An improved and extended internally consistent thermodynamic dataset for phases of petrological interest, involving a new equation of state for solids

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ABSTRACT
The thermodynamic properties of 254 end-members, including 210 mineral end-members, 18 silicate liquid end-members and 26 aqueous fluid species are presented in a revised and updated internally consistent thermodynamic data set. The *PVT* properties of the data set phases are now based on a modified Tait equation of state (EOS) for the solids and the Pitzer & Sterner (1995) equation for gaseous components. Thermal expansion and compressibility are linked within the modified Tait EOS (TEOS) by a thermal pressure formulation using an Einstein temperature to model the temperature dependence of both the thermal expansion and bulk modulus in a consistent way. The new EOS has led to improved fitting of the phase equilibrium experiments. Many new end-members have been added, including several deep mantle phases and, for the first time, sulphur-bearing minerals. Silicate liquid end-members are in good agreement with both phase equilibrium experiments and measured heat of melting. The new dataset considerably enhances the capabilities for thermodynamic calculation on rocks, melts and aqueous fluids under crustal to deep mantle conditions. Implementations are already available in THERMOCALC to take advantage of the new data set and its methodologies, as illustrated by example calculations on sapphirine-bearing equilibria, sulphur-bearing equilibria and calculations to 300 kbar and 2000 °C to extend to lower mantle conditions.

Key words: equation of state; internally consistent dataset; thermodynamic data.

INTRODUCTION

The need for thermodynamic data of sufficient quality to make reliable calculations on rocks continues to grow, particularly to capitalize on new methods of application of phase equilibria that involve increasingly complex solid and fluid solutions, as well as on new advances in software.

The basic philosophy from our earlier summary (Holland & Powell, 1998; hereafter referred to as HP98) is maintained. The thermodynamic data extraction involves using weighted least squares on the different types of data (calorimetric, phase equilibria, natural mineral partitioning) to determine enthalpies of formation of the end-members of the phases. Entropies, volumes, heat capacities, thermal expansions and compressibilities are not derived by regression, but are taken as known in this process. Where they are not known experimentally, they are estimated

as outlined in our earlier papers. The new regression involves determination of the enthalpies of 254 end-members, of which 69 are new to the data set, with an overall fit in which σ_{fit} is 1.09 (σ_{fit} being a goodness-of-fit parameter, identical to $\sqrt{MSWD}$ in geochronology that relates directly to the chi-squared test).

Major methodological changes from HP98 are embodied in this new data set, within the basic philosophy outlined above. They are documented below, along with minor ones that have arisen since HP98, some of which are incorporated in the currently used data set, tc-ds55.txt, from November 2003, but have not been documented properly before.

A list of the chemical compositions of the end-members considered in this study may be found in Table 1. The end-members are listed under the headings orthosilicates and ring silicates (garnet, olivine, etc.), chain silicates (pyroxene and pyroxenoid, amphibole, etc.), sheet silicates (mica, chlorite, etc.), framework silicates, oxides and hydroxides, carbonates, elements, high-pressure phases, gas species, melt species and aqueous species. The new data set itself is given in Table 2. Table 3 lists the calorimetric data used in the dataset generation. Appendix 1 gives the

Group	Abbreviation	End-member	Formula
Garnets & olivines	alm	almandine	$Fe_3Al_2Si_3O_{12}$
	andr	andradite	$Ca_3Fe_2Si_3O_{12}$
	gr	grossular	$Ca_3Al_2Si_3O_{12}$
	knor •	knorringite	$Mg_3Cr_2Si_3O_{12}$
	maj •	majorite	$Mg_4Si_4O_{12}$
	py	pyrope	$Mg_3Al_2Si_3O_{12}$
	spss	spessartine	$Mn_3Al_2Si_3O_{12}$
	chum	clinohumite	$Mg_9Si_4O_{16}(OH)_2$
	fa	fayalite	Fe_2SiO_4
	fo	forsterite	Mg_2SiO_4
	lrn	larnite	Ca_2SiO_4
	mont	monticellite	$CaMgSiO_4$
	teph	tephroite	Mn_2SiO_4
Aluminosilicates	and	andalusite	Al_2SiO_5
	ky	kyanite	Al_2SiO_5
	sill	sillimanite	Al_2SiO_5
	amul •	Al-mullite	$Al_{2.5}Si_{0.5}O_{4.75}$
	smul •	Si-mullite	Al_2SiO_5
	fctd	Fe-chloritoid	$FeAl_2SiO_5(OH)_2$
	mctd	Mg-chloritoid	$MgAl_2SiO_5(OH)_2$
	mnctd	Mn-chloritoid	$MnAl_2SiO_5(OH)_2$
	fst	Fe-staurolite	$Fe_4Al_{18}Si_{7.5}O_{44}(OH)_4$
	mst	Mg-staurolite	$Mg_4Al_{18}Si_{7.5}O_{44}(OH)_4$
	mnst	Mn-staurolite	$Mn_4Al_{18}Si_{7.5}O_{44}(OH)_4$
	tpz	hydroxy-topaz	$Al_2SiO_4(OH)_2$
Other orthosilicates	ak	akermanite	$Ca_2MgSi_2O_7$
	geh	gehlenite	$Ca_2Al_2SiO_7$
	jgd •	julgoldite (FeFe)	$Ca_4Fe_6Si_6O_{21}(OH)_7$
	merw	merwinite	$Ca_3MgSi_2O_8$
	mpm	pumpellyite (MgAl)	$Ca_4MgAl_5Si_6O_{21}(OH)_7$
	fpm	pumpellyite (FeAl)	$Ca_4FeAl_5Si_6O_{21}(OH)_7$
	rnk	rankinite	$Ca_3Si_2O_7$
	sph	sphene	$CaTiSiO_5$
	spu	spurrite	$Ca_5Si_2CO_{11}$
	ty	tilleyite	$Ca_5Si_2C_2O_{13}$
	zrc	zircon	$ZrSiO_4$
Sorosilicates	cz	clinozoisite	$Ca_2Al_3Si_3O_{12}(OH)$
	ep	epidote(ordered)	$Ca_2FeAl_2Si_3O_{12}(OH)$
	fep	Fe-epidote	$Ca_2Fe_2AlSi_3O_{12}(OH)$
	law	lawsonite	$CaAl_2Si_2O_6(OH)_4$
	pmt •	piemontite (ordered)	$Ca_2MnAl_2Si_3O_{12}(OH)$
	zo	zoisite	$Ca_2Al_3Si_3O_{12}(OH)$
	vsv	vesuvianite	$Ca_{19}Mg_2Al_{11}Si_{18}O_{69}(OH)_9$
Cyclosilicates	crd	cordierite	$Mg_2Al_4Si_5O_{18}$
	hcrd	hydrous-cordierite	$Mg_2Al_4Si_5O_{17}(OH)_2$
	fcrd	Fe-cordierite	$Fe_2Al_4Si_5O_{18}$
	mncrd	Mn-cordierite	$Mn_2Al_4Si_5O_{18}$
	osm1	osumilite (1)	$KMg_2Al_5Si_{10}O_{30}$
	osm2	osumilite (2)	$KMg_3Al_3Si_{11}O_{30}$
	fosm	Fe-osumilite	$KFe_2Al_5Si_{10}O_{30}$
High-P phases	apv •	Al-perovskite	$AlAlO_3$
	cpv •	Ca-perovskite	$CaSiO_3$
	cstn •	CaSi-titanite	$CaSi_2O_5$
	fak •	Fe-akimotoite	$FeSiO_3$
	fpv •	Fe-perovskite	$FeSiO_3$
	frw •	Fe-ringwoodite	Fe_2SiO_4
	fwd •	Fe-wadsleyite	Fe_2SiO_4
	mak •	akimotoite	$MgSiO_3$
	mpv •	Mg-perovskite	$MgSiO_3$
	mrw •	Mg-ringwoodite	Mg_2SiO_4
	mwd •	Mg-wadsleyite	Mg_2SiO_4
	phA	phaseA	$Mg_7Si_2O_8(OH)_6$
Pyroxenes & pyroxenoids	acm	acmite	$NaFeSi_2O_6$
	caes •	Ca-eskola pyroxene	$Ca_{0.5}AlSi_2O_6$
	cats	Ca-tschermaks pyroxe	$CaAl_2SiO_6$
	cen •	clino enstatite	$Mg_2Si_2O_6$
	di	diopside	$CaMgSi_2O_6$
	en	enstatite	$Mg_2Si_2O_6$
	fs	ferrosilite	$Fe_2Si_2O_6$
	hed	hedenbergite	$CaFeSi_2O_6$
	hen •	Hi-P clinoenstatite	$Mg_2Si_2O_6$
	jd	jadeite	$NaAlSi_2O_6$
	kos •	kosmochlor	$NaCrSi_2O_6$
	mgts	Mg-tschermaks pyroxe	$MgAl_2SiO_6$
	pren •	protoenstatite	$Mg_2Si_2O_6$
	pswo	pseudowollastonite	$CaSiO_3$
	pxmn	pyroxmangite	$MnSiO_3$

Table 1. The formulae and abbreviations of the end-members of the phases in the internally consistent data set. A bullet beside an abbreviated name indicates that it is a new end-member in the dataset.

Table 1. (*Continued*)

Group	Abbreviation	End-member	Formula
	rhod	rhodonite	$MnSiO_3$
	wal •	walstromite	$CaSiO_3$
	wo	wollastonite	$CaSiO_3$
Amphibole	anth	anthophyllite	$Mg_7Si_8O_{22}(OH)_2$
	cumm	cummingtonite	$Mg_7Si_8O_{22}(OH)_2$
	fact	ferroactinolite	$Ca_2Fe_5Si_8O_{22}(OH)_2$
	fanth	Fe-anthophyllite	$Fe_7Si_8O_{22}(OH)_2$
	fgl	ferroglaucophane	$Na_2Fe_3Al_2Si_8O_{22}(OH)_2$
	gl	glaucophane	$Na_2Mg_3Al_2Si_8O_{22}(OH)_2$
	grun	grunerite	$Fe_7Si_8O_{22}(OH)_2$
	parg	pargasite	$NaCa_2Mg_4Al_3Si_6O_{22}(OH)_2$
	rieb	riebeckite	$Na_2Fe_5Si_8O_{22}(OH)_2$
	tr	tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
	ts	tschermakite	$Ca_2Mg_3Al_4Si_6O_{22}(OH)_2$
Other chain silicates	deer	deerite	$Fe_{18}Si_{12}O_{40}(OH)_{10}$
	fcar	ferrocarpholite	$FeAl_2Si_2O_6(OH)_4$
	fspr	Fe-sapphirine (221)	$Fe_4Al_8Si_2O_{20}$
	mcar	magnesiocarpholite	$MgAl_2Si_2O_6(OH)_4$
	spr4	sapphirine (221)	$Mg_4Al_8Si_2O_{20}$
	spr5	sapphirine (351)	$Mg_3Al_{10}SiO_{20}$
Micas	ann	annite	$KFe_3AlSi_3O_{10}(OH)_2$
	cel	celadonite	$KMgAlSi_4O_{10}(OH)_2$
	east	eastonite	$KMg_2Al_3Si_2O_{10}(OH)_2$
	fcel	ferroceladonite	$KFeAlSi_4O_{10}(OH)_2$
	ma	margarite	$CaAl_4Si_2O_{10}(OH)_2$
	mnbi	Mn-biotite	$KMn_3AlSi_3O_{10}(OH)_2$
	mu	muscovite	$KAl_3Si_3O_{10}(OH)_2$
	naph	sodaphlogopite	$NaMg_3AlSi_3O_{10}(OH)_2$
	pa	paragonite	$NaAl_3Si_3O_{10}(OH)_2$
	phl	phlogopite	$KMg_3AlSi_3O_{10}(OH)_2$
Chlorites	afchl	Al-free chlorite	$Mg_6Si_4O_{10}(OH)_8$
	ames	amesite (14A)	$Mg_4Al_4Si_2O_{10}(OH)_8$
	clin	clinochlore (ordered)	$Mg_5Al_2Si_3O_{10}(OH)_8$
	daph	daphnite	$Fe_5Al_2Si_3O_{10}(OH)_8$
	fsud	ferrosudoite	$Fe_2Al_4Si_3O_{10}(OH)_8$
	mnchl	Mn-chlorite	$Mn_5Al_2Si_3O_{10}(OH)_8$
	sud	sudoite	$Mg_2Al_4Si_3O_{10}(OH)_8$
Other sheet silicates	atg	antigorite	$Mg_{48}Si_{34}O_{85}(OH)_{62}$
	chr	chrysotile	$Mg_3Si_2O_5(OH)_4$
	fpre •	ferri-prehnite	$Ca_2FeAlSi_3O_{10}(OH)_2$
	fstp •	ferrostilpnomelane	$K_{0.5}Fe_5Al_2Si_8O_{18}(OH)_{12.5}$
	fta	ferrotalc	$Fe_3Si_4O_{10}(OH)_2$
	glt •	greenalite	$Fe_3Si_2O_5(OH)_4$
	kao	kaolinite	$Al_2Si_2O_5(OH)_4$
	liz •	lizardite	$Mg_3Si_2O_5(OH)_4$
	minm •	Mg-minnesotaite	$Mg_3Si_4O_{10}(OH)_2$
	minn •	minnesotaite	$Fe_3Si_4O_{10}(OH)_2$
	mstp •	Mg-stilpnomelane	$K_{0.5}Mg_5Al_2Si_8O_{18}(OH)_{12.5}$
	pre	prehnite	$Ca_2Al_2Si_3O_{10}(OH)_2$
	prl	pyrophyllite	$Al_2Si_4O_{10}(OH)_2$
	ta	talc	$Mg_3Si_4O_{10}(OH)_2$
	tap •	prl-talc	$Al_2Si_4O_{10}(OH)_2$
	tats	tschermak-talc	$Mg_2Al_2Si_3O_{10}(OH)_2$
Feldspars & feldspathoid	abh	albite (high)	$NaAlSi_3O_8$
	albite	ab	$NaAlSi_3O_8$
	an	anorthite	$CaAl_2Si_2O_8$
	anl	analcite	$NaAlSi_2O_5(OH)_2$
	cg •	carnegieite (low)	$NaAlSiO_4$
	cgh •	carnegieite (high)	$NaAlSiO_4$
	kcm •	K-cymrite	$KAlSi_3O_7(OH)_2$
	kls	kalsilite	$KAlSiO_4$
	lc	leucite	$KAlSi_2O_6$
	mic	microcline	$KAlSi_3O_8$
	ne	nepheline	$NaAlSiO_4$
	san	sanidine	$KAlSi_3O_8$
Silica minerals	coe	coesite	SiO_2
	crst	cristobalite (high)	SiO_2
	q	quartz	SiO_2
	stv	stishovite	SiO_2
	trd	tridymite (high)	SiO_2
Other framework silicates	heu	heulandite	$CaAl_2Si_7O_{12}(OH)_{12}$
	hol •	hollandite	$KAlSi_3O_8$
	lmt	laumontite	$CaAl_2Si_4O_8(OH)_8$
	me	meionite	$Ca_4Al_6Si_6CO_{27}$
	sdl •	sodalite	$Na_8Al_6Si_6O_{24}Cl_2$
	stlb	stilbite	$CaAl_2Si_7O_{11}(OH)_{14}$
	wa •	Si-wadeite	$K_2Si_4O_9$
	wrk	wairakite	$CaAl_2Si_4O_{io}(OH)_4$

Table 1. (*Continued*)

Group	Abbreviation	End-member	Formula
Oxides	bdy	baddeleyite	ZrO_2
	bix •	bixbyite	Mn_2O_3
	cor	corundum	Al_2O_3
	cup •	cuprite	Cu_2O
	esk •	eskolaite	Cr_2O_3
	fper •	ferropericlase	FeO
	geik	geikielite	$MgTiO_3$
	hem	hematite	Fe_2O_3
	herc	hercynite	$FeAl_2O_4$
	ilm	ilmenite	$FeTiO_3$
	lime	lime	CaO
	mang	manganosite	MnO
	mcor •	MgSi-corundum	$MgSiO_3$
	mft	magnesioferrite	$MgFe_2O_4$
	mt	magnetite	$Fe3O_4$
	NiO	nickel oxide	NiO
	per	periclase	MgO
	picr •	picrochromite	$MgCr_2O_4$
	pnt	pyrophanite	$MnTiO_3$
	ru	rutile	TiO_2
	sp	spinel	$MgAl_2O_4$
	ten •	tenorite	CuO
	usp	ulvospinel	Fe_2TiO_4
Hydroxides	br	brucite	$Mg(OH)_2$
	dsp	diaspore	$AlO(OH)$
	gth	goethite	$FeO (OH)$
Carbonates	ank	ankerite	$CaFe(CO_3)_2$
	arag	aragonite	$CaCO_3$
	cc	calcite	$CaCO_3$
	dol	dolomite	$CaMg(CO_3)_2$
	mag	magnesite	$MgCO_3$
	rhc	rhodochrosite	$MnCO_3$
	sid	siderite	$FeCO_3$
Halides & sulphides	any •	anhydrite	$CaSO_4$
	hlt •	halite	$NaCl$
	lot •	low troilite	FeS
	pyr •	pyrite	FeS_2
	syv •	sylvite	KCl
	tro •	troilite	FeS
	trot •	pyrrhotite	FeS
	trov •	pyrrhotite	$Fe_{0.875}S$
Elements	Cu •	copper	Cu
	diam	diamond	C
	gph	graphite	C
	iron	iron	Fe
	Ni	nickel	Ni
	S •	sulphur	S
Gas species	H2O	water	H_2O
	CO2	carbon dioxide	CO_2
	CO	carbon monoxide	CO
	CH4	methane	CH_4
	O2	oxygen	O_2
	H2	hydrogen	H_2
	S2 •	sulphur gas	S_2
	H2S •	Hydrogen sulphide	H_2S
Melt species	abL	albite liquid	$NaAlSi_3O_8$
	anL	anorthite liquid	$CaAl_2Si_2O_8$
	corL •	corundum liquid	Al_2O_3
	diL	diopside liquid	$CaMgSi_2O_6$
	enL	enstatite liquid	$Mg_2Si_2O_6$
	faL	fayalite liquid	Fe_2SiO_4
	foL	forsterite liquid	Mg_2SiO_4
	h2oL	H2O liquid	H_2O
	hltL •	halite liquid)	$NaCl$
	kspL	K-feldspar liquid	$KAlSi_3O_8$
	lcL •	leucite liquid	$KAlSi_2O_6$
	limL •	CaO liquid	CaO
	neL •	nepheline liquid	$NaAlSiO_4$
	perL •	MgO liquid	MgO
	qL	quartz liquid	SiO_2
	silL	sillimanite liquid	Al_2SiO_5
	syvL •	sylvite (liquid)	KCl
	woL •	wollastonite liquid	$CaSiO_3$

Table 1. (*Continued*)

Group	Abbreviation	End-member	Formula
Aqueous species	H^+	hydrogen ion	$H+$
	Cl^-	chloride ion	Cl^-
	OH^-	hydroxyl ion	HO^-
	Na^+	sodium ion	Na^+
	K^+	potassium ion	K^+
	Ca^{++}	calcium ion	Ca^{2+}
	Mg^{++}	magnesium ion	Mg_2^{2+}
	Fe^{++}	ferrous ion	Fe^{2+}
	Al^{+++}	aluminium ion	Al^{3+}
	CO_3^-	carbonate ion	CO_3^{2-}
	$AlOH_3$	aluminium hydroxide	$Al(OH)_3$
	$AlOH_4^-$	aluminium hydroxide	$AlH_4O_4^-$
	KOH	potassium hydroxide	$K(OH)$
	HCl	hydrogen chloride	HCl
	KCl	potassium chloride	KCl
	$NaCl$	sodium chloride	$NaCl$
	$CaCl_2$	calcium chloride	$CaCl_2$
	$CaCl^+$	calcium chloride	$CaCl^+$
	$MgCl_2$	magnesium chloride	$MgCl_2$
	$MgCl^+$	magnesium chloride	$MgCl^+$
	$FeCl_2$	ferrous chloride	$FeCl_2$
	aqSi	silica (aq)	SiO_2
	HS^- •	sulphide (aq)	HS^-
	HSO_3^- •	sulphite (aq)	HSO_3^-
	SO_4^{2-} •	sulphate (aq)	SO_4^{2-}
	HSO_4^- •	sulphate2 (aq)	HSO_4^-

data sources for the thermodynamic properties, and Appendix 2 is a summary table of the experimental studies used in the data set regression. Appendix 3 provides information on minor changes since the publication of HP98. The table of all the experimentally determined mineral equilibrium brackets used in the least squares analysis and the calculated fit to them is presented in Table S1 as well as at http://www.esc.cam.ac.uk/people/academic-staff/tim-holland and http://www.metamorph.geo.uni-mainz.de/thermocalc/. This is in the form of full computer output from the data extraction program LSQDS. Table S2 contains the activity–composition relations that were used in the generation of the data set.

CHANGES TO METHODOLOGY

The principal differences in methodology from HP98 are outlined before the details of the new data set are presented and discussed.

Equation of state (EOS) for solids

The EOS for solid phases in HP98 involved a thermal expansion expression at 1 bar pressure, with an independent Murnaghan EOS to take the ambient pressure molar volumes to high pressures. To link the expansion and compression terms, a simple linear temperature dependence for the bulk modulus was used. This is now replaced with a more general EOS, and the expansion and compression terms are now linked.

Freund & Ingalls (1989) investigated nine separate EOS to determine which might be most suitable for high pressure work in solids. Their aim was to find a suitable EOS with only two or three adjustable parameters which best fit compression data to very high pressures. The modified Tait equation of Huang & Chow (1974) was one of the best of the equations investigated, in terms of fits to the compression data, and it is adopted here. We then augment this EOS for high temperature use by adding a thermal pressure term, as outlined below, thus integrating the expansion and compression contributions to Gibbs energy. Below, this modified Tait EOS, augmented with a thermal pressure term, is referred to as TEOS.

The 298K (ambient) temperature TEOS, expressed as a three-parameter equation in volume at $T = T_0$ (where $T_0 = 298.15K$) is:

$$\frac{V}{V_0} = 1 - a(1 - (1 + bP)^{-c}) \qquad (1)$$

and, in terms of pressure may be rearranged as:

$$P = \frac{1}{b}\left(\left[\frac{(V/V_0) + a - 1}{a}\right]^{-1/c} - 1\right) \qquad (2)$$

The relationship of the parameters to the bulk modulus and its derivatives at zero pressure is (Freund & Ingalls, 1989):

$$a = \frac{1 + \kappa_0'}{1 + \kappa_0' + \kappa_0\kappa_0''},$$
$$b = \frac{\kappa_0'}{\kappa_0} - \frac{\kappa_0''}{1 + \kappa_0'}, \qquad (3)$$
$$c = \frac{1 + \kappa_0' + \kappa_0\kappa_0''}{\kappa_0'^2 + \kappa_0' - \kappa_0\kappa_0''},$$

where κ_0 is the bulk modulus at ambient conditions,

Table 2a. Molar thermodynamic properties (units: kJ, K, kbar) of the end-members whose formulae can be found in Table 1.

