Cordierite: thermodynamic liquidus phase in peraluminous systems?

Cordierita: ¿fase liquidus termodinámica en sistemas peralumínicos?

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ABSTRACT

Phase relations in the haplogranitic system have been broadly experimentally studied, but there is still an open field of discussion in experimental petrology concerning phase relations in natural granitic systems, Among other ferromagnesian phases occurring in granitoids, cordierite is controversial and its appearance has not jet been constraint. In this preliminar work, we have studied cordierite stability using a thermodynamic data set for temperatures between 750 and 1000 °C and pressures from 3 to 6 kbar. From the results presented here, cordierite could be a saturated phase of the studied system, but nucleation problems in experiments carried out under similar conditions do not reproduce this stability.

RESUMEN

El estudio del sistema haplogranítico ha sido ampliamente abordado por distintos trabajos clásicos de la petrología experimental, sin embargo, existen aún muchas incertidumbres en lo que se refiere a los sistemas graníticos naturales. Estas incertidumbres se refieren a la estabilidad y las relaciones de fases ferromagnesianas en estos sistemas naturales, y entre todas estas fases, la cordierita ha sido la menos estudiada. En este breve trabajo, hemos estudiado la estabilidad de la cordierita en un sistema granítico natural usando bases de datos termodinámicas para condiciones entre 750 y 1100 °C y presiones desde 3 a 6 kbar. Los resultados indican que la cordierita puede ser una fase saturada en este sistema, pero los problemas de nucleación en experimentos realizados en condiciones similares, no reproducen esta estabilidad.

***Key words**: cordierite, peraluminous granites, phase relations, experimental petrology, thermodynamic data, Cabeza de Araya.*

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Cordierite is a typical and characteristic phase of some peraluminous granites of the Spanish Hercynian chain (Corretgé 1971, Bea 1982, Corretgé et al. 1985, Ugidos 1990, Villaseca et al. 1998, Castro et al 1999, Pereira-Gómez & Rodríguez-Alonso, 2000). Both petrographic (Clarke 1995) and experimental evidences (Green (1976), Clemens & Wall (1981), Puziewicz & Johannes (1988), Holtz & Johannes (1991), Vielzeuf & Montel (1994), Castro et al (1999) and Corretgé et al. (2001)) support the magmatic origin of cordierite in many peraluminous granites.

Experiments performed by Green (1976), Holtz & Johannes (1991), Vielzeuf & Montel (1994), Castro et al (1999) and Corretgé et al. (2001) produce or grow magmatic cordierite in partial melting experiments from metapelitic or gneissic rocks as starting materials. In the other hand, Puziewicz & Johannes (1988) produced cordierite crystals in crystallization experiments. They have used a synthetic gel with added synthetic biotite and Al_2SiO_5, the final chemical composition of the starting material being a highly peraluminous biotite+cordierite-rich granite, with absence of CaO which has not been included to avoid kinetic problems with plagioclase crystallization. This absence of CaO prevents clinopyroxene crystallisation, a phase that, as we explain below, could have a strong influence in cordierite crystallization from a melt with a peraluminous composition.

The only experimental work that deals with cordierite crystallized from a glass is Clemens & Wall (1981). They do not specify whether they used a synthetic glass or a glass made from the direct melting of a natural rock with the precise composition, and this may influence the stability of the crystallised phases.

We have performed several experimental runs using a synthetic glass with a monzogranitic composition of the more "basic" sample of the Cabeza de Araya Batolith, as starting material (VSCA, see Table 1). Small "seeds" of natural cordierite and garnet have been added to the synthetic glass in order to overcome the apparent difficulty in nucleating garnet and cordierite (cf. Clemens & Wall 1981). Crystallisation experiments were performed at 4 and 6 kbar between 700 and 975 °C, in all of them, cordierite failed to crystallise and both garnet and cordierite seeds were dissolved in the melt. The liquidus phase was clinopyroxene. This absence of cordierite in our experimental results could mean that it is an undersaturated phase in this melt, but under the light of previous experimental works this cannot be affirmed.

