

Introduction

AX is an activity-composition calculation program for rock-forming minerals. It was never meant to be for public release, and so is not guaranteed to be always robust—however it is freeware and we hope that it will be as useful to you as it has been to us. The program performs by first recalculating the analysis to a mineral formula and then determining the activities of mineral end-members. The uncertainties stemming from typical probe error (0.05wt% minimum + 1.5% relative on each oxide) are propagated to the calculated activities. These are therefore *minimum* errors - they do not take into account activity model uncertainties.

The models used in AX are kept deliberately simple, for two reasons: 1) Natural minerals are more complex than experimentally investigated equivalents, and simpler models probably extrapolate better than elaborate ones; 2) The main use of AX is to supply activities for thermometry and barometry, not to make the most precise phase diagram calculations. The errors involved, stemming from probe analysis, inhomogeneity or incomplete equilibrium, are often as large as any errors arising from simplifying the activity models.

The program is simple and should be relatively obvious even for the new user. The main steps involved are:

1. Create an input file; this may be done either with your favourite editor, or from within AX itself. The data file consists of a line of 11 oxides (these and ONLY these 11 are accepted currently by AX, although they can be placed in any order on the first line of the data file - see the example below).

Each analysis is entered as a pair of lines, the first of which gives the mineral code (g, cpx etc) and a brief title. (A list of the mineral codes can be found from the help menu in the program, and is also given below). The second line gives the oxide wt% values in the SAME order as the oxide names in the list at the top of the file. Data may be tab-, comma-, or space- delimited, and the file is terminated with an asterisk. There should be no blank lines in the file.

An example follows:

```
SiO2 TiO2 Al2O3 Cr2O3 Fe2O3 FeO MnO MgO CaO Na2O K2O
g gt
39.70 0.00 23.20 0.00 0.00 23.60 0.50 7.60 7.00 0.00 0.00
cpx omph
57.20 0.00 12.50 0.00 0.00 4.70 0.00 7.00 10.20 8.00 0.00
*
```

The codes to use in the datafile for the mineral groups are in the table on the next page:

Code	Mineral groups
mu	white micas, including margarite
bi	biotites
amph	amphiboles
fsp	feldspars
ep	epidotes, zoisites
g	garnets
cpx	clinopyroxenes
opx	orthopyroxenes
chl	chlorites
ta	talc
scap	scapolites
ol	olivines
ctd	chloritoid
cd	cordierite
st	staurolites
sp	spinels
carb	carbonates
ilhem	ilmenites and hematites
spr	sapphirines
osm	osumilites

2. Run the program. Double click the AX icon. Mac and Win instructions follow below.

- Windows:

The opening window panel is displayed, which allows you four options. These are

RUN: opens a fileOpen dialog to select an existing datafile which is then run. The resulting output file is then displayed in an editable window.

FILE/EDIT: this button takes you to the editor, opens up a tiny sample datafile which may be used as a template for creating and saving your own new datafile.

EXIT: this closes down the application. The application may also be terminated by double-clicking the close box at the top of the main panel window.

LIST MINERAL ABBREVIATIONS: this button throws up a dialog box showing a list of the mineral abbreviations.

The editor allows only basic functionality such as cut/paste, find/replace, save/saveas etc.

- Mac: You have several menus:

Apple menu. Standard, with an 'about' box.

File menu. Allows you to open and view any text file, and to Quit the application.

Edit Menu. Not usable with this application.

AX Menu. Allows choices of run mode:

- a) Run from file. This will throw up dialog boxes to open an input file and then run.
- b) Interactive. Allows entry of mineral probe data and title. Probe data may be entered as oxide weight percent (in the order shown) or as cations per formula unit.
- c) File Input help. This throws up an example of the format of an input file and asks if you want the example stored to disk as a file named “ax dtest”. This can then be immediately run from the Run from file submenu, or examined and used as a template for other disk files you wish to create.
- d) View a text file. Allows you to open a textfile for viewing (ie to look at your data files or output files – sorry, no editing allowed)

FileType menu. This allows you to select a file creator for your input and output files. If you select MSWord, then all textfiles produced will be Word text files and will open Word on double clicking. If you use a wordprocessor to create files, remember to save the files as “text only”.

Upon completion of a run, the program throws up the outfile in a scrollable window for viewing. You can close this via the file menu or by its go-away box.

3. Examining the output. 3 kinds of output file are generated:

1. AX output: *.out (*o on Mac) – what you see on screen.
2. A tab-delimited file(*.tab) of mineral analysis tables, paged for A4 output.
3. A file suitable for editing and submission to THERMOCALC as input. (Win: thd*.txt; Mac: th d*). AX enters quartz automatically, and H₂O (if hydrous silicates are processed) and/or CO₂ (if carbonates are used).