Group	End-member	$\Delta_f H$	$\sigma(\Delta_f H)$	S	V	C_P a	b	c	d	$\alpha\kappa$ α_0	κ_0	κ_0'	κ_0''	ℓ
Garnet and olivine	Almandine (alm)	−5260.65	1.31	342.00	11.525	0.6773	0	−3772.7	−5.0440	2.12	1900.0	2.98	−0.0016	
	Andradite (andr)	−5769.08	1.56	316.40	13.204	0.6386	0	−4955.1	−3.9892	2.86	1588.0	5.68	−0.0036	
	grossular (gr)	−6642.95	1.46	255.00	12.535	0.6260	0	−5779.2	−4.0029	2.20	1720.0	5.53	−0.0032	
	Knorringite (knor)	−5687.75	3.88	317.00	11.738	0.6130	0.3606	−4178.0	−3.7294	2.37	1743.0	4.05	−0.0023	
	Majorite (maj)	−6050.33	9.62	255.20	11.457	0.7136	−0.0997	−1158.2	−6.6223	1.83	1600.0	4.56	−0.0028	
	Pyrope (py)	−6282.13	1.06	269.50	11.313	0.6335	0	−5196.1	−4.3152	2.37	1743.0	4.05	−0.0023	
	Spessartine (spss)	−5693.65	3.14	335.30	11.792	0.6469	0	−4525.8	−4.4528	2.27	1740.0	6.68	−0.0038	
	Clinohumite (chum)	−9609.82	2.49	443.00	19.785	1.0700	−1.6533	−7899.6	−7.3739	2.91	1194.0	4.79	−0.0040	
	Fayalite (fa)	−1477.74	0.68	151.00	4.631	0.2011	1.7330	−1960.6	−0.9009	2.82	1256.0	4.68	−0.0037	
	Forsterite (fo)	−2172.57	0.57	95.10	4.366	0.2333	0.1494	−603.8	−1.8697	2.85	1285.0	3.84	−0.0030	
	Larnite (lrn)	−2307.04	0.90	127.60	5.160	0.2475	−0.3206	0	−2.0519	2.90	985.0	4.07	−0.0041	1
	Monticellite (mont)	−2251.31	0.52	109.50	5.148	0.2507	−1.0433	−797.2	−1.9961	2.87	1134.0	3.87	−0.0034	
	Tephroite (teph)	−1733.95	1.05	155.90	4.899	0.2196	0	−1292.7	−1.3083	2.86	1256.0	4.68	−0.0037	
Aluminosilicates	Andalusite (and)	−2588.72	0.68	92.70	5.153	0.2773	−0.6588	−1914.1	−2.2656	1.81	1442.0	6.89	−0.0048	
	Kyanite (ky)	−2593.02	0.67	83.50	4.414	0.2794	−0.7124	−2055.6	−2.2894	1.92	1601.0	4.05	−0.0025	
	Sillimanite (sill)	−2585.85	0.68	95.40	4.986	0.2802	−0.6900	−1375.7	−2.3994	1.12	1640.0	5.06	−0.0031	2
	Mullite (amul)	−2485.51	0.91	113.00	5.083	0.2448	0.0968	−2533.3	−1.6416	1.36	1740.0	4.00	−0.0023	
	Mullite (smul)	−2569.28	0.69	101.50	4.987	0.2802	−0.6900	−1375.7	−2.3994	1.36	1740.0	4.00	−0.0023	
	Chloritoid (fctd)	−3208.31	0.80	167.00	6.980	0.4161	−0.3477	−2835.9	−3.3603	2.80	1456.0	4.06	−0.0028	
	Chloritoid (mctd)	−3549.31	0.75	146.00	6.875	0.4174	−0.3771	−2920.6	−3.4178	2.63	1456.0	4.06	−0.0028	
	Chloritoid (mnctd)	−3336.20	1.68	166.00	7.175	0.4644	−1.2654	−1147.2	−4.3410	2.60	1456.0	4.06	−0.0028	
	Staurolite (fst)	−23 755.04	6.34	1010.00	44.880	2.8800	−5.6595	−10642.0	−25.3730	1.83	1800.0	4.76	−0.0026	
	Staurolite (mnst)	−24 246.42	8.60	1034.00	45.460	2.8733	−8.9064	−12688.0	−24.7490	2.09	1800.0	4.76	−0.0026	
	Staurolite (mst)	−25 124.32	6.28	910.00	44.260	2.8205	−5.9366	−13774.0	−24.1260	1.81	1684.0	4.05	−0.0024	
	Topaz (tpz)	−2900.76	0.96	100.50	5.339	0.3877	−0.7120	−857.2	−3.7442	1.57	1315.0	4.06	−0.0031	
Other orthosilicates	Akermanite (ak)	−3865.63	0.94	212.50	9.254	0.3854	0.3209	−247.5	−2.8899	2.57	1420.0	4.06	−0.0029	
	Gehlenite (geh)	−3992.26	1.33	198.50	9.024	0.4057	−0.7099	−1188.3	−3.1744	2.23	1080.0	4.08	−0.0038	2
	Julgoldite (jgd)	−11 809.63	8.50	830.00	31.080	1.7954	−3.7986	−4455.7	−14.8880	2.49	1615.0	4.05	−0.0025	
	Merwinite (merw)	−4545.87	1.36	253.10	9.847	0.4175	0.8117	−2923.0	−2.3203	3.19	1200.0	4.07	−0.0034	
	Pumpellyite (fpm)	−14 033.82	2.63	657.00	29.680	1.7372	−2.4582	−5161.1	−14.9630	2.49	1615.0	4.05	−0.0025	
	Pumpellyite (mpm)	−14 386.75	2.41	629.00	29.550	1.7208	−2.4928	−5998.7	−14.6203	2.47	1615.0	4.05	−0.0025	
	Rankinite (rnk)	−3943.92	1.36	210.00	9.651	0.3723	−0.2893	−2462.4	−2.1813	3.28	950.0	4.09	−0.0043	
	Sphene (sph)	−2601.65	0.96	124.00	5.565	0.2279	0.2924	−3539.5	−0.8943	1.58	1017.0	9.85	−0.0097	1
	Spurrite (spu)	−5847.08	2.23	332.00	14.697	0.6141	−0.3508	−2493.1	−4.1680	3.40	950.0	4.09	−0.0043	
	Tilleyite (ty)	−6368.39	2.21	390.00	17.039	0.7417	−0.5345	−1434.6	−5.8785	3.41	950.0	4.09	−0.0043	
	Zircon (zrc)	−2035.05	1.66	83.03	3.926	0.2320	−1.4405	0	−2.2382	1.25	2301.0	4.04	−0.0018	
Sorosilicates	Clinozoisite (cz)	−6895.42	1.31	301.00	13.630	0.6309	1.3693	−6645.8	−3.7311	2.33	1197.0	4.07	−0.0034	
	Epidote (ep)	−6473.90	1.17	315.00	13.920	0.6133	2.2070	−7160.0	−2.9877	2.34	1340.0	4.00	−0.0030	
	Epidote (fep)	−6027.57	1.23	329.00	14.210	0.5847	3.0447	−7674.2	−2.2443	2.31	1513.0	4.00	−0.0026	
	Lawsonite (law)	−4868.61	0.81	229.00	10.132	0.6878	0.1566	375.9	−7.1792	2.65	1229.0	5.45	−0.0044	
	Piemontite (pmt)	−6543.04	2.70	340.00	13.820	0.5698	2.7790	−5442.9	−2.8126	2.38	1197.0	4.07	−0.0034	
	Zoisite (zo)	−6896.21	1.31	298.00	13.575	0.6620	1.0416	−6006.4	−4.2607	3.12	1044.0	4.00	−0.0038	
	Vesuvianite (vsv)	−42 345.19	8.95	1890.00	85.200	4.4880	−5.7952	−22269.3	−33.4780	2.75	1255.0	4.80	−0.0038	
Cyclosilicates	Cordierite (crd)	−9163.48	1.51	404.10	23.322	0.9061	0	−7902.0	−6.2934	0.68	1290.0	4.10	−0.0031	2
	Cordierite (fcrd)	−8444.02	1.66	461.00	23.710	0.9240	0	−7039.4	−6.4396	0.67	1290.0	4.10	−0.0031	2
	Cordierite (hcrd)	−9449.32	1.52	475.60	23.322	0.9802	0	−7035.9	−6.6808	0.67	1290.0	4.10	−0.0031	2
	Cordierite (mncrd)	−8693.64	3.60	473.00	24.027	0.8865	0	−8840.0	−5.5904	0.69	1290.0	4.10	−0.0031	2
	Osumilite (fosm)	−14 238.91	3.99	762.00	38.320	1.6560	−3.4163	−6497.7	−14.1143	0.49	800.0	4.10	−0.0051	
	Osumilite (osm1)	−14 959.21	3.83	701.00	37.893	1.6258	−3.5548	−8063.5	−13.4909	0.47	810.0	4.10	−0.0051	
	Osumilite (osm2)	−14 799.99	4.05	724.00	38.440	1.6106	−3.4457	−8262.1	−13.1288	0.47	810.0	4.10	−0.0051	
High-pressure phases	akimotoite (fak)	−1142.14	10.12	91.50	2.760	0.1003	1.3328	−4364.9	0.4198	2.12	2180.0	4.55	−0.0022	
	Akimotoite (mak)	−1490.85	0.62	59.30	2.635	0.1478	0.2015	−2395.0	−0.8018	2.12	2110.0	4.55	−0.0022	
	CaSi-titanite (cstn)	−2496.17	2.81	99.50	4.818	0.2056	0.6034	−5517.7	−0.3526	1.58	1782.0	4.00	−0.0022	
	Perovskite (apv)	−1646.76	1.12	51.80	2.540	0.1395	0.5890	−2460.6	−0.5892	1.80	2030.0	4.00	−0.0020	
	Perovskite (cpv)	−1541.73	1.80	73.50	2.745	0.1593	0	−967.3	−1.0754	1.87	2360.0	3.90	−0.0016	
	Perovskite (fpv)	−1084.64	8.14	91.00	2.548	0.1332	1.0830	−3661.4	−0.3147	1.87	2810.0	4.14	−0.0016	
	Perovskite (mpv)	−1443.02	0.69	62.60	2.445	0.1493	0.2918	−2983.0	−0.7991	1.87	2510.0	4.14	−0.0016	
	PhaseA (phA)	−7132.27	1.90	348.00	15.442	0.9640	−1.1521	−4517.8	−7.7247	3.79	1450.0	4.06	−0.0028	
	Ringwoodite (frw)	−1471.79	0.76	140.00	4.203	0.1668	4.2610	−1705.4	−0.5414	2.22	1977.0	4.92	−0.0025	
	Ringwoodite (mrw)	−2127.66	0.78	90.00	3.949	0.2133	0.2690	−1410.4	−1.4959	2.01	1781.0	4.35	−0.0024	
	Wadsleyite (fwd)	−1467.92	0.97	146.00	4.321	0.2011	1.7330	−1960.6	−0.9009	2.73	1690.0	4.35	−0.0026	
	Wadsleyite (mwd)	−2138.50	0.76	93.90	4.051	0.2087	0.3942	−1709.5	−1.3028	2.37	1726.0	3.84	−0.0022	
Pyroxene and pyroxenoid	Acmite (acm)	−2583.50	2.43	170.60	6.459	0.3071	1.6758	−1685.5	−2.1258	2.11	1060.0	4.08	−0.0038	
	Ca-eskola pyroxene (caes)	−3002.01	1.74	127.00	6.050	0.3620	−1.6944	−175.9	−3.5657	2.31	1192.0	5.19	−0.0044	
	Ca-Tschermak pyroxene (cats)	−3310.14	0.80	135.00	6.356	0.3476	−0.6974	−1781.6	−2.7575	2.08	1192.0	5.19	−0.0044	2
	Clinoenstatite (cen)	−3091.12	0.66	132.00	6.264	0.3060	−0.3793	−3041.7	−1.8521	2.11	1059.0	8.65	−0.0082	
	Clinoenstatite high-P (hen)	−3082.74	0.67	131.70	6.099	0.3562	−0.2990	−596.9	−3.1853	2.26	1500.0	5.50	−0.0036	
	Diopside (di)	−3201.69	0.62	142.90	6.619	0.3145	0.0041	−2745.9	−2.0201	2.73	1192.0	5.19	−0.0044	

Table 2a. (*Continued*)

Group	End-member	$\Delta_f H$	$\sigma(\Delta_f H)$	S	V	C_P				$\alpha\kappa$				ℓ
						a	b	c	d	α_0	κ_0	κ_0'	κ_0''	
	Enstatite (en)	−3090.23	0.66	132.50	6.262	0.3562	−0.2990	−596.9	−3.1853	2.27	1059.0	8.65	−0.0082	
	Ferrosilite (fs)	−2388.72	0.81	189.90	6.592	0.3987	−0.6579	1290.1	−4.0580	3.26	1010.0	4.08	−0.0040	
	Hedenbergite (hed)	−2841.92	0.94	175.00	6.795	0.3402	0.0812	−1047.8	−2.6467	2.38	1192.0	3.97	−0.0033	
	Jadeite (jd)	−3025.26	1.67	133.50	6.040	0.3194	0.3616	−1173.9	−2.4695	2.10	1281.0	3.81	−0.0030	
	Kosmochlore (kos)	−2746.80	2.46	149.65	6.309	0.3092	0.5419	−664.6	−2.1766	1.94	1308.0	3.00	−0.0023	
	Mg-Tschermak pyroxene (mgts)	−3196.61	0.73	131.00	6.050	0.3714	−0.4082	−398.4	−3.5471	2.17	1028.0	8.55	−0.0083	
	Protoenstatite (pren)	−3084.57	0.67	137.00	6.476	0.3562	−0.2990	−596.9	−3.1853	2.30	1059.0	8.65	−0.0082	
	Pseudowollastonite (pswo)	−1627.94	0.47	87.80	4.008	0.1578	0	−967.3	−1.0754	2.85	1100.0	4.08	−0.0037	
	Pyroxmangite (pxmn)	−1323.14	0.73	99.30	3.472	0.1384	0.4088	−1936.0	−0.5389	2.80	840.0	4.00	−0.0048	
	Rhodonite (rhod)	−1322.35	0.73	100.50	3.494	0.1384	0.4088	−1936.0	−0.5389	2.81	840.0	4.00	−0.0048	
	Walstromite (wal)	−1625.88	0.48	83.50	3.763	0.1593	0	−967.3	−1.0754	2.54	795.0	4.10	−0.0052	
	Wollastonite (wo)	−1633.75	0.47	82.50	3.993	0.1593	0	−967.3	−1.0754	2.54	795.0	4.10	−0.0052	
Amphibole	Anthophyllite (anth)	−12066.85	2.48	537.00	26.540	1.2773	2.5825	−9704.6	−9.0747	2.52	700.0	4.11	−0.0059	
	Anthophyllite (fanth)	−9624.53	8.80	725.00	27.870	1.3831	3.0669	−4224.7	−11.2576	2.74	700.0	4.11	−0.0059	
	Cummingtonite (cumm)	−12064.71	2.48	538.00	26.330	1.2773	2.5825	−9704.6	−9.0747	2.52	700.0	4.11	−0.0059	
	Ferroactinolite (fact)	−10503.82	2.88	710.00	28.420	1.2900	2.9992	−8447.5	−8.9470	2.88	760.0	4.10	−0.0054	
	Glaucophane (fgl)	−10880.25	5.15	624.00	26.590	1.7629	−11.8992	9423.7	−20.2071	1.83	890.0	4.09	−0.0046	
	Glaucophane (gl)	−11960.24	3.55	530.00	25.980	1.7175	−12.1070	7075.0	−19.2720	1.49	883.0	4.09	−0.0046	
	Grunerite (grun)	−9607.15	3.02	735.00	27.840	1.3831	3.0669	−4224.7	−11.2576	2.74	648.0	4.12	−0.0064	
	Pargasite (parg)	−12664.49	2.27	635.00	27.190	1.2802	2.2997	−12359.5	−8.0658	2.80	912.0	4.09	−0.0045	
	Riebeckite (rieb)	−10024.77	5.30	695.00	27.490	1.7873	−12.4882	9627.1	−20.2755	1.80	890.0	4.09	−0.0046	
	Tremolite (tr)	−12304.56	2.17	553.00	27.270	1.2602	0.3830	−11455.0	−8.2376	2.61	762.0	4.10	−0.0054	
	Tschermakite (ts)	−12555.30	1.77	533.00	26.800	1.2448	2.4348	−11965.0	−8.1121	2.66	700.0	4.10	−0.0054	
Other chain silicates	Deerite (deer)	−18341.50	6.45	1650.00	55.740	3.1644	−2.7883	−5039.1	−26.7210	2.75	630.0	4.12	−0.0065	
	Carpholite (fcar)	−4411.57	1.01	251.10	10.695	0.6866	−1.2415	186.0	−6.8840	2.21	525.0	4.14	−0.0079	
	Carpholite (mcar)	−4771.22	0.79	221.50	10.590	0.6830	−1.4054	291.0	−6.9764	2.43	525.0	4.14	−0.0079	
	Sapphirine (fspr)	−9659.86	5.87	485.00	19.923	1.1329	−0.7348	−10420.2	−7.0366	1.96	2500.0	4.04	−0.0017	
	Sapphirine (spr4)	−11022.40	3.10	425.50	19.900	1.1331	−0.7596	−8816.6	−8.1806	2.05	2500.0	4.04	−0.0016	
	Sapphirine (spr5)	−11135.69	3.83	419.50	19.750	1.1034	0.1015	−10957.0	−7.4092	2.06	2500.0	4.04	−0.0016	
Mica	annite (ann)	−5144.23	3.19	418.00	15.432	0.8157	−3.4861	19.8	−7.4667	3.80	513.0	7.33	−0.0143	
	Celadonite (cel)	−5834.87	2.83	290.00	13.957	0.7412	−1.8748	−2368.8	−6.6169	3.07	700.0	4.11	−0.0059	
	Celadonite (fcel)	−5468.47	2.86	330.00	14.070	0.7563	−1.9147	−1586.1	−6.9287	3.18	700.0	4.11	−0.0059	
	Eastonite (east)	−6330.48	3.04	318.00	14.738	0.7855	−3.8031	−2130.3	−6.8937	3.80	530.0	7.33	−0.0143	
	Margarite (ma)	−6242.11	1.40	265.00	12.964	0.7444	−1.6800	−2074.4	−6.7832	2.33	1000.0	4.08	−0.0041	
	Mn-biotite (mnbi)	−5477.59	4.85	433.00	15.264	0.8099	−5.9213	−1514.4	−6.9987	3.80	530.0	7.33	−0.0143	
	Muscovite (mu)	−5976.56	2.90	292.00	14.083	0.7564	−1.9840	−2170.0	−6.9792	3.07	490.0	4.15	−0.0085	
	Na-phlogopite (naph)	−6171.92	1.99	318.00	14.450	0.7735	−4.0229	−2597.9	−6.5126	3.28	513.0	7.33	−0.0143	
	Paragonite (pa)	−5942.91	1.81	277.00	13.211	0.8030	−3.1580	217.0	−8.1510	3.70	515.0	6.51	−0.0126	
	Phlogopite (phl)	−6214.95	2.90	326.00	14.964	0.7703	−3.6939	−2328.9	−6.5316	3.80	513.0	7.33	−0.0143	
Chlorites	Al-free chlorite (afchl)	−8728.65	2.27	439.00	21.570	1.1550	−0.0417	−4024.4	−9.9529	2.04	870.0	4.09	−0.0047	
	Amesite (ames)	−9039.80	1.96	413.00	20.710	1.1860	−0.2599	−3627.2	−10.6770	2.00	870.0	4.09	−0.0047	
	Clinochlore (clin)	−8909.23	1.55	437.00	21.140	1.1708	−0.1508	−3825.8	−10.3150	2.04	870.0	4.09	−0.0047	
	Daphnite (daph)	−7116.71	3.20	584.00	21.620	1.1920	−0.5940	−4826.4	−9.7683	2.27	870.0	4.09	−0.0047	
	Mn-chlorite (mnchl)	−7702.37	8.36	595.00	22.590	1.1365	−0.5243	−5548.1	−8.9115	2.23	870.0	4.09	−0.0047	
	Sudoite (fsud)	−7900.11	2.08	456.00	20.400	1.4663	−4.7365	−1182.8	−14.3880	2.08	870.0	4.09	−0.0047	
	Sudoite (sud)	−8626.91	1.65	395.00	20.300	1.4361	−4.8749	−2748.5	−13.7640	1.99	870.0	4.09	−0.0047	
Other sheet silicates	Antigorite (atg)	−71416.61	15.14	3600.00	175.480	9.6210	−9.1183	−35941.6	−83.0342	2.60	496.0	6.31	−0.0127	
	Chrysotile (chr)	−4360.96	0.98	221.30	10.746	0.6247	−2.0770	−1721.8	−5.6194	2.20	628.0	4.00	−0.0064	
	Fe-talc (fta)	−4798.43	4.24	352.00	14.225	0.5797	3.9494	−6459.3	−3.0881	1.80	430.0	6.17	−0.0144	
	Greenalite (glt)	−3297.65	1.69	310.00	11.980	0.5764	0.2984	−3757.0	−4.1662	2.28	630.0	4.00	−0.0063	
	Kaolinite (kao)	−4122.10	0.78	203.70	9.934	0.4367	−3.4295	−4055.9	−2.6991	2.51	645.0	4.12	−0.0064	
	Lizardite (liz)	−4369.14	1.08	212.00	10.645	0.6147	−2.0770	−1721.8	−5.6194	2.20	710.0	3.20	−0.0045	
	Minnesotaite (minn)	−4819.29	1.49	355.00	14.851	0.5797	3.9494	−6459.3	−3.0881	1.80	430.0	6.17	−0.0144	
	Minnesotaite (minm)	−5866.01	10.26	263.90	14.291	0.6222	0	−6385.5	−3.9163	1.80	430.0	6.17	−0.0144	
	Prehnite (fpre)	−5766.75	1.35	320.00	14.800	0.7371	−1.6810	−1957.3	−6.3581	1.58	1093.0	4.01	−0.0037	
	Prehnite (pre)	−6202.10	1.11	292.80	14.026	0.7249	−1.3865	−2059.0	−6.3229	1.58	1093.0	4.01	−0.0037	
	Prl-talc (tap)	−5589.24	1.03	245.00	13.450	0.7845	−4.2948	1251.0	−8.4959	4.50	370.0	10.00	−0.0271	
	Pyrophyllite (prl)	−5640.68	1.01	239.00	12.804	0.7845	−4.2948	1251.0	−8.4959	4.50	370.0	10.00	−0.0271	
	Stilpnomelane (fstp)	−12550.45	9.09	930.20	37.239	1.9443	−1.2289	−4840.2	−16.6350	3.68	513.0	7.33	−0.0143	
	Stilpnomelane (mstp)	−14288.03	25.51	847.40	36.577	1.8622	−1.4018	−8983.1	−14.9230	3.71	513.0	7.33	−0.0143	
	Talc (ta)	−5897.17	1.16	259.00	13.625	0.6222	0	−6385.5	−3.9163	1.80	430.0	6.17	−0.0144	
	Tschermak-talc (tats)	−5992.20	0.98	259.00	13.510	0.5495	3.6324	−8606.6	−2.5153	1.80	430.0	6.17	−0.0144	
Feldspar and feldspathoid	Albite (ab)	−3935.49	1.69	207.40	10.067	0.4520	−1.3364	−1275.9	−3.9536	2.36	541.0	5.91	−0.0109	2
	Albite-high (abh)	−3921.49	1.68	224.30	10.105	0.4520	−1.3364	−1275.9	−3.9536	2.40	541.0	5.91	−0.0109	
	Analcite (anl)	−3307.25	1.68	232.00	9.740	0.6435	−1.6067	9302.3	−9.1796	2.76	400.0	4.18	−0.0104	
	Anorthite (an)	−4232.70	0.79	200.50	10.079	0.3705	1.0010	−4339.1	−1.9606	1.41	860.0	4.09	−0.0048	2
	Carnegieite-high (cgh)	−2077.99	1.76	135.00	5.670	0.2292	1.1876	0	−1.9707	4.67	465.0	4.16	−0.0089	
	Carnegieite-low (cg)	−2091.70	1.76	118.70	5.603	0.1161	8.6021	−1992.7	0	4.50	465.0	4.16	−0.0089	
	Kalsilite (kls)	−2122.89	2.91	136.00	6.052	0.2420	−0.4482	−895.8	−1.9358	3.16	514.0	2.00	−0.0039	