Sample	VSCA	Cordierite	IT516 melts
Analysis		Average 33	Average 23
SiO_2	72.48	47.93	72.30
TiO_2	0.44	0.19	0.58
Al_2O_3	14.49	31.67	14.69
FeO	2.49	11.88	3.83
MnO	0.00	0.24	0.03
MgO	0.62	4.71	0.87
CaO	1.15	0.04	0.25
Na_2O	3.63	0.92	2.33
K_2O	4.69	0.19	5.12
Total	100	97.77	100.00
#Mg			
Average		0.41	0.29
St dev		0.027	
Range		0.38-0.51	

Table I.- Chemical composition of synthetic glass used in our crystallization experiments: VSCA; cordierites from the Cabeza de Araya Batholith (average of 33 analysis) and melt composition of the melt produced in partial melting experiments (IT516melts) in which cordierite was stable.

Tabla I.- Composición química del vidrio sintético VSCA usado en nuestros experimentos de cristalización, de las cordieritas del Batolito de Cabeza de Araya (promedio de 33 análisis) y del fundido generado en experimentos de fusión parcial (IT516melts) en los que la cordierita era estable.

1bar, 298,15 ºK	$\Delta_fG^{Pr,Tr}$	$\Delta_fH^{Pr,Tr}$	$S^{Pr,Tr}$	$V^{Pr,Tr}$
Cordierite Berman (1988)	-8651.515	-9158.727	417.970	23.311
Cordierite Saxena (1989)		-9164.869	411.000	

Table II.- Thermodynamic data from Berman (1988) and Saxena (1989). See text for explanation.

Tabla II.- Datos termodinámicos de Berman (1988) y Saxena (1989). Ver la explicación en el texto.

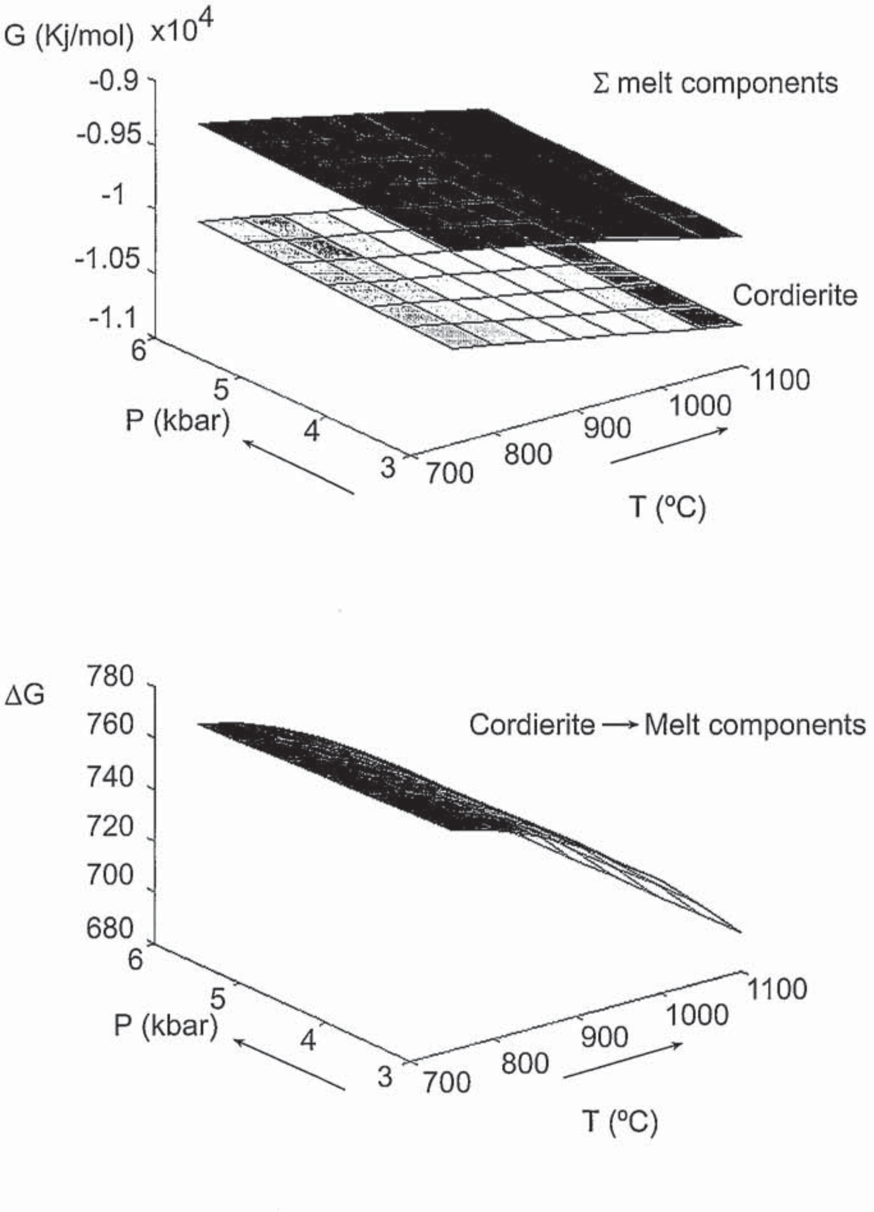

Fig. 1.- G of cordierite and Ómelt components and DG for the pressure – temperature space considered. See explanation in the text.