N.B. Eliminate all doubtful end-member data before running THERMOCALC (either because of disequilibrium character - e.g. retrograde phases, or because the end-member is the dilute end-member on a solvus limb - see below.

Some notes:

- On tiny values for activity: Some minerals will have very small activities simply because there are many sites on which mixing occurs. To decide whether a calculated activity is too tiny to be reliable, use the following rule of thumb: for a mineral where mixing is dominated by mixing on n sites, raise the activity to the power of $1/n$ and check that the result lies in the range 0.1–1.0. This is effectively normalising to an equivalent one-site solution where we would be suspicious of activities for mole fractions less than 0.1 unless good Henry’s law constants are available. As an example, although for garnet ($n=3$) an activity of 0.008 might seem at first sight to be far too small to be reliable, this would be equivalent to 0.2 on a one-site basis and would probably be acceptable. AX does not print activities which are far smaller than their uncertainties.
- Dilute limbs of a solvus: Avoid end-members on the “dilute” limb of a solvus - ie do not use the paragonite activity in a K-rich white mica, or the muscovite or celadonite

end-members in a paragonite. The uncertainties on wrong-limb end-members are prohibitively large.

- Published thermobarometer calibrations: Many published thermometers or barometers rely on very specific recipes for activities for successful use. Do not use AX activities in such formulations, particularly in sensitive cation exchange equilibria (e.g. garnet–clinopyroxene thermometers), or solvus thermometers (e.g. two pyroxene thermometers).

Output produced by AX with the above example datafile is

```
-----
g gt
  2-site mixing + Regular solution gammas
  Ferric from: Cation Sum = 8 for 12 oxygens
  W: py.alm=2.5, gr.py=33, py.andr=73, alm.andr=60, spss.andr=60 kJ
```

oxide	wt % cations			activity	sd	%
SiO2	39.70	2.988	py	0.051	0.0122	24
TiO2	0.00	0.000	gr	0.0176	0.00579	33
Al2O3	23.20	2.059	alm	0.10	0.0170	17
Cr2O3	0.00	0.000	spss	0.0000009	0.00000051	59
Fe2O3	0.00	0.000	andr	-	-	-
FeO	23.60	1.486				
MnO	0.50	0.032				
MgO	7.60	0.853				
CaO	7.00	0.565				
Na2O	0.00	0.000				
K2O	0.00	0.000				

totals	101.61	7.982				

```
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cpx omph
  Assumed P2/n ordered pyroxene: ideal coupled mixing
  Ferric from: Cation Sum = 4 for 6 oxygens
```

oxide	wt % cations			activity	sd	%
SiO2	57.20	2.024	di	0.35	0.0348	10
TiO2	0.00	0.000	hed	0.13	0.0213	16
Al2O3	12.50	0.521	jd	0.52	0.052	10
Cr2O3	0.00	0.000	cats	-	-	-
Fe2O3	0.00	0.000	acm	-	-	-
FeO	4.70	0.139				
MnO	0.00	0.000				
MgO	7.00	0.369				
CaO	10.20	0.387				
Na2O	8.00	0.549				
K2O	0.00	0.000				

totals	99.61	3.990				

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Activities of mineral end-members for average P , average T , and average PT calculations may be estimated with the help of the program AX which accepts raw microprobe data in the form of oxide weight percents and performs standard mineral recalculations, with attempts at ferric iron estimation. The program calculates activities for end-members which can then be used for rock calculations in THERMOCALC. The assumptions used in deriving the activities and in estimation of ferric iron are listed briefly below. (R_{\max} is the maximum allowed ratio of ferric to ferrous iron; HP90 is Holland & Powell 1990, J. Met. Geol. 8, 89–124. HP98 is Holland & Powell 1998, J. Met. Geol. 16, 309–343.)

For more information on some of the mineral groups, see

- 1) HP90 p 100 & especially HP98 p 315–318
- 2) www pages at www.esc.cam.ac.uk/astaff/holland/

• Clinopyroxene

Ferric from: Cation Sum = 4 for 6 oxygens, $R_{\max}=0.95$. Wood & Banno model (M1–M2 mixing only) used. If $Na < 0.3$ then disordered C2/c *calcic cpx* is assumed with nonideal mixing. e.g. $a_{di} = X_{Ca,M2}X_{Mg,M1}\gamma_{di}$

Nonideality is approximated by renormalising to the set of end-members di-hed-cats-jd-en with symmetric formalism interaction energies (kJ):