Table 2a. (*Continued*)

Group	End-member	$\Delta_f H$	$\sigma(\Delta_f H)$	S	V	C_P a	b	c	d	α_0	κ_0	κ_0'	κ_0''	ℓ
	Leucite (lc)	−3029.23	2.82	198.50	8.826	0.3698	−1.6332	684.7	−3.6831	1.85	450.0	5.70	−0.0127	2
	Microcline (mic)	−3975.33	2.80	214.30	10.871	0.4488	−1.0075	−1007.3	−3.9731	1.65	583.0	4.02	−0.0069	
	Nepheline (ne)	−2094.54	1.75	124.40	5.419	0.2727	−1.2398	0	−2.7631	4.63	465.0	4.16	−0.0089	1
	Sanidine (san)	−3966.68	2.80	214.30	10.871	0.4488	−1.0075	−1007.3	−3.9731	1.65	583.0	4.02	−0.0069	2
Silica minerals	Coesite (coe)	−907.02	0.27	39.60	2.064	0.1078	−0.3279	−190.3	−1.0416	1.23	979.0	4.19	−0.0043	
	Cristobalite (crst)	−904.24	0.27	50.86	2.745	0.0727	0.1304	−4129.0	0	0	160.0	4.35	−0.0272	
	Quartz (q)	−910.70	0.27	41.43	2.269	0.0929	−0.0642	−714.9	0	0	730.0	6.00	−0.0082	1
	Stishovite (stv)	−876.39	0.49	24.00	1.401	0.0681	0.6010	−1978.2	−0.0821	1.58	3090.0	4.60	−0.0015	
	Tridymite (trd)	−907.08	0.27	44.10	2.800	0.0749	0.3100	−1174.0	−0.2367	0	150.0	4.36	−0.0291	
Other framework silicates	Heulandite (heu)	−10 545.09	1.80	783.00	31.700	1.5048	−3.3224	−2959.3	−13.2972	1.57	274.0	4.00	−0.0146	
	Hollandite (hol)	−37 91.94	5.27	166.20	7.128	0.4176	−0.3617	−4748.1	−2.8199	2.80	1800.0	4.00	−0.0022	
	Laumontite (lmt)	−7262.64	1.12	465.00	20.370	1.0134	−2.1413	−2235.8	−8.8067	1.37	860.0	4.09	−0.0048	
	Meionite (me)	−13 841.95	2.61	752.00	33.985	1.3590	3.6442	−8594.7	−9.5982	1.82	870.0	4.09	−0.0047	
	K-cymrite (kcm)	−4232.63	2.81	281.50	11.438	0.5365	−1.0090	−980.4	−4.7350	3.21	425.0	2.00	−0.0047	
	Sodalite (sdl)	−13405.41	10.54	910.00	42.130	1.5327	4.7747	−2972.8	−12.4270	4.63	465.0	4.16	−0.0089	
	Stilbite (stlb)	−10 896.63	2.23	710.00	32.870	1.5884	−3.2043	−3071.6	−13.9669	1.51	860.0	4.09	−0.0048	
	Wadeite (wa)	−4271.79	6.46	254.00	10.844	0.4991	0	0	−4.3501	2.66	900.0	4.00	−0.0044	
	Wairakite (wrk)	−6662.40	1.11	380.00	19.040	0.8383	−2.1460	−2272.0	−7.2923	1.49	860.0	4.09	−0.0048	
Oxides	Baddelyite (bdy)	−1100.34	1.63	50.40	2.115	0.1035	−0.4547	−416.2	−0.7136	2.00	953.0	3.88	−0.0041	
	Bixbyite (bix)	−959.00	1.09	113.70	3.137	0.1451	2.3534	721.6	−1.0084	2.91	2230.0	4.04	−0.0018	
	Corundum (cor)	−1675.33	0.75	50.90	2.558	0.1395	0.5890	−2460.6	−0.5892	1.80	2540.0	4.34	−0.0017	
	Cuprite (cup)	−170.60	0.11	92.40	2.344	0.1103	0	0	−0.6748	3.33	1310.0	5.70	−0.0043	
	Eskolaite (esk)	−1137.35	4.31	83.00	2.909	0.1190	0.9496	−1442.0	−0.0034	1.59	2380.0	4.00	−0.0017	
	Geikielite (geik)	−1568.97	0.89	73.60	3.086	0.1510	0	−1890.4	−0.6522	2.15	1700.0	8.30	−0.0049	
	Hematite (hem)	−825.65	0.68	87.40	3.027	0.1639	0	−2257.2	−0.6576	2.79	2230.0	4.04	−0.0018	1
	Hercynite (herc)	−1953.09	0.85	113.90	4.075	0.2167	0.5868	−2430.2	−1.1783	2.06	1922.0	4.04	−0.0021	2
	Ilmenite (ilm)	−1230.43	0.84	109.50	3.169	0.1389	0.5081	−1288.8	−0.4637	2.40	1700.0	8.30	−0.0049	1
	Lime (lime)	−634.61	0.50	38.10	1.676	0.0524	0.3673	−750.7	−0.0510	3.41	1130.0	3.87	−0.0034	
	Manganosite (mang)	−385.55	0.41	59.70	1.322	0.0598	0.3600	−31.4	−0.2826	3.69	1645.0	4.46	−0.0027	
	Mg-corundum (mcor)	−1474.43	2.87	59.30	2.635	0.1478	0.2015	−2395.0	−0.8018	2.12	2110.0	4.55	−0.0022	
	Magnesioferrite (mft)	−1442.29	2.71	121.00	4.457	0.2705	−0.7505	−999.2	−2.0224	3.63	1857.0	4.05	−0.0022	1
	Magnetite (mt)	−1114.51	0.95	146.90	4.452	0.2625	−0.7205	−1926.2	−1.6557	3.71	1857.0	4.05	−0.0022	1
	Ni-oxide (NiO)	−239.47	0.36	38.00	1.097	0.0477	0.7824	−392.5	0	3.30	2000.0	3.94	−0.0020	1
	Periclase (per)	−601.55	0.27	26.50	1.125	0.0605	0.0362	−535.8	−0.2992	3.11	1616.0	3.95	−0.0024	
	Periclase (fper)	−271.97	2.05	60.60	1.206	0.0444	0.8280	−1214.2	0.1852	7.43	1520.0	4.90	−0.0032	
	Picrochromite (picr)	−1762.60	3.28	118.30	4.356	0.1961	0.5398	−3126.0	−0.6169	1.80	1922.0	4.04	−0.0021	2
	Pyrophanite (pnt)	−1361.99	2.16	105.50	3.288	0.1435	0.3373	−1940.7	−0.4076	2.40	1700.0	8.30	−0.0049	
	Rutile (ru)	−944.37	0.78	50.50	1.882	0.0904	0.2900	0	−0.6238	2.24	2220.0	4.24	−0.0019	
	Spinel (sp)	−2301.26	0.84	82.00	3.978	0.2229	0.6127	−1686.0	−1.5510	1.93	1922.0	4.04	−0.0021	2
	Tenorite (ten)	−156.10	2.18	42.60	1.222	0.0310	1.3740	−1258.0	0.3693	3.57	2000.0	3.94	−0.0020	
	Ulvospinel (usp)	−1491.10	1.01	180.00	4.682	−0.1026	14.2520	−9144.5	5.2707	3.86	1857.0	4.05	−0.0022	
Hydroxides	Brucite (br)	−925.65	0.30	63.20	2.463	0.1584	−0.4076	−1052.3	−1.1713	6.20	415.0	6.45	−0.0155	
	Diaspore (dsp)	−999.86	0.38	34.50	1.786	0.1451	0.8709	584.4	−1.7411	3.57	2280.0	4.04	−0.0018	
	Goethite (gth)	−561.79	0.35	60.30	2.082	0.1393	0.0147	−212.7	−1.0778	4.35	500.0	4.03	−0.0016	
Carbonates	Ankerite (ank)	−1970.62	0.77	188.46	6.606	0.3410	−0.1161	0	−3.0548	3.46	914.0	3.88	−0.0043	2
	Aragonite (arag)	−1207.82	0.46	89.80	3.415	0.1923	−0.3052	1149.7	−2.1183	6.14	614.0	5.87	−0.0096	1
	Calcite (cc)	−1207.88	0.46	92.50	3.689	0.1409	0.5029	−950.7	−0.8584	2.52	733.0	4.06	−0.0055	1
	Dolomite (dol)	−2325.76	0.58	156.10	6.429	0.3589	−0.4905	0	−3.4562	3.28	943.0	3.74	−0.0040	2
	Magnesite (mag)	−1110.93	0.32	65.50	2.803	0.1864	−0.3772	0	−1.8862	3.38	1028.0	5.41	−0.0053	
	Rhodochrosite (rhc)	−892.28	0.41	98.00	3.107	0.1695	0	0	−1.5343	2.44	953.0	3.88	−0.0041	
	Siderite (sid)	−762.22	0.57	93.30	2.943	0.1684	0	0	−1.4836	4.39	1200.0	4.07	−0.0034	
Sulphides and halides	Anhydrite (any)	−1434.40	3.50	106.90	4.594	0.1287	4.8545	−1223.0	−0.5605	4.18	543.8	4.19	−0.0077	
	Halite (hlt)	−411.30	0.22	72.10	2.702	0.0452	1.7970	0	0	11.47	238.0	5.00	−0.0210	
	Pyrite (pyr)	−171.64	1.28	52.90	2.394	0.0373	2.6715	−1817.0	0.6493	3.10	1395.0	4.09	−0.0029	
	Pyrrhotite (trot)	−99.03	1.34	65.50	1.819	0.0502	1.1052	−940.0	0	5.68	658.0	4.17	−0.0063	1
	Pyrrhotite (trov)	−96.02	1.17	57.50	1.738	0.0511	0.8307	−669.7	0	5.94	658.0	4.17	−0.0063	1
	Troilite (lot)	−102.16	0.48	60.00	1.818	0.0502	1.1052	−940.0	0	4.93	658.0	4.17	−0.0063	1
	Troilite (tro)	−97.76	0.48	70.80	1.819	0.0502	1.1052	−940.0	0	5.73	658.0	4.17	−0.0063	1
	Sylvite (syv)	−436.50	0.22	82.60	3.752	0.0462	1.7970	0	0	11.09	170.0	5.00	−0.0294	
Elements	Copper (Cu)	0	0.00	33.14	0.711	0.0124	0.9220	−379.9	0.2335	3.58	1625.0	4.24	−0.0026	
	Diamond (diam)	2.00	0.06	2.38	0.342	0.0243	0.6272	−377.4	−0.2734	0.49	4465.0	1.61	−0.0004	
	Graphite (gph)	0.00	0.00	5.74	0.530	0.0510	−0.4429	488.6	−0.8055	1.67	312.0	3.90	−0.0125	
	Iron (iron)	0.00	0.00	27.09	0.709	0.0462	0.5159	723.1	−0.5562	3.56	1640.0	5.16	−0.0031	1
	Nickel (Ni)	0.00	0.00	29.87	0.659	0.0498	0	585.9	−0.5339	4.28	1905.0	4.25	−0.0022	1
	Sulphur (S)	0.00	0.00	32.05	1.551	0.0566	−0.4557	638.0	−0.6818	6.40	145.0	7.00	−0.0063	
Gas species	Methane (CH$_4$)	−74.81	0.37	186.26	0	0.1501	0.2063	3427.7	−2.6504	0	0	0	0	
	Carbon monoxide (CO)	−110.53	0.19	197.67	0	0.0457	−0.0097	662.7	−0.4147	0	0	0	0	
	Carbon dioxide (CO$_2$)	−393.51	0.08	213.70	0	0.0878	−0.2644	706.4	−0.9989	0	0	0	0	
	Hydrogen (H$_2$)	0.00	0.00	130.70	0	0.0233	0.4627	0	0.0763	0	0	0	0	
	Hydrogen sulphide (H$_2$S)	−20.30	0.44	205.77	0	0.0474	1.0240	615.9	−0.3978	0	0	0	0	

Table 2a. (*Continued*)

Group	End-member	$\Delta_f H$	$\sigma(\Delta_f H)$	S	V	C_P				$\alpha\kappa$				ℓ
						a	b	c	d	α_0	κ_0	κ_0'	κ_0''	
	Oxygen (O$_2$)	−0.00	0.00	205.20	0	0.0483	−0.0691	499.2	−0.4207	0	0	0	0	
	Sulphur gas (S$_2$)	128.54	0.32	231.00	0	0.0371	0.2398	−161.0	−0.0650	0	0	0	0	
	Water (H$_2$O)	−241.81	0.02	188.80	0	0.0401	0.8656	487.5	−0.2512	0	0	0	0	
Melt species	Albite liq (abL)	−3926.05	1.69	149.90	10.858	0.3580	0	0	0	3.37	176.0	14.35	−0.0815	4
	Anorthite liq (anL)	−4277.91	0.84	29.00	10.014	0.4300	0	0	0	5.14	210.0	6.38	−0.0304	4
	Corundum liq (corL)	−1632.02	1.02	14.90	3.369	0.1576	0	0	0	7.03	150.0	6.00	0	4
	Diopside liq (diL)	−3193.70	0.70	42.10	7.288	0.3340	0	0	0	8.51	249.0	8.04	−0.0323	4
	Enstatite liq (enL)	−3096.58	0.80	−4.00	6.984	0.3536	0	0	0	6.81	218.0	7.20	−0.0330	4
	Fayalite liq (faL)	−1463.04	0.71	96.00	4.677	0.2437	0	0	0	10.71	290.0	10.42	−0.0359	4
	Forsterite liq (foL)	−2237.32	0.60	−62.00	4.312	0.2694	0	0	0	9.20	362.0	10.06	−0.0278	4
	Water liq (h$_2$oL)	−295.01	0.03	45.50	1.460	0.0800	0	0	0	46.33	46.2	1.50	−0.0325	4
	Halite liq (hltL)	−392.99	0.23	80.10	2.938	0.0720	−0.3223	0	0	29.50	64.0	4.61	−0.0720	4
	K-feldspar liq (kspL)	−3980.06	2.80	132.20	11.431	0.3680	0	0	0	4.93	174.0	6.84	−0.0393	4
	Leucite liq (lcL)	−3068.37	2.82	102.00	8.590	0.2870	0	0	0	6.70	175.0	7.00	−0.0394	4
	Lime liq (limL)	−692.37	0.52	−47.50	1.303	0.0990	0	0	0	17.50	362.0	10.06	−0.0278	4
	Nepheline liq (neL)	−2116.71	1.76	52.90	5.200	0.2165	0	0	0	13.70	250.0	7.37	−0.0295	4
	Periclase liq (perL)	−654.14	0.36	−64.30	0.839	0.0990	0	0	0	22.60	362.0	10.06	−0.0278	4
	Quartz liq (qL)	−921.03	0.27	16.30	2.730	0.0825	0	0	0	0	220.0	9.46	−0.0430	4
	Sillimanite liq (silL)	−2594.05	1.79	10.00	6.051	0.2530	0	0	0	4.08	220.0	6.36	−0.0289	4
	Sylvite liq (syvL)	−417.41	0.23	94.50	3.822	0.0669	0	0	0	30.10	56.0	4.65	−0.0830	4
	Wollastonite liq (woL)	−1642.20	0.51	22.50	3.965	0.1674	0	0	0	6.69	305.0	9.38	−0.0308	4
Aqueous species	H$^+$	0	0.00	0	0	0	0	0	0	0	0	0	0	3
	Cl$^-$	−167.08	0.11	56.73	1.779	0	0	0	0	0	0	0	0	3
	OH$^-$	−230.02	0.11	−10.71	−0.418	0	0	0	0	0	0	0	0	3
	Na$^+$	−240.30	0.11	58.40	−0.111	0	19.1300	0	0	0	0	0	0	3
	K$^+$	−252.17	0.11	101.04	0.906	0	7.2700	0	0	0	0	0	0	3
	Ca^{++}	−543.30	1.09	−56.50	−1.806	0	−6.9000	0	0	0	0	0	0	3
	Mg^{++}	−465.96	1.09	−138.10	−2.155	0	−4.6200	0	0	0	0	0	0	3
	Fe^{++}	−90.42	3.28	−107.11	−2.220	0	0	0	0	0	0	0	0	3
	Al^{+++}	−527.23	1.64	−316.30	−4.440	0	0	0	0	0	0	0	0	3
	CO$_3^{--}$	−675.23	0.11	−50.00	−0.502	0	0	0	0	0	0	0	0	3
	AlOH$_3$	−1251.85	1.09	53.60	0	0	0	0	0	0	0	0	0	3
	AlOH$_4^-$	−1495.78	1.09	126.90	0	0	0	0	0	0	0	0	0	3
	KOH	−473.62	1.31	109.62	−0.800	0	9.4500	0	0	0	0	0	0	3
	HCl	−162.13	0.87	56.73	1.779	0	9.0300	0	0	0	0	0	0	3
	KCl	−400.03	1.42	184.81	4.409	0	5.4300	0	0	0	0	0	0	3
	NaCl	−399.88	1.20	126.09	2.226	0	19.1300	0	0	0	0	0	0	3
	CaCl2	−877.06	1.31	46.00	3.260	0	13.6900	0	0	0	0	0	0	3
	CaCl$^+$	−701.28	1.75	27.36	0.574	0	−6.9000	0	0	0	0	0	0	3
	MgCl$_2$	−796.08	2.29	−22.43	2.920	0	23.9900	0	0	0	0	0	0	3
	MgCl$^+$	−632.48	0.87	−81.37	0.126	0	−4.6200	0	0	0	0	0	0	3
	FeCl$_2$	−375.34	3.28	109.88	2.700	0	45.0300	0	0	0	0	0	0	3
	aqSi	−887.81	0.68	46.35	1.832	0	17.7500	0	0	0	0	0	0	3
	HS$^-$	−16.04	5.46	68.00	2.065	0	0	0	0	0	0	0	0	3
	HSO$_3^-$	−623.82	5.46	139.00	3.330	0	0	0	0	0	0	0	0	3
	SO$_4^{2-}$	−906.12	5.46	18.80	1.388	0	0	0	0	0	0	0	0	3
	HSO$_4^-$	−885.70	5.46	125.04	3.520	0	0	0	0	0	0	0	0	3

$\Delta_f H$ is the regressed enthalpy of formation from the elements; $\sigma(\Delta_f H)$ is 1SD on the enthalpy of formation; S is the entropy; V the volume (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 and κ are thermal expansion and bulk modulus; α_0 is the thermal expansion parameter; κ_0, κ_0' and κ_0'' are the bulk modulus (at 298 K, 1 bar) and its first and second pressure derivatives; ℓ is a flag, 1 signifying a phase transition described via Landau theory and 2 signifying a phase transition described via Bragg-Williams theory, 3 signifies an aqueous species and 4 signifies a melt end-member.

$$\kappa_0 = -V \left(\frac{\partial P}{\partial V} \right)_T \bigg|_{P_0, T_0},$$

and κ_0' and κ_0'' are the first and second derivatives of κ_0 with pressure also at ambient conditions. Conversely,

$$\kappa_0 = \frac{1}{abc},$$

$$\kappa_0' = \frac{c+1}{ac} - 1, \tag{4}$$

$$\kappa_0'' = \frac{b}{a}(1-a)(c+1).$$

By substituting equation (3) into equation (1) or (2) and setting $\kappa_0'' = 0$, TEOS reduces to the simpler two-parameter Murnaghan equation, with

$$a = 1, \quad b = \frac{\kappa_0'}{\kappa_0} \quad \text{and} \quad c = \frac{1}{\kappa_0'}$$

and

$$\frac{V}{V_0} = (1 + bP)^{-c},$$

as used in HP98, with, as a default there, $\kappa_0' = 4$ (or $c = \frac{1}{4}$).

A major advantage of the three-parameter TEOS over Murnaghan is that the inclusion of the second

Table 2b. Landau theory parameters used for end-members in the data set.

	Tc	S_{max}	V_{max}
lrn	1710	10.03	0.0500
sph	485	0.40	0.0050
q	847	4.95	0.1188
ne	467	10.00	0.0800
hem	955	15.60	0
NiO	520	5.70	0
ilm	1900	12.00	0.0200
mt	848	35.00	0
mft	665	17.00	0
cc	1240	10.00	0.0400
arag	1240	9.00	0.0450
trot	598	12.00	0.0410
tro	598	12.00	0.0410
lot	420	10.00	0
trov	595	10.00	0.0160
iron	1042	8.30	0
Ni	631	3.00	0

Tc is the critical temperature at 1 bar, S_{max} and V_{max} are the entropy and volume of disordering at Tc. See Holland & Powell (1998) for further details.

Table 2c. Symmetric formalism (SF; a generalized Bragg–Williams theory) parameters used for end-members in the data set.

	ΔH	ΔV	W	W_V	n	Fac
sill	4.75	0.0100	4.75	0.0100	1	0.25
geh	7.51	0.0900	7.50	0.0900	1	0.80
crd	36.71	0.1000	36.70	0.1000	2	1.50
hcrd	36.71	0.1000	36.70	0.1000	2	1.50
fcrd	36.71	0.1000	36.70	0.1000	2	1.50
mncrd	36.71	0.1000	36.70	0.1000	2	1.50
cats	3.80	0.0100	3.80	0.0100	1	0.25
ab	14.00	0.0420	13.00	0.0420	3	0.90
san	8.65	0.0240	8.50	0.0240	3	0.80
an	42.01	0.1000	42.00	0.1000	1	2.00
lc	11.61	0.4000	11.60	0.4000	2	0.70
sp	8.00	0	1.20	0	2	0.50
herc	18.30	0	13.60	0	2	1.00
picr	8.00	0	1.20	0	2	0.50
dol	11.91	0.0160	11.90	0.0160	1	1.00
ank	11.91	0.0160	11.90	0.0160	1	1.00

ΔH and ΔV are the total enthalpy and volume of disordering, W and W_V are the interaction energy terms used in $W = W_H + PW_V$, n is the number of Si disordering with each Al, and fac is a scaling factor on the energy of disordering. See Holland & Powell (1996a,b) for further details.

Table 2d. Values for $d\kappa_0/dT$, the temperature dependence of the bulk modulus for melt end-members in the data set.

	$d\kappa_0/dT$
SyvL	−0.02000
hltL	−0.01500
perL	−0.04100
limL	−0.04100
corL	−0.03500
qL	−0.03500
h2oL	−0.00001
foL	−0.04400
faL	−0.05500
woL	−0.02000
enL	−0.02400
diL	−0.03730
silL	−0.02900
anL	−0.05500
kspL	−0.00900
abL	−0.02600
neL	−0.00800
lcL	0

See Holland & Powell (1998) for further details.

Table 2e. $C_{P,aq}$, the augmented b term in the heat capacity for aqueous species in the modified density model of Anderson *et al.*, (1991), $C_p^* = C_p^\circ + bT$.

