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# Survival of zincian staurolite to upper amphibolite facies metamorphic grade

ZINCIAN staurolite is found as a relict phase in rocks of upper amphibolite facies on the verge of anatexis. In quartz-poor metasediments, zincian staurolite survives in sillimanite-free domains, while staurolite which may have been relatively zinc-poor is inferred to have reacted out in domains now containing sillimanite and corundum. Survival to such a high grade appears to be a result of the stabilising influence of the zinc and the paucity of reactant quartz.

## Geology

Rocks of the late Proterozoic Dalradian Supergroup which crop out in east Glen Muick, Scotland [NGR NO 39], were metamorphosed to upper amphibolite-facies regional grade during the Caledonian orogeny. They form part of Barrow's sillimanite zone, and record conditions of 750 °C and 7–8 kbar, which are some of the highest temperatures and pressures reached in the Scottish Dalradian (Baker and Droop, 1983). The Crinan subgroup in this area consists of predominantly semipelitic to pelitic metasediments and amphibolites, interbanded on scales ranging from a few centimetres to several tens of metres. The peak metamorphic assemblage in pelites is quartz + plagioclase + K-feldspar + biotite ± garnet ± sillimanite + accessories (zircon, apatite, ilmenite, magnetite), and in the metabasic rocks is hornblende + plagioclase + quartz ± garnet ± clinopyroxene + accessories (titanite, magnetite, pyrite, zircon). The stability of K-feldspar + sillimanite in the absence of muscovite in pelitic rocks and the presence of clinopyroxene in metabasic rocks of suitable composition indicates peak metamorphism in the upper amphibolite facies. In the sillimanite–K-feldspar-bearing rocks there are kyanite cores to some fibrolitic sillimanite, and rare relic inclusions of kyanite and staurolite within garnet, which attest to the lower grade part of the prograde history of the gneisses. For the most part, however, these earlier metamorphic assemblages have been entirely obliterated. Metamorphic grade drops steadily to the SE, with pelitic assemblages including kyanite, staurolite and muscovite dominating in Glen Doll and Glen Clova [NGR NO 37], some 20 km south of Glen Muick (Chinner, 1965).

Both metasediments and metabasites are gneissose, and the metasediments are frequently migmatitic. Four main fold phases have affected the area, and fabric studies indicate that peak metamorphic conditions were reached syn- to post-F2 folding (Goodman *et al.*, 1991). Banded gneisses and stromatic migmatites follow the dominant S2 fabric, and were folded during the D3 episode. The metamorphic grade remained high during D3, however, with diffuse migmatitic leucosome cutting F3 folds, and localised anatexis related to D3 shear zones. The D4 deformation episode was accompanied by minor retrogression.

## Mineralogy

Zincian staurolite is found in one metasedimentary unit of unusual paragenesis in east Glen Muick [NGR NO 36559180]. The rocks are quartz-poor metasediments, being dominantly plagioclase, K-feldspar and biotite, with a small amount of quartz and abundant garnets. The zincian staurolite is found as fractured grains cored by the zincian spinel, gahnite, in domains which contain no sillimanite and very little quartz. Domains with abundant prismatic sillimanite contain small amounts of staurolite, and here corundum is also present. Accessory minerals are apatite, zircon and opaques, the opaque suite being unusual in that it is dominated by sulphide minerals, rather than the more typical oxides.

Gahnite is found only within the zincian staurolite, suggesting that zincian staurolite grew during reactions consuming gahnite. The staurolite has clean, unreactive contacts with garnet, biotite and feldspar; nowhere is it observed in contact with quartz or sillimanite. In places the staurolite–feldspar contacts are marked by some alteration, involving the formation of white micas. This is probably part of the late retrogression which caused minor chloritisation of some biotite and garnet.

The staurolite-bearing rocks are banded gneisses, passing into migmatites, the granitic (as opposed to trondjemitic) composition of the leucosome being a reflection of the unusual rock composition. These rocks were probably quartz-poor sediments initially; extraction of quartz into the leucosome would have further depleted the melanosome in quartz. Prevalent metamorphic conditions were probably intense enough for dehydration melting, rather than a process of subsolidus differentiation, to be the cause of migmatisation (Le Breton and Thompson, 1988).

The elongate minerals—biotite, sillimanite and staurolite—are oriented parallel to the stromatic banding. This banding is folded by F3 folds, a deformation phase responsible for the fracturing of staurolite and the kinking of biotite and sillimanite. These minerals were therefore formed prior to D3 deformation, and were present under peak metamorphic conditions, synchronous with migmatisation.

