Cordierite as a sensor of fluid and melt distribution in crustal metamorphism

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Introduction

Cordierite, $(Mg,Fe)_2Al_4Si_5O_{18}\cdot(nCO_2,mH_2O)$, can incorporate both the major volatile species in crustal metamorphism, CO_2 and H_2O, within its structure and may be produced over a wide pressure-temperature range through processes involving different fluid regimes, such as melting and metasomatic fluid infiltration. As a consequence this mineral is potentially a powerful sensor of the CO_2 and H_2O contents of fluids and melts involved in crustal metamorphism, providing that post-formation leakage of channel constituents is not significant. In fluid-saturated cases the absolute abundance of channel volatiles and X_{CO_2} (CO_2/CO_2+H_2O) in cordierite is a function of pressure, temperature and X_{CO_2} in the coexisting fluid (Johannes & Schreyer, 1981). However, when a free volatile phase is not present the channel volatile contents will instead depend upon the distribution of H_2O and CO_2 between cordierite and other phases, the most important of which is melt. Hence, knowledge of both the total volatile content and H_2O-CO_2 composition of cordierite is required to discriminate between fluid-present and fluid-absent (melt-present) conditions, and spatial data on volatile distribution needed to assess the resilience of cordierite to leakage of channel volatiles.

Sims analysis and calibration

A new SIMS (secondary ion mass spectrometry) method for determining the volatile contents of cordierite has been developed to enable discrimination of melt- and volatile-present processes in high-grade metamorphism. SIMS has marked advantages over other forms of volatile analysis, as H and C are determined simultaneously on a small volume of sample (*c.* 700 μm^3). This enables the spatial variations in H_2O and CO_2 within and between grains to be determined.

Carbon and hydrogen abundances have been determined using the Cameca ims-4f ion microprobe at the University of Edinburgh. SIMS $^{12}C/^{28}Si$ and $^{1}H/^{28}Si$ isotope ratios obtained using a negative secondary beam and measured on 25 μm spot analyses of reference samples analysed using independent methods (e.g. stepped-heating mass spectrometry, H-extraction) have been used to derive CO_2 and H_2O calibration curves, tested against reference grains analysed along with unknowns in all SIMS sessions. Background levels for H and C are 44 ppm H and 110–130 ppm C, equating to 0.04 wt % for both H_2O and CO_2 and analytical precision is to ± 0.06 wt %.

Some applications

Cordierite in migmatites and melts: melt-cordierite partitioning. Field and textural relations in many metapelite-dominated granulites suggest that cordierite has been produced through peritectic vapour-absent melting of biotite in the presence of sillimanite. In such cases, fluid-undersaturated cordierite would be anticipated as volatile contents would be controlled by cordierite-melt partitioning. SIMS analysis of cordierites from patch leucosomes and veins from several terranes (e.g. Arunta, Cooma, Prydz Bay, Madagascar, Willyama) preserve low H_2O and CO_2 contents of 0.3–0.4 wt % and 0.5–1.0 wt % respectively, and hence are significantly depleted in total volatiles compared with the saturation curves of Vry *et al.* (1990) for appropriate P-T conditions (fig. 1). Despite typcal channel occupancies of only 20–40 %, no cordierite analytical populations are consistent with simple H_2O loss, and rimward zoning to higher volatile contents in some samples suggests retention of original volatile contents.

Both the low total volatile contents and relatively high X_{CO_2} in the migmatitic cordierites are considered to reflect equilibration with melts in a fluid-undersaturated metamorphic environment. A cordierite-melt H_2O partitioning experiment conducted at 900°C and 7 kbar has been analysed using SIMS, yielding partitioning value, K_w [= H_2O(melt)/H_2O(cordierite)], of 3±0.3. This is significantly lower than the K_w deduced for vapour-saturated conditions where felsic melts are expected to contain up to 13 wt% H_2O (K_w = 6–7). Given the present uncertainties, water

