Abrupt transition in H_2O activity in the melt-present zone of a thermal aureole: Evidence from H_2O contents of cordierites

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DATA REPOSITORY 2001036

Petrography of analyzed rocks

Six-figure sample numbers: Harker Collection, University of Cambridge.

Accessory minerals in brackets. ²: Retrograde alteration product.

Mineral name abbreviations from Kretz (1983).

MD1 (126525)

Lithology: Andalusite-cordierite-muscovite-hornfels

(high-silica pelite from the Islay Quartzite)

Locality: NN11402719 ca. 900 m from contact with Quarry Diorite.

Assemblage: And + Crd + Bt + Ms + Kfs + Pl + Qtz (+ Ilm + Ap + Tur + Zrn)

Texture: A regional S_2 crenulation cleavage is overgrown statically by ragged helicitic

0.2 to 1.5 mm long poikiloblasts of Crd and And, commonly elongated parallel to S_2 . Crd poikiloblasts show minimal alteration and have inclusions of Ms, Bt and Ilm; analyses are from the largest inclusion-free areas. Ms forms fine-grained aggregates of aligned flakes defining (i) the S_2 crenulation cleavage, and (ii) a folded S_1 cleavage within 0.5 mm-wide lithons between S_2 cleavage planes. Bt forms irregular cross-cutting flakes up to 1 mm long but is also aligned mimetically in S_2 . Kfs forms granoblastic polygonal grains up to 0.4 mm diameter, and also as thin $(10-20 \,\mu\text{m})$ rims around equant Qtz grains

contacting mica.

MM187

Lithology: Corundum-andalusite-cordierite-Kfeldspar-hornfels

(low-silica pelite from the Leven Schist)

Locality: NN12052830 ca. 380 m from contact with Quarry Diorite.

Assemblage: And $+ Crd + Crn + Bt + Kfs + Pl (+ Ms^2 + Ilm + Ap + Zrn)$

Texture: A typical hornfels with granoblastic/poikiloblastic texture. Crd is abundant

and forms rarely-twinned anhedral ellipsoidal poikiloblasts and polycrystalline

patches (up to 3 x 2 mm, enclosing Bt and Ilm) with a weak shape fabric

controlled by the former S₂ crenulation cleavage; sericitic and pinitic alteration are minimal. Subgrains and subgrain-free grains range in size from ca. 0.01 to

0.5 mm. And occurs as abundant randomly oriented irregular anhedral

poikiloblasts up to 3 mm long. Crn forms small equant ragged poikiloblasts up to 0.5 mm across, locally rimmed by retrograde Ms. Bt is fine-grained and decussate. Kfs is fine-grained granoblastic polygonal orthoclase microperthite.

MM171

Spinel-andalusite-cordierite-Kfeldspar-hornfels Lithology:

(low-silica pelite from the Leven Schist)

Locality: NN12412878 ca. 160 m from contact with Quarry Diorite.

Assemblage: And + Crd + Spl + Crn + Bt + Kfs + Pl (+ Ms² + Ilm + Ap + Zrn)

Texture: A fine-grained granoblastic/poikiloblastic hornfels which is very fresh except

> within 1 mm of localized cracks where retrograde sericitization is intense. Crd forms abundant large randomly oriented irregular ellipsoidal poikiloblasts, up to 3mm long, with typical subgrain structure. Subgrains and subgrain-free grains range in size from ca. 0.01 to 0.7 mm. Inclusions of Bt, Ilm and Spl are common in Crd, though inclusion-free areas up to 0.5 mm across occur; Crd analyses were obtained from such areas in grains remote from zones of intense sericitization. And and Crn form skeletal poikiloblasts. Spl forms abundant eu/subhedral green crystals up to 250 µm across. Bt occurs as irregular

randomly oriented flakes.

MM166A

Migmatitic garnet-cordierite-Kfeldspar-hornfels Lithology:

(low-silica pelite from the Leven Schist)

Locality: NN12482896 ca. 100 m from contact with Quarry Diorite.