Analysis of the zincian staurolite shows that it contains >2 wt.% ZnO, while the gahnite inclusions contain up to 17 wt.% ZnO (Table 1). Garnet and biotite are somewhat richer in Mg and poorer in Fe in the rocks containing zincian staurolite than in more typical pelitic metasediments in the area, while the feldspars are of typical composition. Ragged staurolite relics in sillimanite-bearing domains are relatively zinc-poor (Table 1); apart from this, the minerals show no significant variation in composition between staurolite-bearing/sillimanite-free and sillimannite-bearing domains.

### Staurolite-forming reactions

Staurolite forms under greenschist facies conditions by continuous reactions such as:

$$\text{Chl} + \text{Ms} \rightleftharpoons \text{St} + \text{Bt} + \text{Qtz} + H_2O$$

and discontinuous reactions such as:

**TABLE 1. Representative microprobe analyses of zincian staurolite and gahnite from east Glen Muick**

| Weight % | staurolite 1 | staurolite 2 | staurolite 3 | staurolite 4 | gahnite | gahnite |
|---|---|---|---|---|---|---|
| $SiO_2$ | 26.46 | 26.08 | 25.04 | 25.11 | 0.05 | n.d. |
| $TiO_2$ | 0.28 | 0.33 | 0.65 | 0.57 | n.d. | n.d. |
| $Al_2O_3$ | 53.48 | 53.48 | 54.17 | 55.36 | 55.60 | 55.11 |
| $Cr_2O_3$ | 0.07 | 0.14 | 0.17 | 0.12 | 0.70 | 0.76 |
| FeO | 13.69 | 13.22 | 13.36 | 13.39 | 23.25 | 24.32 |
| MnO | 0.23 | 0.27 | 0.28 | 0.22 | 0.20 | 0.12 |
| MgO | 1.93 | 1.64 | 1.38 | 1.32 | 2.78 | 2.82 |
| ZnO | 2.43 | 2.13 | 2.32 | 1.92 | 16.92 | 16.35 |
| $V_2O_5$ | n.d. | n.d. | n.d. | n.d. | 0.09 | 0.31 |
| Total | 98.57 | 97.29 | 97.37 | 98.01 | 99.59 | 99.79 |
| Formula | Units | | | | | |
| Si | 7.41 | 7.37 | 7.10 | 7.05 | 0.01 | n.d. |
| Ti | 0.06 | 0.07 | 0.14 | 0.12 | n.d. | n.d. |
| Al | 17.65 | 17.82 | 18.12 | 18.32 | 15.35 | 15.22 |
| Cr | 0.02 | 0.03 | 0.04 | 0.03 | 0.13 | 0.14 |
| $Fe^{2+}$ | 3.21 | 3.13 | 3.17 | 3.14 | 4.21 | 4.28 |
| $Fe^{3+}$ | | | | | 0.35 | 0.48 |
| Mn | 0.06 | 0.06 | 0.07 | 0.05 | 0.04 | 0.02 |
| Mg | 0.81 | 0.69 | 0.58 | 0.55 | 0.97 | 0.98 |
| Zn | 0.50 | 0.45 | 0.49 | 0.40 | 2.92 | 2.83 |
| V | n.d. | n.d. | n.d. | n.d. | 0.02 | 0.05 |
| Total | 29.72 | 29.62 | 29.71 | 29.66 | 24 | 24 |

Staurolite 1,2 and 3 from sillimanite-free domain; staurolite 4 from sillimanite-bearing domain. Staurolite formulae recalculated to 46 oxygen atoms; all Fe as FeO. Spinel formulae recalculated to 24 cations, 32 oxygen atoms. n.d. = not detected.

$$\text{Chl} + \text{Ms} + \text{Grt} \rightleftharpoons \text{St} + \text{Bt} + \text{Qtz} + \text{H}_2\text{O}$$

(Winkler, 1979, p. 223; mineral abbreviations after Kretz, 1983).

The staurolite seen in lower grade rocks in Glen Doll and Glen Clova would have formed by such reactions (Chinner, 1965); it contains considerably less zinc than the staurolite in east Glen Muick (Schumacher, 1985). Gahnite can be present in greenschist facies metasediments (Moore and Reid, 1989), and in such a case, zincian staurolite would be formed by a reaction analogous to the above, such as

$$\text{Chl} + \text{Ms} + \text{Zn–Spl} \rightleftharpoons \text{Zn–St} + \text{Bt} + \text{Qtz} + \text{H}_2\text{O}.$$

## Staurolite-breakdown reactions

Staurolite is the only common silicate phase which can incorporate significant amounts of zinc in rocks of the amphibolite facies. Zinc substitutes for tetrahedrally co-ordinated divalent iron (Deer *et al.*, 1982, p. 822), and partitions strongly into staurolite due to the lack of other suitable cation sites. At higher metamorphic grade, as staurolite begins to react out, zinc is increasingly concentrated in the staurolite which remains.