Fig. 1.- G de la cordierita y del sumatorio de los components del melt e DG para el espacion presión –tempertura considedrado. Ver la explicación en el texto

In order to test the stability of cordierite from a suitable granite melt composition we have carried out a thermodynamic study based on MELTS Supplemental Calculator software (Ghiorso & Sack 1995) and Saxena´s (1989) Inspector of Thermodynamic Data Software v. 2.2., and the following starting statements:

a) Seed nucleation of minerals from a melt should be possible if the condition of equality of chemical potentials of components in heterogeneous systems has been accomplished.

b) Choosing liquid components in a way similar to the proposal of Ghiorso & Sack (1995) for other mineral phases, growth of cordierite from a suitable melt reaction must be as the following:

$(Mg,Fe)_2Al_4Si_5O_{18} = (½Mg_2SiO_4 + ½ Fe_2SiO_4) + Al_2O_3 + 4SiO_2$

In the case of hydrous cordierite *n* molecules of water can be also be considered:

$(Mg,Fe)_2Al_4Si_5O_{18}nH_2O$

c) Taking into account that in Cabeza de Araya cordierites are always close to #Fe = 0.50 (average 0.41, st dev 0.027, range 0.38-0.51) (Table 1), equals quantities of $MgSiO_4$ and $FeSiO_4$ have to be considered in our calculations.

For our purposes thermodynamic cordierite $Mg_2Al_4Si_5O_{18}$ data from Saxena (1989) are considered. The differences between these data and data used by Berman (1988) are small as can be seen in Table 2.

a) Σi niμi of melt components

P(kbar)/ T (ºC)	750	800	850	900	950	1000	1050	1100
3	-9491,2855	-9558,5015	-9627,7735	-9699,012	-9772,1375	-9847,0735	-9923,7475	-10002,105
3,5	-9480,2615	-9547,439	-9616,6805	-9687,881	-9760,972	-9835,8755	-9912,515	-9990,8405
4	-9469,2775	-9536,427	-9605,63	-9676,8	-9749,8525	-9824,7205	-9901,326	-9979,613
4,5	-9458,3465	-9525,4575	-9594,6245	-9665,755	-9738,774	-9813,604	-9890,175	-9968,426
5	-9447,4605	-9514,5365	-9583,6635	-9654,756	-9727,739	-9802,533	-9879,065	-9957,276
5,5	-9436,6175	-9503,654	-9572,7455	-9643,8025	-9716,7425	-9791,495	-9867,9935	-9946,169
6	-9425,824	-9492,8185	-9561,8675	-9632,887	-9705,7915	-9780,505	-9856,958	-9935,094

b) G = *f*(P,T) of cordierite

P(kbar)/ T (ºC)	750	800	850	900	950	1000	1050	1100
3	-10256,6	-10319,5	-10382,4	-10445,3	-10508,2	-10571,1	-10634	-10696,9
3,5	-10245	-10307,9	-10370,8	-10433,7	-10496,6	-10559,5	-10622,4	-10685,3
4	-10233,3	-10296,2	-10359,1	-10422	-10484,9	-10547,8	-10610,7	-10673,6
4,5	-10221,6	-10284,5	-10347,4	-10410,3	-10473,2	-10536,1	-10599	-10661,9
5	-10210	-10272,9	-10335,8	-10398,7	-10461,6	-10524,5	-10587,4	-10650,3
5,5	-10198,3	-10261,2	-10324,1	-10387	-10449,9	-10512,8	-10575,7	-10638,6
6	-10186,7	-10249,6	-10312,5	-10375,4	-10438,3	-10501,2	-10564,1	-10627

c) ΔG of the saturation reaction

P(kbar)/ T (ºC)	750	800	850	900	950	1000	1050	1100
3	765,315	760,999	754,627	746,288	736,063	724,027	710,253	694,795
3,5	764,738	760,461	754,119	745,819	735,628	723,625	709,885	694,459
4	764,022	759,773	753,470	745,200	735,047	723,079	709,374	693,987
4,5	763,254	759,043	752,776	744,545	734,426	722,496	708,825	693,474
5	762,540	758,363	752,136	743,944	733,861	721,967	708,335	693,024
5,5	761,682	757,546	751,354	743,198	733,157	721,305	707,706	692,431
6	760,876	756,782	750,633	742,513	732,509	720,695	707,142	691,906