Assemblage: $Grt + Crd + Bt + Kfs + Pl + Qtz (+ Spl + Ms^2 + Ilm + Ap + Zrn)$

Texture: A fine- to medium-grained migmatitic hornfels. Indistinct leucosomes rich in

> finer-grained Crd-rich mesosomes, forming stripes that follow the former S₂ crenulation cleavage. Grt forms relatively inclusion-free eu/subhedral crystals up to 2 mm across, mainly within leucosomes. Crd is abundant and occurs both as eu/subhedral twinned crystals (up to 0.7 x 0.4 mm), especially in leucosomes, and as elongated granoblastic polycrystalline patches (up to 3 x 1 mm) aligned parallel to leucosomes. The patches commonly contain Ilm and Bt inclusions and locally clusters of tiny green Spl granules. The Crd is fresh, though some grains are altered to sericite within ca. 20 µm of their grain boundaries. Subgrains and subgrain-free grains range in size from <0.03 to 0.7 mm. Bt forms randomly oriented flakes up to 0.5 mm long. Kfs occurs as granoblastic-polygonal to blocky subhedral crystals of microcline

Kfs + Qtz (average grainsize ca. 0.5 mm) alternate on a 2-3 mm scale with

microperthite, mostly within leucosomes. Otz is mostly granoblastic, but locally forms cuspate grains interstitial to blocky Kfs in leucosomes.

MM166D

Lithology: Spinel-sillimanite-cordierite-Kfeldspar-hornfels

(low-silica pelite from the Leven Schist)

Locality: NN12442896 ca. 70 m from contact with Quarry Diorite.

Assemblage: And + Sil + Crd + Spl + Crn + Bt + Kfs + Pl (+ Ilm + Ap + Zrn)

Texture: A fine- to medium-grained granoblastic/poikiloblastic hornfels with a high

degree of textural equilibrium. Crd+Bt±Kfs-rich layers alternate with Spl+Crd+And+Sil+Crn-rich ones. The minerals show no visible alteration except within 100 μm of rare cracks. Crd is abundant and forms (i) ellipsoidal polycrystalline patches up to 5 x 3 mm, mostly aligned parallel to the layering, and (ii) isolated eu/subhedral twinned prisms (<0.05 mm to 1 mm across), especially adjacent to Bt. Elongated ragged poikiloblasts of And, up to 1cm long, are locally replaced by small Sil prisms in parallel alignment. Green Spl is spatially associated with Crd, Al₂SiO₅ and Crn and forms subhedral granules, mostly in subequant clusters (up to 3 mm diameter) but also as isolated grains up to 0.5 mm across. Crn forms small irregular grains. Bt is decussate and forms subhedral books of low aspect ratio. The Kfs is

orthoclase microperthite and occurs both as blocky grains up to 1.5 mm across and as poikilitic patches interstitial to euhedral cordierite. The larger Pl grains

are antiperthitic.

MM198C

Lithology: Migmatitic orthopyroxene-cordierite-plagioclase-hornfels

(meta-greywacke from the Leven schist)

Locality: NN12492912 ca. 15 m from contact with Quarry Diorite.

Assemblage: Mesosomes: Opx + Crd + Bt + Pl + Qtz (+ Ilm)

Leucosomes: $Crd \pm Opx + Bt + Pl + Qtz (+ Ilm + Chl^2 + Ms^2 + Ap + Zrn)$

Texture: A migmatite with distinct irregular medium-grained leucosome veins up to 8

mm wide in a dark, fine-grained matrix (mesosome) of biotite-rich hornfels. All analysed Crd grains are from leucosomes. The *leucosomes* have igneous textures, with eu/subhedral Crd, Opx and Pl from 0.1 to 2 mm across. Opx is

strongly pleochroic and locally altered to Chl. Crd is relatively free of inclusions: where abundant it is euhedral to interstitial Otz, but where rar

inclusions; where abundant it is euhedral to interstitial Qtz, but where rare it forms poikilitic patches up to 6mm across enclosing granoblastic Qtz. Both Crd and Pl are heavily sericitized in places. Crd analyses were obtained as far from altered regions as possible in the least altered grains. The *mesosomes* are composed of very fine-grained (ca. 100 mm) homogeneous Opx-Bt-Pl-rich hornfels in which skeletal Opx prisms are set randomly in a granoblastic

Bt+Pl+Crd matrix.

MD9A (126531)

Lithology: Migmatitic spinel-sillimanite-cordierite-Kfeldspar-hornfels

(low-silica pelite, probably originally from the Leven Schist)

Locality: NN112283. From a <10 cm diameter xenolith within the Quarry Diorite.

