Calculate garnet mineral chemistry from electron microprobe data

how the FeO is recalculated as Fe^{2+} and Fe^{3+}

Enami, Masaki *et* al., (1995) A mechanism for Na incorporation in garnet: An example from garnet in orthogneiss from the Su-Lu terrane, eastern China.

Recap: Garnet Properties

$X^{2+}_3\ Y^{3+}_2\ Si_3\ O_{12}$
X stands for Ca, Fe^{2+}, Mn, and Mg
Y stands for Al, Cr, and Fe^{3+}

Crystal system: Cubic
Cleavage: none
Fracture: conchoidal to uneven
Hardness: 6.5-7.5

Members of the Garnet group are:
Pyrope - $Mg_3Al_2Si_3O_{12}$
Almandine - $Fe^{2+}_3Al_2Si_3O_{12}$
Spessartine - $Mn_3Al_2Si_3O_{12}$
Grossular - $Ca_3Al_2Si_3O_{12}$
Andradite - $Ca_3Fe^{3+}_2Si_3O_{12}$
Uvarovite - $Ca_3Cr_2Si_3O_{12}$

Electron Microprobe Data

TABLE 2. Representative analyses of Na-Y garnet in the Su-Lu orthogneisses and Y-rich pegmatite

	Orthogneiss							Pegmatite*
	91TF03a			91TF03b	91TFX01	91H01	91M02	GSJ-M18062
	(Al-gar)	(Fe^{3+}-gar)	(Fe^{3+}-gar)	(Fe^{3+}-gar)	(Al-gar)	(Al-gar)	(Al-gar)	(Al-gar)
Weight percent oxides								
SiO_2	36.1	34.1	33.8	35.0	36.9	36.8	38.2	34.7
TiO_2	0.26	0.44	0.33	0.45	0.14	0.18	0.10	0.00
Al_2O_3	20.1	4.91	4.76	2.47	20.6	17.9	20.6	19.9
Y_2O_3	1.19	1.49	2.10	0.89	0.76	1.02	0.33	3.15
Er_2O_3	—	0.14	—	—	—	—	—	—
Yb_2O_3	0.24	0.21	0.43	0.16	0.06	0.24	0.07	0.56
FeO**	14.6	22.6	22.2	25.1	11.1	20.7	13.3	15.8
MnO	21.7	14.1	13.3	6.18	28.0	9.85	6.21	24.5
MgO	0.03	0.26	0.24	0.04	0.03	0.11	0.14	0.00
ZnO	—	0.02	0.10	0.04	0.07	0.00	0.02	0.01
CaO	3.48	18.1	18.5	26.8	3.61	12.0	20.6	1.64
Na_2O	0.372	0.093	0.094	0.021	0.244	0.236	0.079	0.093
Total	98.1	96.5	95.9	97.2	101.5	99.0	99.6	100.4
Cations = 8								
Si	3.010	2.967	2.966	2.984	2.978	3.011	3.009	2.895
Ti	0.016	0.029	0.022	0.029	0.008	0.011	0.006	0.000
Al	1.975	0.504	0.492	0.248	1.959	1.726	1.912	1.956
Y	0.053	0.069	0.098	0.040	0.033	0.045	0.014	0.140
Er	—	0.004	—	—	—	—	—	—
Yb	0.006	0.006	0.012	0.004	0.002	0.006	0.002	0.014
Fe^{3+}†	0.000	1.441	1.438	1.685	0.073	0.217	0.056	0.116
Fe^{2+}†	1.018	0.203	0.190	0.104	0.676	1.199	0.821	0.986
Mn	1.533	1.039	0.988	0.446	1.914	0.682	0.414	1.731
Mg	0.004	0.034	0.032	0.005	0.003	0.013	0.017	0.000
Zn		0.001	0.006	0.003	0.004	0.000	0.001	0.001
Ca	0.311	1.688	1.739	2.448	0.312	1.052	1.738	0.146
Na	0.060	0.016	0.016	0.003	0.038	0.037	0.012	0.015

Note: abbreviations are: Al-gar = aluminian garnet; Fe^{3+}-gar = ferrian garnet. K is below detection limits.

* Yttrian garnet in Y-rich pegmatite described by Iimori (1938) and Wakita et al. (1969).

** Total Fe as FeO.

† Calculated values (see text).

