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Multiple-reaction geobarometry for olivine-bearing igneous rocks

American Mineralogist

Supplementary Material 3

Thermodynamic dataset and activity-composition models refined for the calculations of average P

Molar thermodynamic properties (units: kJ, K, kbar) of the end-members. Data are from the Holland and Powell (2011) dataset, its updated version 6.3, generated 29 March, 2016.

Phase	End-member	$\Delta_f H$	$\sigma(\Delta_f H)$	S	V	C_P				ακ			
						a	b	c	d	α_0	κ_0	κ'_0	κ''_0
Olivine	Fayalite (fa)	-1477.54	0.68	151.00	4.631	0.2011	1.7330	-1960.6	-0.9009	2.82	1256.0	4.68	-0.0037
	Forsterite (fo)	-2172.46	0.57	95.10	4.366	0.2333	0.1494	-603.8	-1.8697	2.85	1285.0	3.84	-0.0030
Pyroxene	Acmite (acm)	-2583.28	2.43	170.60	6.459	0.3071	1.6758	-1685.5	-2.1258	2.11	1060.0	4.08	-0.0038
	Ca-Tschermak (cats)	-3310.10	0.80	135.00	6.356	0.3476	-0.6974	-1781.6	-2.7575	2.08	1192.0	5.19	-0.0044
	Diopside (di)	-3201.79	0.62	142.90	6.619	0.3145	0.0041	-2745.9	-2.0201	2.73	1192.0	5.19	-0.0044
	Jadeite (jd)	-3025.39	1.67	133.50	6.040	0.3194	0.3616	-1173.9	-2.4695	2.10	1281.0	3.81	-0.0030
	Enstatite (en)	-3090.00	0.66	132.50	6.262	0.3562	-0.2990	-596.9	-3.1853	2.27	1059.0	8.65	-0.0082
	Ferrosilite (fs)	-2388.55	0.81	189.90	6.592	0.3987	-0.6579	1290.1	-4.0580	3.26	1010.0	4.08	-0.0040
Plagioclase	H-albite (abh)	-3921.34	1.68	224.30	10.105	0.4520	-1.3364	-1275.9	-3.9536	2.41	541.0	5.91	-0.0109
	Anorthite (an)	-4232.72	0.79	200.50	10.079	0.3705	1.0010	-4339.1	-1.9606	1.41	860.0	4.09	-0.0048
	Sanidine (san)	-3966.76	2.80	214.30	10.871	0.4488	-1.0075	-1007.3	-3.9731	1.66	583.0	4.02	-0.0069
Spinel	Hercynite (herc)	-1949.53	0.85	113.90	4.075	0.1849	1.4170	-3674.8	-0.4040	2.06	1922.0	4.04	-0.0021
	Magnetite (mt)	-1114.21	0.95	146.90	4.452	0.2625	-0.7205	-1926.2	-1.6557	3.71	1857.0	4.05	-0.0022
	Picrochromite (picr)	-1764.35	3.28	118.30	4.356	0.1961	0.5398	-3126.0	-0.6169	2.60	1922.0	4.04	-0.0021
	Spinel (sp)	-2300.34	0.84	80.63	3.978	0.2005	0.6252	-2996.4	-0.8884	1.93	1922.0	4.04	-0.0021
	Ulvospinel (usp)	-1494.00	1.01	171.00	4.682	0.1295	4.8696	-3739.0	0.6902	3.86	1470.00	4.00	-0.0027

$\Delta_f H$ is the regressed enthalpy of formation from the elements (kJ/mol); $\sigma(\Delta_f H)$ is the 1σ on the enthalpy of formation derived from the regression; S is the entropy (J/mol/K); V the volume (kJ/kbar); all properties at 1 bar and 298 K; a, b, c and d are the coefficients in the heat capacity polynomial $C_p = a + bT + cT^{-2} + dT^{-1/2}$; α_0 is the thermal expansion; κ_0, κ_0', κ_0'' are the bulk modulus (at 298 K, 1bar) and its first and second pressure derivatives.