Assemblage: Mesosomes: And $+ Sill + Crd + Spl + Crn + Kfs + Bt + Ilm (+ Ms^2 + Bt^2)$

Leucosomes: Kfs + Pl + Qtz + Bt \pm Crd (+ Ms² + Zrn + Opaque)

Texture: Fine-grained granoblastic/poikiloblastic hornfels containing a few 1-2 mm

thick leucosome veins and patches. The rock is fresh apart from within ca. 0.5 mm of a crack where there is extensive micaceous alteration of the high-grade

minerals. In the *mesosomes*, abundant fresh Crd forms interlocking

polycrystalline patches and poikiloblasts up to 3 mm across in which are set ragged poikiloblasts of Crn, abundant small irregular crystals of And (partially replaced by Sil), and rare granules of green Spl. The *leucosomes* are rich in Kfs and cannot therefore be offshoots of the enclosing diorite. Qtz is mainly interstitial to blocky, subhedral microcline crystals, and minor Pl decorates Kfs

grain boundaries. Bt is rare. Subhedral twinned prisms of Crd occurs in one

pod-like leucosome patch.

Ion probe analysis conditions

A defocused 25 μ m, O primary-beam with an energy of approximately 10.5 keV was applied. The extraction energy was 4.5 keV and the offset energy was 100 eV. Secondary ions were measured sequentially on an electron multiplier ion counting system. Count rates measured for H and C were ratioed to 28 Si for all samples except MD1 for which 30 Si was used. Standards were used to derive CO₂ and H₂O calibrations. Isotopic ratios obtained from the Etive cordierites were tested against standard cordierites in all SIMS sessions. The background levels for H₂O and CO₂ were 0.025 and 0.322 wt%, respectively, and analytical precision was ± 0.06 wt%.

Calculation of nH₂O of cordierite

The mole fraction of H_2O in the channel site of cordierite, nH_2O , was calculated from the weight percentage measured by SIMS using the following method:-

For each rock, take the mean composition of cordierites analysed by EPMA (as weight percent oxides of Si, Ti, Al, Cr, Fe, Mn, Mg, Ca, Zn, Na and K). (N.B. Each mean composition will be close to, but not necessarily identical to, the representative cordierite analyses listed in Table A2.)

For each water analysis:-

- 1. Normalise the anhydrous oxide wt.% of the average cordierite in the respective rock (from EPMA) to 100-x, where x is the wt.% H₂O measured by SIMS.
- 2. Divide each oxide wt.% value by the molecular weight of the respective oxide to obtain the molecular proportion of the oxide in the cordierite.
- 3. Multiply each oxide molecular proportion by the number of oxygen atoms per molecule of respective oxide to obtain the relative atomic proportion of oxygen associated with each oxide in the cordierite.
- 4. Sum the relative atomic proportions of oxygen for all oxides except H₂O to obtain an oxgen total (p). Normalise the atomic oxygen in all oxides except H₂O to 18.00 by multiplying each relative atomic proportion of oxygen (from 3) by 18/p to obtain the number of oxygen atoms associated with each oxide in the cordierite formula, as cast on the basis of 18(O) anhydrous.
- 5. Multiply the relative atomic proportion of oxygen associated with H₂O (from 3) by 18/p to obtain the number of oxygen atoms associated with molecular H₂O in the cordierite formula, as cast on the basis of 18(O) anhydrous. This is the number of H₂O molecules per molecule of cordierite, and is therefore equal to the mole fraction of H₂O in the channel site, nH₂O.

6. Multiply the number of oxygens associated with each oxide (from 4) by the number of cations per molecule of respective oxide and divide by the number of oxygens per oxide molecule to obtain the cation proportions for the cordierite formula on the basis of 18(O) anhydrous.

 $n\rm H_2O$ values calculated using the cordierite analyses listed in Table A2 differ from those calculated using mean cordierites by a maximum of 0.002. Generally the values are identical.

