated from loss on ignition at 1000°C (LOI), FeO, H_2O^- and CO_2. Fluorine was not considered in the H_2O determinations, and yet might have contributed to the LOI, thereby explaining the somewhat high analytical totals.

Samples R22517 and 10503 were analyzed under the direction of Andrew Christy by the following methods at the Australian National University: (1) XRF of 12-22 eutectic borate disks at a flux to sample ratio of about 6.5 to 1 – F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, Mn, Fe; (2) 0.1g gram of sample was digested for typically 2-3 days with

2g crystalline NH_4F and 15 ml concencrated HNO_3 in a sealed 125 ml HDPE bottle in a water bath at 60ºC. The resulting liquid was diluted to ca. 100 ml volume with ultrapure water and analyzed in a Varian Vista Pro axial ICP-AES. Several spectral lines were selected for each of Cr and V. Concentrations were calibrated against solutions made from mixtures of commercial single-element standards. (3) laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) of 3:1 sample:flux Li borate discs with ArF+ (193 nm) laser power 60-70 mJ, laser pulse frequency of 5 Hertz, spot size ca. 200 microns, dwell time on each mass number 10 milliseconds, and a scan time of 1.01 seconds – Be, Sc, Ni, Cu, Zn, Ga, Ge, As, Br, Rb, Sr, Y, Zr, Nb, Mo, Ag, Cd, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, Pb, Bi, Th, and U. Twenty seconds of background were collected before opening laser shutter and drilling sample for 40 seconds. Mass numbers ^{29}Si, ^{44}Ca, ^{49}Ti and ^{55}Mn were collected as potential internal standards, but ^{44}Ca or ^{49}Ti were actually used depending on which element was more abundant in the sample. External standard data for the laser ablation were collected from NIST 612 glass at the start and finish of ablation and after every 10 samples. Raw MS counts were processed by (i) subtraction of average of 20 seconds background counts collected for each analyte immediately prior to each sample. (ii) normalization of background-subtracted counts against those of an internal standard analyte. This eliminates most of the variation due to flow variations, decrease of yield with increasing hole depth, etc. (iii) mean and standard deviations were calculated for a set of internally standardized data after inspection for outliers. (iv) absolute concentration calculated by scaling internally standardized mean against absolute concentration of

analyte in NIST 612 and of internal standard in NIST 612 and in sample (as determined by XRF).

Electron microprobe analysis

Minerals were analyzed in carbon-coated polished thin sections by MGY for constituents with Z > 8 with a wavelength dispersive Cameca SX 100 electron microprobe (EMP) at the University of Maine (15 kV accelerating voltage, 10 nA beam current and 10 µm spot size). Natural silicates and oxides were used as standards and data were processed using the X-Phi correction scheme proposed by Merlet (1994). Fluorine in biotite was analyzed using the TAP crystal and a polylithionite standard. Each tabulated compositions is an average of five 20 s analyses at a given spot; less commonly, only 3 or 4 analyses have been averaged; rarely fewer (e.g., see Electronic Appendix 4 available for downloading on the web site http://www.petrology.oxfordjournals.org). Conditions permitting, we attempted to obtain 3 spot analyses on different grains of each mineral or textural variety thereof (e.g., for orthopyroxene, cores and rims of coarse-grained, coronal) per thin section.

In order to better assess compositional heterogeneity in orthopyroxene and garnet, profiles were obtained using wavelength dispersive spectrometers, 15kV, 40nA, a focused beam, and a dwell time of 1 second.

Ion microprobe analysis

Secondary ion mass spectrometry (SIMS) was conducted on gold-coated polished thin sections using a Cameca ims 4f ion microprobe at the University of New Mexico (UNM) by UNM-Sandia National Laboratories consortium up until late 2001. Further analyses were conducted on the same instrument when it was moved to UNM Department of Earth and Planetary Sciences. Every effort was made to carry out the ion and electron

microprobe analyses at the same spots so that the analyses could be combined. Ion imaging was used to assist in locating sample spots. Tabulated analyses refer to the same spot analyzed with the electron microprobe; in a few cases, they are averages for two or more such spots as indicated in the tables.

Analyses were made using primary $^{16}O^{-}$ ions accelerated through a nominal potential of 10 kV. A primary beam current of 10 nA was focused on the sample over a spot diameter of 10-15 µm. Sputtered secondary ions were energy-filtered using a sample offset voltage of 50 V, energy window of ± 25 V. In mineral matrices with high Be and relatively low Al (i.e. sapphirine) a mass resolution of ~320 (routine operating conditions) were sufficient to measure $^{9}Be^{+}$. However, at low Be and relatively high Al moderate mass resolution (~1000-1100) was sufficient to separate the $^{9}Be^{+}$ and $^{27}Al^{3+}$ signals. Acquisition times for 10 counting cycles at each spot were 5 s ($^{7}Li^{+}$), 5 s ($^{9}Be^{+}$), 10 s ($^{11}B^{+}$) and 5 s ($^{30}Si^{+}$) (low resolution) and 4 s ($^{9}Be^{+}$), 2 s ($^{9}Al^{3+}$) and 2 s ($^{30}Si^{+}$) (moderate resolution). The analytical procedure included counting on a background position to monitor detection noise.