Clinopyroxene model (after the "augite" model of Green et al. 2016)

End-members and cation distribution:

	M1				M2				T	
	Mg	Fe^{2+}	Al	Fe^{3+}	Mg	Fe^{2+}	Ca	Na	Si	Al
di	1	0	0	0	0	0	1	0	2	0
cenh	1	0	0	0	1	0	0	0	2	0
cfs	0	1	0	0	0	1	0	0	2	0
jd	0	0	1	0	0	0	0	1	2	0
acm	0	0	0	1	0	0	0	1	2	0
cats	0	0	1	0	0	0	1	0	1	1
cfm	1	0	0	0	0	1	0	0	2	0

Site fractions (calculated from the input compositional variable, see Supplementary Material 2):

$$x_{Mg}^{M1} = 1 - j - x - y + jx + xy + \frac{Q_{fm}}{2}(1 - j - z)$$

$$x_{Fe^{2+}}^{M1} = x - jx - xy - \frac{Q_{fm}}{2}(1 - j - z)$$

$$x_{Al}^{M1} = j + y - f$$

$$x_{Mg}^{M2} = 1 - j - x - z - \frac{Q_{fm}}{2}(1 - j - z) + jx + xz$$

$$x_{Fe^{2+}}^{M2} = x + \frac{Q_{fm}}{2}(1 - j - z) - jx - xz$$

$$x_{Ca}^{M2} = z$$

$$x_{Na}^{M2} = j$$

$$x_{Si}^{T} = 1 - \frac{y}{2}$$

$$x_{Al}^{T} = \frac{y}{2}$$

Ideal activities:

$$a_{di}^{ideal} = x_{Mg}^{M1} x_{Ca}^{M2} (x_{Si}^{T})^{\frac{1}{2}}$$

$$a_{cenh}^{ideal} = x_{Mg}^{M1} x_{Mg}^{M2} (x_{Si}^{T})^{\frac{1}{2}}$$

$$a_{cfs}^{ideal} = x_{Fe^{2+}}^{M1} x_{Fe^{2+}}^{M2} (x_{Si}^{T})^{\frac{1}{2}}$$

$$a_{jd}^{ideal} = x_{Al}^{M1} x_{Na}^{M2} (x_{Si}^{T})^{\frac{1}{2}}$$

$$a_{acm}^{ideal} = x_{Fe^{3+}}^{M1} x_{Na}^{M2} (x_{Si}^{T})^{\frac{1}{2}}$$

$$a_{cats}^{ideal} = \sqrt{2}\, x_{Al}^{M1} x_{Ca}^{M2} (x_{Si}^{T} x_{Al}^{T})^{\frac{1}{4}}$$

$$a_{cfm}^{ideal} = x_{Mg}^{M1} x_{Fe^{2+}}^{M2} (x_{Si}^{T})^{\frac{1}{2}}$$

End-member proportions:

$$p_{di} = z - y$$

$$p_{cenh} = 1 - j - x - z - \frac{Q_{fm}}{2}(1 - j - z) + jx + xz$$

$$p_{cfs} = x - \frac{Q_{fm}}{2}(1 - j - z) - jx - xy$$

$p_{jd} = j - f$
$p_{acm} = f$
$p_{cats} = y$
$p_{cfm} = Q_{fm}(1 - j - z) + xy - xz$

Interaction energies (P in kbar):

$W_{ij}(kJ)$	cenh	cfs	jd	acm	cats	fmc
di	29.8-0.03P	23.0-0.03P	26.0	21.0	8.0-0.01P	21.5-0.03P
cenh		7.0	35.0	30.0	31-0.29P	4.0
cfs			25.0	21.0	29.0	4.0
jd				5.0	20.0	30.0
acm					25.0	34.0
cats						30.0

Asymmetry parameters for mixing (Holland & Powell, 2003) are: $\propto_{cenh}=\propto_{cfs}=\propto_{cfm}= 1$, $\propto_{di}=\propto_{jd}=\propto_{acm}= 1.2$ and $\propto_{cats}= 1.9$.

Gibbs energies (kJ) of the end-members not in the Holland & Powell (2011) dataset:

$G_{cenh}(P,T) = G_{en}(P,T) + 1.75 - 0.001T + 0.024P$
$G_{cfs}(P,T) = G_{fs}(P,T) + 4.20 - 0.00375T + 0.0675P$
$G_{cfm}(P,T) = \frac{1}{2}\left[G_{cenh}(P,T) + G_{cfs}(P,T)\right] - 3.52 - 0.00238T + 0.0458P$

Olivine model (after Hackler and Wood 1989)

End-members and cation distribution:

	M1		M2		T
	Mg	Fe^{2+}	Mg	Fe^{2+}	Si
fo	1	0	1	0	1
fa	0	1	0	1	1
olfm	1	0	0	1	1

Site fractions:

$x_{Mg}^{M1} = 1 - \left(x - \frac{1}{2}Q_{fm}\right)$
$x_{Fe}^{M1} = x - \frac{1}{2}Q_{fm}$
$x_{Mg}^{M2} = 1 - \left(x + \frac{1}{2}Q_{fm}\right)$
$x_{Fe}^{M2} = x + \frac{1}{2}Q_{fm}$