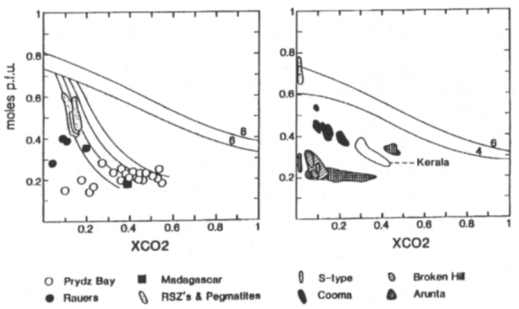

FIG. 1. Plots of number of moles of volatiles per formula unit of cordierite (n) versus XCO_2 for selected suites analysed using SIMS (total number of analyses = 500). Contours of channel saturation for pressures of 4, 6, and 8 kbars (based on Vry *et al.*, 1990) and model H_2O-loss curves (steep curves) can be compared with the cordierite volatile populations. Note the large volatile deficiencies defined for cordierites from migmatites from several areas (Rauer Group, Cooma, Prydz Bay, Madagascar, Arunta, Broken Hill) and high H_2O and total volatiles for retrograde shear zones (RSZ's), pegmatites and S-type granites. Kerala cordierites are volatile-undersaturated for a regional metamorphism at 5-6 kbar.

contents of the melts coexisting with CO_2-poorer cordierites in some of the migmatite terrains studied using SIMS are encouragingly consistent with independent experimental studies on dehydration melting.The relationships between migmatites and and discordant S-type granitoids have been examined in several low-pressure/high-temperature terrains. At Mt Stafford, CO_2-poor cordierites in segregated S-type granite leucosomes are clearly distinct from cordierites in the patch migmatites, which contain mixed H_2O-CO_2 fluids. The extensive melting at Mt Stafford, coupled with the lack of CO_2 in the main leucosome type, suggests open-system behaviour with the influx of fluids derived from subjacent crystallising granitoids. Cordierites in other S-type granites and pegmatites are also H_2O-rich and close to volatile-saturated (Fig. 1), and signify formation either during wet melting or from a melt approaching saturation in H_2O.

Cordierite volatile compositions and CO_2 flooding hypotheses. The marked fractionation of CO_2 between cordierite and vapour demonstrated by Johannes & Schreyer (1981) has led to the general acceptance of CO_2-rich cordierite as evidence for carbonic metamorphism in granulites (Armbruster *et al.*, 1982; Santosh *et al.*, 1993). However, CO_2-bearing cordierites from the Kerala Khondalite Belt are undersaturated in volatiles with respect to the saturation curves of Vry *et al.* (1990) at the P-T conditions suggested for CO_2-infiltration and arrested charnockite formation in the region (Fig. 1). The presence of a free fluid phase (H_2O-CO_2) at the metamorphic peak is not supported by the cordierite data, and precludes models of CO_2-flooding under peak metamorphic conditions (Santosh *et al.*, 1993).

Late metamorphic fluid channelling and metasomatism in the Reynolds Range. Although peak-metamorphic CO_2 infiltration is not considered to be a general process of granulite formation, post-peak fluid infiltration may be an important feature of many high grade terrains. The role of late metamorphic fluid channelling, layer parallel fluid flow, and related metasomatism in low-P/high-T terranes has been investigated using cordierites from adjacent pelite and K-leached cordierite-orthoamphibole layers in the Reynolds Range, where interlayered marbles display layer-specific development of wollastonite. Cordierites coexisting with orthoamphibole ± orthopyroxene in the infiltration zones contrast with those in the normal sillimanite-microcline-biotite metapelites in preserving higher H_2O, lower CO_2, and enhanced X_{H_2O} values. These results support a model of infiltration of a water-rich fluid, with an X_{H_2O} greater than 0.6 based on data of Johannes and Schreyer (1981), at pressures of *c.* 2–2.5 kbar. These pressures are 1–2 kbar lower than those estimated for the peak metamorphism in this area but are consistent with independent evidence that the high-temperature fluid infiltration post-dated significant decompression of the regional terrain.

Conclusions

Simultaneous analysis of cordierite volatile compositions using SIMS demonstrates that channel constituents are often retained and hence provide a record of fluid- and melt-related processes in high-grade metamorphism. Cordierite-melt volatile partitioning, important in many granulites, requires further experimental study before cordierite can be used to monitor melt compositions accurately. The role of fluid infiltration in either forming or modifying granulite assemblages can be evaluated through careful textural studies of cordierite parageneses coupled with the chemical and spatial information provided by SIMS volatile analysis.

References

Armbruster, Th., Schreyer, W. and Hoefs, J., (1982) *Contrib. Miner. Petrol.*, **81**, 262–267.