Absolute concentrations of each element were calculated using empirical relationships of measured $^{9}Be^{+}$ / $^{30}Si^{+}$, $^{7}Li^{+}$ / $^{30}Si^{+}$ and $^{11}B^{+}$ / $^{30}Si^{+}$ ratios (normalized to known SiO_2 content). The light element concentrations in the unknowns were derived from working curves based on measurements of various mineral and glass standards; these curves were constructed from plots of SiO_2 wt% * $^{9}Be^{+}$ / $^{30}Si^{+}$, $^{7}Li^{+}$ / $^{30}Si^{+}$ or $^{11}B^{+}$ / $^{30}Si^{+}$ count ratio vs. ppm element or wt% oxide of Li, Be or B. Standards used for sapphirine, sillimanite, biotite, orthopyroxene, and garnet were surinamite (no. 2292C) and khmaralite (2234L) for Be (SiO_2 wt% and Be/Si ratios from Barbier *et al.,* 1999,

2002); dravite (108796), elbaite (98144) and/or schorl (112566) for Li (SiO_2 wt%, Li/Si ratio from Dyar *et al.,* 2001), and on one or more of the above tourmalines plus prismatine (112233) for B (SiO_2 wt% and B/Si ratio from Dyar *et al.,* 2001 and Cooper, 1997, respectively). The Be/Si and B/Si ratios had been determined by single-crystal structure refinement (SREF) in surinamite, tourmaline and prismatine or by SREF and SIMS combined (khmaralite), whereas Li/Si ratio had been determined by atomic absorption (tourmaline); SiO_2 content was determined by electron microprobe analysis.

Standards for Li, Be and B in cordierite, feldspars, quartz were three synthetic granitic glasses doped with 0.73-0.74 wt% Li_2O, 0.57, 1.11 and 3.33 wt% BeO, and 0.48-0.49 wt% B_2O_3 (Evensen, 1997; Evensen & London, 2002, 2003; Evensen *et al.,* 1999; Evensen, personal communication).

In another two sessions involving B only, sillimanite B content was calibrated using working curves based on B contents measured in four sillimanite samples by prompt gamma neutron activation analysis (Paul, 2005). One of these samples ("Kerrick's") gave a calibration discrepant with the three others, so B data calibrated with only this sample had to be scaled to correct for the discrepancy.

Repeated calibrations of the three doped glasses using the minerals as standards gave a 1σ precision of ± 8% for Be determinations and ± 6-9 % for B and Li determinations (see Electronic Appendix 8 available for downloading on the web site http://www.petrology.oxfordjournals.org). We interpret the 1σ precision to be a measure of the reproducibility of the SIMS, so that variations in excess of 10% in a given sample are suggestive of compositional heterogeneity. The 1σ precision for B is 16% in surinamite, but 45% in khmaralite, and 30-43% for Li in both minerals. It is likely values

of 30% or more reflect compositional heterogeneity. The SIMS value for Be in prismatine BM1940,39 agrees with Be determined by atomic absorption, whereas the SIMS Li content is discrepant (see Electronic Appendix 8 available for downloading on the web site http://www.petrology.oxfordjournals.org).

The averages for the glasses are 20-30% higher than the amounts measured by ICP-AES. This discrepancy is attributed to a difference in matrix, which resulted in differences in relative ion yields between surinamite and khmaralite on the one hand, and glasses on the other. Consequently, we have not used the glasses as standards except for tectosilicates and cordierite.

We explored in a very preliminary fashion the possibility of using $^{9}Be^{+}$ / $^{27}Al^{3+}$ and $^{9}Be^{+}$ / $^{57}Fe^{+}$ to calibrate Be contents in spinel using a magnesiotaaffeite-6*N*'3*S* (musgravite) from Dove Bugt, East Greenland, analyzed by electron microprobe and Be content assumed to be stoichiometric. Measurements on spinel associated with musgravite gave 46 ± 11 ppm Be (n = 3) when calibrated with $^{9}Be^{+}$ / $^{27}Al^{3+}$ and 28 ppm Be (n = 1) when calibrated with $^{9}Be^{+}$ / $^{57}Fe^{+}$, and those on spinel in 2234A, 23 ± 2 ppm Be (n = 3) and 15 ± 1 ppm Be (n = 3), respectively, *i.e.*, calibration using $^{27}Al^{3+}$ is 60-65% higher. It is also much less precise; the peak for $^{27}Al^{3+}$ has several orders of magnitude fewer counts than the peak for $^{57}Fe^{+}$. Data for spinel in sample 2234B was calibrated using only $^{27}Al^{3+}$, so the average Be content reported in Electronic Appendix 6 (available for downloading on the web site http://www.petrology.oxfordjournals.org) is the measured value divided by 1.63 to correct for the discrepancy. Ongoing studies by Shearer *et al.* (2000), Papike *et al.* (2002) and Righter (2002) indicate that normalization

of trace elements to Fe for the analysis of spinels is the more appropriate analytical approach

Analyzing sections without carbon coating eliminated the B contamination that Grew *et al.* (2000) suspected was present in the carbon. New analyses did not confirm the relatively high B contents (to 21 ppm) in sillimanite and sapphirine reported by these authors in quartz-rich paragneisses from Christmas Point and Mount Pardoe.

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