Ideal activities:

$a_{fo}^{ideal} = x_{Mg}^{M1}x_{Mg}^{M2}$
$a_{fa}^{ideal} = x_{Fe}^{M1}x_{Fe}^{M2}$
$a_{olfm}^{ideal} = x_{Mg}^{M1}x_{Fe}^{M2}$

End-member proportions:

$$p_{fo} = 1 - \left(x + \frac{1}{2}Q_{fm}\right)$$
$$p_{fa} = x - \frac{1}{2}Q_{fm}$$
$$p_{olfm} = Q_{fm}$$

Interaction energies:

$W_{ij}(kJ)$	fa	olfm
fo	8.0	4.0
fa		4.0

Gibbs energies (kJ) of the end-members not in the Holland & Powell (2011) dataset:

$$G_{olfm}(P,T) = \frac{1}{2}\left[G_{fa}(P,T) + G_{fo}(P,T)\right] - 8.0 - 0.003T + 0.02P$$

Spinel model (after Bryndzia and Wood 1990, and T.J.B. Holland, pers. Comm.)

End-members and cation distribution:

	M					
	Fe^{2+}	Fe^{3+}	Al	Mg	Cr	Ti
sp	0	0	2	1	0	0
herc	1	0	2	0	0	0
mt	1	2	0	0	0	0
picr	0	0	0	1	2	0
usp	2	0	0	0	0	1

Site fractions:

$$x^M_{Fe^{2+}} = \tfrac{1}{3}x + x\tfrac{1}{3}ti$$
$$x^M_{Fe^{3+}} = \frac{2}{3}f$$
$$x^M_{Al} = \frac{2}{3} - \frac{2}{3}(cr + f + ti)$$
$$x^M_{Mg} = \frac{1}{3} - \frac{1}{3}(x - ti) - x\frac{1}{3}ti$$
$$x^M_{Cr} = \frac{2}{3}cr$$
$$x^M_{Ti} = \frac{1}{3}ti$$

Ideal activities:

$$a^{ideal}_{sp} = \frac{27}{4}(x^M_{Al})^2 x^M_{Mg}$$

$$a_{herc}^{ideal} = \frac{27}{4}(x_{Al}^{M})^2 x_{Fe^{2+}}^{M}$$

$$a_{mt}^{ideal} = \frac{27}{4}\left(x_{Fe^{3+}}^{M}\right)^2 x_{Fe^{2+}}^{M}$$

$$a_{picr}^{ideal} = \frac{27}{4}(x_{Cr}^{M})^2 x_{Mg}^{M}$$

$$a_{usp}^{ideal} = \frac{27}{4}\left(x_{Fe^{2+}}^{M}\right)^2 x_{Ti}^{M}$$

End-member proportions:

$p_{sp} = 1 - (cr + x - ti) - xti$
$p_{herc} = x - f - 2ti + xti$
$p_{mt} = f$
$p_{picr} = cr$
$p_{usp} = ti$

Interaction energies:

$W_{ij}(kJ)$	herc	mt	picr	usp
sp	4.0	56.0	23.0	50.0
herc		32.0	16.0	30.0
mt			36.0	40.0
picr				50.0

Modifications to end-members Gibbs energies (kJ):

$G_{sp}^{mod}(P,T) = G_{sp}(P,T) + 5.0$
$G_{herc}^{mod}(P,T) = G_{herc}(P,T) + 5.0$

Plagioclase model (Holland and Powell 2003)

End-members and cation distribution:

	A		
	Ca	Na	K
an	1	0	0
abh	0	1	0
san	0	0	1

Site fractions:

$x_{Ca}^{A} = ca$
$x_{Na}^{A} = 1 - ca - k$
$x_{K}^{A} = k$

Ideal activities:

$a_{an}^{ideal} = x_{Ca}^{A}$
$a_{abh}^{ideal} = x_{Na}^{A}$
$a_{san}^{ideal} = x_{K}^{A}$

End-member proportions:

$p_{an} = ca$
$p_{abh} = 1 - k - ca$
$p_{san} = k$

Interaction energies:

$W_{ij}(kJ)$	abh	san
an	15.0	40.0
abh		25.1-0.0108T+0.338P

Asymmetry parameters for mixing (Holland & Powell, 2003) are: $\propto_{an}=\propto_{san}= 1$ and $\propto_{abh}= 0.643$.

Modifications to end-members Gibbs energies (kJ):

$G_{abh}^{mod}(P,T) = G_{abh}(P,T) + 0.57 - 0.00412T$