AX program - general

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 endmembers. 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 exactly 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 11 oxide names in the list at the top of the file. Data may be tab-, comma-, or space- delimited, and the file is termnated with an asterisk followed by a hard return.

   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
*
```

2. Run the program. Double click the AX icon.

3. Examining the output. 3 kinds of output file (assuming that your input file is named axeg.txt) are generated:

   1. AX output file - what you see on screen (as axeg_o.txt).

   2. A file suitable for editing and submission to THERMOCALC as input (as axeg_tcd.txt). AX enters quartz automatically, and H2O (if hydrous silicates are processed) and/or CO2 (if carbonates are used).

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

   3. A table file with analyses tabulated in columns of oxide weight percent above cation values in traditional manner (as axeg_tab.txt).

Some further notes on activities:

- A note 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 endmembers 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 endmembers in a paragonite. The uncertainties on wrong-limb endmembers 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).

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
stp	stilpnomelanes
pmp	pumpellyites
pre	prehnites

Mineral end-member activity models

Activities of mineral endmembers 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

HP90 p 100, HP98 p 315–318, HP2011 p 348-351

and Jennings & Holland (2015) *J. Pet.* **56**, 869–892.

- **Clinopyroxene**

  Ferric from: Cation Sum = 4 for 6 oxygens, R_{max}=0.95.

  M1–M2 mixing with $\frac{1}{4}$-entropy of mixing on T sites used. If Na < 0.4 or Na > 0.6 then disordered C2/c cpx is assumed with nonideal mixing. e.g. $a_{di} = X_{Ca,M2} X_{Mg,M1} X_{Si,T}^{\frac{1}{2}} \gamma_{di}$, $a_{cats} = 1.41421\, X_{Ca,M2} X_{Al,M1} X_{Si,T}^{\frac{1}{4}} X_{Al,T}^{\frac{1}{4}} \gamma_{cats}$

  Cpx is recast into the following end-members: di ($CaMgSi_2O_6$), hed ($CaFeSi_2O_6$), cats ($CaAlSiAlO_6$), jd ($NaAlSi_2O_6$), acm ($NaFe^{3+}Si_2O_6$), oen ($MgMgSi_2O_6$), tip ($CaTiAl_2O_6$), crp ($CaCrSiAlSiO_6$), mnp ($MnMgSi_2O_6$) and caes ($Ca_{\frac{1}{2}}\square_{\frac{1}{2}}AlSi_2O_6$). Non-ideality is accounted for by symmetric formalism among end-members di-hed-cats-jd-acm-oen with interaction energies (kJ):

W	hed	cats	jd	acm	oen
di	3	12	26	24	29
hed		12	24	24	34
cats			6	6	45
jd				0	40
acm					40

  The remaining interactions are set to zero.

  Otherwise, (if $0.4 >$ Na < 0.6), P2/n ***omphacite*** is assumed. Ideal coupled mixing is assumed as an approximation (jd-di-hed-acm).

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

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

if Al,M1 > Na,M2 then $a_{\rm jd} = X_{\rm Na,M2}$ else $a_{\rm jd} = X_{\rm Al,M1}$, $a_{\rm acm} = X_{\rm Fe^{3+},M1}$

- **Orthopyroxene**

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

  M1–M2 mixing with $\frac{1}{4}$-entropy of mixing on T sites used.

  e.g. $a_{\rm en} = X_{\rm Mg,M2} X_{\rm Mg,M1} X_{\rm Si,T}^{\frac{1}{2}} \gamma_{\rm en}$, $a_{\rm mgts} = 1.41421\, X_{\rm Mg,M2} X_{\rm Al,M1} X_{\rm Si,T}^{\frac{1}{4}} X_{\rm Al,T}^{\frac{1}{4}} \gamma_{\rm mgts}$

  Opx is recast into the following end-members: en ($MgMgSi_2O_6$), fs ($FeFeSi_2O_6$), mgts ($MgAlSiAlO_6$), odi ($CaMgSi_2O_6$), mes ($MgFe^{3+}SAlO_6$), cren ($MgCrSiAlO_6$), tip ($CaTiAl_2O_6$), ojd ($NaAlSi_2O_6$), mnp ($MnMgSi_2O_6$) and mges ($Mg_{\frac{1}{2}}\square_{\frac{1}{2}}AlSi_2O_6$). Non-ideality is accounted for by symmetric formalism among end-members en-fs-mgts-odi-mes-cren with interaction energies (kJ):

W	fs	mgts	odi	mes	cren
en	2	12	32	8	8
fs		7	24	10	10
mgts			75	2	2
odi				30	30
mes					2

  The remaining interactions are set to zero.