	$C_{P,aq}$
Na^+	0.0306
K^+	0.0072
$AlOH_3$	0.1015
$AlOH_4^-$	0.0965
HCl	0.0540
$CaCl_2$	0.0343
$CaCl^+$	0.0400
$MgCl_2$	0.0186
$MgCl^+$	0.1126
$FeCl_2$	0.0124
aqSi	0.0283
SO_4^-	0.2680
HSO_4^-	0.0220

See Holland & Powell (1998) for further details.

derivative of bulk modulus gives more flexibility, and allows extrapolation to very high pressures in a sensible fashion when the size and sign of κ_0'' is known. Although Freund & Ingalls (1989) state that experiments do not allow this term to be determined to better than 100% error, their applications suggest that all the successful EOS do seem to point to a fairly uniform but small negative value of κ_0'' for the range of elements and compressible compounds investigated. Jackson & Niesler (1982) suggested that $\kappa_0'' \approx -\phi/\kappa_0$, where ϕ is a small number between 0 and 10, and this was confirmed for periclase by Jacobs & Oonk (2000). More importantly, a negative value for κ_0'' is shown to be a requirement in the analysis of Stacey (2005), and should therefore be implemented in such an EOS. Here, to maintain this

requirement for a small negative κ_0'', we adopt the heuristic $\kappa_0'' = -\kappa_0'/\kappa_0$, with ϕ chosen to scale with κ_0' (see below). With this, the isothermal TEOS can be written in two-parameter form as:

$$\frac{V}{V_0} = -\kappa_0' + (1 + \kappa_0')\left(1 + \frac{\kappa_0'(2 + \kappa_0')}{\kappa_0(1 + \kappa_0')}P\right)^{-1/(\kappa_0'(2+\kappa_0'))},$$

or as

$$\frac{V}{V_0} = 1 - \sqrt{\frac{1+c}{c}}(1 - (1 + bP)^{-c}). \quad (5)$$

The relationship between TEOS and the commonly used third-order Birch-Murnaghan, can be seen in series expansion. The latter can be written as:

$$P = 3f(1 + 2f)^{5/2}(\kappa_0 + \frac{3}{2}\kappa_0(\kappa_0' - 4)f)$$

with the Eulerian strain $f = 1/2(y^{2/3} - 1)$, and $y = V_0/V$. Now, Murnaghan in terms of y is:

Table 3a. Regressed values for enthalpy of formation (kJ/mol) from the elements and their uncertainties compared with the compilation of Robie & Hemingway (1995). The $\Delta_f H$ and corresponding standard deviation (σ) are from the original data tabulation, for ambient conditions. The e^* are residuals, the difference between fitted values and tabulated values, normalised to σ. The fitted values and their standard deviations are given in Table 2. hat is the diagonal element of the hat matrix.

	$\Delta_f H$	σ	e^*	hat
fo	−2173.00	2.00	−0.22	0.07
fa	−1478.20	1.40	−0.34	0.20
teph	−1731.50	3.00	0.82	0.10
lrn	−2306.70	3.00	0.11	0.08
py	−6285.00	4.00	−0.72	0.06
alm	−5264.70	5.00	−0.81	0.06
gr	−6643.00	3.00	−0.02	0.20
andr	−5771.00	5.90	−0.32	0.06
and	−2589.90	2.00	−0.59	0.10
ky	−2593.80	2.00	−0.39	0.10
sill	−2586.10	2.00	−0.13	0.10
ak	−3865.40	3.00	0.08	0.08
crd	−9161.50	5.90	0.34	0.06
sph	−2602.90	3.00	−0.41	0.09
zrc	−2034.20	3.10	0.27	0.24
en	−3091.20	3.00	−0.32	0.04
cen	−3091.10	3.00	0.01	0.04
fs	−2390.40	6.00	−0.28	0.02
di	−3201.50	2.00	0.10	0.08
jd	−3029.30	3.60	−1.12	0.18
cats	−3306.30	5.00	0.77	0.02
rhod	−1321.60	2.00	0.38	0.11
pxmn	−1322.30	2.00	0.42	0.11
wo	−1634.80	1.40	−0.75	0.09
pswo	−1627.60	1.40	0.25	0.09
prl	−5640.00	1.50	0.46	0.38
ta	−5897.20	2.00	−0.02	0.28
kao	−4120.10	4.00	0.50	0.03
chr	−4360.00	3.00	0.32	0.09
ab	−3935.00	2.60	0.19	0.35
abh	−3921.00	5.00	0.10	0.10
mic	−3974.60	3.90	0.19	0.43
san	−3965.60	4.10	0.26	0.39
an	−4234.00	3.00	−0.43	0.06
q	−910.70	0.50	−0.01	0.25
trd	−907.00	4.00	0.02	0.00
coe	−905.60	2.10	0.67	0.01
ne	−2092.10	3.90	0.63	0.17
cg	−2089.30	4.00	0.60	0.16
anl	−3310.10	5.00	−0.57	0.09
lime	−635.10	0.90	−0.54	0.26
ru	−944.00	0.80	0.46	0.79
per	−601.60	0.30	−0.18	0.70
fper	−260.00	5.00	−0.03	0.42
mang	−385.20	0.50	0.71	0.57
cor	−1675.70	1.30	−0.28	0.28
hem	−826.20	1.30	−0.43	0.23
bix	−959.00	1.00	0	1.00
NiO	−239.30	0.40	0.44	0.69
pnt	−1360.10	4.00	0.47	0.24
ilm	−1232.00	2.50	−0.63	0.09
bdy	−1100.60	1.70	−0.15	0.77
ten	−156.10	2.00	0	1.00
cup	−170.60	0.10	0	1.00
sp	−2299.10	2.00	1.08	0.15
mt	−1115.73	2.10	−0.58	0.17
mft	−1441.50	3.00	0.26	0.68
usp	−1493.80	3.00	−0.90	0.09
picr	−1762.60	3.00	0	1.00
br	−924.50	2.00	0.58	0.02
dsp	−1000.60	5.00	−0.15	0.00
gth	−562.60	2.10	−0.39	0.02
cc	−1207.40	1.30	0.37	0.11
arag	−1207.40	1.40	0.30	0.09
mag	−1113.30	4.00	−0.59	0.01
sid	−760.60	3.00	0.54	0.03
rhc	−892.90	0.50	−1.24	0.58
dol	−2324.50	1.50	0.84	0.13
syv	−436.50	0.20	0	1.00
hlt	−411.30	0.20	0	1.00
pyr	−171.50	1.70	0.08	0.48
lot	−101.00	3.00	0.39	0.02
trov	−97.50	5.00	−0.30	0.05
any	−1434.40	3.20	0	1.00
diam	1.90	0.10	−1.01	0.26
S_2	128.60	0.30	0.19	0.98
H_2S	−20.60	0.70	−0.42	0.33

	Reaction	$T\,°C$	H (cal)	σ	H (298)	e^*	hat	
mwd	mwd = fo	702	30.0	3.0	32.3	−0.6	0.02	Akaogi et al. (1989)
mrw	mrw = fo	702	39.1	2.6	43.6	−0.5	0.04	Akaogi et al. (1989)
mrw	mrw = mwd	702	9.1	2.6	11.2	0.1	0.01	Akaogi et al. (1989)
fwd	fwd = fa	702	9.6	1.3	9.6	−0.2	0.23	Akaogi et al. (1989)
frw	frw = fa	702	3.8	2.4	5.5	−0.2	0.02	Akaogi et al. (1989)
frw	frw = fwd	702	−5.8	2.7	−4.1	−0.1	0.07	Akaogi et al. (1989)
mak	mak = mpv	697	−51.1	6.6	−51.0	−0.5	0.00	Akaogi & Ito (1993)
mak	2mak = en	697	118.2	8.6	121.8	1.5	0.01	Ashida et al. (1988)
mrw	mrw = mpv + per	697	−96.8	5.8	−92.8	−1.7	0.01	Navrotsky (1995)
mag	mag = per + CO_2	25	−116.8	1.0	−116.8	−0.9	0.03	Chai & Navrotsky (1993)
cc	cc = lime + CO_2	25	−178.3	1.2	−178.3	1.2	0.04	Chai & Navrotsky (1993)
dol	dol = per + lime + $2CO_2$	25	−304.3	1.9	−304.3	−0.9	0.03	Chai & Navrotsky (1993)
sill	sill = cor + q	697	−2.4	1.2	−0.5	−0.6	0.00	Charlu et al. (1975)
and	and = cor + q	697	−5.0	1.2	−3.6	−0.7	0.00	Anderson et al. (1977)
ky	ky = cor + q	697	−8.3	1.2	−7.1	−0.1	0.00	Anderson & Kleppa (1969)
sp	sp = per + cor	697	−22.5	1.2	−25.7	−1.1	0.01	Charlu et al. (1975)
py	py = 3per + cor + 3q	697	−74.1	5.5	−69.8	0.1	0.01	Charlu et al. (1975)
py	2py = 3en + 2cor	700	55.5	8.6	61.0	0.5	0.00	Charlu et al. (1975)
fo	fo = 2per + q	750	−59.5	1.9	−58.0	0.4	0.04	Brousse et al. (1984)
en	en = 2per + 2q	697	−67.9	3.5	−66.8	−0.3	0.01	Brousse et al. (1984)
mont	mont = lime + per + q	750	−104.8	1.7	−103.4	0.6	0.03	Brousse et al. (1984)
ak	ak = 2lime + per + 2q	750	−178.2	1.6	−172.5	0.6	0.11	Brousse et al. (1984)
crd	crd = 2per + 2cor + 5q	697	−68.9	3.0	−58.6	−0.8	0.02	Charlu et al. (1975)
spr4	spr4 = 4per + 4cor + 2q	697	−85.7	4.0	−87.7	1.4	0.04	Kleppa & Newton (1975)
di	di = lime + per + 2q	697	−146.4	1.7	−143.6	0.3	0.04	Charlu et al. (1975)
wo	wo = lime + q	697	−89.9	1.5	−87.8	0.4	0.03	Charlu et al. (1975)
pswo	pswo = lime + q	697	−83.3	1.3	−80.3	1.8	0.04	Charlu et al. (1975)
an	an = wo + cor + q	727	−13.5	1.5	−10.7	1.5	0.03	Zhu et al. (1993)
rhod	rhod = mang + q	713	−26.4	1.3	−24.4	1.3	0.22	Navrotsky & Coons (1976)
rhod	rhod = pxmn	713	0.2	2.0	0.2	−0.3	0.00	Navrotsky & Coons (1976)
zrc	zrc = q + bdy	25	−24.0	3.0	−24.0	0.0	0.01	O'Neill 2006
ky	ky = sill	701	−6.2	1.2	−6.8	0.3	0.00	Holm & Kleppa (1966)
and	and = sill	701	−2.8	1.0	−3.3	−0.4	0.01	Holm & Kleppa (1966)
hcrd	hcrd = crd + H2O	25	−42.5	3.0	−42.5	0.5	0.00	Carey & Navrotsky (1992)
clin	2clin = ames + afchl	25	−50.0	1.0	−50.0	0	1.00	This study
ep	2ep = fep + cz	25	−25.0	10.0	−25.0	0.0	0.00	Holland & Powell (1998)
ab	ab = abh	25	−14.0	0.1	−14.0	−0.0	0.98	Holland & Powell (1996)
mic	mic = san	25	−8.6	0.1	−8.6	−0.0	1.00	Holland & Powell (1996)
cg	cg = cgh	693	−8.1	1.0	−13.7	0.0	0.00	Richet et al. (1990)
stv	stv = coe	25	29.9	1.2	29.9	−0.6	0.10	Liu et al. (1996)
CO_2	CO_2 = gph + O_2	25	−393.5	0.1	−393.5	0.1	0.98	Robie & Hemingway (1985)
H_2O	$2H_2O = 2H_2 + O_2$	25	−483.6	0.0	−483.6	−0.0	1.00	Robie & Hemingway (1985)
H_2S	$H_2S = 2H_2 + S$	25	−20.6	0.6	−20.6	−0.5	0.45	Robie & Hemingway (1985)
CH_4	CH_4 = gph + $2H_2$	25	−74.8	0.3	−74.8	0	1.00	Robie & Hemingway (1985)
CO	2CO = 2gph + O_2	25	−221.1	0.3	−221.1	0	1.00	Robie & Hemingway (1985)
aqSi	aqSi = q	25	22.9	0.6	22.9	0	1.00	Holland & Powell (1998)
corL	corL = cor	2050	107.5	5.4	42.8	−0.1	0.04	Richet & Bottinga (1986)
diL	diL = di	1397	137.7	7.0	8.1	0.0	0.00	Lange et al. (1991)
faL	faL = fa	1217	90.0	3.0	14.0	−0.2	0.00	Richet & Bottinga (1986)
foL	foL = fo	1890	114.0	15.0	−61.0	0.3	0.00	Richet & Bottinga (1986)
anL	anL = an	1557	134.0	3.0	−38.2	2.3	0.01	Richet & Bottinga (1986)
abL	abL = abh	1120	64.5	3.0	−6.9	−0.8	0.00	Richet & Bottinga (1986)
kspL	kspL = san	1200	63.0	5.0	−14.4	−0.2	0.00	Richet & Bottinga (1986)
qL	qL = crst	1726	8.9	2.0	−17.0	−0.1	0.00	Richet & Bottinga (1986)
enL	enL = en	1561	155.6	12.0	−9.8	−0.3	0.00	Richet & Bottinga (1986)
woL	woL = pswo	1544	57.3	2.9	−14.5	−0.1	0.00	Richet & Bottinga (1986)
neL	neL = ne	1447	46.3	2.0	−22.2	−0.0	0.00	Richet & Bottinga (1986)
lcL	lcL = lc	1686	40.0	10.0	−38.4	0.1	0.00	Estimated, this study
cgh	cgh = neL	1526	−21.7	3.0	39.7	0.3	0.00	Estimated, this study
perL	perL = per	2825	77.0	10.0	−53.7	−0.1	0.00	This study, Howald (1992)
limL	limL = lime	2572	52.0	10.0	−57.9	−0.0	0.00	This study, Howald (1992)
lot	lot = iron + S	25	−102.6	3.0	−102.6	−0.1	0.02	Evans et al. (2010)
pyr	pyr = iron + 2S	25	−171.6	1.7	−171.6	−0.0	0.48	Evans et al. (2010)

Table 3b. Oxide and reaction calorimetry. Enthalpies (kJ), with uncertainty (σ), are given at T and 298K. e^* is the normalised enthalpy residual, and hat is the diagonal element of the hat matrix.

$$P = \frac{\kappa_0}{\kappa_0'}(y^{\kappa_0'} - 1). \qquad (6)$$

Accepting that this EOS works well at small compression, TEOS, equation (2), and third-order Birch–Murnaghan, equation (6), can be expanded in terms of $y^{\kappa_0'}$ around 1 (i.e. no compression). For TEOS to the third power in $y^{\kappa_0'} - 1$ this gives

$$P = \frac{\kappa_0}{\kappa_0'}(y^{\kappa_0'} - 1)\left(1 + \frac{1}{6}\kappa_0''\frac{\kappa_0}{\kappa_0'^{\,2}}(y^{\kappa_0'} - 1)^2 + \cdots\right), \quad (7)$$

and for third-order Birch–Murnaghan

$$P = \frac{\kappa_0}{\kappa'_0}(y^{\kappa'_0} - 1)$$

$$\left(1 + \frac{1}{6}\left\{\left(7 - \kappa'_0 - \frac{143}{9\kappa'_0}\right)\frac{\kappa'_0}{\kappa_0}\right\}\frac{\kappa_0}{\kappa_0'^2}(y^{\kappa'_0} - 1)^2 + \cdots\right),$$

(8)

with this written such that the term in curly brackets corresponds to

$$(\kappa''_0)_{bm3} = \left(\frac{\partial^2 \kappa}{\partial P^2}\right)_T\bigg|_{P_0,T_0} = \left(7 - \kappa'_0 - \frac{143}{9\kappa'_0}\right)\frac{\kappa'_0}{\kappa_0}.$$

(9)

This brings out that in third-order Birch–Murnaghan, κ''_0 is specified by κ_0 and κ'_0, in contrast to TEOS where κ''_0 is a free parameter to be determined from data (or, e.g. via the heuristic above). Note that the term in brackets in equation (9) is close to -1 for $\kappa'_0 \approx 4$, in relation to the heuristic adopted above to approximate κ''_0. Note also that fourth-order Birch–Murnaghan reduces to third order if the adjustable parameter $(\kappa''_0)_{bm4}$ is substituted with the above expression for $(\kappa''_0)_{bm3}$. Analogously fourth-order Birch–Murnaghan reduces to third-order Birch–Murnaghan, approximately, if the above heuristic, $\kappa''_0 = -(\kappa'_0/\kappa_0)$ is adopted. Similar to third-order Birch–Murnaghan, in the so-called universal EOS of Vinet (e.g. Stacey, 2005), κ''_0 is specified by κ_0 and κ'_0

$$(\kappa''_0)_{vinet} = \left(\frac{\partial^2 \kappa}{\partial P^2}\right)_T\bigg|_{P_0,T_0} = \left(-\frac{1}{2} - \frac{\kappa'_0}{4} + \frac{19}{36\kappa'_0}\right)\frac{\kappa'_0}{\kappa_0}$$

(10)

and an exactly equivalent expression to equation (8) can be written for it.

The EOS adopted here, equation (1), or with the κ''_0 heuristic, equation (5), is derived only for ambient temperature. We may extend it to high temperature by adding a thermal pressure term P_{th} to equation (2), and using the relationship (Anderson, 1997):

$$P_{th} = \int_{T_0}^{T} \alpha\kappa dT\bigg|_V.$$

(11)

For the very few phases that there are sufficient data, Anderson (1997) showed that there is no simple relationship to use for $\alpha\kappa$ as a function of T, with $\alpha\kappa$ for some phases becoming constant to high-T, while others increase or decrease slightly. Rearranging the Grüneisen relation gives $\alpha\kappa = (\gamma/V)C_v$, and noting that γ/V is nearly independent of temperature, the form of $\alpha\kappa$ should have the shape of a heat capacity function, rising to an approximately constant value. That this is approximately so may be seen for the phases tabulated in Anderson & Isaak (1995) and illustrated here for their forsterite data in Fig. 1a. Here we adopt the simplest regularization that $\alpha\kappa$ becomes constant to high-T, taking an Einstein function to represent how $\alpha\kappa$ decreases to zero as temperature decreases to 0K:
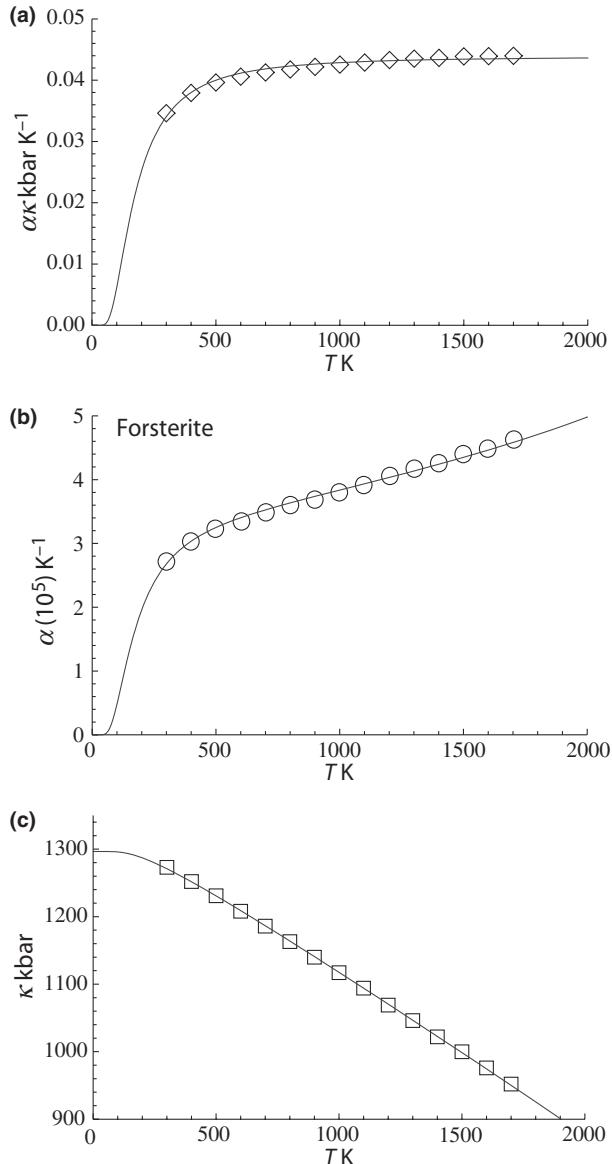
Fig. 1. For forsterite, (a) $\alpha\kappa$, (b) α and (c) κ, are shown as a function of temperature, at 1 bar. The shape of the temperature dependence is a consequence of the involvement of the Einstein function in the thermal pressure term. The symbols are data from Anderson & Isaak (1995) and the curves are Tait equation of state fits to their data. The Anderson and Isaak data are used here because they present separate values for α and κ, but for the thermodynamic data set itself we have preferred to use the experimental molar volumes listed in Appendix 1.

$$\xi = \frac{u^2 e^u}{(e^u - 1)^2}$$

with $u = \theta/T$, and θ the Einstein temperature. For equation (11), $\alpha\kappa$ is written as $\alpha\kappa = n\xi$, where n is a normalization constant, equal to $\alpha\kappa$ at infinite temperature, so $n = \alpha_0\kappa_0(1/\xi_0)$, and $\alpha\kappa = \alpha_0\kappa_0(\xi/\xi_0)$, with α_0, κ_0 and ξ_0 being the values of α, κ and ξ at ambient temperature. Then, using equation (11)

$$P_{th} = \int_{T_0}^{T} \alpha_0 \kappa_0 \frac{\xi}{\xi_0} dT = \alpha_0 \kappa_0 \frac{1}{\xi_0} \int_{T_0}^{T} \alpha_0 \kappa_0 \xi dT$$
$$= \alpha_0 \kappa_0 \frac{\theta}{\xi_0} \left(\frac{1}{e^u - 1} - \frac{1}{e^{u_0} - 1} \right).$$

Writing $P = P|_{T_0} + P_{th}$, this may be rearranged in volume explicit form as:

$$\frac{V}{V_0} = 1 - a(1 - (1 + b(P - P_{th}))^{-c}). \quad (12)$$

Integrating V with respect to P gives the G contribution

$$G|_{P,T} - G|_{P_0,T}$$
$$= PV_0 \left(1 - a + \frac{a\left((1 - bP_{th})^{1-c} - (1 + b(P - P_{th}))^{1-c}\right)}{b(c-1)P} \right) \quad (13)$$

This EOS contains an implicit thermal expansion at ambient pressure conditions. At $P = 0$, the thermal expansion α is:

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P \Big|_{P_0}$$
$$= \alpha_0 \frac{\xi}{\xi_0} \left(\frac{1}{(1 - bP_{th})(a + (1 - a)(1 - bP_{th})^c)} \right).$$

The compressibility is also a function of temperature and pressure, given by

$$\kappa = -V \left(\frac{\partial P}{\partial V} \right)_T$$
$$= \kappa_0 (1 + b(P - P_{th}))(a + (1 - a)(1 + b(P - P_{th}))^c).$$

The form of TEOS for thermal expansion is shown in Fig. 1b, with the characteristic shape provided by the Einstein function, and in Fig. 1c the implicit negative temperature dependence of the bulk modulus. These curves are fits of TEOS to the experimental data for forsterite tabulated in Anderson & Isaak (1995). Use of the expressions above necessitates a value for the Einstein temperature θ for each end-member. Only very rarely are accurate thermal expansion data made at temperatures below ambient, thus making direct determination of θ by data fitting effectively impossible. We have found that the value of θ needs only to be known approximately, and affects mainly the low temperature thermal expansion and volume behaviour. An approximate value for θ is derived for each end-member from the measured entropy (or via Holland, 1989). Thus for end-member i the value of θ_i is given by the empirical relationship, $\theta_i = 10636/(S_i/n_i + 6.44)$, where S_i is the molar entropy (in J K^{-1}mol^{-1}) of i and n_i is the number of atoms in i.

