AX62 program - general

AX62 is an activity-composition calculation program for rock-forming minerals. It has been updated (from AX) for use with the 2011 dataset of Holland & Powell. 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 AX62 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 AX62 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 AX62 itself. The data file consists of a line of exactly 11 oxides (these and ONLY these 11 are accepted currently by AX62, although they can be placed in any order on the first line of the data file – see the example below).
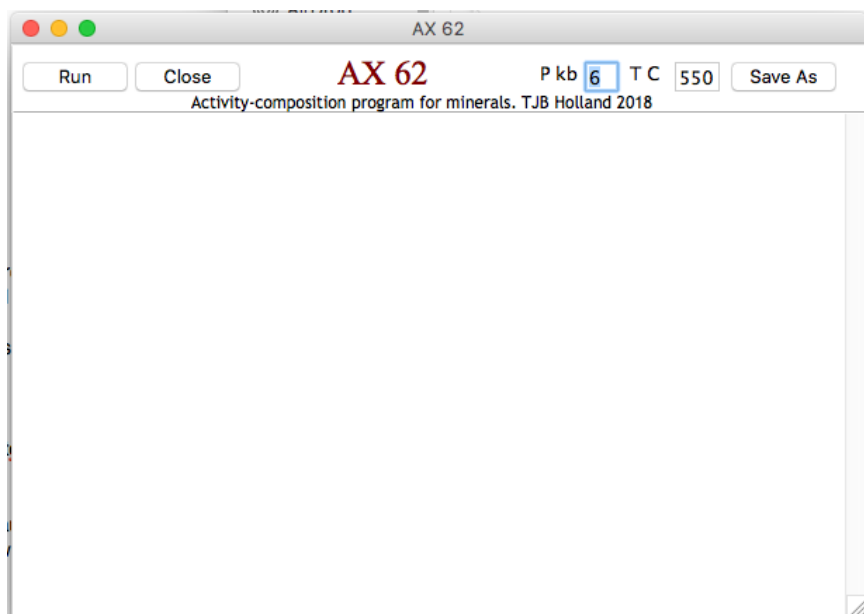
   Each analysis is entered as a pair of lines, the first of which gives the mineral code (g, cpx etc) and a brief title. (A list of the mineral codes can be found from the help menu in the program, and is also given below). The second line gives the oxide wt% values in the SAME order as the 11 oxide names in the list at the top of the file. Data may be tab-, comma-, or space- delimited, and the file is terminated 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 on AX62, set an approximate pressure and temperature in the boxes at the top, and then hit Run button. The AX62 output file will appear in the scrollable text area. Hit the Close button and examine output files.

3. Output files. 3 kinds of output file (assuming that your input file, from the examples folder, is named axeg.txt) are generated:

1. AX62 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). AX62 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 low-fraction 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. AX62 does not print activities which are far smaller than their uncertainties.

- 'Wrong' end of a solvus:

  Avoid low-fraction endmembers on the 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 AX62 activities in such formulations, particularly in sensitive cation exchange equilibria (e.g. garnet–clinopyroxene thermometers), or solvus thermometers (e.g. two pyroxene thermometers).

Mineral code abbreviations

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 AX62 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)

Refs: HP90: Holland & Powell 1990, J. Met. Geol. 8, 89–124. HP98: Holland & Powell 1998, J. Met. Geol.16, 309–343. Also: Jennings & Holland (2015) J. Pet. 56, 869–892, Holland et al. (2018) J. Pet. 59, 889–900.

AX62 has been **updated** (from AX62) to comply with activity models in the most recent papers including: Diener et al. (2007) J. Met. Geol. 25, 631–656, and White et al. (2014) J. Met. Geol. 32, 261–286.

- **Clinopyroxene**

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

  1. If Na < 0.4 or Na > 0.6 then disordered C2/c cpx is assumed. M1–M2 mixing with half-entropy of mixing on T sites used. 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 ($MgMgSi_2O_6$). Minor components tip ($CaTiAl_2O_6$), crp ($CaCrSiAlSiO_6$), mnp ($MnMgSi_2O_6$) and caes ($Ca_{\frac{1}{2}}\square_{\frac{1}{2}}AlSi_2O_6$) are assumed to mix ideally. The mixing model approximates that of Holland et al. (2018) J. Pet. 59, 889–900.

  2. 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 $a_{di} = X_{Ca,M2}$ 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

- **Orthopyroxene**

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

  M1–M2 mixing with half-entropy of mixing on T sites used, and 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 ($MgCrSiAlO_6$); minor end-members tip ($CaTiAl_2O_6$), ojd ($NaAlSi_2O_6$), mnp ($MnMgSi_2O_6$) and mges ($Mg_{\frac{1}{2}}\square_{\frac{1}{2}}AlSi_2O_6$) assumed to mix ideally. The mixing model approximates that of Holland et al. (2018) J. Pet. 59, 889–900.