My Calculations

91TF03a	weight %	MW	moles of oxide	moles oxygen	moles cation	Normalized cations 8 cations	Normalized oxygens 8 cations		
SiO2	34.1	60.08	0.56757656	1.13515313	0.56757656	**2.967437963**	5.934875926		
TiO2	0.44	79.9	0.00550688	0.01101377	0.00550688	**0.02879142**	0.057582841		
Al2O3	4.91	101.96	0.04815614	0.14446842	0.09631228	**0.503545657**	0.755318485		
Y2O3	1.49	225.809	0.0065985	0.01979549	0.01319699	**0.068997318**	0.103495977		
Er2O3	0.14	382.517	0.000366	0.00109799	0.00073199	**0.003827053**	0.00574058		
Yb2O3	0.21	394.077	0.00053289	0.00159867	0.00106578	**0.005572183**	0.008358275		
FeO	22.6	71.85	0.31454419	0.31454419	0.31454419	**~~1.644518866~~**	1.644518866	Fe2+	1.441289
MnO	14.1	70.94	0.19875952	0.19875952	0.19875952	**1.039166462**	1.039166462	Fe3+	0.20323
MgO	0.26	40.3	0.00645161	0.00645161	0.00645161	**0.033730711**	0.033730711		
ZnO	0.02	81.389	0.00024573	0.00024573	0.00024573	**0.001284758**	0.001284758		
CaO	18.1	56.08	0.32275321	0.32275321	0.32275321	**1.687437761**	1.687437761		
Na2O	0.093	61.98	0.00150048	0.00150048	0.00300097	**0.015689842**	0.007844921		
Total	96.5			**2.157382**	**1.530146**	5.670139367	**11.27935556**	0.720644	

O- Factor	
8 cation	5.22826
12 oxygen	5.562297

Normalized cations 12 oxygens	Normalized oxygens 12 oxygens		
3.154835058	6.309670116		
0.030609631	0.061219263		
0.53534514	0.80301771		
0.073354577	0.110031866		
0.004068736	0.006103104		
0.005924073	0.00888611		
~~1.74837211~~	1.74837211	Fe2+	0.016681
1.10479101	1.10479101	Fe3+	1.731692
0.035860844	0.035860844		
0.001365892	0.001365892		
1.794001382	1.794001382		
0.016680673	0.008340337		
8.505209127	**11.99165974**	0.00834	

Step 1 & 2

1. Divide the weight percentage of each oxide by the molecular weight of that oxide = moles of oxide
2. Multiply the resulting moles of oxide by the number of oxygens in the formula = moles of oxygen

91TF03a	weight %	molecular weight	moles of oxide	moles oxygen
SiO2	34.1	60.08	0.567576565	1.13515313
TiO2	0.44	79.9	0.005506884	0.01101377
Al2O3	4.91	101.96	0.04815614	0.14446842
Y2O3	1.49	225.809	0.006598497	0.01979549
Er2O3	0.14	382.517	0.000365997	0.00109799
Yb2O3	0.21	394.077	0.000532891	0.00159867
FeO	22.6	71.85	0.314544189	0.31454419
MnO	14.1	70.94	0.198759515	0.19875952
MgO	0.26	40.3	0.006451613	0.00645161
ZnO	0.02	81.389	0.000245733	0.00024573
CaO	18.1	56.08	0.32275321	0.32275321
Na2O	0.093	61.98	0.001500484	0.00150048
Total	96.5			**2.1573822**

Step 3 & 4

3. Multiply the resulting moles of oxide by the number of cations in the formula unit = moles of cations.
4. Normalization constant: obtained by dividing the number of oxygens (or cations) in the structural formula by the sum of the moles of oxygen ions (or sum of moles of cation).

91TF03a	weight %	molecular weight	moles of oxide	moles oxygen	moles cation
SiO2	34.1	60.08	0.567576565	1.13515313	0.56757656
TiO2	0.44	79.9	0.005506884	0.01101377	0.00550688
Al2O3	4.91	101.96	0.04815614	0.14446842	0.09631228
Y2O3	1.49	225.809	0.006598497	0.01979549	0.01319699
Er2O3	0.14	382.517	0.000365997	0.00109799	0.00073199
Yb2O3	0.21	394.077	0.000532891	0.00159867	0.00106578
FeO	22.6	71.85	0.314544189	0.31454419	0.31454419
MnO	14.1	70.94	0.198759515	0.19875952	0.19875952
MgO	0.26	40.3	0.006451613	0.00645161	0.00645161
ZnO	0.02	81.389	0.000245733	0.00024573	0.00024573
CaO	18.1	56.08	0.32275321	0.32275321	0.32275321
Na2O	0.093	61.98	0.001500484	0.00150048	0.00300097
Total	96.5			**2.1573822**	**1.5301457**

Oxygen Factor	
8 cations	5.22826
12 oxygen	5.5623

Step 5 & 6

5. Multiply the moles of oxygen by the normalization constant (5.56=12 oxygen/total moles of oxygen, 2.157).
6. Multiply the moles of cation by the normalization constant (5.22 = 8 cations/total moles of cations, 1.53).