W	hed	cats	jd	en
di	3	7	24	30
hed		4	24	20
cats			20	24
jd				24

If $Na > 0.7$ then disordered C2/c *sodic pyroxene* is assumed with nonideality approximated by renormalising to the set of end-members jd-acm-di-hed with symmetric formalism interaction energies (kJ):

W	acm	di	hed
jd	0	24	24
acm		24	24
di			3

Otherwise, (if $0.3 > Na < 0.7$), P2/n *omphacite* is assumed. Ideal coupled mixing is assumed as an approximation (jd-di-hed-acm).

if $Mg,M1 > Ca,M2$ then $a_{di} = X_{Ca,M2}$ else $a_{di} = X_{Mg,M1}$

if $Fe,M1 > Ca,M2$ then $a_{hed} = X_{Ca,M2}$ else $a_{hed} = X_{Fe,M1}$

if $Al,M1 > Na,M2$ then $a_{jd} = X_{Na,M2}$ else $a_{jd} = X_{Al,M1}$

$a_{acm} = X_{Fe^{3+},M1}$

• Orthopyroxene

Ferric from: Cation Sum = 4 for 6 oxygens, $R_{\max}=0.2$. The Wood & Banno model (M1–M2 mixing only) is used. e.g. $a_{en} = X_{Mg,M2}X_{Mg,M1}\gamma_{en}$

Nonideality is approximated by renormalising to the set of end-members en-fs-mgts-di with symmetric formalism interaction energies (kJ):

W	fs	mgts	di
en	1	0	30
fs		1	28
mgts			30

• Olivine

Ferric from: Cation Sum = 3 for 4 oxygens, $R_{\max}=0.1$

Mixing on sites used (M1–M2). e.g. $a_{fo} = X_{Mg,M2}X_{Mg,M1}\gamma_{fo}$

Nonideality is approximated by renormalising to the set of end-members fo-fs with symmetric formalism interaction energy 4.0 kJ per site ($W_{fo,fa} = 8$ kJ)

- **Talc**

Ferric from: Cation Sum = 7 for 11 oxygens, $R_{\max}=0.1$

Ideal mixing on sites model of Holland & Powell 1998 is used. e.g. $a_{\text{ta}} = X_{\text{Mg,M1}} X_{\text{Mg,M2}}^2 X_{\text{Si,T1}}^2$

- **Garnet**

Ferric from: Cation Sum = 8 for 12 oxygens, $R_{\max}=0.99$

2 site mixing model for ideal mixing part e.g. $a_{\text{py}} = X_{\text{Mg,M2}}^3 X_{\text{Al,M1}}^2 \gamma_{\text{py}}$

Nonideality is approximated by renormalising to the set of end-members py-gr-alm-spss-andr with symmetric formalism interaction energies (kJ):

W	gr	alm	spss	andr
py	33	2.5	0	73
gr		0	0	0
alm			0	60
spss				60

- **Epidote**

Ferric from: $\text{Si} + \text{Al} + \text{Fe}^{3+} = 6$ for 12.5 oxygens, $R_{\max}=0.99$

2 site mixing and ordering model of Holland & Powell 1998, involving end-members clinozoisite (cz AlAl), epidote (ep AlFe) and ferric-epidote (fep FeFe). e.g.

$$a_{\text{cz}} = X_{\text{Ca,M2}} X_{\text{Al,M1}} X_{\text{Al,M3}} \gamma_{\text{cz}}$$

$$a_{\text{ep}} = X_{\text{Ca,M2}} X_{\text{Al,M1}} X_{\text{Fe}^{3+},\text{M3}} \gamma_{\text{ep}}$$

$$a_{\text{fep}} = X_{\text{Ca,M2}} X_{\text{Fe}^{3+},\text{M1}} X_{\text{Fe}^{3+},\text{M3}} \gamma_{\text{fep}}$$

Nonideality is approximated by renormalising to the set of end-members cz-ep-fep. The proportion of fep acts as an order parameter and is determined at the temperature selected in the program. The symmetric formalism interaction energies (kJ):

W	ep	fep
cz	0	15.40
ep		3

$\Delta H = -26.10$ kJ for the reaction $\text{cz} + \text{fep} = 2 \text{ep}$

- **Feldspar**

Ferric: all iron taken as ferric.

If $\text{Ca} < 0.05$, then **plagioclase feldspar** is assumed, with the ordered model of Holland & Powell 1992 (model 1)

If $\text{Ca} > 0.05$, then **alkali feldspar** is assumed. The subregular solution model of Waldbaum & Thompson 1969 is used. Tetrahedral mixing terms are ignored.