Derivation of equation 2

A paraphrase of Kurepin's (1985) derivation of equation 2 is reproduced here. For any balanced dehydration reaction, the following equation is approximately true at equilibrium:

$$0 = \Delta H_{1,298}^{o} - T\Delta S_{1,298}^{o} + (P - 1)\Delta V_{s} + RT \ln K + hRT \ln \left(\frac{f_{H2O.P,T}}{f_{H2O.1,T}}\right)$$

where P is pressure, T is absolute temperature, is the standard state enthalpy change of reaction, is the standard state entropy change of reaction, ΔV_s is the volume change of reaction solids, R is the gas constant, R is the equilibrium constant, R is the number of molecules of R_2O evolved per mole of reaction, $R_{P,T}$ is the fugacity of R_2O at the R and R of interest, and R is the fugacity of R_2O at 1 bar and the R of interest. The assumptions inherent in this equation are that (i) compressibilities and thermal expansivities of solid components are negligible or effectively cancel, so that R is independent of R and R and R and R and R are independent of R (i.e. the sum of the heat capacities of reactants is exactly equal to that for products). (The second assumption is not strictly true for dehydration reactions, but may be justified in certain cases, see below).

For the reaction

$$Mg_2Al_4Si_5O_{18} \cdot H_2O = Mg_2Al_4Si_5O_{18} + H_2O$$
 cordierite cordierite fluid

 $\Delta V_s = 0$, since the presence or absence of H_2O in the channel site in cordierite has no effect on its molar volume, and h = 1. Assuming that the $Mg_2Al_4Si_5O_{18}$ part of the cordierite molecule has the same molar heat capacity in hydrous and anhydrous cordierite, and that free H_2O has

the same molar heat capacity as the H_2O in the channel site of hydrous cordierite, ΔH° and ΔS° may be justifiably assumed to be independent of T. The equilibrium constant is given by:

$$K = \left(\frac{a_{MgCrd} \cdot a_{H2O}}{a_{MgCrd \cdot H2O}}\right)$$

where $a_{\rm MgCrd}$ is the activity of anhydrous cordierite, $a_{\rm MgCrd,H2O}$ is the activity of hydrous cordierite, and $a_{\rm H2O}$ is the activity of H₂O. Because substitution of a given amount of Fe for Mg can be assumed to reduce $a_{\rm MgCrd}$ and $a_{\rm MgCrd,H2O}$ by the same amount, cordierite activity can be modelled simply as a function of the occupancy of the channel site (i.e. as a one-site solution). If, as in the case of the studied Etive cordierites, H₂O is the only volatile species to enter the channel site in significant quantities, and if the site contains no other ions, and if H₂O molecules mix with vacancies on that site ideally, then $a_{\rm MgCrd,H2O} = X_{\rm H2O}^{\rm crd}$ and $a_{\rm MgCrd} = 1 - X_{\rm H2O}^{\rm crd}$. Thus

$$K = \left(\frac{\left(1 - X_{H2O}^{crd}\right). a_{H2O}}{X_{H2O}^{crd}}\right) = \left(\frac{\left(1 - n\right). a_{H2O}}{n}\right)$$

and

$$0 = \Delta H^{o} - T\Delta S^{o} + RT \ln \left(\frac{(1-n) \cdot a_{H2O} \cdot f_{P,T}}{n \cdot f_{1,T}} \right)$$

Recognising that $f_{1,T}$ is approximately 1 bar (Burnham et al., 1969), rearranging this yields equation [2]:

$$a_{H_2O} = \frac{n}{f_{P,T}(1-n)} \exp\left[\frac{T\Delta S^{\circ} - \Delta H^{\circ}}{RT}\right].$$

Error Propagation

The error in each of the aH_2O values tabulated in Table 1 was calculated by propagating errors in the thermodynamic data, P, T and n through equation 2 using the standard formulae.

The error in the thermodynamic data, manifested in the term $T\Delta S^{\circ}$ - ΔH° (the top line of the term in square brackets in equation 2), was calculated on the basis of the quoted error of $\pm 6\%$ in Mirwald and Schreyer's (1979) measurements of H₂O in experimentally equilibrated cordierites.

The error in n (and hence in 1-n) was taken as the 1σ sample standard deviation in the measured values (see Tables 1 and A3).

The contribution to the error in aH_2O caused by uncertainty in P was treated by considering the error in the fugacity of water, f, the only P-sensitive term in equation 2. The error in f was taken to be the average actual deviation in f consequent upon a P difference of 0.4 kbar, i.e. the average of $(f_{T, 2.4\text{kbar}} - f_{T, 2.0\text{kbar}})$ and $(f_{T, 2.0\text{kbar}} - f_{T, 1.6\text{kbar}})$.

The error in T was assumed to be $\pm 30^{\circ}$.

