

Cordierite-Melt H₂O and CO₂ partitioning

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Experiments

Experiments aimed at defining the distribution of water between cordierite and melts ($D_w = \text{H}_2\text{O}(\text{melt})/\text{H}_2\text{O}(\text{crd})$) have now been performed at 800, 900 and 1000 °C and 3, 5 and 7 kbar. The charges consist of a gel corresponding in composition to peraluminous granite and natural cordierite evacuated using stepped heating mass spectrometry methods at Royal Holloway, University of London. The natural cordierite has an Mg/Mg+Fe (XMg) value (0.66) close to that for equilibrium with the melt (XMg=0.25) at 5.0 kbar and 900 °C, and is placed at one end of the charge as crushed grains (125-250 μm). In reversal runs H₂O-saturated cordierite equilibrated with pure H₂O prior to the experiment, but following evacuation of any original H₂O and CO₂, has been run with the melt under vapour-undersaturated conditions. Different quantities of H₂O have been added to the cordierite-gel charges using a microsyringe so that D_w can be measured for a wide range of H₂O contents in the experimental phases.

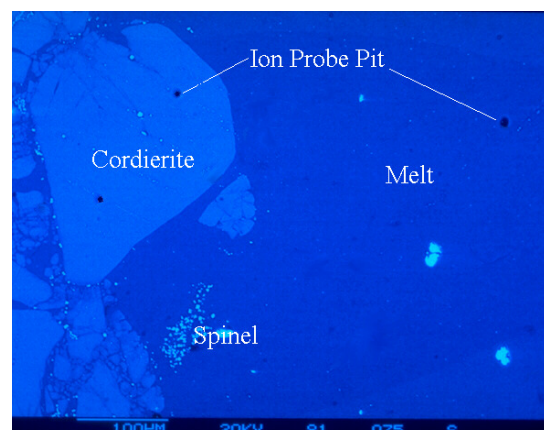
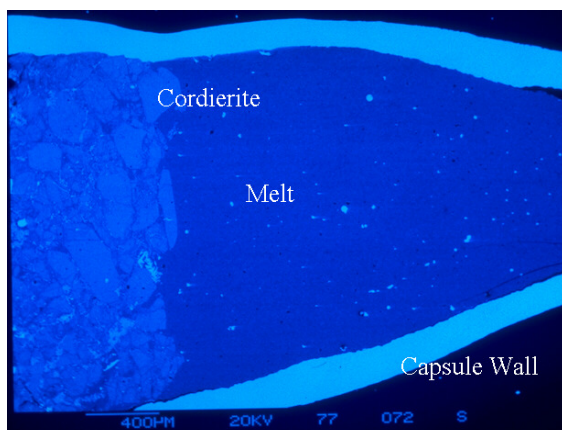
Further experiments have been carried out using cordierite with:

- different starting XMg of 0.87 to assess the significance, if any, of Mg/Fe ratio on volatile content
- a sandwich of evacuated cordierite/melt/saturated cordierite, to assess the approach to equilibrium in a series of experiments run for times between 2 hours and 2 weeks

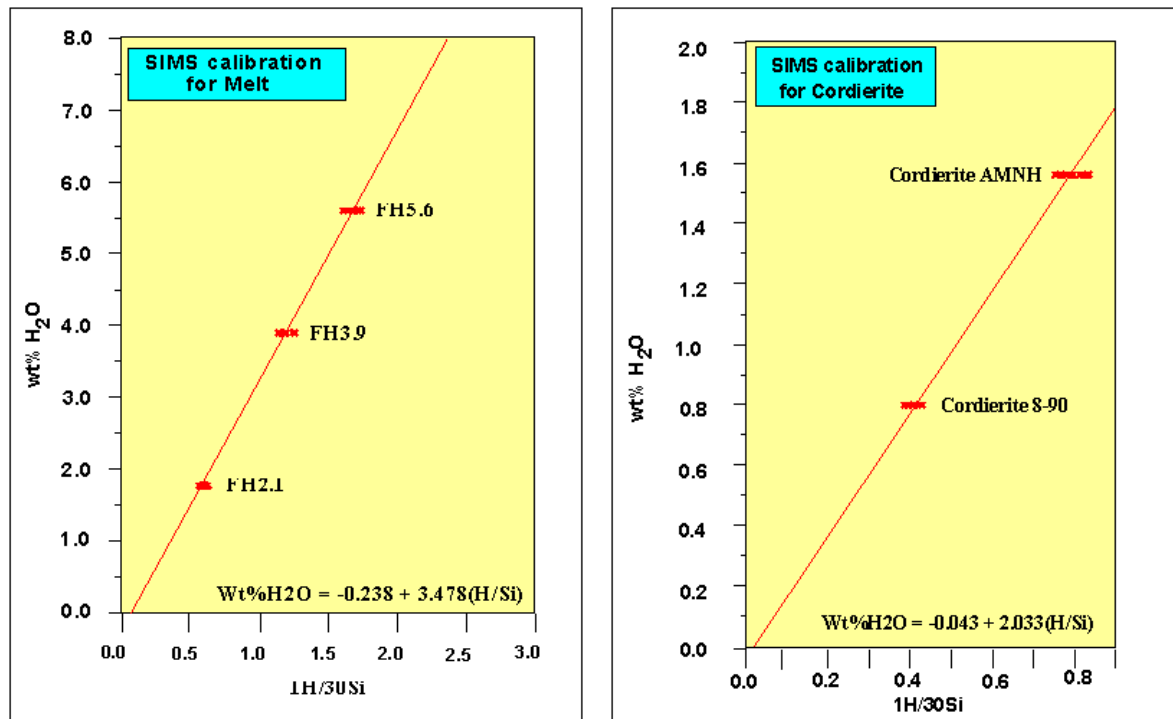
A series of experiments aimed at determining the effect of CO₂ on the partitioning, D_w , at 5 kbar and 900 °C have been performed in a similar way to those outlined above, but adding silver oxalate to the starting gel mix as a source of CO₂.