- **Scapolite**

Ferric: all iron is taken as ferrous.

Ideal mixing on large cations site, ignoring tetrahedral terms. e.g.

$$a_{\text{me}} = X_{\text{Ca,A}}^4$$

$$a_{\text{miz}} = 9.48 X_{\text{Ca,A}}^3 X_{\text{Na,A}}$$

- **Chloritoid**

Ferric from: Cation Sum = 4 for 6 oxygens. $R_{\max} = 0.2$

For the half formula size used, there is one M2 site (Fe, Mg, Mn) and half a M1 site (Al, Fe^{3+}) and so: $a_{\text{mctd}} = X_{\text{Mg,M2}} X_{\text{Al,M1}}^{0.5} \gamma_{\text{mctd}}$

Nonideality is approximated by renormalising to the set of end-members mctd-fctd-mnctd with symmetric formalism interaction energies (kJ)

W	fctd	mnctd
mctd	1.5	1.5
fctd		1.5

- **Amphibole**

Ferric from: The method of Holland & Blundy 1993.

The ideal mixing part follows mixing on sites, following Holland & Powell 1998 (which allows only half the configurational entropy contribution from tetrahedral sites). Thus

$$a_{\text{tr}} = X_{\square, A} X_{\text{Ca}, \text{M4}}^2 X_{\text{Mg}, \text{M13}}^3 X_{\text{Mg}, \text{M2}}^2 X_{\text{Si}, \text{T1}}^2 \gamma_{\text{tr}}$$

For *calcic amphiboles*, taken when $X_{\text{Ca}, \text{M4}} > 0.5$, nonideality is approximated by renormalising to the set of end-members tr-fact-ts-parg-gl-fits-kpa with symmetric formalism interaction energies (following Dale, Holland & Powell, 2000) (kJ)

W	fact	ts	parg	gl	fits	kpa
tr	11.4	20.8	29.3	35.3	88.3	12.0
fact		0	11.4	15.0	88.3	-37.8
ts			18.2	15.0	0.0	-23.8
parg				84.5	88.3	12.0
gl					88.3	50.8
fits						88.3

For *sodic amphiboles*, here taken when $X_{\text{Na}, \text{M4}} > 0.5$, nonideality is approximated by renormalising to the simple set of end-members gl-fgl-rieb with symmetric formalism interaction energies (kJ)

W	fgl	rieb
gl	10	10
fgl		0

For *Fe-Mg amphiboles*, taken when $X_{\text{Ca}, \text{M4}} < 0.3$ and $X_{\text{Na}, \text{M4}} < 0.3$, nonideality is approximated by renormalising to the simple set of end-members cum-grun with a symmetric formalism interaction energy $W_{\text{cum}, \text{gr}} = 17.5$ (kJ). This approximates the behaviour modelled in Holland & Powell (1996) in the metamorphic temperature range.

- **Chlorite**

Ferric from: Cation Sum = 10 for 14 oxygens. $R_{\text{max}} = 0.2$

Mixing is taken from Holland, Baker & Powell (1998), simplified for chlorites more aluminous than clinochlore (Al assumed ordered into the M4 site). e.g.

$$a_{\text{clin}} = 4X_{\text{Mg}, \text{M23}}^4 X_{\text{Mg}, \text{M1}} X_{\text{Al}, \text{M4}} X_{\text{Al}, \text{T2}} X_{\text{Si}, \text{T2}} \gamma_{\text{clin}}$$

Nonideality is approximated by renormalising to the set of end-members clin-daph-ames with symmetric formalism interaction energies (kJ)

W	daph	ames
clin	2.5	18
daph		20.5

- **White mica**

Ferric from: Tet + Oct cation sum = 6.05 for 11 oxygens. $R_{\text{max}} = 0.7$

Mixing is taken from Holland & Powell (1998) e.g.

$$a_{\text{mu}} = 4X_{\text{K}, A} X_{\square, \text{M1}} X_{\text{Al}, \text{M2}} X_{\text{Al}, \text{M3}} X_{\text{Al}, \text{T1}} X_{\text{Si}, \text{T1}} \gamma_{\text{mu}}$$

For *margarites*, here taken when $X_{\text{Ca}, A} > 0.5$, nonideality is approximated by a regular solution of Ca-Na- \square on the A site (i.e the small amount of K is ignored) with interaction energies (kJ)

W	Ca	\square
Na	14.5	14
Ca		14

For *paragonites*, here taken when $X_{\text{Na}, A} > 0.5$, nonideality is approximated as follows: for margarite activity the solid solution is treated as a ternary Ca-Na- \square as above; for muscovite and paragonite activities the solid solution is treated as a ternary K-Na- \square (ignoring the small Ca content) with a DQF increment to the muscovite free energy: (kJ)