The total error incorporates contributions from pressure and thermodynamic data which are systematic and thus cannot be responsible for between-sample variations. Non-systematic errors were also calculated for each of the samples, incorporating contributions from $n{\rm H}_2{\rm O}$ and T only.

Figure caption

A1. Variation in H₂O activity in Etive aureole with distance from Quarry Quartz-Diorite. Note abrupt change in H₂O activity near sillimanite isograd. Error bars indicate magnitude of non-systematic errors.

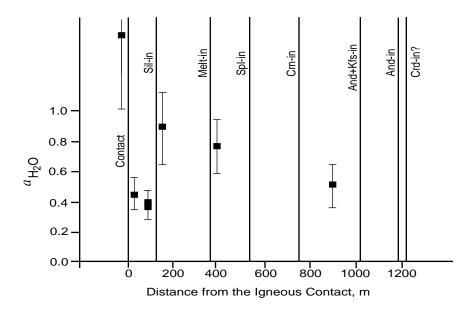


Table A1. Summary of metamorphic assemblages (normal type) and model KFMASH reactions (bold type) in silica-rich and silica-poor pelites from the southern segment of the etive Aureole. C: KFMASH-continuous reaction; D: KFMASH-discontinuous reaction.

Mineral Zone / Isograd		Silica-rich pelites	Silica-poor pelites			
II	Cordierite Zone	Crd + Bt + Ms + Qtz	Crd + Bt + Ms + Qtz			
	Andalusite Isograd	$Crd + Ms = And + Bt + Qtz + H_2O$ (C)				
III	Andalusite Zone	Crd + And + Bt + Ms + Qtz	Crd + And + Bt + Ms + Qtz			
	Andalusite + K-feldspar Isograd	Ms + Qtz = And	$Ms + Qtz = And + Kfs + H_2O$ (D)			
IV	Andalusite + K-feldspar Zone	Crd + And + Bt + Kfs + Qtz	(Crd + And + Bt + Ms + Kfs not seen)			
		$Bt + And + Qtz = Crd + Kfs + H_2O$ (C)	-			
	Corundum Isograd	-	$\mathbf{Ms} = \mathbf{Kfs} + \mathbf{Crn} + \mathbf{H}_2\mathbf{O} (\mathbf{D})$			
V	Corundum Zone	Crd + And + Bt + Kfs + Qtz	Crd + And + Crn + Bt + Kfs			
		$Bt + And + Qtz = Crd + Kfs + H_2O$ (C)	$Bt + And = Crd + Crn + Kfs + H_2O (C)$			
	Spinel Isograd	-	Bt + And = Spl + Crd + Crn + Kfs + H2O (D)			
		Crd + And + Bt + Kfs + Qtz	Crd + And + Spl + Crn + Bt + Kfs			
		$Bt + And \pm Crd + Kfs + Qtz + H_2O = melt (D)$	-			
VI	Spinel Zone	Crd + And + Bt + Kfs + Qtz + melt	Crd + And + Spl + Crn + Bt + Kfs			
	_	Bt + And + Qtz = Grt + Crd + Kfs + melt (D)	? Bt + And = Spl \pm Crd + Crn + Kfs + melt (D)			
	_	Grt + Crd + Bt + Kfs + Qtz + melt	Crd + And + Spl + Crn + Bt + Kfs + melt			
	Sillimanite Isograd	-	And = Sill (D)			
VII	Sillimanite Zone	Grt + Crd + Bt + Kfs + Qtz + melt	$Crd + Sill + Spl + Crn \pm Bt + Kfs + melt$			

N.B. Melting reactions in silica-poor pelites are uncertain. High-grade spinel- and biotite-bearing assemblages are not strictly within the KFMASH system owing to appreciable contents of Fe⁺⁺⁺ in spinel and Ti and F in biotite.

Table A2. Representative electron microprobe analyses of cordierite.