Normalized cations	Normalized oxygens
8 cations	8 cations
2.967437963	5.934875926
0.02879142	0.057582841
0.503545657	0.755318485
0.068997318	0.103495977
0.003827053	0.00574058
0.005572183	0.008358275
1.644518866	1.644518866
1.039166462	1.039166462
0.033730711	0.033730711
0.001284758	0.001284758
1.687437761	1.687437761
0.015689842	0.007844921
5.670139367	11.27935556

Normalized cations	Normalized oxygens
12 oxygens	12 oxygens
3.154835058	6.309670116
0.030609631	0.061219263
0.53534514	0.80301771
0.073354577	0.110031866
0.004068736	0.006103104
0.005924073	0.00888611
1.74837211	1.74837211
1.10479101	1.10479101
0.035860844	0.035860844
0.001365892	0.001365892
1.794001382	1.794001382
0.016680673	0.008340337
8.505209127	11.99165974

Step 7

Left hand column: notice that the oxygens do not total to 12 as would be expected from the garnet formula.

Some oxygen is missing, indicating that some of the Fe is in the 3+ state. We can estimate how much by converting Fe^{2+} into Fe^{3+}:

$2FeO + O = Fe_2O_3$.

Normalized oxygens 8 cations
5.934875926
0.057582841
0.755318485
0.103495977
0.00574058
0.008358275
1.644518866
1.039166462
0.033730711
0.001284758
1.687437761
0.007844921
11.27935556

Normalized oxygens 12 oxygens
6.309670116
0.061219263
0.80301771
0.110031866
0.006103104
0.00888611
1.74837211
1.10479101
0.035860844
0.001365892
1.794001382
0.008340337
11.99165974

Step 7

Notice that for every Fe^{3+} cations we convert into $2Fe^{2+}$, we will get an additional oxygen. We need to add 0.7206444 (8-cations) or 0.008340257 (12-oxygen) to bring the total to 12.

Normalized oxygens 8 cations		
5.934875926		
0.057582841		
0.755318485		
0.103495977		
0.00574058		
0.008358275		
1.644518866	Fe2+	1.441289
1.039166462	Fe3+	0.20323
0.033730711		
0.001284758		
1.687437761		
0.007844921		
11.27935556	0.7206444	

Normalized oxygens 12 oxygens		
6.309670116		
0.061219263		
0.80301771		
0.110031866		
0.006103104		
0.00888611		
1.74837211	Fe2+	0.016681
1.10479101	Fe3+	1.731692
0.035860844		
0.001365892		
1.794001382		
0.008340337		
11.99165974	0.0083403	

Step 7

- For 8 cations:

Fe^{2+} = 2 x 0.7206444 = 1.441289

Fe^{3+} = 1.1644518866 - 1.441289 = 0.20323

- For 12 oxygens:

Fe^{2+} = 2 x 0.008340257 = 0.016680515

Fe^{3+} = 1.74837211 - 0.016680515 = 1.731691595

BUT a re-calculation of Fe(II), Fe(III) ***here*** is meaningless

Normalized cations	Normalized oxygens		
8 cations	8 cations		
2.967437963	5.934875926		
0.02879142	0.057582841		
0.503545657	0.755318485		
0.068997318	0.103495977		
0.003827053	0.00574058		
0.005572183	0.008358275		
1.644518866	1.644518866	Fe2+	1.441289
1.039166462	1.039166462	Fe3+	0.20323
0.033730711	0.033730711		
0.001284758	0.001284758		
1.687437761	1.687437761		
0.015689842	0.007844921		
5.670139367	**11.27935556**	0.720644	

Normalized cations	Normalized oxygens		
12 oxygens	12 oxygens		
3.154835058	6.309670116		
0.030609631	0.061219263		
0.53534514	0.80301771		
0.073354577	0.110031866		
0.004068736	0.006103104		
0.005924073	0.00888611		
1.74837211	1.74837211	Fe2+	0.016681
1.10479101	1.10479101	Fe3+	1.731692
0.035860844	0.035860844		
0.001365892	0.001365892		
1.794001382	1.794001382		
0.016680673	0.008340337		
8.505209127	**11.99165974**	0.00834	

Results

91TF03a	Normalized cations
	8 cations
SiO2	2.967437963
TiO2	0.02879142
Al2O3	0.503545657
Y2O3	0.068997318
Er2O3	0.003827053
Yb2O3	0.005572183
FeO	1.644518866
MnO	1.039166462
MgO	0.033730711
ZnO	0.001284758
CaO	1.687437761
Na2O	0.015689842

Fe2+	1.441289
Fe3+	0.20323

91TF03a	Normalized cations
	12 oxygens
SiO2	3.154835058
TiO2	0.030609631
Al2O3	0.53534514
Y2O3	0.073354577
Er2O3	0.004068736
Yb2O3	0.005924073
FeO	1.74837211
MnO	1.10479101
MgO	0.035860844
ZnO	0.001365892
CaO	1.794001382
Na2O	0.016680673

Note that if we don't adjust the Fe^{2+}/Fe^{3+} ratio, we get an unrealistic excess of Si (> 3 moles per formula unit).

91TF03a
(Fe^{3+}-gar)

Si	2.967
Ti	0.029
Al	0.504
Y	0.069
Er	0.004
Yb	0.006
Fe^{3+}†	1.441
Fe^{2+}†	0.203
Mn	1.039
Mg	0.034
Zn	0.001
Ca	1.688
Na	0.016