Staurolite can be consumed by reactions which generate sillimanite, such as

$$\text{St} + \text{Ms} + \text{Qtz} \rightleftharpoons \text{Sil} + \text{Bt} + \text{H}_2\text{O}$$

and $\text{St} + \text{Ms} + \text{Qtz} \rightleftharpoons \text{Sil} + \text{Grt} + \text{Bt} + \text{H}_2\text{O}$,

or in the absence of muscovite

$$\text{St} + \text{Qtz} \rightleftharpoons \text{Sil} + \text{Grt} + \text{H}_2\text{O}$$

(Yardley, 1989 p. 72).

The reactions involving muscovite take place at a lower grade than the staurolite + quartz reaction (Winkler, 1979, p. 229), so staurolite can persist to higher grades in muscovite-free assemblages, such as those in east Glen Muick.

Within the staurolite-bearing rocks of east Glen Muick, domains with abundant sillimanite have very little staurolite, with the relics that remain containing less zinc than in the sillimanite-free domains. Reactions such as those above have presumably consumed the zinc-poor staurolite and generated sillimanite. The paucity of quartz in the rock has led to the stability of corundum in these domains.

Staurolite of higher zinc content remained stable under the high grade conditions necessary for migmatisation due to the stabilising influence of the zinc and the lack of available reactant quartz, hence the sillimanite-free domains.

## Comparison with zincian staurolite from other localities

In Dalradian rocks at Portsoy, zincian staurolite is found in muscovite-free semipelitic migmatites (Ashworth, 1975). It is considered to be formed during retrogression associated with migmatisation, and is morphologically distinct from staurolite in the regional assemblage. It also differs from the zincian staurolite of east Glen Muick by being in reactive association with garnet and biotite in cordierite-bearing rocks.

Zincian staurolite reported from Glen Doll is also considered to have formed during retrogression (Schumacher, 1985) and occurs in lower amphibolite facies metasediments. It is generally much lower in zinc than the Glen Muick examples, being typically <1.5% zinc. In the aureole of the post-orogenic Glen Doll diorite, the staurolite is consumed during thermal metamorphism which generates cordierite and andalusite in pelitic rocks (Schumacher, 1985). Gahnite is a product of the thermal reaction of staurolite, in contrast to the staurolite–gahnite relations in east Glen Muick.

Moore and Reid (1989) describe zincian staurolite forming after gahnite in muscovite-free assemblages in the Namaqualand Metamorphic Complex, but invoke retrogressive hydration, as does Beach (1973), for the staurolite–spinel association in sheared Lewisian gneisses. The preservation of regional metamorphic textures, and lack of evidence for overprinting thermal metamorphism or pervasive retrogression indicate that the zincian staurolite of east Glen Muick differs from the above examples, and is most likely to be a relict regional phase.

Spry and Scott (1986) list several occurrences of gahnite and zincian staurolite in the Appalachians and Scandinavian Caledonides, and point out that they are not always in unequivocal reactive contact and may in fact form together (which cannot entirely be discounted for the rocks in east Glen Muick). The gahnite–zincian staurolite association is related to the metamorphism of stratabound base metal ore deposits. Gahnite, and possibly zincian staurolite, are formed during greenschist facies metamorphism and desulphidation of sphalerite. There is no evidence that mineralisation of ore grade exists in east Glen Muick. The rocks with zincian staurolite do, however, contain sulphide minerals instead of the usual opaque oxide suite. The sulphide grains are mainly pyrite, but there is some chalcopyrite, and up to 2% cobalt has been found in pyrite. This suggests that the rock composition may reflect the effects of minor exhalative mineralisation. This could be related to hydrothermal activity associated with intrusion of high level sills now present as large metabasite bodies, or it could be an early manifestation of the extrusive activity which generated the metavolcanic rocks at a higher stratigraphical level.

In east Glen Muick, staurolite persists as a relict phase in upper amphibolite-facies rocks on the verge of anatexis. It survives to these exceptionally high grades as a result of the stabilising influence of zinc, and the low availability of reactant quartz. The paragenesis differs from those previously described in the literature, and is an additional example of the occurrence of staurolite at anomalously high metamorphic grade.

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# Sector-zoning of epidote in the Sanbagawa schists and the question of an epidote miscibility gap

IN the controversy over the presence of a miscibility gap in the epidote solid-solution series first proposed by Strens (1965), Raith (1976) used compositional data from a suite of rocks from the southern Tauern Window area, Austria, to support the concept of a miscibility gap. In our work on the low-grade Sanbagawa schists in central Shikoku, Japan, we have accumulated a large quantity of compositional data for epidotes from a wide range of rock-types and metamorphic