Sample	MM198C	MM166A	MM166D	MM171	MM187	MD1 [†]	MD9 [†]
SiO_2	48.93	47.99	47.67	47.42	47.27	48.43	48.16
TiO_2	0.00	0.14	0.09	0.04	0.04	0.00	0.00
Al_2O_3	32.57	32.58	32.67	32.37	32.34	33.16	32.93
Cr_2O_3	0.08	0.03	0.03	0.00	0.00	-	-
FeO*	9.15	11.77	11.66	11.64	12.10	9.99	12.18
MnO	0.24	0.17	0.17	0.23	0.17	0.17	0.14
MgO	8.22	6.57	6.51	6.49	6.37	7.00	5.96
CaO	0.02	0.05	0.06	0.00	0.03	0.02	0.00
ZnO	0.00	0.00	0.02	0.08	0.00	-	-
Na ₂ O	0.21	0.25	0.31	0.51	0.49	0.00	0.00
K_2O	0.04	0.03	0.00	0.02	0.00	0.07	0.00
Total	99.46	99.58	99.19	98.80	98.81	98.84	99.37
	Number of a	toms on the b	pasis of 18 ox	ygens			
Si	5.01	4.97	4.95	4.95	4.95	5.00	4.99
Ti	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Al	3.93	3.97	4.00	3.99	3.99	4.03	4.02
Cr	0.00	0.00	0.00	0.00	0.00	_	-
Fe	0.78	1.02	1.01	1.02	1.06	0.86	1.06
Mn	0.02	0.01	0.01	0.02	0.01	0.02	0.01
Mg	1.25	1.01	1.00	1.01	0.99	1.08	0.92
Ca	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Zn	0.00	0.00	0.00	0.00	0.00	-	-
Na	0.04	0.05	0.06	0.10	0.10	0.00	0.00
K	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Total	11.03	11.04	11.03	11.09	11.10	11.00	11.00

^{*} Fe total as Fe^{2+}

[†] From Droop and Treloar (1981).

Table A3. Water contents of cordierites in the Etive aureole. Isotopic ratios are from SIMS. SD = sample standard deviation.

Sample	¹ H/ ²⁸ Si	Wt% H ₂ O	Mean wt%	n H ₂ O	Mean n H ₂ O
MM166D M. Sill Zone T=750°C P=2kbar	0.1206 0.1145 0.1109 0.1113 0.1031 0.1255	0.947 0.898 0.869 0.872 0.806 0.986	0.896 (SD=0.063)	0.329 0.311 0.301 0.302 0.279 0.342	0.311 (SD=0.022)
MM166A L. Sill Zone T=725°C P=2kbar	0.1205 0.1041 0.1097 0.1165	0.946 0.814 0.859 0.913	0.883 (SD=0.058)	0.328 0.282 0.398 0.317	0.306 (SD=0.020)
MM198C U. Sill Zone T=800°C P=2kbar	0.1214 0.1091 0.1343 0.1145 0.1236 0.1170 0.1086 0.1230 0.1164 0.1187 0.1226 0.1223 0.1313	0.953 0.854 1.057 0.898 0.971 0.918 0.850 0.966 0.913 0.932 0.963 0.961 1.033	0.944 (SD=0.060)	0.327 0.292 0.363 0.308 0.333 0.315 0.291 0.331 0.313 0.319 0.330 0.329 0.354	0.323 (SD=0.021)
MM187 L. Spl Zone T=650°C P=2kbar	0.1892 0.1740 0.1950 0.1684 0.1758 0.1738 0.1864 0.1947	1.500 1.377 1.546 1.332 1.392 1.376 1.477 1.544	1.443 (SD=0.084)	0.525 0.481 0.541 0.465 0.487 0.481 0.517 0.541	0.505 (SD=0.029)
MM171 U. Spl Zone T=700°C P=2kbar	0.1677 0.1703 0.1963 0.2083 0.2054 0.2126 0.1839 0.1744 0.1698 0.1907	1.326 1.347 1.557 1.654 1.630 1.688 1.457 1.380 1.343	1.489 (SD=0.139)	0.463 0.470 0.544 0.579 0.570 0.591 0.509 0.482 0.469 0.529	0.521 (SD=0.049)
MD9 Xenolith T=850°C P=2kbar	0.1878 0.1938 0.2250 0.2464	1.488 1.537 1.788 1.691	1.694 (SD=0.222)	0.519 0.536 0.625 0.591	0.592 (SD=0.079)
	¹ H/ ³⁰ Si				
MD1 And+Kfs Zone T=575°C P=2kbar	0.5659 0.5295 0.5540 0.4672	1.355 1.264 1.325 1.108	1.263 (SD=0.110)	0.467 0.435 0.457 0.381	0.435 (SD=0.038)