- **Olivine**

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

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

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

- **Talc**

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

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

- **Garnet**

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

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

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

W	gr	alm	spss	andr	uvar
py	30	4.1	9.2	87	51
gr		4.5	0.3	2.0	2.0
alm			1.9	61	25
spss				32	32
andr					2.0

- **Epidote**

  Ferric from: Al + Fe^{3+} + Cr + Ti $\leq$ 3 for 12.5 oxygens. Fe^{2+} is made when the sum above is greater than 3.0; otherwise all Fe is Fe^{3+}. R_{max} = 0.99

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

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

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

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

  Nonideality is approximated by renormalising to the set of endmembers 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

  ΔH = -26.10 kJ for the reaction cz + fep = 2 ep

- **Feldspar**

  Ferric: all iron taken as ferric.

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

If 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.

  $a_{\mathrm{me}} = X^4_{\mathrm{Ca,A}}$

  $a_{\mathrm{miz}} = 9.48 X^3_{\mathrm{Ca,A}} X_{\mathrm{Na,A}}$

- **Chloritoid**

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

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

  Nonideality is approximated by renormalising to the set of endmembers 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

  $a_{\mathrm{tr}} = X_{\Box,A} X^2_{\mathrm{Ca,M4}} X^3_{\mathrm{Mg,M13}} X^2_{\mathrm{Mg,M2}} X^2_{\mathrm{Si,T1}} \gamma_{\mathrm{tr}}$

  For ***calcic amphiboles***, taken when $X_{\mathrm{Ca,M4}} > 0.5$, nonideality is approximated by renormalising to the set of endmembers tr-fact-ts-parg-gl-fits-kpa with symmetric formalism interaction energies (following Dale, et al., 2005) (kJ)

W	fact	ts	parg	gl	fits	kpa
tr	10	20	33	65	20	0
fact		12.5	-1.9	39.3	12.5	0
ts			-38.5	25	0	0
parg				50	-38.5	0
gl					45.9	0
fits						0

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

W	fgl	rieb
gl	10	10
fgl		0

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

- **Chlorite**

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

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

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

  Nonideality is approximated by renormalising to the set of endmembers 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. $\mathrm{R_{max}} = 0.7$

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

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

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

W	Ca	□
Na	14.5	14
Ca		14

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

W	Na	□
K	22.8	14
Na		14

DQF (mu) = -3.28 kJ

For ***muscovite-phengites***, here taken when $X_{\mathrm{K,A}} > 0.5$, nonideality is approximated by renormalising to the set of endmembers 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. $\mathrm{R_{max}} = 0.15$

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

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

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

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

ΔH = -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. $a_{\rm crd} = X^2_{\rm Mg,M}\gamma_{\rm crd}$

  Nonideality is approximated by renormalising to the set of endmembers crd-frcd-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. $a_{\rm fst} = X^4_{\rm Fe,M}$

- **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.

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

  Nonideality is approximated by renormalising to the set of endmembers 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:

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

- **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.:

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

- **Carbonates**

  Ferric from: all ferrous

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

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

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

  Nonideality is approximated by renormalising to the set of endmembers 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.

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

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

- **stilpnomelane**

  Ferric from: cation sum (less K,Na,Ca) = 15 for 24.25 oxygens. $R_{\mathrm{max}} = 0.75$

  Regular solution for 5-site mixing, W = 4 kJ per site

  $a_{\mathrm{mstp}} = X^5_{\mathrm{Mg,M1}} \gamma_{\mathrm{mstp}}$

  $a_{\mathrm{fstp}} = X^5_{\mathrm{Fe,M1}} \gamma_{\mathrm{fstp}}$

- **pumpellyite**

  Ferric from: Al + Cr + Ti + Fe3 = 5 for 24.5 oxygens. $R_{\mathrm{max}} = 0.9$

  Ideal mixing on sites:

  $a_{\mathrm{mapm}} = X_{\mathrm{Mg,M3}} X_{\mathrm{Al,M2}} X^4_{\mathrm{Al,M1}}$

  $a_{\mathrm{fapm}} = X_{\mathrm{Fe,M3}} X_{\mathrm{Al,M2}} X^4_{\mathrm{Al,M1}}$

$a_{\mathrm{julg}} = X_{\mathrm{Fe,M3}} X_{\mathrm{Fe^{3+},M2}} X^4_{\mathrm{Fe^{3+},M1}}$

- **prehnite**

  Ferric from: Cation Sum = 7 for 11 oxygens. $R_{max} = 0.99$

  Ideal one site Fe^{3+}–Al mixing

  $a_{\mathrm{pre}} = 1 - X_{\mathrm{Fe^{3+}}}$

  $a_{\mathrm{fpre}} = X_{\mathrm{Fe^{3+}}}$