Origin of hydrous cordierite—a reply

I AGREE with Allen's comments (previous paper) on the 1470±60 Ma whole-rock isochron (recalculated to 1440 Ma using new decay constants) obtained from four phlogopite-bearing granulites from near Johannsen's Mine (Iyer et al., 1976). Recent ⁴⁰Ar/³⁹Ar total fusion ages on refractory minerals of some of the rocks used for this isochron show ages of 1690 and 1750 Ma for PM230 opx and PM215 opx, respectively (Baksi and Wilson, in prep.). The same techniques, applied to PM230 qtz and PM215 sapphirine, however, suggest excess argon and anomalous ages of over 2000 Ma.

Allen's comments on the excess argon in the cordierites are pertinent, and underline the problems of its origin.

A major part of Allen's paper is his discussion of the source of the water in the cordierites. In my 1978 paper I pointed out that much water can normally be fairly loosely held within the channels of cordierite. I also noted that total dehydration of my samples did not take place in the laboratory until well above 1000 °C at 1 atm. This was much higher than expected in the light of research which showed a gradual loss of water from cordierites between 200 and 700 °C at 1 atm. (Schreyer and Yoder, 1964). It was for that reason that I suggested that some (perhaps most) of the H_2O+ , possibly as OH, may have replaced oxygens in the tetrahedra of the cordierite. Following acceptance of my manuscript, papers by Cohen et al. (1977) and Goldman et al. (1977) showed that there is no evidence for OH or H replacing components in the tetrahedral framework of their hydrous cordierites. Goldman et al. (1977) record considerably higher temperatures for dehydration, namely 800 °C at 1 atm., and yet another sample lost no water up to 775 °C. These cordierites are not specifically designated to have formed within the granulite facies. Newton's (1972) work points out that cordierite in granulites should be stabilized by H₂O to higher pressures than anhydrous cordierite. I suggest that it should not be inconsistent with the generally low P_{H_2O} of a granulite terrain to conceive that cordierite can initially form with $c.1\% H_2O + ...$

Indeed the presence of tightly held water (H_2O+) is not uncommon in some so-called anhydrous minerals. H_2O+ has been found in many of my granulite minerals by careful analyses carried out on mineral separates of extreme purity (>99.9%). Orthopyroxene and clinopyroxene

commonly yield H_2O+ values of $\sim 0.30\%$, and some fall within the range 0.40 to 0.55%. A phlogopitic sapphirine-bearing rock from the Archaean of Western Australia (42265 UWA) is very similar to the Strangways Range rock, PM215, that was used for the 1440 Ma Rb-Sr isochron referred to above. The water contents, as determined by L. Sutherland (weight %), are:

	$H_2O +$	H_2O-
bronzite	0.34	0.03
cordierite	1.08	0.02

As a check on these data the samples were recently dehydrated by R. Hall who heated them to 1000 °C at 1 atm using a thermogravimetric balance. After an initial slight increase in weight in both minerals from about 200 to 300 °C (probably due to oxidation of the small amount of FeO in the samples) there was loss of weight throughout the temperature range. For cordierite, however, this was particularly rapid from 600 to 900 °C. A dehydration plateau was not reached in either mineral, even at 1000 °C. The loss of weight for bronzite was 0.22% and is lower than $H_2O +$ recorded by the modified Penfield tube technique. This may reflect the greater oxidation of the sample by the later method. The loss of weight for cordierite (1.67%) is high, but the relative contributions of H₂O, Ar, and other fluids to this loss are unknown. It is clear that the H₂O + of this Archaean cordierite is tightly held, and identical in amount to those Proterozoic cordierites under discussion. It appears, then, that the hydrous cordierites described in my paper are not unique to the Strangways Range and the postulated hydration during Allen's M3 event.

Allen cites textural evidence in support of the reaction: anhydrous cordierite+water = aluminous anthophyllite+sillimanite+quartz. An alternative interpretation, however, is that the influx of water acted as a catalyst, initiating reactions in hydrous cordierite that may or may not involve fixation of new water in the products. If the breakdown products only occur where water is introduced to anhydrous cordierite, and if it becomes fixed in the reaction, then the cores of 'corroded' cordierites should still be essentially anhydrous. However, it is in these cores that I have repeatedly found $\sim 1\%$ water.

Clearly in this region there has been movement

of various fluids on several occasions. Measurement of ¹⁸O/¹⁶O and D/H is well advanced on many presumed M3 and other phases and on the alteration products of the cordierites. These data will be reported elsewhere and should provide restraints on models of origin.

The oxygen isotopes of the cordierites of my paper (δ^{18} O ranging from 1.97 to 3.11%) must not be considered in isolation. Coexisting quartz and hypersthene yield δ^{18} O values consistent with a metamorphic temperature of 760 °C (Wilson and Baksi, 1978). Many other δ^{18} O values have been measured on coexisting minerals and whole-rocks (Wilson and Baksi, in prep.). These show that the presence of cordierite makes no difference to the generally low 18 O values found in these rocks. For example, the anomalous low 18 O values are widespread and are also found in many two-pyroxene plagioclase granulites (with very low Rb/Sr ratios) in locations devoid of cordierite-bearing rocks or phlogopite-bearing rocks.

Allen's deductions from oxygen isotope temperatures need qualification. The most reliable estimate of temperature is 760 °C, referred to above, and the cordierite's temperature may well be the same, but this can only be assumed on textural grounds (Wilson and Baksi, 1978). Recent laboratory calibrations involving biotite (Hoernes and Friedrichsen, 1978) suggest that Δ quartz-biotite of about 4°_{00} indicates about 620 °C (thus generally confirming the estimates of Bottinga and Javoy, 1975) rather than 760 °C. However, in view of the probable composite nature of the biotite sample, we had already stated that temperature estimates using this biotite could have little meaning.

An important problem is the source and age of the fluids depleted in ¹⁸O. Allen states that the M3 metasomatic event 'appears to be related to the formation of the Wuluma Granite—Ingula Migmatite Complex... dated at [about] 1450 Ma...'.

Recent isotope and geochemical work (Wilson, in prep.) shows that the $\delta^{18}O$ values of Wuluma (about $6.3\%_{00}$) are too high to be a source of the widespread $\delta^{18}O$ values of the granulites. However, they could be compatible with Wuluma being a repository of the somewhat higher $-^{18}O$ anatectic material extracted from deep crustal slabs, thus rendering the granulites more depleted in ^{18}O and some other components.

I currently favour a combination of two processes: a pre-granulite depletion by reaction with low – ¹⁸O waters of unknown origin, and granulite metamorphism wherein the higher – ¹⁸O partial melts were removed during one of the early granulite episodes. Possibly a reason why such extreme ¹⁸O depletions as are found in the Strangways Range are not found in every granulite terrain is that it would be uncommon to have a coincidence of both processes (Wilson and Baksi, in prep.).

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