TEOS relates the volume at any P–T to the standard state volume with only three adjustable parameters (κ_0, κ_0' and α_0). The data set includes a term for κ_0'' to anticipate for the rare occasion where a value other than $\kappa_0'' = -(\kappa_0'/\kappa_0)$ might be warranted. Fitting TEOS to volume data for phases where volumes have been measured to very high pressures and temperatures (grossular garnet, stishovite and periclase) and for phases where simultaneous high temperature and high pressure measurements have been made (magnesite, dolomite, aragonite, brucite, grossular, andradite, jadeite and muscovite) shows that it behaves very well (see Fig. 3), in fitting all the data, whether at ambient pressures and high temperatures, ambient temperature and high pressures or at combined high pressures and temperatures.

As an example, the data for stishovite to 2300 kbar are shown in Fig. 2a where the lower pressure data (up to 500 kbar) of Andrault et al. (2003) have been fitted with TEOS and, on extrapolation, appear to fit nicely the very high pressure data of Luo et al. (2002). The extrapolatory power of TEOS is seen to be excellent. Also shown in Fig. 2b is the volume thermal expansion data and the good form of the fit to the data. The way
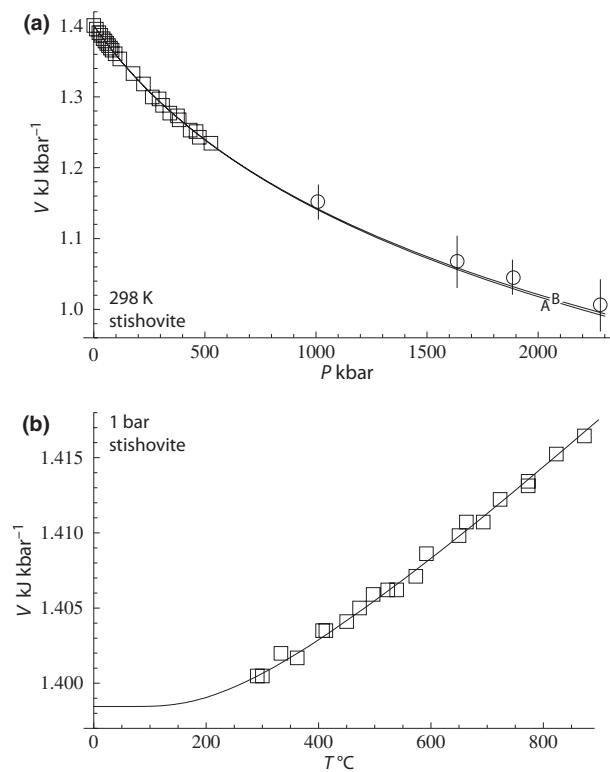
Fig. 2. Stishovite volume data. (a) Precise data of Andrault et al. (2003) up to 500 kbar (squares) and the very high pressure data of Luo et al. (2002) to 2500 kbar (circles with error bars). Error bars for the lower pressure data are smaller than the symbols. Calculated curves: A – fit to low pressure data of Andrault et al., only; B – fit to all data with experimental uncertainties. (b) Volume expansion data of Ito et al. (1974) and the calculated fit.
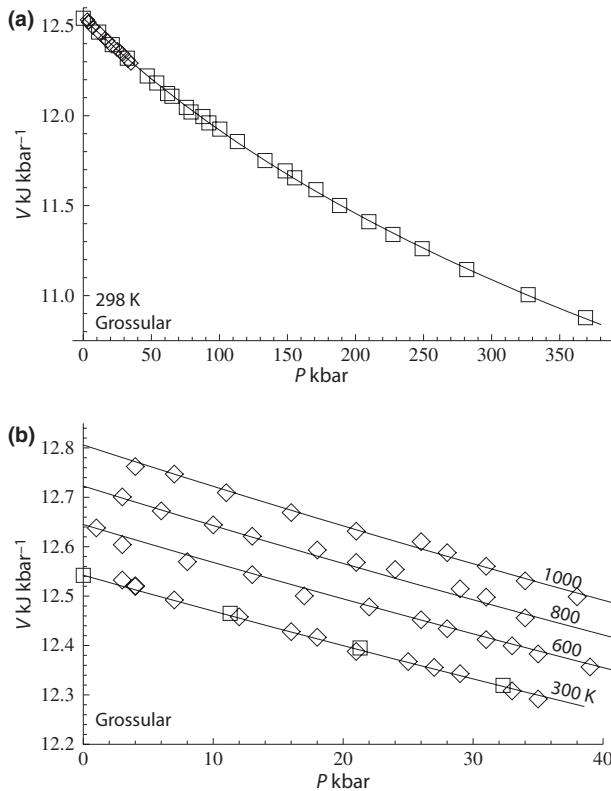
Fig. 3. Experimental data of Pavese *et al.* (2001a,b) and the fitted curves from Tait equation of state. (a) The 298 K data to 360 kbar; (b) the high pressure–high temperature data to 1000 K and 40 kbar.

volume levels off at low temperature is a reflection of the way thermal expansion drops off to zero (Fig. 1) at low temperatures. Figure 3 illustrates the fit of the high pressure volume data for grossular from Pavese *et al.* (2001a,b), first as a function of pressure to over 350 kbar, and second as a function of both pressure and temperature to 1000 K and 40 kbar. TEOS appears to have a form that is well suited to represent such data.

Although using TEOS in place of Murnaghan makes little difference to the derived thermodynamic data, two related factors have led to significant improvement in the overall data fitting. First, not restricting the value of κ' to 4.0 has allowed better extrapolations to very high pressure, and second (and more significantly) the incorporation of the implicit thermal expansion and the consequent temperature dependence of bulk modulus κ through the thermal pressure has made the volume behaviour at high pressures and temperatures more reliable.

Equation of state for fluid phases

Pure fluid species

The EOS for fluids used in HP98 was the CORK equation (Holland & Powell, 1991) which was derived

for the purposes of extrapolation to high pressures. The equations of Pitzer & Sterner (1995) have now been substituted in place of CORK for both H_2O and CO_2 for the following two reasons: (i) the CORK expressions did not fit the volumes for H_2O in the region of the critical point closely (fig. 2 of Holland & Powell, 1991), and (11) the CORK expressions involved a piecewise continuous transition in compressibility at 2 kbar which made for difficulties in root-finding algorithms for free energy. The differences between CORK and Pitzer & Sterner (1995) volumes and free energies are minor for H_2O, and virtually indistinguishable for CO_2. Change to the Pitzer & Sterner equations necessitated minor compensating adjustments in entropy for a number of hydrous phases. The CORK equation is, however, retained for calculating volumes and fugacities of CO, CH_4, H_2, S_2 and H_2S because of its ease in application of the corresponding-states principle. The constants for the CORK expressions for COH gases are taken from Holland & Powell (1991), table 2. For S_2 and H_2S the critical constants are taken from Reid *et al.* (1977) and used with equation (9) in Holland & Powell (1991).

Mixing in fluids

Mixtures of gases, such as H_2O and CO_2, as well as other species in the COHS system are now handled via a Van Laar model as described in Holland & Powell (2003), in which the volumes of the end-members control the asymmetry parameters directly, which allows a controlled extrapolation to very high pressures. Because the mixing properties are very similar to those generated by the modified Redlich–Kwong EOS, the latter were used to derive Van Laar parameters for all other COHS gas end-members. The COH a_{ij} values are from Holland & Powell (2003), and the remaining ones from Evans *et al.* (2010). This change has led to an overall reduction in the misfit between mixed silicate-carbonate experiments and thermodynamic data.

The earlier HP98 paper also involved aqueous solution thermodynamic properties, based on a modification of the Anderson density model (Anderson *et al.* 1991) which is retained here. A problem never addressed satisfactorily for aqueous fluids at geological conditions is that of the transition from the dilute region, where Debye–Huckel type (infinite dilution standard state) models are typically used, to the high ionic strength electrolytes such as saturated salt solutions where Raoult's Law type standard states are used. Progress towards resolving this has been made by Evans & Powell (2005), who devised a model which slides smoothly between the two types of behaviour, allowing a single activity–composition expression to be used for mixed aqueous electrolytes and dissolved COHS gas species. An example where such calculations have been used is given below and further examples may be found in Evans *et al.* (2010).

Use of univariant and divariant experimentally determined equilibria involving solid solutions

A new feature of this data set is the use of univariant equilibria in solving for enthalpies and mixing properties of solid solutions simultaneously. As an example, the univariant reaction sapphirine + quartz = orthopyroxene + sillimanite in the MAS system has been determined experimentally by Newton (1972), Hensen, (1972) and Chatterjee & Schreyer (1972). Along the length of this reaction, from 1050 °C to 1475 °C, the compositions of pyroxene and sapphirine change. By fitting simultaneously to a set of independent reactions between the end-members, the enthalpies of all end-members (spr4, spr5, en, mgts, sill, q) may be optimized together. Consideration of the variation of mixing properties, via the interaction energies ($W_{en-mgts}$ and $W_{spr4-spr5}$) also allowed these values to be refined.

As well as univariant reactions, many divariant equilibria were also fitted in the same manner, allowing easy refinement of mixing energies for a number of solid solutions involved across different reactions. This was particularly helpful in refining the properties of the chlorites in MASH (clin, ames, afchl) through the experiments of Baker & Holland (1996), Jenkins (1981) and Jenkins & Chernosky (1986). It has also been used in a number of Fe–Mg and other exchange equilibria between silicates and between silicates and carbonates.

Order–disorder and Landau models

Treatment of order–disorder in HP98 was done with a Landau tricritical model to account for the sharp lambda peaks in the heat capacity exhibited at the phase transition temperatures in such end-members. This was convenient in making a simple representation of the order–disorder characteristics in stoichiometric phases, but is not satisfactory when dealing with solid solutions involving disordering behaviour because the Landau expansion does not correctly incorporate the configurational entropy associated with cation ordering. We now represent many order disorder transitions with a macroscopic Bragg–Williams type of model, the SF or symmetric formalism of Holland & Powell (1996a,b)). End-members now characterized by the SF model include sillimanite, gehlenite, cordierite, albite, K-feldspar, anorthite, spinel, hercynite, dolomite, ankerite. Using the SF model allows solid solutions involving these end-members to be constructed with standard configurational entropies and thus activity–composition expressions, making them much easier to be used in multicomponent solid-solution phase equilibrium calculations.

Melt species

Following on from the initial modelling of simple granitic systems (Holland & Powell, 2001) and its extension into partial melting of pelitic compositions (White et al., 2001), the data for melt components has improved considerably over those initially presented in HP98. The principal differences lie in enforcing the heat of melting as a constraint, where known, in addition to fitting the experimental $P-T$ curves and changes introduced through the relaxation of $\kappa' = 4$ constraint. Many melt end-members now have their properties consistent with experiments which go to high pressures (e.g. qL to 60 kbar, faL to 70 kbar, foL to 153 kbar). In addition, several new melt end-members have been introduced since HP98 [perL (MgO), limL (CaO), corL (Al_2O_3), wolL ($CaSiO_3$), neL ($NaAlSiO_4$), lcL ($KAlSi_2O_6$), KCl and NaCl liquids].

The new thermal expansion expressions used in TEOS are not suitable for melt end-members, as they are based on a vibrational model. The experimental data currently available do not warrant anything more elaborate than constant thermal expansion at the temperatures investigated (Lange, 1997), and so the constant thermal expansion and linear temperature dependence of bulk modulus as in HP98 is retained for melt end-members.

NEW END-MEMBERS IN THE DATA SET

The following is a brief outline of additions to the data set in a mineral group or system context; all the new end-members are indicated in Table 1. Changes in activity–composition relations that are implicit in data set generation for these and other end-members are included below in the next subsection.

For the first time, sulphides and sulphur-bearing minerals and fluid species have been incorporated into the data set. The details are published in Evans et al. (2010) and encompass the solid phases pyrite (FeS_2), troilite (FeS), pyrrhotites (solid solution between hypothetical end-member trot, FeS and vacancy-bearing trov, $Fe_{0.875}S$), anhydrite ($CaSO_4$), elemental sulphur S, gaseous S_2 and H_2S as well as aqueous species HS^-, HSO_3^-, SO_4^{2-} and HSO_4^-. Troilite is described as a low temperature form (lot) from 298 K up to 420 K and a high temperature form (tro) above 420 K. These solids are complicated, involving two lambda transitions in troilites (one at 420 K, one at 598K) and a lambda transition in trov at 595 K. Examples of phase diagram calculations, including pseudosections involving mixed silicates, carbonates and sulphides may be found in Evans et al. (2010).

Several new pyroxene end-members are now included. Clinoenstatite (cen, $Mg_2Si_2O_6$) and proto-enstatite (pren) are new end-members whose enthalpy of formation and entropy are derived from experiments of Atlas (1952), Chen & Presnall (1975) and Boyd & England (1965). A calcium-eskola pyroxene end-member (caes, $Ca_{0.5}\square_{0.5}AlSi_2O_6$) is introduced to account for vacancy substitutions seen in calcic pyroxene at high pressures, and is calibrated on the experimental results of Gasparik (1984). The activity

model used assumes that some short-range ordering between Si–Al on tetrahedral and Mg–Al on octahedral sites can be accommodated by reducing the tetrahedral entropy of mixing to a quarter of the configurational contribution. This then gives the activities of caes and cats in a binary pyroxene as $a_{caes} = 2X_{Ca,M2}^{0.5}X_{\square,M2}^{0.5}X_{Si,T}^{0.5}\gamma_{caes}$ and $a_{cats} = 1.414213$ $X_{Ca,M2}X_{Si,T}^{0.25}X_{Al,T}^{0.25}\gamma_{cats}$ with activity coefficients from a regular solution with $W_{caes,cats} = -15$ kJ.

Chromium-bearing end-members are now included: the oxide eskolaite (esk, Cr_2O_3), the pyroxene kosmochlor (kos, $NaCrSi_2O_6$), the garnet knorringite (knor, $Mg_3Cr_2Si_3O_{12}$) and the spinel picrochromite (picr, $MgCr_2O_4$). We have fitted the experiments on the exchange reaction $2jd + picr = 2kos + sp$, assuming that jd–kos is ideal and that the sp–picr solid solution is non-ideal with a symmetrical interaction energy $W_{picr,sp} = 25$ kJ (Carroll Webb & Wood, 1986). We have not added a large entropy increment to knorringite (as done by Klemme, 2004, and Klemme et al., 2000, who assumed that the low-T anomaly seen in the heat capacity of uvarovite applies to knorringite), and thus we have been able to fit the slope and positions of both the reactions $2knor = 3en + 2esk$ (Turkin et al., 1983) and $knor + fo = picr + 2en$ (Klemme, 2004). The P–T slope of the experimental brackets of Irifune et al. (1982) for $2knor = 3en + 2esk$ are incompatible with the other studies and with the thermodynamic data.

Carnegieite and high-carnegieite (cg, cgh, $NaAlSiO_4$) are fitted to the experiments of Bowen & Greig (1925), Greig & Barth (1938) and Cohen & Klement (1967). These data depend on those for nepheline, and are in turn used to determine those for nepheline liquid and sodalite.

Stilpnomelane with end-members ferrostilpnomelane (fstp, $K_{0.5}(Fe_5Al)[Si_8Al]O_{22}(OH)_{4.5}\cdot4H_2O$) and magnesiostilpnomelane (mstp, $K_{0.5}(Mg_5Al)[Si_8Al]O_{22}(OH)_{4.5}\cdot4H_2O$) is now included. The formula for stilpnomelane is not fully known, but the chosen formula units are based on Eggleton (1972) simplified and normalized to 8 Si pfu. The activities are given by assuming that octahedral Al resides on one site, with Fe and Mg mixing on five sites, so that $a_{fstp} = X_{Fe}^5\gamma_{fstp}$ and $a_{mstp} = (1 - X_{Fe})^5\gamma_{mstp}$ with activity coefficients from a regular solution with $W_{fstp,mstp} = 20$ kJ. The data for the end-members are derived from the reaction $28fstp = 14ann + 5grun + 21alm + 79q + 156H_2O$ and the partitioning of Fe and Mg between stilpnomelane and chlorite (Miyano & Klein, 1989).

Minnesotaite [minn, $Fe_3Si_4O_{10}(OH)_2$] and its Mg equivalent [minm, $Mg_3Si_4O_{10}(OH)_2$] are derived from the experiments of Engi (1983) for the reaction $2minn = 3fa + 5q + 2H_2O$ along with data for partitioning of Fe and Mg between carbonate and minnesotaite of Klein (1974). The activities are given by assuming that Fe and Mg mix on three sites, so that $a_{minn} = X_{Fe}^3\gamma_{minn}$ and $a_{minm} = (1 - X_{Fe})^3\gamma_{minm}$ with activity coefficients from a regular solution with $W_{minn,minm} = 12$ kJ.

Greenalite [glt, $Fe_3Si_2O_5(OH)_4$] was derived using reactions $glt + 2q = minn + H_2O$ and $2glt + 5min = 3grun + 6H_2O$ using the constraints discussed by Rasmussen et al. (1998).

Considering pumpellyite, in addition to the original MgAl pumpellyite in HP98 data are presented for a solid solution between three end-members, the MgAl end-member [mpm, $Ca_4MgAlAl_4Si_6O_{21}(OH)_7$], the FeAl end-member [fpm, $Ca_4FeAlAl_4Si_6O_{21}(OH)_7$] and the $FeFe^{3+}$ end-member julgoldite [jgd, $Ca_4FeFe_5^{3+}Si_6O_{21}(OH)_7$] are included. As in HP98, the mpm end-member is derived from the experiments of Schiffman & Liou (1980), while data for the iron analogue are taken from the Fe–Mg partition between pumpellyite and chlorite of Evans (1990). The jgd end-member is derived from the Fe^{3+}–Al partitioning data between epidote and pumpellyite given by Cho et al. (1986). Ordering of Mg and Fe onto a single M2a site is assumed for these pumpellyites and activities are given by

$$a_{mpm} = X_{Mg,M2a}X_{Al,M2b}X_{Al,M1}^4,$$
$$a_{fpm} = X_{Fe,M2a}X_{Al,M2b}X_{Al,M1}^4$$

and

$$a_{jgd} = X_{Fe,M2a}X_{Fe^{3+},M2b}X_{Fe^{3+},M1}^4.$$

Talc now includes a pyrophyllitic end-member [tap, $Al_2Si_4O_{10}(OH)_2$] fitted to the experimental compositions reported by Newton (1972). All experiments involving aluminous talc (e.g. Chernosky, 1978; Massonne et al., 1981; Massonne, 1989; Massonne & Schreyer, 1989; Hoschek, 1995) have been fitted with a model involving both the tschermak substitution and the pyrophyllite-like substitution.

Prehnite now includes a ferric end-member [fpre, $Ca_2AlFeSi_3O_{10}(OH)_2$]. Ferric iron is assumed to substitute for Al on one octahedral site only, and the activity relations simplify to $a_{fpre} = X_{Fe}\gamma_{fpre}$ and $a_{pre} = (1 - X_{Fe})\gamma_{pre}$ with activity coefficients from a regular solution with $W_{pre,fpre} = 1$ kJ. The data for fpre are derived from the Fe^{3+}–Al partitioning data between epidote and prehnite given by Cho et al. (1986).

The halide minerals halite (hlt, NaCl) and sylvite (syv, KCl) and their molten equivalents (hltL and syvL) are included in the data set. The enthalpies of formation of halite and sylvite are taken from Robie & Hemingway (1995), and the molten end-members from fitting to the melting curves to 20 kbar pressure from Clark (1966). The experimental data of Aranovich & Newton (1997, 1998) involving concentrated brines (KCl and NaCl) in equilibrium with brucite and periclase may now be reproduced by direct calculation with the new data set.

Sapphirine has been a difficult phase to quantify thermodynamically, largely because available experiments have not been able to involve characterization of the composition of the sapphirine. A new model for sapphirine is adopted here, based on the revision of

Kelsey *et al.* (2004), which involves the 2:2:1 end-members spr4 ($Mg_4Al_8Si_2O_{20}$) and fspr ($Fe_4Al_8Si_2O_{20}$) and the 3:5:1 end-member spr5 ($Mg_3Al_{10}SiO_{20}$). The activity relations, as discussed below, are found by optimization of the fit to the experimental data on sapphirine equilibria (Boyd & England, 1959; Hensen, 1972; Newton, 1972; Seifert, 1974; Doroshev & Malinovskiy, 1974; Malinovsky & Doroshev, 1975; Ackermand *et al.*, 1975; Arima & Onuma, 1977; Perkins *et al.*, 1981; Podlesskii, 1996; Fockenberg, 2008). In the fitting process, the compositions of sapphirine are predicted; they fall in the range $x_{spr5} = 0.36$–0.45 for most of the high pressure experiments, but do rise to $x_{spr5} = 0.60$ when coexisting with mullite. The fit to all these experiments is now quite good. Although a similar quality fit to the H_2O-absent subset of the data in MAS was made by Podlesskii *et al.* (2008), their data set was only constrained within this subset of MAS rather than by all the other phases and equilibria used in this study.

Mullite is a complex solid solution involving an end-member of sillimanite composition (Al_2SiO_5) into which the substitution $Si + 1/2O = Al + 1/2\square$ occurs. This could in principle extend from Al_2SiO_5 ($x = 0$) to a Si-free end-member $Al_2AlO_{4.5}$ ($x = 1$), where x is the amount of the substitution above, but in practice rarely extends beyond $x = 0.5$ (Cameron, 1977). We have elected to use this intermediate composition (amul, $Al_2Si_{0.5}Al_{0.5}O_{4.75}$) as the aluminous end-member in mullite in part because natural compositions rarely become more aluminous than this and in part because of the strong ordering of Al + Si and O + $\square$. These two different ordering patterns (Al + Si and O + $\square$) lead to two different symmetries, P_cnnm and P_cbnm and an overall structure with an incommensurate modulation (Angel *et al.*, 1991). Rather than attempt a detailed, and probably incorrect, activity model for this solid solution we take a pragmatic approach that assumes that the high degrees of Al,Si and $\square$,O ordering can be approximated by a simple two-site mixture of the end-members, such that $a_{amul} = x_{amul}^2 \gamma_{amul}$ and $a_{smul} = (1 - x_{amul})^2 \gamma_{smul}$. Mullite enthalpies (for smul and amul) and the interaction energy ($W_{smul,amul}$) are derived from the experiments on the reactions muscovite + quartz = mullite + sanidine + H_2O (Segnit & Kennedy, 1961), pyrophyllite = mullite + quartz + H_2O (Carr & Fyfe, 1960), cordierite + corundum = sapphirine + mullite (Seifert, 1974) and the melting equilibria cristobalite + mullite + liquid and mullite + corundum + liquid (Klug *et al.*, 1987). The calculated compositions of mullite are close to that of sillimanite at low temperatures and reproduce the aluminous compositions observed by Klug *et al.* (1987) at the melting temperatures. Calculations involving this mullite are included below.

Lizardite, one of the serpentine group minerals (with antigorite and chrysotile) is now included in the data set. Its properties are assumed to be like those of chrysotile, but with slightly smaller values for volume

and entropy (Evans, 2004; Hilairet *et al.*, 2006). We have accordingly also lowered the heat capacity and compressibility of lizardite. The enthalpy for lizardite, following the arguments of Evans (2004), is derived from accepting that lizardite transforms (metastably) to chrysotile between 413 and 431 °C at 2 kbar (Chernosky, 1975). The calculated stability of lizardite extends only up to 170 °C at 2 kbar where it breaks down to antigorite + brucite. More work needs to be done to determine unambiguously the stability of lizardite relative to chrysotile. The new measured compressibilities for lizardite and chrysotile (Hilairet *et al.*, 2006) and for antigorite (Bose & Navrotsky, 1998) are used, allowing good fits to antigorite in very high pressure experiments (Wunder & Schreyer, 1997; Bose & Navrotsky, 1998; Pawley, 1998).