SIMS Analysis

Forty **experimental charges** have been analysed for the H₂O contents in **cordierite and melt** using SIMS. All charges have also been characterised



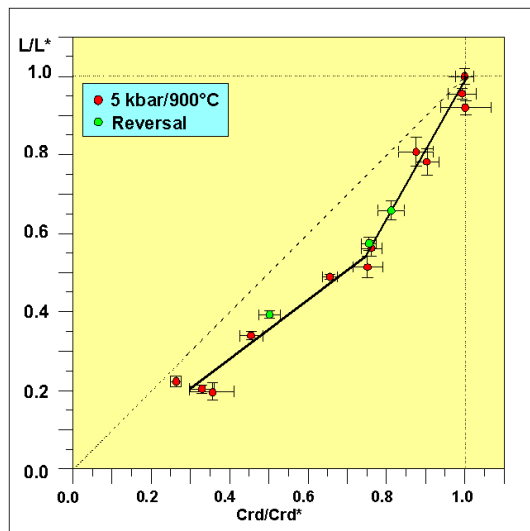
using the electron microprobe and BSE photographs. All SIMS analyses in the Cordierite-melt-H₂O system have been obtained using an O⁻ primary beam at 8 nA primary current and measuring positive secondary ions (¹H⁺, ³⁰Si⁺) with the ion counts determined at an energy offset of 75eV ± 20eV. Each analysis involves 30 cycles of H and Si counts following 5 minutes burn-in. The mean of the isotope ratios of the last 10 cycles is taken as the final analysis value. Analyses are expressed as isotopic ratios of ¹H/³⁰Si and converted to wt% H₂O by comparison with the standards of *melts* or *cordierites*.



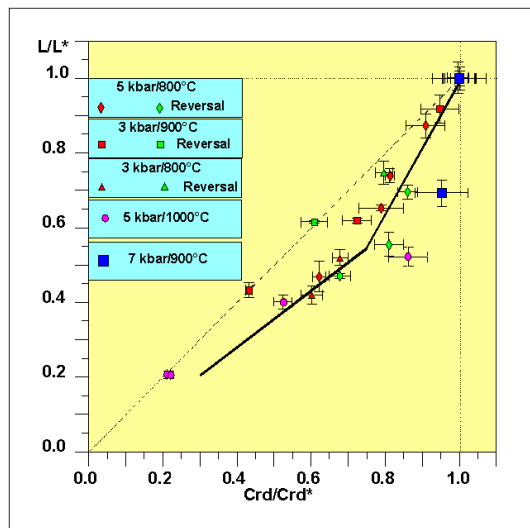
Several experimental charges have been analysed for H₂O and CO₂ using SIMS in negative secondary mode. In this case an O⁻ primary beam at 8 nA primary current has been used and negative secondary ions (¹H⁻, ¹²C⁻, ²⁸Si⁻) measured with the ion counts determined at an energy offset of 80eV ± 20eV. Each analysis involves 30 cycles of H and Si counts following 5 minutes burn-in. The mean of the isotope ratios of the last 10 cycles is taken as the final analysis value. Analyses are expressed as isotopic ratios of ¹H/²⁸Si and ¹²C/²⁸Si, and converted to wt% H₂O and CO₂ respectively by comparison with the standard cordierites or melts.

Presentation of Results

Results of the experiments over a P-T range are presented below and show the H₂O contents of the phases normalised against those at saturation for the ambient P-T condition. The newly-measured data obtained at 3-7 kbar and 900 °C and at 800-1000 °C and 5 kbar are mutually consistent, and broadly agree with the 900 °C, 5 kbar normalised distribution. The increase in Dw with H₂O in melt defined at 900 °C is confirmed by the new data, and in addition Dw at saturation increases with increasing T, as predicted from our previous studies. Maximum H₂O contents in melts and cordierite at 800 and 1000 °C again agree well with extrapolations of independent studies (Holtz & Johannes, 1994; Mirwald et al., 1979).



