

# matters arising

## Palaeogeotherms: implications of disequilibrium in garnet lherzolite xenoliths

FRASER AND LAWLESS<sup>1</sup> have pointed out that, because of the different diffusion mechanisms involved, the two-pyroxene geothermometer<sup>2,3</sup> and the garnet-orthopyroxene geobarometer<sup>4,5</sup> commonly used<sup>6-8</sup> in the interpretation of the pressure-temperature equilibration conditions and depths of derivation of garnet lherzolite xenoliths in kimberlites may be out of phase and thus generate a spurious apparent geotherm. Whilst this may be the case it should, however, be noted that the lines of constant  $K$  for garnet-orthopyroxene equilibria in Fig. 1 of Fraser and Lawless<sup>1</sup> are, in the depth range of interest, effectively sub-parallel to geotherms independently calculated<sup>9</sup> from heat flow-production studies. This essentially makes it impossible to determine whether geotherms calculated from xenolith data are real or spurious in the way suggested.

Their Fig. 1 thus highlights the critical importance of the temperature estimates to the depths of origin inferred for such xenoliths. Their further discussion, therefore, purporting to demonstrate the different diffusion blocking temperatures for element exchange reactions between various mineral pairs in garnet lherzolite xenoliths is crucial but quite unconvincing and rather misleading.

Fraser and Lawless attempted to test the possibility that diffusion between pyroxenes and garnets is less rapid than between coexisting pyroxenes by comparing the distribution coefficients for Mg-Fe<sup>2+</sup> exchange between garnet-clinopyroxene and garnet-orthopyroxene pairs with temperatures based on the Ca-Mg exchange between coexisting pyroxenes<sup>3</sup>. They interpreted the arrays of data points in their Fig. 2 as indicating that Mg-Fe<sup>2+</sup> exchange between pyroxenes and garnet is effectively blocked below ~1,100 °C whilst lower temperatures continue to be monitored by Ca-Mg exchange between coexisting pyroxenes. In reaching this conclusion they ignored the fact that the xenoliths concerned have probably been derived from an appreciable depth zone in the mantle and hence may be expected to have equilibrated over a range of pressures as well as temperatures. Furthermore, clearly both Mg-Fe<sup>2+</sup> exchange between pyroxenes and garnets and Ca-Mg exchange between coexisting pyroxenes depend on pressure as well as temperature, although there are uncertainties as to the magnitudes of the

pressure dependence of these exchange reactions<sup>2,10-13</sup>. Certainly it is unreasonable for Fraser and Lawless to expect that the xenoliths would plot along lines defining the temperature dependence of the Mg-Fe<sup>2+</sup> distribution coefficients at effectively one particular pressure. Indeed the experimental evidence of Råheim and Green<sup>12</sup> that  $(\text{Mg}/\text{Fe}^{2+})_{\text{cpx}}/(\text{Mg}/\text{Fe}^{2+})_{\text{gnt}}$  decreases with temperature but increases with pressure suggests that the arrays of points on Fig. 2 of Fraser and Lawless may simply reflect the combined pressure/temperature effects on the distribution coefficients involved.

The variation in  $(\text{Mg}/\text{Fe}^{2+})_{\text{cpx}}/(\text{Mg}/\text{Fe}^{2+})_{\text{gnt}}$  between garnet-clinopyroxene pairs in different metamorphic environments<sup>14,15,19</sup> indicates that Mg-Fe<sup>2+</sup> exchange is normally effective at temperatures well below 1,100 °C. Krogh<sup>16</sup>, Råheim and Green<sup>17</sup>, for example, have described both prograde and retrograde variations in this distribution coefficient in eclogite assemblages which indicate that above ~700 °C, diffusion rates even in garnets are fast enough to chemically homogenise the minerals. At lower temperatures Mg-Fe<sup>2+</sup> exchange is not completely blocked but is restricted to the extent that pronounced zoning is produced and retained, especially in the garnets<sup>16</sup>.

Thus contrary to the impression given by Fraser and Lawless and to the interpretation which they place on their Fig. 2, petrographic<sup>16-19</sup> and experimental<sup>2,10-12</sup> evidence indicate that Mg-Fe<sup>2+</sup> exchange reactions between pyroxenes and garnets probably provide far more sensitive geothermometers below 1,100 °C than the Ca-Mg exchange between coexisting pyroxenes. However, the magnitude of the pressure effect on the Mg-Fe<sup>2+</sup> exchange reactions in garnet lherzolite assemblages and reliable estimates of the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratios in these minerals<sup>19</sup> must first be determined before one can hope to obtain geologically meaningful temperatures from even these geothermometers and hence calculate valid geotherms.

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FRASER AND LAWLESS reply—We completely agree<sup>1</sup> with Carswell that the similarity between the temperature dependence of the garnet-orthopyroxene geobarometer<sup>2</sup> and likely geothermal gradients makes it difficult to use this reaction to distinguish between the effects of differences in blocking temperatures and temperature-pressure distributions obtained from samples which have equilibrated at different depths along such geothermal gradients.

In the absence of a suitable alternative geobarometer with a different slope it is difficult to distinguish between these two possibilities or indeed some combination of both. It is, however, unsound to make Carswell's *a priori* assumption that the xenoliths in question are derived from different depths and to use such an assumption to require that the nodules show an appreciable effect of pressure on Fe<sup>2+</sup>-Mg distribution coefficients. This may indeed be the case as may bulk-compositional effects such as we have mentioned<sup>1</sup>. However, the observed departure of garnet-pyroxene Fe<sup>2+</sup>-Mg distribution coefficients from the equilibrium values at 30 kbar is equally consistent with increased departure from equilibrium at lower temperature. The extent of low temperature Fe<sup>2+</sup>-Mg exchange observed in the eclogitic assemblages of Krogh<sup>3</sup> and Råheim and Green<sup>4</sup> results from equilibration over long periods of geological time and cannot be directly compared with the proposed retrograde effects on garnet lherzolite nodules resulting from relatively rapidly changing temperature-pressure conditions during movement towards the Earth's surface before final eruption of the kimberlite.

These important questions can only be resolved by independent tests. The calibration of an alternative geobarometer with different slope is clearly important. Moreover, the bulk chemical homogeneity of the phases in the xenoliths