Table III.- a) $S_i n_i m_i$ of melt components $4SiO_2 + 2Al_2O3 + 1/2Fe_2SiO_4 + 1/2Mg_2SiO_4$ obtained from MELTS Supplemental Calculator, b) G = ¦(P,T) of cordierite and c) DG of the saturation reaction $(Mg,Fe)_2Al_4Si_5O_{18} = (½Mg_2SiO_4 + ½ Fe_2SiO_4) + Al_2O_3 + 4SiO_2$.

Tabla III.- a) $S_i n_i m_i$ de los components del fundido $4SiO_2 + 2Al_2O3 + 1/2Fe_2SiO_4 + 1/2Mg_2SiO_4$ obtenidos a partir de MELTS Supplemental Calculator, b) G = ¦(P,T) de la cordierita y c) DG de la reacción de saturación $(Mg,Fe)_2Al_4Si_5O_{18} = (½Mg_2SiO_4 + ½ Fe_2SiO_4) + Al_2O_3 + 4SiO_2$.

For a (Mg,Fe)-cordierite, the Margules parameters are:

$W_{12} = 1830.6$

$W_{21} = 1830.6$

And considering that $V_{G,1-2}$ @ $V_{G,2-1}$, the Margules equation which has to be used to calculate the Gibbs free energy (G_m^{ex}) in a real cordierite with a certain #Mg is:

$G_m^{ex} = (1-X_2)X_2W_G$

Table 1 shows the composition (average of 33 analysis) of cordierites in the Cabeza de Araya granites, with an average #Mg = 0.41, the Gibbs free energy for this natural Cabeza de Araya cordierite is: $G_m^{ex} = -442.82$, which has to be added to the data obtained for G = ¦(P,T) (Saxena 1989) of Mg- cordierite. Chemical analysis of melt compositions from partial melting experiments (Corretgé et al. 2001) in which cordierite was a stable growing phase are also shown in Table 1. We have used this melt composition to obtain the thermodynamic data for the melt components using MELTS Supplemental Calculator (Ghiorso & Sack 1995).

Results

Table 3 shows a) $S_i n_i m_i$ of melt components $4SiO_2 + 2Al_2O3 + 1/2Fe_2SiO_4 + 1/2Mg_2SiO_4$ obtained from MELTS Supplemental Calculator, b) G = ¦(P,T) of cordierite and c) DG of the saturation reaction $(Mg,Fe)_2Al_4Si_5O_{18} = (½Mg_2SiO_4 + ½ Fe_2SiO_4) + Al_2O_3 + 4SiO_2$, taking into account that enthalpies and entropies of melting of melt components are considered in MELTS's dataset.

As it is shown in Table 3c, DG is always positive under the considered temperature-pressure conditions. Fig.1 shows graphically this DG, and it hints that cordierite is the stable phase instead of melt components.

Discussion and Conclusions

Cordierite is a saturated phase in the system FMAS between 3 and 6 kbar and 750 and 1100ºC. Nucleation problems in the experimental procedures using a more complex system (CKNFMASH) may be due to metastability of different mineral phases observed in our experiments which take FeO, MgO and CaO from the melt, and Al_2O_3 through CaTs components, as it is observed in clinopyroxene that was grown in our runs, or preference nucleation of other minerals due to particular structure of the melt which could impose structural conditions, as avoidance of Al-O-Al linkages in the tetrahedral network of the melt (Lowenstein 1954, Herrero et al. 1985).

It can also be argued the possibility of magmatic growth of cordierite from a peritectic reaction as observed in the partial melting experiments (Corretgé et al. 2001) of the type: A + B crd +liquid, in the source region of these granites. It is possible that, at the conditions of emplacement, this reaction is not stable, therefore it may not be reproduced in our crystallisation experiments.

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