➤ Roozeboom plots showing the distribution of H₂O between cordierite and melt normalised against the phases H₂O contents at saturation. Normalised H₂O "occupancy" for each phase (e.g. Crd/Crd*) is defined as [H₂O (measured) / H₂O* (saturation)] P,T. Data obtained at 5.0 kbar, 900 °C define a clear trend shown as a solid line (note kink at melt/melt*=0.55). The maximum H₂O contents in cordierite and melt (i.e. Crd* and Melt*) are 1.7 and 10.0 wt% respectively (Carrington and Harley 1996).



➤ The data obtained in the range 800-1000 °C and 3-7 kbar mostly fit the same normalised distribution, showing that pressure and temperature are not the principal determinants of H₂O partitioning between cordierite and melt.

Reversed experiments using H₂O-saturated and evacuated cordierites equilibrated with the same melt demonstrate that equilibrium is approached (for H₂O contents) in less than 2 days. The further experiments carried out using a considerably more magnesian cordierite (XMg=0.85) yielded a D_w values consistent with the data obtained at the same P-T for the less magnesian cordierite (XMg=0.66), confirming that there is no measurable Fe-Mg compositional dependence of D_w and therefore the H₂O content in cordierite.

Difficulties have been encountered in measuring melt glass standard material for H₂O and CO₂ in negative SIMS mode at low CO₂ contents (<1000 ppm). Experimental granitic melts in equilibrium with cordierite of moderate CO₂ content (< 1 wt%) appear to contain less than 800 ppm CO₂. There is a very strong fractionation of CO₂ into the cordierite (up to 0.84 wt%) over melt, yielding a D_c (CO₂(melt)/CO₂(crd)) of 0.1-0.3. At 900 °C and 5 kbar, the total amount of volatiles in cordierite at saturation is shown to decrease with increasing XCO₂ in the cordierite channels, with moles p.f.u. decreasing from over 0.65 at XCO₂ of <0.05 to 0.45 at XCO₂ of 0.26 (c.f. Johannes & Schreyer, 1981). Melts in equilibrium with these cordierites also show a decrease in H₂O as XCO₂ (crd) increases, so that the

calculated D_w for fluid-saturated but CO_2 -bearing conditions (4.4-3.9) decreases compared with the pure H_2O case (5.5-6.0) and are comparable to D_w values otherwise obtained for low water activities in the H_2O -only system. These preliminary results confirm the suggestion from the available data on natural cordierites in migmatites (Harley, 1994; Fitzsimons, 1994) that cordierites with moderate X_{CO_2} channel volatiles ($X_{\text{CO}_2}=0.2-0.5$) can coexist with melts that contain little CO_2 and are undersaturated in H_2O compared with the pure water system.

Future Work

A thermodynamic model is currently being developed to define the relationships between water activity, D_w and the H_2O contents of cordierite and melt. This model, which utilises the Burnham approach for melts and a one-site channel model for cordierite, predicts the observed relations very well at 900°C and 5 kbar and will be extended to the rest of our experimental data set. The effects of CO_2 on the systematics developed from the H_2O studies and the fractionation of H_2O - CO_2 between cordierite and melt will be extended into fluid-undersaturated systems and over a wider range of X_{CO_2} in the cordierite, at 900°C and 5 kbar. Experiments in the H_2O - CO_2 system at other P-T conditions will also be analysed by SIMS to test the predictive capacity of the model derived from the H_2O dataset and the detailed 900°C, 5 kbar H_2O - CO_2 data.

References

- Carrington D.P. and Harley S.L. (1996)** Cordierite as a monitor of fluid and melt water contents in the lower crust: an experimental calibration. *Geology* 24 647-650.
- Harley S.L. (1994)** Cordierite as a sensor of fluid and melt distribution in crustal metamorphism. VM Goldschmidt Conference Extended Abstracts, *Min. Mag.*, 58A, 374-375.
- Fitzsimons I.C.W. (1994)** Cordierite migmatites from East Antarctica: geochemical constraints on volatile distribution during crustal anatexis. VM Goldschmidt Conference Extended Abstracts, *Min. Mag.*, 58A, 274-275.
- Holtz F. and Johannes W. (1994)** Maximum and minimum water contents of granitic melts: implications for chemical and physical properties of ascending magmas. *Lithos*, 32, 149-159.
- Johannes W. and Schreyer W. (1981)** Experimental introduction of CO_2 and H_2O into Mg-cordierite. *Am. J. Sci.*, 281, 299-317.
- Mirwald P.W., Maresch W.V. and Schreyer W. (1979)** Der Wassergehalt von Mg-cordierit zwischen 500° und 800°C sowie 0.5 und 11 kbar. *Fortschr. Mineralogie*, 57, 101-102.

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