- **Olivine**

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

Mixing on sites used (M1–M2) and nonideality is approximated by renormalising to the set of endmembers fo–fs with symmetric formalism interaction energy 4.0 kJ per site ($W_{\text{fo,fa}} = 8$ kJ)

- **Talc**

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

  Nonideal mixing model of Holland & Powell 2011 is used.

- **Garnet**

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

  2 site mixing model for ideal mixing part is coupled with the mixing model in White et al. (2014).

- **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+}. $R_{\text{max}} = 0.99$

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

- **Feldspar**

  Ferric: all iron taken as ferric.

  The simple ternary (Ca–Na–K) mixing model from Holland & Powell (2003, CMP 145, 492-501) is used.

- **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. $R_{\text{max}} = 0.2$

  Mixing model from White et al. (2014)

- **Amphibole**

  Ferric from: The method of Holland & Blundy 1993.

  Mixing model from Diener et al. (2007)

  1. xCaM4 < 0.3 and xNaM4 < 0.3

     An Fe–Mg amphibole assumed, involving renormalising to end-members cumm and grun.
  2. CaM4 > 0.5

     Calcic or Na-Ca amphibole assumed. End-members: tr, fact, ts, parg, gl, fits, kpa
  3. NaM4 > 0.4

     A sodic amphibole assumed and is renormalised to the end-members gl–fgl–rieb–tr

- **Chlorite**

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

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

- **White mica**

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

  Mixing is taken from Coggon & Holland (2002, JMG 20, 683–696) and updated in

- **Biotite**

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

  Mixing model from White et al. (2014)

- **Cordierite**

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

  Mixing model from White et al. (2014) for hydrated cordierites at P and T

- **Staurolite**

  Ferric from: 5% of Fe as Fe^{3+} assumed

  Mixing model from White et al. (2014)

- **Spinel**

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

  3-site random mixing model of Bryndzia & Wood (1990) as used in Jennings & Holland (2015). End-members: sp-herc-pcr-mt.

- **Sapphirine**

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

  Mixing model of Wheller & Powell 2014 (JMG 32, 287–299)

- **Osumilite**

  Ferric from: Cation Sum = 18 for 30 oxygens, R_{max}=0.4
  mixing: [K,Na] (Al,Mg,Fe, Fe3) Si10 [Al,Si]2 O30
  Mixing on sites model for Holland & Powell 2011 dataset

  $a_{osma} = X_{K,A} X_{Mg,M1}^2 X_{Al,T1} X_{Al,T2}^2$
  $a_{osmm} = 4 X_{K,A} X_{Mg,M1}^2 X_{Mg,T1} X_{Al,T2} X_{Si,T2}$
  $a_{osfa} = X_{K,A} X_{Fe,M1}^2 X_{Al,T1} X_{Al,T2}^2$
  with non-ideality given by a regular solution (kJ):

W	osmm	osfa
osma	10	4
osmm		14

- **Carbonates**

  Ferric from: all ferrous

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

  Nonideality assumes $W_{FeMg,M1} = 4.0$ kJ

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

  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	23	18	15
mag		4	18
sid			8

- **Ilmenite-hematite**

  Ferric from: Cation Sum = 2 for 3 oxygens.

  Simple 2-site asymmetric mixing in ordered ilm-hem is used.
  (Fe, Fe^{3+}, Mg,Mn) (Ti,Fe^{3+})O_3
  e.g. $a_{\text{ilm}} = X_{\text{Fe,M1}} X_{\text{Ti,M2}}$ etc

  Non-ideal W's below, with asymmetry parameters $\alpha = 1$ for all
  except hem with $\alpha = 1.3$

W	hem	pnt	gei
ilm	31	2	4
hem		30	33
pnt			4

  These parameters to match approximately-known solvi in Chinner
  (1960, JPet 1, 178), Lindsley (1973, BGSA 84, 657) and Itsaya &
  Otsuki (1978, J Japan Ass Min Pet Econ Geol 73, 359).

- **stilpnomelane**

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

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

  $a_{\text{mstp}} = X_{\text{Mg,M1}}^5 \gamma_{\text{mstp}}$

  $a_{\text{fstp}} = X_{\text{Fe,M1}}^5 \gamma_{\text{fstp}}$

- **pumpellyite**

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

  Ideal mixing on sites:

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

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

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

- **prehnite**

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

  Ideal one site Fe^{3+}–Al mixing

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

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