The new modified TEOS for solids allows reliable extrapolation of mineral volumes to very high pressures, and so we are starting to accumulate a set of thermodynamic data for phases at deep mantle pressures and temperatures. We present preliminary data on the end-members ferropericlase (fper, FeO), Mg-wadsleyite (mwd, Mg_2SiO_4), Fe-wadsleyite (fwd, Fe_2SiO_4), Mg-ringwoodite (mrw, Mg_2SiO_4), Fe-ringwoodite (frw, Fe_2SiO_4), Mg-perovskite (mpv, $MgSiO_3$), Fe-perovskite (fpv, $FeSiO_3$), Al-perovskite (apv, $AlAlO_3$), Ca-perovskite (cpv, $CaSiO_3$), Mg-akimotoite (mak, $MgSiO_3$), Fe-akimotoite (fak, $FeSiO_3$), majorite garnet (maj, $Mg_4Si_4O_{12}$), high-pressure clinoenstatite (hen, $Mg_2Si_2O_6$), Ca-Si-titanite (cstn, $CaSi_2O_5$), walstromite (wal, $CaSiO_3$), MgSi-corundum (mcor, $MgSiO_3$), K-cymrite (kcm, $KAlSi_3O_8.H_2O$), wadeite (wa, $K_2Si_24O_9$) and hollandite (hol, $KAlSi_3O_8$). Experimental details for the equilibria used to extract the data may be found in Appendix 2. These data are tied into, and are consistent with the thermodynamic data for end-members at lower *P–T* (crustal) conditions.

Mixing model changes

Since HP98 we have changed slightly some solid solution models used in the data set generation. Only the ones which directly affect the fitted enthalpies are discussed here.

For MgAl orthopyroxene, the entropy of mixing is taken over octahedral and tetrahedral sites rather than the earlier octahedral site only model as in Wood & Banno (1973). This is done to facilitate multi-component extensions to the model involving other substitutions. We take only a one-fourth of the full tetrahedral site entropy as an approximation for Al–Si and Mg–Al ordering, writing the activities of en and mgts as $a_{en} = X_{Mg,M1}X_{Si,T}^{1/2}\gamma_{en}$ and $a_{mgts} = \sqrt{2}X_{Mg,M1}X_{Si,T}^{1/4}X_{Al,T}^{1/4}\gamma_{mgts}$, with the activity coefficients taken from a macroscopic regular model (symmetric formalism; Powell & Holland, 1993a,b) with $W_{en,mgts} = 13.0 - 0.15P$ kJ derived from the measurements of Al

solubility in aluminous pyroxenes coexisting with other phases in the data set, principally garnet and spinel.

For tremolite–tschermakite amphibole, we now take the tetrahedral contribution to be only one-fourth that of the full configurational entropy, as in the pyroxenes above, as was done in Diener *et al.* (2007) to make a comprehensive amphibole mixing model from natural and experimental data. Allowing a small cummingtonite component, the activities are written as

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

$$a_{ts} = 2 X^2_{Ca,M4} X^2_{Al,M2} X^{1/2}_{Si,T} X^{1/2}_{Al,T} \gamma_{mgts} \text{ and}$$

$$a_{cumm} = X^2_{Mg,M4} X^2_{Mg,M2} X_{Si,T1} \gamma_{mgts}$$

with the activity coefficients taken from a regular model with $W_{tr,ts} = 20$ kJ, $W_{tr,cumm} = 45$ kJ and $W_{ts,cumm} = 70$ kJ derived from the experiments of Jenkins (1994), Hoschek (1995) and the results of Diener *et al.* (2007).

Chlorite has been slightly simplified since HP98, keeping the basic model the same, but relaxing the degree of ordering required slightly. This has come about in part due to using the X-ray calibration of chlorite compositions from Jenkins & Chernosky (1986), Roots (1994) and Shirozu & Momoi (1972) rather than the data of Baker & Holland (1996) which yielded slightly lower volumes than the other studies. This has affected the adopted molar volumes of the clin, ames and afchl end-members. The molar volume of daph has been changed from the old value (213.4 J bar^{-1}) taken from Helgeson *et al.* (1978) and Holdaway & Lee (1977) to 216.2 J bar^{-1} from Parra *et al.* (2005) as, even though their measurements are quite scattered, they are in better agreement with the measured data of James *et al.* (1976), Vidal *et al.* (2001) and with simple exchange models involving chlorite and biotite, olivine, orthopyroxene and chloritoid. In addition the entropy of clinochlore and daphnite have been taken from Bertoldi *et al.* (2007) with an extra 11.5 J K^{-1} added for tetrahedral site configurational entropy. The entropies of afchl and ames were adjusted slightly in fitting to the phase equilibrium experimental results. The heat capacities were taken from Bertoldi *et al.* (2007), the thermal expansion from Nelson & Guggenheim (1993) and compressibility from Pawley *et al.* (2002). The mixing energies are very similar to those of the earlier data set $W_{afchl,clin} = 17$ kJ, $W_{afchl,ames} = 20$ kJ and $W_{clin,ames} = 17$ kJ with an enthalpy of -50.0 kJ for the internal equilibrium afchl + ames = 2 clin.

Epidote has also been slightly modified since HP98. The heat capacities of zoisite and clinozoisite have been refitted to high temperatures using a simple vibrational model. The values for both polymorphs are now very similar, with clinozoisite being very slightly lower than zoisite. The heat capacity of epidote is similarly extrapolated to high temperatures, fitting the experimental data of Kiseleva *et al.* (1974) and the entropy of epidote is taken from Kiseleva & Ogorodova (1987). The entropy of cz and fep end-members are adjusted slightly to fit phase equilibrium data for the reaction epidote = anorthite + garnet + hematite + quartz + H$_2$O from Holdaway (1972) and Liou (1973). The activity model is the same as in HP98, but the mixing energies are changed (simplified) to $W_{cz,fep} = 3$ kJ, $W_{cz,ep} = 1$ kJ and $W_{ep,fep} = 1$ kJ. These small values are based on a value for $W_{Al,Fe^{3+}} = 2$ kJ for Al–Fe^{3+} mixing in grossular-andradite garnet derived from fitting the experiments of Holdaway (1972) for coexisting garnet + anorthite + wollastonite + quartz. The enthalpy of the internal equilibrium fep + cz = 2ep is -25.0 kJ to account for the degree of order in natural epidote (Dollase, 1973; Bird & Helgeson, 1980).

Talc now incorporates a pyrophyllite as well as a tschermak substitution. The mixing properties are assumed to be given by an ideal solution of the three end-members, ta, tats and tap (see above). The activities are given by

$$a_{ta} = X_{Mg,M1} X^2_{Mg,M23} X^2_{Si,T2},$$

$$a_{tap} = X_{\square,M1} X^2_{Al,M23} X^2_{Si,T2} \text{ and}$$

$$a_{tats} = 16 X_{Mg,M1} X_{Mg,M23} X_{Al,M23} X_{Al,T2} X_{Si,T2}$$

Sapphirine, following the treatment in Kelsey *et al.* (2004) involves two end-members spr4 and spr5 (see above) related by a tschermak substitution. The activities for the binary are given by $a_{spr4} = X^2_{Mg,M3} X_{Si,T3} \gamma_{spr4}$ and $a_{spr5} = X^2_{Al,M3} X_{Al,T3} \gamma_{spr5}$, with gammas found from a regular model with $W_{spr4,spr5} = 10.0 - 0.2P$ kJ.

Pyrrhotite is treated as a non-ideal solid solution of trov and trot (see above), with activities given by $a_{trov} = 1.4576 X^{7/8}_{Fe,M2} X^{1/8}_{\square,M2} \gamma_{trov}$ and $a_{trot} = X_{Fe,M2} \gamma_{trot}$. The activity coefficients may be found from a regular model with $W_{trov,trot} = -3.19$ kJ. More details may be found in Evans *et al.* (2010).

There are many additional changes to the data set, mainly relating to changes to thermodynamic parameters taken as assumed in data set generation (entropy, volume, heat capacity, etc.), and in the use of newer experimental data on phase stability that can be included in data set generation. Some changes are very minor and may be found by comparison with the tables in HP98, whereas others are more significant and are listed briefly in Appendix 3. One change that may be of greatest import to metamorphic petrologists is highlighted here, and concerns the aluminium silicate phases kyanite, andalusite and sillimanite. The choice of the Holdaway (1971) experiments, as opposed to those of Richardson *et al.* (1969) for the and = sill reaction is no longer arbitrarily imposed as a constraint. Instead, we prefer to return to the situation in our earlier data sets (Holland & Powell, 1985;

1998) in which no and = sill experimental brackets were used, and a triple point is allowed to emerge from the multitude of other equilibria involved in the data set. The calculated triple point from data in this study lies at 4.3 kbar, 534 °C, in between that of Holdaway (1971) and Richardson *et al.* (1969). The fact that the relaxation of the and = sill constraint yields a triple point almost identical to that advocated by Pattison *et al.* (2002) on the basis of field, petrographic and phase equilibria arguments, suggested to us that the combined reaction data used in the regression provide a reasonable justification of this decision.

EXAMPLES OF CALCULATED PHASE EQUILIBRIA

The following examples are of calculated phase equilibria highlighting new features of the internally consistent data set. All calculations were undertaken with THERMOCALC (Powell & Holland, 1988, 1998), and the activity–composition relations adopted are given in Table S2.

Sapphirine

Calculations in the literature on sapphirine phase equilibria using the Holland and Powell data set have used a special upgrade of the HP98 data set (tc-ds55s), for example, Kelsey *et al.* (2004), Baldwin *et al.* (2007) and Taylor-Jones & Powell (2010). The origin of the

upgrade was that the fitting of the available experimental data in the fifth update of Holland & Powell (1998) in November 2003, tc-ds55 – the extant standard data set – was considered to be partially degraded by inclusion of the sapphirine experimental data. Now, as discussed above, a successful incorporation of the sapphirine end-members into the data set has been undertaken.

Sapphirine equilibria are important geologically as they have been used widely in higher temperature rocks in which sapphirine-bearing mineral assemblages occur to estimate P–T conditions of metamorphism. Phase equilibria in the simple systems MgO–Al_2O_3–SiO_2 (MAS) and MgO–Al_2O_3–SiO_2–H_2O (MASH) are experimentally determined, so they in turn constrain the corresponding thermodynamic data of the mineral end-members Figure 4 shows the calculated phase equilibria in the systems MgO–Al_2O_3–SiO_2, with the ultimate stability of sapphirine, and sapphirine + quartz indicated. The main invariant points (a–d) are at a slightly lower pressure (< 0.4 kbar) and higher temperature (< 30 °C) than those calculated with tc-ds55s. Note that mullite-bearing equilibria, at the highest temperature on Fig. 4, can now be calculated.

Not specifically shown in Fig. 4 are the corresponding MASH equilibria as these can be easily envisaged in Fig. 4. Addition of H_2O to MAS affects only equilibria involving cordierite, at least until melt is stabilized. Thus, on addition of H_2O, the MAS invariant points become MASH univariant lines
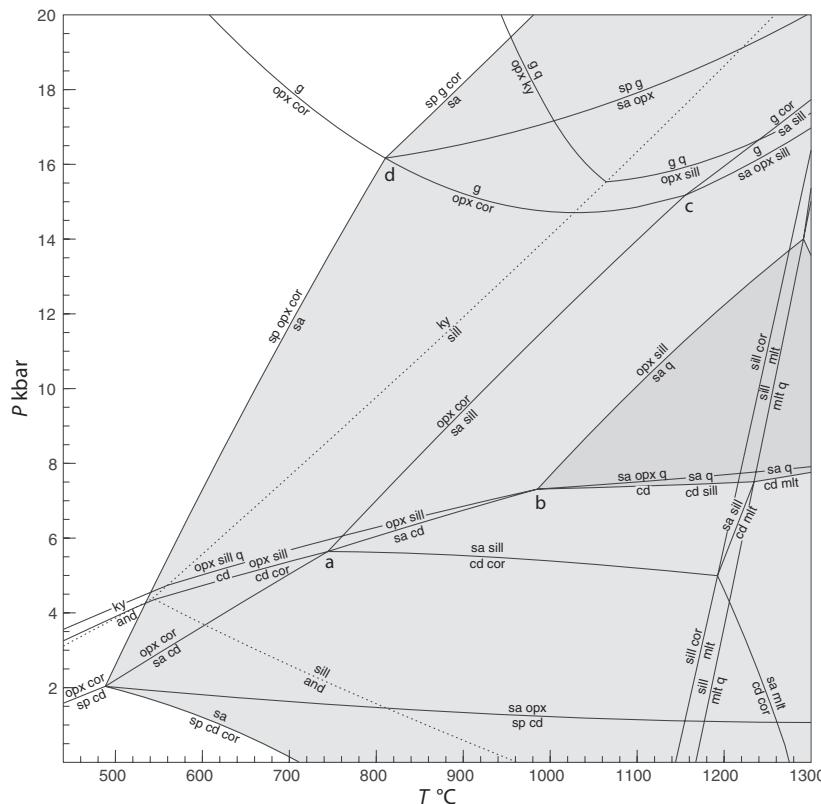
Fig. 4. P–T projection for sapphirine equilibria in the MgO–Al_2O_3–SiO_2 system, showing the maximum stability fields for sa (light shading) and sa + q (darker shading). Phases: g, garnet; sa, sapphirine; cor, corundum; sp, spinel; opx, orthopyroxene; ky, kyanite; and, andalusite; sill, sillimanite; cd, cordierite; mlt, mullite; q, quartz. a, b, c, d are invariant points from which FeO–MgO–Al_2O_3–SiO_2 univariants emerge (see Fig. 5). For *a–x* relationships used, see Table S2.
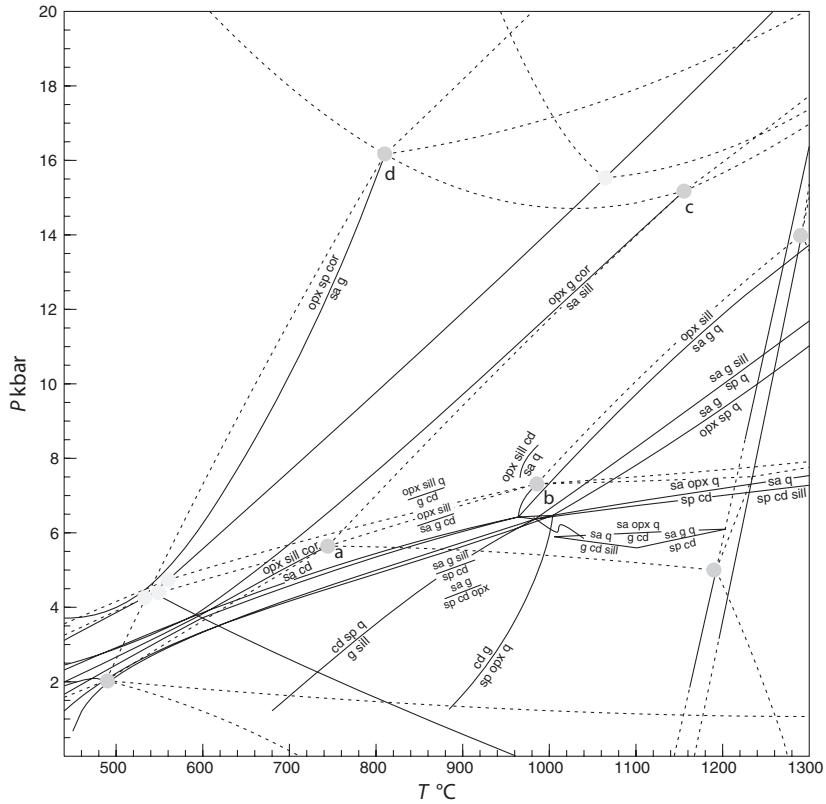
Fig. 5. *P–T* projection for sapphirine equilibria in the FeO–MgO–Al$_2$O$_3$–SiO$_2$ system (full curves) and the MgO–Al$_2$O$_3$–SiO$_2$ subsystem (dashed curves). a, b, c, d are invariant points in MAS from which FMAS univariants emerge. Close to MAS invariant point *b* is the triangle of FMAS invariant points deduced by Hensen (1972) – although his experiments contained trace H$_2$O and were at somewhat higher pressures (see text). For *a–x* relationships used, see Table S2.

coincident with reactions not involving cordierite (or [cd], i.e. cd-out) MAS univariant lines. These extend up *P–T* from invariant points, a and b, in Fig. 4.

Extension of the phase equilibria from MAS into the FeO-bearing system, FMAS, is shown in Fig. 5. Out of each MAS univariant point comes a FMAS univariant line, depending on which phases involved more easily incorporate FeO. Focussing on point b, the [sp] FMAS univariant extends *down* temperature until garnet is stabilized, and the resulting FMAS invariant point is the lower temperature one of the familiar triangle of FMAS invariant points (as shown in the adjacent inset on Fig. 5). Extending into FMASH, the [cd] FMAS univariant reactions go up to higher *P–T* from this triangle of FMAS invariant points to become the FMASH univariants. As discussed in Kelsey *et al.* (2004) and Baldwin *et al.* (2007), the classic experimental results of Hensen (1972) are in (at least) FMASH, not FMAS, and so occur at rather higher *P–T* than those shown in Fig. 5, corresponding to the small amount of water in his experiments.

Sulphur

As outlined above, the scope for calculating phase equilibria involving aqueous solutions, CHOS fluids and also sulphides and sulphate is now considerably increased (see above; also Evans & Powell, 2007; Evans

et al., 2010). Calculated equilibria among magnetite, hematite, pyrite, pyrrhotite, anhydrite and siderite, in the presence of calcite, are shown in Fig. 6. These are simple end-members, apart from pyrrhotite, for which the non-stoichiometry is modelled as described in Evans *et al.* (2010), and outlined above. Focussing on phase equilibria at 5 kbar, Fig. 7 shows a back-projection of the phase relationships onto the pyrrhotite one-phase field for assemblages with calcite + graphite.

The fields on Fig. 6 are labelled with tetrahedral compatibility diagrams. Simpler triangular compatibility diagrams can be drawn for graphite-, and for pyrite-saturated, conditions. Whereas compatibilty diagrams of various sorts are commonly best adapted for representing mineral stabilities for geological processes (e.g. Powell *et al.*, 2005), conventionally such relationships for the minerals involved here are represented on intensive variable diagrams, involving for example log activities. An equivalent diagram, calculated at 5 kbar and 500° C, in terms of chemical potentials, is shown in Fig. 8. The top surface of the μ-μ-μ box is for graphite presence. Note that the μ-μ-μ invariant points (a–d in Fig. 8) correspond to tie tetrahedra in the compatibility diagrams in Fig. 6. The calculations were performed on these divariant equilibria using the calcmu script in THERMOCALC, with μ_C calculated from $\mu_{CO_2} - 2\mu_O$, and μ_S calculated from $\mu_{SO_2} - 2\mu_O$. Only the higher μ_C relationships are shown (for simplicity): from the compatibility diagram
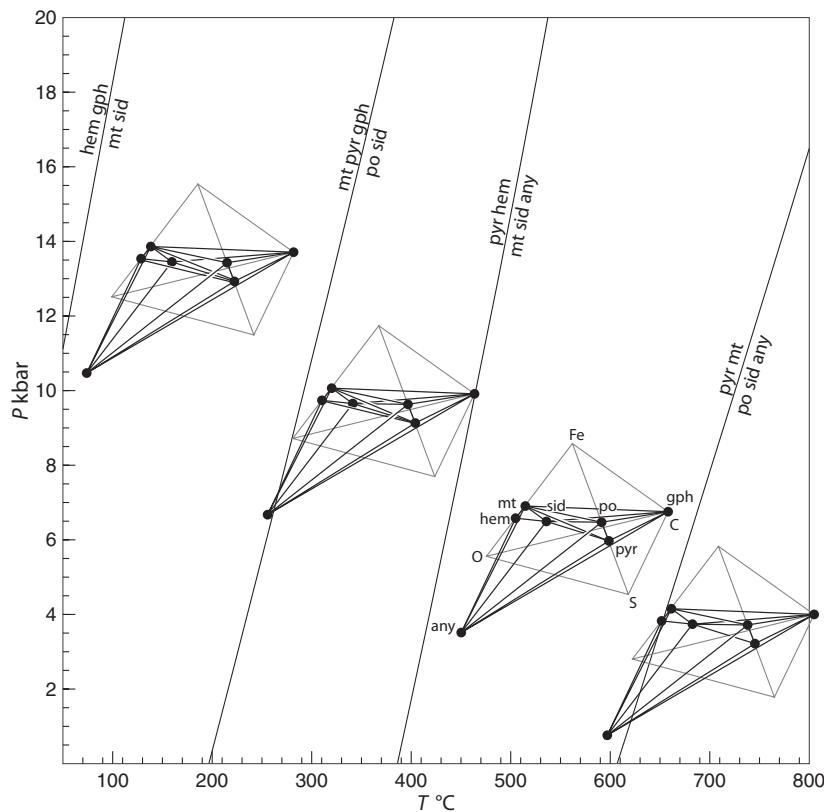
Fig. 6. *P–T* projection for CaO–FeO–C–O–S with excess calcite (cc) to show calculated equilibria among the phases hem (hematite), mt (magnetite), gph (graphite), sid (siderite), po (pyrrhotite), pyr (pyrite), any (anhydrite). Compatibility tetrahedra are shown – see text for discussion.
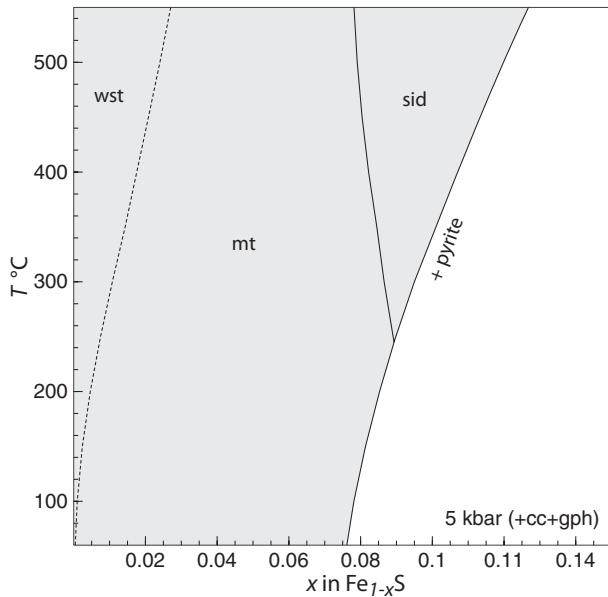
Fig. 7. *T–y(po)* diagram at 5 kbar, with excess calcite and graphite, showing the calculated composition of pyrrhotite coexisting with wustite (wst), magnetite (mt), siderite (sid) and pyrite.