W	Na	\square
K	22.8	14
Na		14

DQF (mu) = -3.28 kJ

For ***muscovite-phengites***, here taken when $X_{K,A} > 0.5$, nonideality is approximated by renormalising to the set of end-members mu-pa-cel-fcel with symmetric formalism interaction energies (kJ)

W	pa	cel	fcel
mu	12 + 0.4P	0	0
pa		14 + 0.2P	14 + 0.2P
cel			0

DQF (pa) = 1.42 + 0.4P kJ

- **Biotite**

Ferric from: Tet + Oct cation sum = 6.9 for 11 oxygens. $R_{\max} = 0.15$

Mixing is taken from the ordering model of Powell & Holland (1999) e.g.:

$$a_{\text{phl}} = 4X_{K,A}X_{\text{Mg},\text{M1}}X_{\text{Mg},\text{M3}}^2X_{\text{Al},\text{T1}}X_{\text{Si},\text{T1}}\gamma_{\text{phl}}$$

Nonideality is approximated by renormalising to the set of end-members phl-ann-east-obi with symmetric formalism interaction energies (kJ)

W	ann	east	obi
phl	9	10	3
ann		-1	6
east			10

$\Delta H = -32.3$ kJ for the reaction ann + phl = 2 obi

- **Cordierite**

Ferric from: Cation Sum = 11 for 18 oxygens, $R_{\max}=0.2$

Mixing on M sites only is used. e.g. $a_{\text{crd}} = X_{\text{Mg},\text{M}}^2\gamma_{\text{crd}}$

Nonideality is approximated by renormalising to the set of end-members crd-fcrd-mncrd with symmetric formalism interaction energies (kJ)

W	fcrd	mncrd
crd	1.5	1.5
fcrd		0

- **Staurolite**

Ferric from: all ferrous assumed

Ideal mixing on 4 M sites only is used, e.g. $a_{\text{fst}} = X_{\text{Fe},\text{M}}^4$

- **Spinel**

Ferric from: Cation Sum = 3 for 4 oxygens. Max Ratio = 0.9;

If an ***aluminous spinel*** (Al > 1.0) then a 3-site mixing model is used, e.g.

$$a_{\text{sp}} = X_{\text{Mg},\text{M}}^2X_{\text{Al},\text{T}}\gamma_{\text{sp}}$$

Nonideality is approximated by renormalising to the set of end-members sp-herc-mt with symmetric formalism interaction energies (kJ)

W	herc	mt
sp	2	41
herc		39

For ***magnetites*** (Al < 1.0) the model involves simple ideal mixing in inverse spinels:

$$a_{\text{mt}} = X_{\text{Fe}^{3+},\text{M}}^2X_{\text{Fe},\text{T}}$$

- **Sapphirine**

Ferric from: Cation Sum = 14 for 20 oxygens, $R_{\max}=0.7$

Ideal mixing on sites model of Holland & Powell 1998

- **Osumilite**

Ferric from: Cation Sum = 18 for 30 oxygens, $R_{\max}=0.4$

Ideal mixing on sites model of Holland & Powell 1998 e.g.:

$$a_{\text{osm1}} = X_{K,A}X_{\text{Mg},\text{M1}}^2X_{\text{Al},\text{T1}}^3X_{\text{Al},\text{T2}}^2$$

- **Carbonates**

Ferric from: all ferrous

For *dolomite-ankerites*, a 2-site model is used e.g. $a_{\text{dol}} = X_{\text{Ca,M2}}X_{\text{Mg,M1}}\gamma_{\text{dol}}$

Nonideality assumes $W_{\text{FeMg,M1}} = 3.0$ kJ

For *calcite-magnesite-siderite-rhodachrosite* disordered carbonates a simple 1-site model is used e.g. $a_{\text{cc}} = X_{\text{Ca,M}}\gamma_{\text{cc}}$

Nonideality is approximated by renormalising to the set of end-members cc-mag-sid-rhc with symmetric formalism interaction energies (kJ)

W	mag	sid	rhc
cc	22	18	0
mag		4	0
sid			0

- **Ilmenite-hematite**

Ferric from: Cation Sum = 2 for 3 oxygens.

Simple 2-site mixing in ordered ilm-hem is used.

$$a_{\text{ilm}} = X_{\text{Fe,M1}}X_{\text{Ti,M2}}$$

$$a_{\text{hem}} = X_{\text{Fe}^{3+},\text{M1}}X_{\text{Fe}^{3+},\text{M2}}$$