Fig. 8. $\mu(C) - \mu(S) - \mu(O)$ box at 5 kbar, 500 °C showing the fields for mt (magnetite), sid(siderite), any (anhydrite), pyr (pyrite) and po (pyrrhotite). The top surface is graphite-saturated. Invariant points a–d correspond with the compatibility tie-tetrahedra in Fig. 6.

mt + hem + sid + any (at $\mu_C = -52.0$) and pyr + po + mt + any (at $\mu_C = -60.3$)

If the mineral assemblages are considered to be in equilibrium with a CHOS fluid, the composition can be calculated with THERMOCALC. So for example, considering the tie tetrahedron pyr + po + mt + sid with a fluid involving the end-members, H_2O–CO_2–CH_4–H_2–CO–H_2S–S_2 at 5 kbar and 500° C, the proportions of these end-members are:

it can be seen that at lower μ_C (moving away from the C apex), successive invariant points in the μ-μ-μ box, will involve pyr + mt + sid + any (at $\mu_C = -45.0$),

$$H_2O = 0.549,$$

$$CO_2 = 0.450,$$

$$CH_4 = 3.1210^{-7},$$

$$H_2 = 1.3910^{-5},$$

$$H_2S = 6.2310^{-4},$$

$$S_2 = 2.2310^{-9}.$$

Phase equilibria at deep mantle pressures

A new departure in this data set is the inclusion of phases which become stable in the deeper parts of the Earth's mantle. The thermodynamic data now allow calculation of P–T grids in chosen chemical systems, and pseudosections for bulk compositions applicable to model mantle materials. This is an expanding field of endeavour, both experimentally and in modelling, and we present some examples of the types of phase diagram which may be calculated with this data set using THERMOCALC.

The first example is a P–T projection in the MgO–SiO$_2$ system (Fig. 9) involving the phases olivine, wadsleyite (wad), ringwoodite (ring), high-pressure cpx (hcpx), akimotoite (aki), perovskite (pv), periclase (per) and stishovite (stv). The diagram pertains to pressures above the breakdown of orthopyroxene. The inferences that can be made from the MS system about mantle mineralogy are somewhat limited, and so we calculate a P–T diagram showing the MAS reactions emerging from the MS invariant points on introduction of alumina into the system (Fig. 10). Three stable invariant points ensue, labelled A, B and C in the figure, and these are the starting points for FMAS univariant reactions in the Fe-bearing system (arrow-ended curves in Fig. 10). These enable construction of the rather more petrologically interesting pseudosection for fixed bulk composition allowing portrayal of the different FMAS assemblages on the P–T diagram.

Figure 11 shows the pseudosection calculated for the Kilbourne Hole peridotite bulk composition (Takahash, 1986; Walter, 1998), simplified into the FMAS system. It is immediately clear that the nature of the 660 km transition ($\sim$230 kbar) is likely to be more complex than that commonly interpreted from experimental data in smaller subsystems, changing through several assemblages involving incoming of perovskite and periclase. The range and variety of assemblages developed in P–T space shows how difficult it will be to perform and interpret experimental charges in chemically complex systems. Addition of calcium will further complicate the pattern of mineral assemblages, and such a calculation will be presented elsewhere. A word of caution is in order here, as there are a couple of major sources of uncertainty in the experiments used to
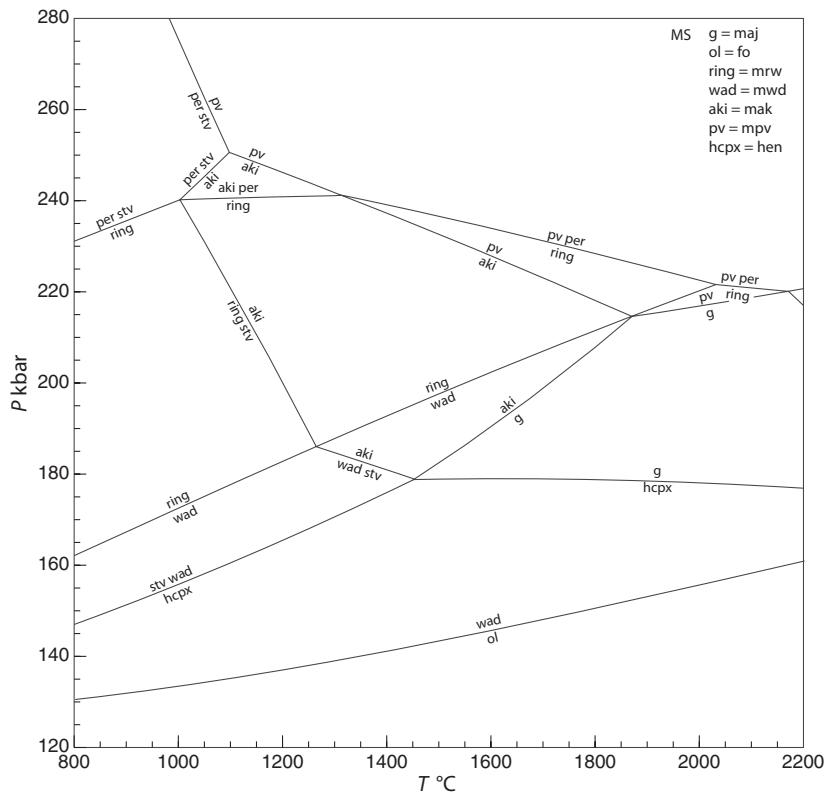
Fig. 9. P–T projection for deep mantle phases in MgO–SiO$_2$. Phases: pv, perovskite; aki, akimotoite (ilmenite); per, periclase; ring, ringwoodite; wad, wadsleyite; g, majorite garnet; stv, stishovite; hcpx, high-pressure clinoenstatite; ol, olivine. Legend provides the end-member names as used in THERMOCALC.
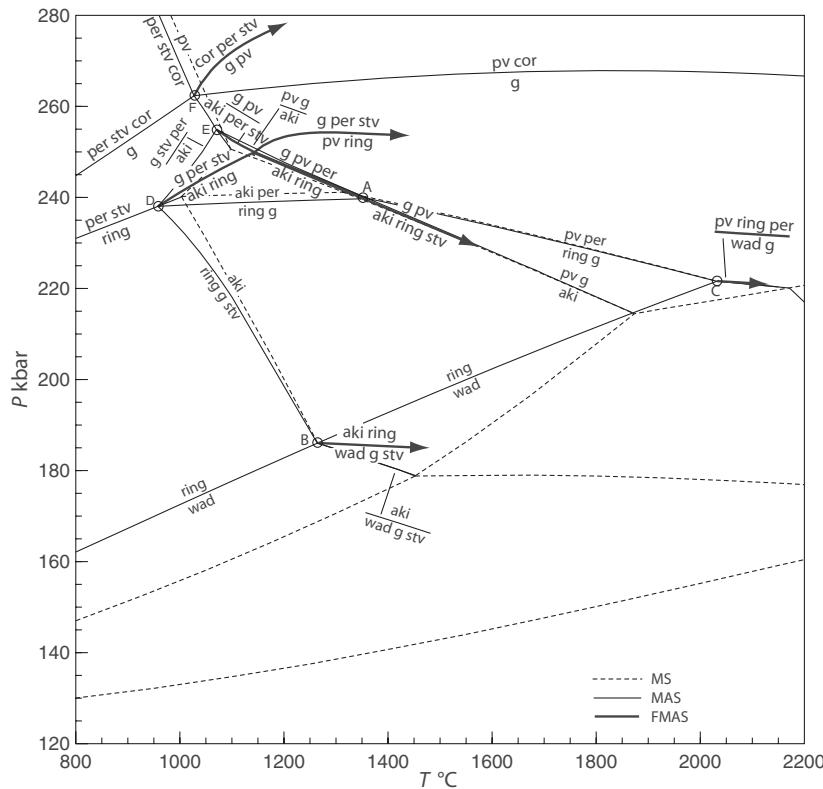
Fig. 10. *P–T* projection for deep mantle phase in MgO–Al$_2$O$_3$–SiO$_2$. Full thin curves are univariant equilibria in MAS and thin dashed curves are the MS equilibria. There are six MAS invariant points (A, B, C, D, E, F) with emergent FeO–MgO–Al$_2$O$_3$–SiO$_2$ univariants shown by heavy lines and arrowed ends, as well as one full FMAS invariant point close to 250 kbar and 1200 °C. cor, corundum; other phase names as in Fig. 9. For *a–x* relationships used, see Table S2.
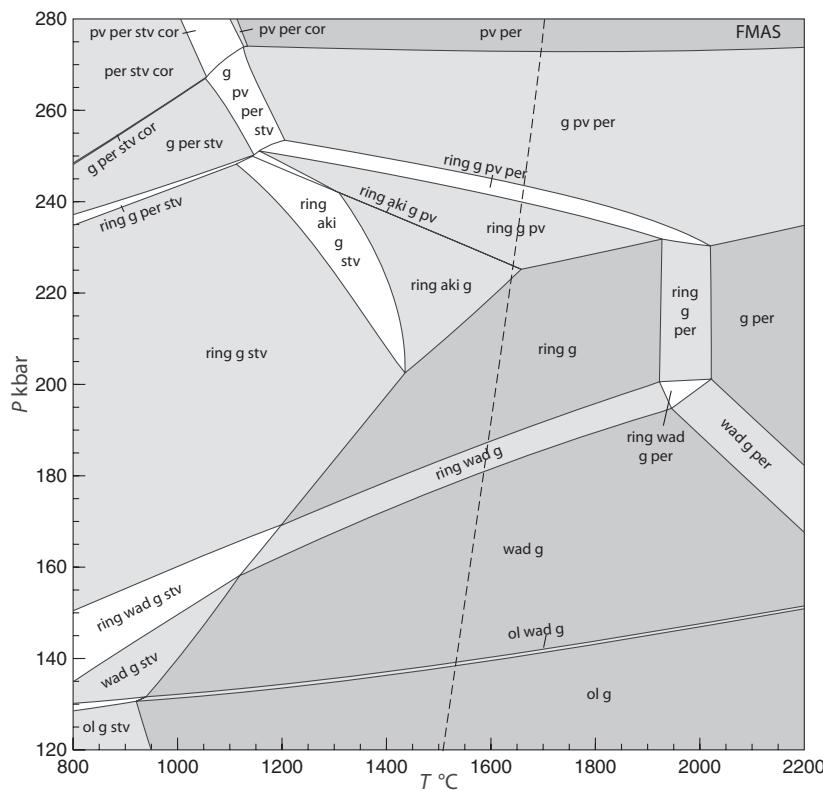
Fig. 11. *P–T* pseudosection for FeO–MgO–Al$_2$O$_3$–SiO$_2$ with a bulk composition corresponding to the Kilbourne Hole peridotite KLB-1 (Walter, 1998). The bulk composition sees short sections of some of the univariant curves in Fig. 10, but only below about 1400 °C and 240 kbar and so typical mantle geotherms are likely to pass to somewhat higher temperatures and may not intersect them. The dashed line represents one estimated geotherm smoothed from Stixrude & Lithgow-Bertelloni (2007). The lowest pressure part of this diagram is metastable with respect to inclusion of high-pressure cpx which was not considered for this diagram. cor, corundum; other phase names as in Fig. 9. For *a–x* relationships used, see Table S2.

derive these data. First, pressures and temperatures for the same experimental boundaries are often inconsistent among different investigators, and second, the pressure scale to be used in the experiments has not yet been satisfactorily resolved. Thus, the calculated equilibria may require adjustment in future as these experimental problems are resolved.

DISCUSSION

The internally consistent thermodynamic data set described here is a major improvement on previous ones because all the calorimetric and experimental data published in the 13 years since HP98 are now considered and incorporated if appropriate, and this increases the reliability of the data and expands the scope (via the incorporation of the new end-members that has become possible). The increase in reliability of the data set, in relation to the end-members already present in HP98, stems from the better implicit cross-checking between equilibria that involve the same end-members (the 'internal consistency') as new data become available. In detail, if before there was an equilibrium with high 'hat' (see HP98, table 7, or Table S1 here) – a measure of how constraining that equilibrium is – then addition of data involving that end-member will reduce the hat for the equilibria involved. Also additional data may simply suggest that equilibria taken to be correct in the past should now be considered untrustworthy and not used in data set generation. Methodological improvements also contribute to reliability. The expansion of scope is self-evident in the addition of a large number of new end-members, but also arises as a consequence of the methodological improvements that now allow calculations at high P–T, and in S-bearing systems, for example.

The ongoing development of the internally consistent thermodynamic data set is largely dependent on the calorimetric and phase equilibria experimental community, without whose best efforts our work will tend to founder. Although we think this data set is a substantial step forward in the quest for this aspect of quantification of petrological processes, much needs to be done. Obvious things are needed, for example the proper characterization of the phases in experimental charges and measurement of unit cell volumes to high pressures and temperatures, particularly those made at high temperatures at elevated pressures. As may be readily seen from Appendix 1, there remain many end-members for which no measured thermal expansion, compressibility or heat capacity values as yet exist. For some, for example, those fictive end-members which do not exist stably in nature or are not readily synthesized experimentally, such measurements will never be available but could in principle be calculated from molecular simulations. For many others in the table new measurements would be most welcome. Applications to well-characterized rocks from well-established

geological settings will provide critical input to the evaluation of the data set, and we welcome feedback relating to this from people using the data set. Of course such applications are equally reliant on the activity–composition relations used for the phases involved, as well as a realistic appraisal of the likely geological processes involved in rock formation.

In generation of the data set, the enthalpies of formation of the end-members are solved for in the weighted least squares approach. As a part of this, the uncertainty on these enthalpies are calculated, as well as the correlations between them (e.g. Powell & Holland, 1993a,b). These uncertainties can be considered as reflecting 'known unknowns' about the end-member properties. If in fact data used in the generation of the data set are incorrect, because the data were not sufficiently dense to identify this, then this amounts to 'unknown unknowns' about the end-member properties (the results are incorrect, and we have no way of knowing about it). The former source of uncertainty can be accounted for in error propagation calculations, but the latter cannot be handled in this way and introduce a bias in the results if, later, such problems are recognized. It is for this reason that validation of the data set via more experimental studies, and/or appropriate applications is important.

In using the data set, the uncertainties inherent in the data set can be propagated through calculations using THERMOCALC, as is done routinely in average P–T calculations, but also can be done for P–T projection and pseudosection calculations (via the calcsdnle script). So, for example considering Fig. 5, the uncertainty on the positions of the invariant points that form the highlighted triangle at around 6 kbar and 1000 °C, from the data set uncertainties, at 2σ level, in {kbar,°C}, are {$6.4 \pm 0.8, 964 \pm 142$}, {$6.4 \pm 1.0, 983 \pm 88$} and {$6.5 \pm 0.6, 1004 \pm 40$}, with increasing temperature. If the uncertainties on the interaction parameters of the phases (Table S2) are also included, as they can be as outlined in Powell & Holland (2008), the uncertainties will be yet larger. These uncertainties are for the invariant points individually, and a way of looking at the *correlations* between the positions of the points as a consequence of the uncertainties is not yet implemented. It is conceivable that the uncertainties simply translate the triangle of points, rather than cause them to be involved in an inversion of topology. Work is in progress to address this aspect of uncertainties in calculated phase diagrams. Uncertainties, but with the same problem of not being able to ascertain correlations, can be done for pseudosection calculations. So, in Fig. 11, looking at the point on the divariant field, ring + g + pv + per, where the modes of pv and per are zero, the calculated uncertainty just with data set uncertainties is {$231.8 \pm 8.0, 1928 \pm 326$}. In the case of propagated uncertainties for calculations at these conditions, the agreement of a pressure scale for experimental studies, as well as the reaching of a

consensus on the position of end-member equilibria in P–T, should dramatically reduce the size of the uncertainties.

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SUPPORTING INFORMATION

Additional Supporting Information may be found in the online version of this article:

Table S1. Complete LSQDS output for data set generation.

Table S2. Activity-composition relationships.

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Appendix 1: Sources for thermodynamic data

Group	End-member	S	V	C_p	α	κ
Garnet and olivine	almandine (alm)	3	4	0, 3	5	6
	andradite (andr)	1	1	1	46	46
	grossular (gr)	42	1	43, 44	45, 46	46
	knorringite (knor)	0	47	0	0	0
	majorite (maj)	33	26	33	33	26
	pyrope (py)	0, 1	3	34	35	36, 37
	spessartine (spss)	38	39	38	40	41
	clinohumite (chum)	0	20	0	0	21
	fayalite (fa)	1	1	13	14, 15	16
	forsterite (fo)	1	1	1	10, 11	10, 12
	larnite (larn)	1	1	1	0	0
	monticellite (mont)	0, 1	1	1	18	19
	tephroite (teph)	1	1	1	17	0
Aluminosilicates	andalusite (and)	1	1	52	53	54
	kyanite (ky)	1	1	52	53	55
	sillimanite (sill)	1	1	52	53	54
	mullite (amul)	0	7	0	8	9
	mullite (smul)	0	7	0	8	9
	chloritoid (mctd)	61	59	61	62	63
	chloritoid (fctd)	61	64	61	62	63
	chloritoid (mnctd)	0	0	0	62	63
	staurolite (mst)	0	65	0	57	58
	staurolite (fst)	0	60	0	57	58
	staurolite (mnst)	0	0	0	57	58
	topaz (tpz)	0	66	0	40	0
Other orthosilicates	akermanite (ak)	2	2	2	2	0
	gehlenite (geh)	79	60	1	40	0
	julgoldite (jgd)	0	78	0	0	0
	merwinite (merw)	1	65	1	40	0
	pumpellyite (mpm)	0	77	0	0	0
	pumpellyite (fpm)	0	0	0	0	0
	rankinite (rnk)	1	1	1	40	0
	sphene (sph)	1	1	1, 88	89	90
	spurrite (spu)	1	1	0	0	0
	tilleyite (ty)	0	80	0	0	0
	zircon (zrc)	1	1	1	40	91
Sorosilicates	clinozoisite (cz)	0	71	0	69	70
	epidote (ep)	72	73	72	69	70, 74
	epidote (fep)	0	0	0	0	0
	lawsonite (law)	67	1	0, 67	69	76
	piemontite (pmt)	0	75	0	0	0
	zoisite (zo)	0, 67	68	0, 67	69	70
	vesuvianite (vsv)	0	49	0	50	51
Cyclosilicates	cordierite (fcrd)	81	86	81	83	84, 85
	cordierite (hcrd)	81	0	0	83	84, 85
	cordierite (crd)	81, 82	1	81	83	84, 85
	cordierite (mncrd)	0	0	0	83	84, 85
	osumilite (osm1)	18	18	18	0	0
	osumilite (osm2)	18	18	18	0	0
	osumilite (fosm)	18	18	18	0	0
High-pressure silicates	akimotoite (fak)	0, 33	22	33	0, 33	33
	akimotoite (mak)	0, 33	22	33	33	26
	caSi-titanite (cstn)	0	247	0	0	247
	perovskite (apv)	0, 27	22	0	0, 32	26
	perovskite (cpv)	0	246	0	0, 32	246
	perovskite (fpv)	0	249	0	0	249
	perovskite (mpv)	0, 27	22	32	32	26
	phase A (phA)	0	87	0	87	87
	ringwoodite (mrw)	0, 27	22	23	28	26
	ringwoodite (frw)	0	26	29, 30	31	30
	wadsleyite (mwd)	0	22	23	24	25
	wadsleyite (fwd)	0	22	0	0	26
Pyroxenes and pyroxenoid	acmite (acm)	1	60	1	92	93
	Ca-tschermak's pyroxene (cats)	94	94	94	94	0
	Ca-Eskola pyroxene (caes)	0	95	0	0	0
	clinoenstatite (cen)	0	96	97, 98	40	0
	clinoenstatite (hen)	0	102	0	0	107
	diopside (di)	1	99	1	100	101
	enstatite (en)	1	1	1	40	102
	ferrosilite (fs)	1	103	1	103	104
	hedenbergite (hed)	105	105	105	92	106
	jadeite (jd)	1	1	108	92, 109	109
	kosmochlore (kos)	0	110	0	92	111
	Mg-tschermak's pyroxene (mgts)	0	112	0	0	0
	protoenstatite (pren)	0	60	0, 1	113	102
	pseudowollastonite (pswo)	1	1	0, 114	40	0
	pyroxmangite (pxmn)	1	1	1	115	115
	rhodonite (rhod)	1	1	1	115	115
	walstromite (wal)	248	248	0, 114	0,40	0, 116
	wollastonite (wo)	1	60	114	40	116

Appendix 1. (*Continued*)

Group	End-member	S	V	C_p	α	κ
Amphiboles	actinolite (fact)	0	120	0	0	0
	anthophyllite (anth)	1	1	0	0	0
	anthophyllite (fanth)	0	0	0	0	0
	cummingtonite (cumm)	0	126	0	0	0
	glaucophane (gl)	123	124	123	124	119
	glaucophane (fgl)	0	0	0	0	0
	grunerite (grun)	0	127	0	0	128
	pargasite (parg)	0	122	0	103	119
	riebeckite (rieb)	0	125	0	0	0
	tremolite (tr)	0, 1	117	118	242	119
	tschermakite (ts)	0	121	0	0	0
Other chain silicates	deerite (deer)	0	129	0	0	129
	carpholite (mcar)	130	131	130	0	0
	carpholite (fcar)	130	132	130	0	0
	sapphirine (spr4)	0	133, 134	0	0	0
	sapphirine (spr5)	0	133, 134	0	0	0
	sapphirine (fspr)	0	0	0	0	0
Mica	annite (ann)	0	60	0	0	0
	biotite (mnbi)	0	0	0	0	0
	celadonite (cel)	0	135	0	137	138
	celadonite (fcel)	0	136	0	137	138
	eastonite (east)	0	139	0	0	0
	margarite (ma)	1	1	1	140	0
	muscovite (mu)	1	1	1	137	138
	paragonite (pa)	1	1	1, 141	137	138
	phlogopite (phl)	1	1	1	142	143
	phlogopite (naph)	0	144	0	0	0
Chlorite	chlorite (afchl)	145	146, 147, 148	145	149	150
	chlorite (mnchl)	0, 145	0	0	149	150
	amesite (ames)	0	146, 147, 148	145	149	150
	clinochlore (clin)	145	146, 147, 148	145	149	150
	daphnite (daph)	145	151	145	149	150
	sudoite (sud)	152	0	0	149	150
	sudoite (fsud)	0	0	0	149	150
Other sheet silicates	antigorite (atg)	0	158	159	0	160
	chrysotile (chr)	1	1	1	0	162
	lizardite (liz)	0	162	1	0	162
	greenalite (glt)	0	161	0	0	0
	kaolinite (kao)	1	1	1	0	0
	minnesotaite (min)	0	155	0	0	0
	minnesotaite (minm)	0	0	0	0	0
	stilpnomelane (mstp)	0	0, 155	0	0	0
	stilpnomelane (fstp)	0	155	0	0	0
	prehnite (pre)	67	67	67	0	156
	prehnite (fpre)	0	157	0	0	156
	pyrophyllite (prl)	1	22	153	0	150
	talc (ta)	22	1	1	154	150
	talc (fta)	0	0	0	154	150
	talc (tap)	0	0	153	0	150
	talc (tats)	0	0	0	154	150
Feldspar and feldspathoid	albite (ab)	1	1	1	163	164
	albite (abh)	0, 1	0, 1	1	163	164
	analcite (anl)	1	1	0	0	177
	anorthite (an)	1	1	167	168	169
	carnegieite (cg)	1	1	1	0	0
	carnegieite (cgh)	1	178	1	0	0
	kalsilite (kls)	1	179	1	179, 180	181
	leucite (lc)	1	182	0, 1	182	181
	microcline (mic)	1	1	1	165	166
	nepheline (ne)	1	1	1	40	177
	sanidine (san)	1	165	1	165	166
Silica minerals	coesite (coe)	0, 174	1	174	0	0
	cristobalite (crst)	0, 1	0, 1	1	0	0
	quartz (q)	1	1	1, 173	0	173
	stishovite (stv)	0, 1	1	33	175	176
	tridymite (trd)	0, 1	0, 1	0, 1	0	0
Other framework silicates	heulandite (heu)	187	187	0	0	244
	hollandite (hol)	171	172	172	172	172
	laumontite (lmt)	0	186	0	0	0
	meionite (me)	0, 183	183	0	184	185
	K-cymrite (kcm)	0	170	0	170	170
	sodalite (sdl)	245	245	245	0, 40	0, 177
	stilbite (stb)	0	188	0	0	0
	wadeite (wa)	171	170	170	172	171
	wairakite (wrk)	0	1	0	0	0
Oxides	baddeleyite (bdy)	1	1	1	40	205
	bixbyite (bix)	1	1	199	0	0
	corundum (cor)	1	1	199	200	201
	corundum (mcor)	0	0	0	0	0
	cuprite (cup)	1	1	1	0	206
	eskolaite (esk)	1	1	1	0	202

Appendix 1. (*Continued*)

Group	End-member	S	V	C_p	α	κ
	geikielite (geik)	1	1	0, 1	0	0
	hematite (hem)	1	1	1	40	202
	hercynite (herc)	209	1	0	40	0
	Ilmenite (ilm)	1	1	1	204	204
	lime (lime)	1	1	1	189	190
	magnesioferrite (mft)	210	1	1	0	0
	magnetite (mt)	1	1	1	40	208
	manganosite (mang)	1	1	1	197	198
	nickel oxide (NiO)	1	1	1	0	203
	periclase (per)	1	1	193	194	195, 196
	picrochromite (picr)	211	1	1	0	0
	pyrophanite (pnt)	1	1	0, 1	0	0
	rutile (ru)	1	1	1	191	192
	spinel (sp)	0, 1	1	1	207	208
	tenorite (ten)	1	1	1	0	0
	ulvospinel (usp)	1	1	1	0	0
	ferropericlase (fper)	0, 1	26	1	40	26
Hydroxides	brucite (br)	1	1	0, 1	212, 213	213, 214
	diaspore (dsp)	1	22	0, 1	215	216
	goethite (gth)	1	1	0	0	0
Carbonates	ankerite (ank)	0	227	0	0	226
	aragonite (arag)	1	1	0, 1	40, 219	219
	calcite (cc)	1	1	0, 1	217	218
	dolomite (dol)	1	22	0, 1	224, 225	225, 226
	magnesite (mag)	1	1	0, 1	217, 220, 221	220, 221
	rhodochrosite (rhc)	1	1	1	222	223
	siderite (sid)	0, 1	22	0, 1	0	177
Halides and S-bearing	anhydrite (any)	1	1	235	236	177
	halite (hlt)	1	1	1	228	228
	pyrite (pyr)	1	1	229	40	230
	pyrrhotite (trot)	0	231	0, 233	231	232
	pyrrhotite (trov)	0	231	0, 233	231	232
	troilite (tro)	0	231	0, 233	231	232
	troilite (lot)	0	231	0, 233	234	232
	sylvite (syv)	1	1	1	228	228
Elements	copper (Cu)	1	1	1	40	238
	diamond (diam)	1	1	1	40	240
	graphite (gph)	1	1	1	40	239
	iron (iron)	1	1	0, 1	40	237
	nickel (Ni)	1	1	0, 1	40	177
	sulphur (S)	1	1	1	243	241
Gas species	methane (CH$_4$)	1	–	1	–	–
	carbon monoxide (CO)	1	–	1	–	–
	carbon dioxide (CO$_2$)	1	–	1	–	–
	hydrogen (H$_2$)	1	–	1	–	–
	hydrogen sulphide (H$_2$S)	1	–	1	–	–
	sulphur gas (S$_2$)	1	–	1	–	–
	water (H$_2$O)	1	–	1	–	–
	oxygen (O$_2$)	1	–	1	–	–

Sources for entropy (*S*), molar volume (*V*), heat capacity (*C$_p$*), thermal expansion (α) and incompressibility (κ) data.

0 Estimated or optimised in this study
1 Robie & Hemingway, 1995
2 Hemingway *et al.*, 1986
3 Newton & Harlov (1993)
4 Geiger *et al.*, 1987
5 Skinner, 1956
6 Takahashi & Liu, 1970
7 Cameron, 1977
8 Schneider & Eberhard, 1990
9 Balzar & Ledbetter, 1993
10 Hazen, 1976
11 Kajiyoshi, 1986
12 Downs *et al.*, 1996
13 Robie *et al.*, 1982
14 Smyth, 1975
15 Suzuki *et al.*, 1981
16 Williams *et al.*, 1990
17 Okajima *et al.*, 1978
18 Lager & Meagher, 1978
19 Sharp *et al.*, 1986
20 Yamamoto & Akimoto, 1977
21 Ross & Crichton, 2001
22 Smyth & McCormick, 1995
23 Ashida *et al.*, 1987
24 Suzuki, 1980
25 Jacobs & de Jong, 2005
26 Stixrude & Lithgow-Bertelloni, 2005
27 Fei *et al.*, 1990
28 Suzuki, 1979
29 Watanabe, 1982
30 Jacobs & Oonk, 2001

31 Mao *et al.*, 1969
32 Gillet *et al.*, 2000
33 Saxena, 1996
34 Tequi *et al.*, 1991
35 Suzuki & Anderson, 1983
36 Hazen & Finger, 1989
37 Zhang *et al.*, 1998
38 Dachs *et al.*, 2009
39 Hsu, 1968
40 Skinner, 1966
41 Leger *et al.*, 1990
42 Westrum *et al.*, 1979
43 Bosenick *et al.*, 1996
44 Thieblot *et al.*, 1999
45 Isaak *et al.*, 1992
46 Pavese *et al.*, 2001a,b
47 Irifune *et al.*, 1982
48 Holland *et al.*, 1996
49 Hochella *et al.*, 1982
50 Tribaudino & Prencipe, 1999
51 Tribaudino & Prencipe, 2001
52 Hemingway *et al.*, 1991
53 Winter & Ghose, 1979
54 Burt *et al.*, 2006
55 Comodi *et al.*, 1997
56 Cameron, 1977
57 Gibbons *et al.*, 1981
58 Grevel *et al.*, 1998
59 Chopin & Schreyer, 1983
60 Robie *et al.*, 1967
61 Koch-Müller *et al.*, 2002

62 Ivaldi *et al.*, 1988
63 Comodi *et al.*, 1992
64 Rao & Johannes, 1979
65 Schreyer & Seifert, 1969
66 Wunder *et al.*, 1993
67 Perkins *et al.*, 1980
68 Chatterjee, 1976
69 Pawley *et al.*, 1996
70 Comodi & Zanazzi, 1997
71 Jenkins *et al.*, 1985
72 Kiseleva *et al.*, 1974
73 Bird & Helgeson, 1980
74 Holland *et al.*, 1996
75 Keskinen & Liou, 1979
76 Boffa-Ballaran & Angel, 2003
77 Schiffman & Liou, 1980
78 Artioli *et al.*, 2003
79 Hemingway & Robie, 1984
80 Harker, 1959
81 Dachs & Geiger, 2008
82 Paukov *et al.*, 2006
83 Mirwald *et al.*, 1984
84 Mirwald, 1981
85 Schlenker *et al.*, 1977
86 Mukhopadhyay & Holdaway, 1994
87 Pawley & Wood, 1995
88 Manon *et al.*, 2008
89 Malcherek, 2001
90 Angel *et al.*, 1999a,b
91 Hazen & Finger, 1979
92 Cameron *et al.*, 1973

93 Kandelin & Weidner, 1988
94 Haselton *et al.*, 1984
95 McCormick, 1986
96 Stephenson *et al.*, 1966
97 White, 1919
98 Wagner, 1932
99 Krupka *et al.*, 1985a
100 Finger & Ohashi, 1976
101 McCormick *et al.*, 1989
102 Hugh-Jones & Angel, 1994
103 Sueno *et al.*, 1976
104 Kandelin & Weidner, 1988
105 Haselton *et al.*, 1987
106 Zhang & Hafner, 1992
107 Kung *et al.*, 2005
108 Hemingway *et al.*, 1998
109 Zhao *et al.*, 1997
110 Carroll Webb & Wood, 1986
111 Origlieri *et al.*, 2003
112 Gasparik & Newton, 1984
113 Jackson *et al.*, 2003
114 Richet *et al.*, 1991
115 Pinckney & Burnham, 1988
116 Vaidya *et al.*, 1973
117 Hewitt, 1975
118 Krupka *et al.*, 1985b
119 Comodi *et al.*, 1991
120 Jenkins & Bozhilov, 2003
121 Jenkins, 1994
122 Lykins & Jenkins, 1992
123 Holland, 1988

124 Jenkins & Corona, 2006
125 Ernst, 1962
126 Evans & Ghiorso, 1995
127 Ghiorso & Evans, 2002
128 Zhang et al., 1992
129 Lattard & LeBreton, 1994
130 Bertoldi et al., 2006
131 Chopin & Schreyer, 1983
132 Viswanathan & Seidel, 1979
133 Seifert, 1974
134 Chatterjee & Schreyer, 1972
135 Schmidt et al., 2001
136 Coggon & Holland, 2002
137 Guggenheim et al., 1987
138 Comodi & Zanazzi, 1995
139 Circone et al., 1991
140 Symmes, 1986
141 Holland, 1979
142 Russell & Guggenheim, 1999
143 Pavese et al., 2003
144 Carman, 1974
145 Bertoldi et al., 2007
146 Baker & Holland, 1996
147 Jenkins & Chernosky, 1986
148 Roots, 1994
149 Nelson & Guggenheim, 1993
150 Pawley et al., 2002
151 Parra et al., 2005
152 Vidal, 1992
153 Krupka et al., 1979
154 Pawley et al., 1995
155 Miyano & Klein, 1989

156 Detrie et al., 2009
157 Rose & Bird, 1987
158 Mellini et al., 1987
159 King et al., 1967
160 Bose & Navrotsky, 1998
161 Rasmussen et al., 1998
162 Hilairet et al., 2006
163 Winter et al., 1979
164 Downs et al., 1994
165 Hovis et al., 1999
166 Allan & Angel, 1997
167 Richet & Fiquet, 1991
168 Grundy & Brown, 1974
169 Angel, 2004
170 Fasshauer et al., 1997
171 Yong et al., 2006
172 Akaogi et al., 2004
173 Dorogokupets, 1995
174 Hemingway et al., 1998
175 Ito et al., 1974
176 Andrault et al., 2003; Luo et al., 2002
177 Birch, 1966
178 Richet et al., 1990
179 Carpenter & Cellai, 1996
180 Hovis et al., 2003
181 Fasshauer et al., 1998
182 Palmer et al., 1989
183 Baker & Newton, 1994
184 Baker, 1962
185 Hazen & Sharp, 1988
186 Liou, 1971a
187 Cho et al., 1987

188 Liou, 1971b
189 Fiquet et al., 1999
190 Richet et al., 1988
191 Sugiyama & Takeuchi, 1991
192 Hazen & Finger, 1981
193 Richet & Fiquet, 1991
194 Dubrovinsky & Saxena, 1997
195 Fei, 1999
196 Hazen, 1976
197 Suzuki et al., 1979
198 Jeanloz & Rudy, 1987
199 Richet et al., 1992
200 Aldebert & Traverse, 1984
201 D'Amour et al., 1978
202 Finger & Hazen, 1980
203 Clendenen & Drickamer, 1966
204 Wechsler & Prewitt, 1984
205 Leger et al., 1993
206 Werner & Hochheimer, 1982
207 Fiquet et al., 1999
208 Finger et al., 1986
209 Klemme & Van Miltenburg, 2003
210 Klemme & Ahrens, 2005
211 Klemme et al., 2000
212 Fei & Mao, 1993
213 Fukui et al., 2003
214 Catti et al., 1995
215 Pawley et al., 1996
216 Xu et al., 1994
217 Markgraf & Reeder, 1985
218 Redfern & Angel, 1999
219 Martinez et al., 1996

220 Fiquet & Reynard, 1999
221 Zhang et al., 1997
222 Rao & Murthy, 1970
223 Martens et al., 1982
224 Reeder & Markgraf, 1986
225 Martinez et al., 1996
226 Ross & Reeder, 1992
227 Davidson et al., 1993
228 Walker et al., 2004
229 Chase, 1998
230 Adams & Williamson, 1923
231 Tenailleau et al., 2005
232 King & Prewitt, 1982
233 Gronvold & Stolen, 1991,1992
234 Taylor, 1970
235 Majzlan et al., 2002
236 Evans, 1979
237 Takahashi et al., 1968
238 Vaidya & Kennedy, 1971
239 Zhao & Spain, 1989
240 Alexandrov et al., 1987
241 Luo & Ruoff, 1993
242 Sueno et al., 1973
243 Wallis et al., 1986
244 Comodi et al., 2001
245 Sharp et al., 1989
246 Shim et al., 2000
247 Angel et al., 1999a,b
248 Chatterjee et al., 1984
249 Walter et al., 2004.

Appendix 2: Summary table of equilibria used for fitting the data set.

1) 2knor = 3en + 2esk (Irifune et al., 1982)
2) 2knor = 3en + 2esk (Turkin et al., 1983)
3) knor + fo = picr + 2en (Klemme, 2004)

Equilibrium: crpx crsp (Carroll Webb & Wood, 1986), involving:
4) 2kos + sp = 2jd + picr
5) lot = tro (fix at transition)

Equilibrium: po S$_2$ (Rau, 1976), involving:
6) 16trov = 14trot + S$_2$
7) 8trov + H$_2$ = 7trot + H$_2$S (Lin, 1976)

Equilibrium: po S$_2$ (Toulmin & Barton, 1964), involving:
8) 16trov = 14trot + S$_2$

Equilibrium: po pyr S$_2$ (Toulmin & Barton, 1964), involving next two reactions:
9) 14trot + S$_2$ = 16trov
10) 2trot + S$_2$ = 2pyr

Equilibrium: po pyr S$_2$ (Schneeberg, 1973), involving next two reactions:
11) 16trov = 14trot + S$_2$
12) 2pyr = 2trot + S$_2$

Equilibrium: iron tro fluid2 (Rosenqvist, 1954), involving:
13) iron + H$_2$S = tro + H$_2$

Equilibrium: iron tro fluid2 (Alcock & Richardson, 1951), involving:
14) iron + H$_2$S = tro + H$_2$
15) en = pren (Atlas, 1952; Chen & Presnall, 1975)
16) diam = gph (Kennedy & Kennedy, 1976)
17) q = trd (Ostrovsky, 1966)
18) trd = crst (Ostrovsky, 1966)
19) q = crst (Ostrovsky, 1966; Jackson, 1976)
20) coe = q (Bose & Ganguly, 1995)
21) coe = q (Bohlen & Boettcher, 1982; Gasparik, 1984)
22) stv = coe (Zhang et al., 1996)
23) arag = cc (Boettcher & Wyllie, 1968)
24) arag = cc (Crawford & Hoersch, 1972)
25) arag = cc (Johannes & Puhan, 1971)
26) arag = cc (Goldsmith & Newton, 1969)
27) arag = cc (Irving & Wyllie, 1975)
28) arag = cc (Suito et al., 2001)
29) arag + mag = dol (Morlidge et al., 2006)
30) arag + sid = ank (Morlidge et al., 2006)
31) cen = en (Boyd & England, 1965)
32) hen = en (Pacalo & Gasparik, 1990)
33) hen = cen (Angel et al., 1992)
34) mwd + stv = hen (Sawamoto, 1987; Kanzaki, 1987)
35) maj = 2hen (Ohtani, 1991)
36) 2mwd + 2stv = maj (Ohtani, 1991)
37) mwd = fo (Katsura & Ito, 1989; Fei & Bertka, 1999)

38) mrw = mwd (Katsura & Ito, 1989; Fei et al., 2004)
39) 2mak = mwd + stv (Sawamoto, 1987; Kanzaki, 1987)
40) 4mpv = maj (Katsura & Ito, 1989; Ohtani 1991)
41) mpv = mak (Katsura & Ito, 1989; Ohtani 1991)
42) mpv = mak (Ito & Takahashi, 1989)
43) frw = fa (Yagi et al., 1987; Akimoto et al., 1965, 1967)
44) fwd = fa (Fei & Bertka, 1999; Frost, 2003; Katsura & Ito, 1989; Akimoto, 1987)

Equilibrium: ol wd rg (Fei & Bertka, 1999; Frost, 2003; Katsura & Ito, 1989; Akimoto, 1987), involving next three reactions:
45) fwd = fa
46) mwd = fo
47) mwd = mrw
48) mpv + per = mrw (Shim et al., 2001; Ito & Takahashi 1989; Fei et al., 2004)
49) per + cor = sp (Akaogi et al., 1989)

Equilibrium: pv aki (Ito & Yamada, 1982), involving next two reactions:
50) fpv = fak
51) mpv = mak

Equilibrium: aki rg stv (Ito & Yamada, 1982), involving next two reactions:
52) 2mak = mrw + stv
53) 2fak = frw + stv

Equilibrium: rg mwu stv (Ito & Yamada, 1982), involving next two reactions:
54) mrw = 2per + stv
55) frw = 2fper + stv

Equilibrium: pv aki rg mwu (Ito & Yamada, 1982), involving next three reactions:
56) fpv = fak
57) mpv = mak
58) 2mpv + frw = 2fpv + mrw

Equilibrium: pvk crn py (Hirose et al., 2001; Kubo & Akaogi, 2000), involving next three reactions:
59) cor = apv
60) mcor = mpv
61) py = 3mpv + cor
62) wo = pswo (Osborn & Schairer, 1941; Huang & Wyllie, 1975)
63) wal = wo (Chatterjee et al., 1984; Essene, 1974)
64) lrn + cstn = 3wal (Gasparik et al., 1994)
65) 3cpv = lrn + cstn (Gasparik et al., 1994)
66) cc = lime + CO$_2$ (Smyth & Adams, 1923)
67) cc = lime + CO$_2$ (Baker, 1962)
68) cc + q = wo + CO$_2$ (Zhu, Newton & Kleppa, 1993)
69) cc + q = wo + CO$_2$ (Jacobs & Kerrick, 1981)
70) cc + q = wo + CO$_2$ (Ziegenbein & Johannes, 1974)
71) cc + q = wo + CO$_2$ (Greenwood, 1967a,b; Harker & Tuttle, 1956)
72) cc + q = wo + CO$_2$ (Aranovich & Newton, 1999)
73) cc + q = wo + CO$_2$ (Haselton et al., 1978)
74) 3cc + 2wo = ty + CO$_2$ (Zharikov & Shmulovich, 1969)
75) ty = spu + CO$_2$ (Zharikov & Shmulovich, 1969)
76) spu + 4wo = 3rnk + CO$_2$ (Zharikov & Shmulovich, 1969)
77) spu + rnk = 4lrn + CO$_2$ (Zharikov & Shmulovich, 1969)

Appendix 2. (*Continued*)

78) ta + 2en = anth (Chernosky *et al.*, 1985)
79) br = per + H_2O (Barnes & Ernst, 1963)
80) br = per + H_2O (Aranovich & Newton, 1996)
81) br = per + H_2O (Schramke *et al.,* 1982; Irving *et al.*, 1977)
82) br = per + H_2O (Irving *et al.*, 1977)
83) br = per + H_2O (Kanzaki, 1991)
84) 2ta = 3en + 2q + $2H_2O$ (Chernosky, 1976a,b; Chernosky *et al.*, 1985; Skippen, 1971)
85) 2ta = 3en + 2q + $2H_2O$ (Chernosky *et al.*, 1985)
86) 2ta = 3en + 2q + $2H_2O$ (Jenkins *et al.*, 1991)
87) 2ta = 3en + 2q + $2H_2O$ (Aranovich & Newton, 1999)
88) 2ta = 3en + 2coe + $2H_2O$ (Pawley & Wood, 1995)
89) 2fo + 2ta = 5en + $2H_2O$ (Chernosky, 1976a,b; Chernosky *et al.*, 1985)
90) 2fo + 2ta = 5en + $2H_2O$ (Pawley, 1998)
91) 2anth = 7en + 2q + $2H_2O$ (Chernosky & Autio, 1979)
92) 7ta = 3anth + 4q + $4H_2O$ (Chernosky & Autio, 1979)
93) 2anth + 2fo = 9en + $2H_2O$ (Chernosky *et al.*, 1985)
94) 9ta + 4fo = 5anth + $4H_2O$ (Chernosky *et al.*, 1985)
95) br + chr = 2fo + $3H_2O$ (Johannes, 1968; Kitahara *et al.*, 1966)
96) 5chr = ta + 6fo + $9H_2O$ (Chernosky, 1982; Kitahara *et al.*, 1966)
97) liz = chr (Chernosky, 1975)
98) 17liz = atg + 3br (Evans, 2004)
99) atg = 4ta + 18fo + $27H_2O$ (Evans *et al.*, 1976)
100) atg = 4ta + 18fo + $27H_2O$ (Wunder & Schreyer, 1997)
101) atg = 14fo + 10cen + $31H_2O$ (Wunder & Schreyer, 1997)
102) atg = 14fo + 10cen + $31H_2O$ (Wunder & Schreyer, 1997)
103) atg = 14fo + 10en + $31H_2O$ (Bose & Navrotsky, 1998)
104) 2br + cen = 2fo + $2H_2O$ (Wunder & Schreyer, 1997)
105) atg + 14ta = 45en + $45H_2O$ (Pawley, 1996)
106) phA = 3br + 2fo (Pawley & Wood, 1995)
107) 6atg + 226fo = 62phA + 153en (Bose & Navrotsky, 1998)
108) anth = cumm (Ghiorso & Evans, 2002)

Equilibrium: cum enfs ol q H_2O (Fonarev & Korolkov, 1980), involving next two reactions:
109) 2cumm = 7en + 2q + $2H_2O$
110) 2grun = 7fs + 2q + $2H_2O$
111) chum = 4fo + per + H_2O (Duffy & Greenwood, 1979)
112) chum = 4fo + per + H_2O (Pawley, 2000)
113) chum = 4fo + br (Pawley, 2000)
114) 4fo + br = chum (Wunder, 1998)
115) 4fo + br = chum (Wunder, 1998)
116) mag = per + CO_2 (Harker & Tuttle, 1955; Goldsmith & Heard, 1962)
117) mag = per + CO_2 (Johannes & Metz, 1968; Philipp & Girsperger, 1990; Koziol & Newton, 1995)
118) mag = per + CO_2 (Irving & Wyllie, 1975)
119) 2mag + 2q = en + $2CO_2$ (Johannes, 1969)
120) 2mag + 2q = en + $2CO_2$ (Koziol & Newton, 1995)
121) 2mag + 2coe = en + $2CO_2$ (Haselton *et al.*, 1978)
122) 2mag + en = 2fo + $2CO_2$ (Haselton *et al.*, 1978; Koziol & Newton, 1998)
123) ta + 5mag = 4fo + $5CO_2$ + H_2O (Greenwood, 1967a,b)
124) 2wo + 2mont = di + merw (Yoder, 1968)
125) wo + mont = ak (Yoder, 1968)
126) di + merw = 2ak (Yoder, 1968)
127) di + 3mont = fo + 2ak (Walter, 1963; Yoder, 1968)
128) 2di + ta = tr (Jenkins *et al.*, 1991)
129) di + 2mag = en + dol (Brey *et al.*, 1983)
130) spu + 2mont = 2merw + cc (Walter, 1965)
131) 2tr = 3en + 4di + 2q + $2H_2O$ (Yin & Greenwood, 1983)
132) 2tr = 3en + 4di + 2q + $2H_2O$ (Boyd, 1959)
133) 2tr = 3en + 4di + 2q + $2H_2O$ (Jenkins *et al.*, 1991)
134) 2tr + 2fo = 5en + 4di + $2H_2O$ (Jenkins, 1983)
135) dol = cc + per + CO_2 (Goldsmith, 1980)
136) dol = cc + per + CO_2 (Harker & Tuttle, 1955)
137) *dol + 2q = di + $2CO_2$* (Slaughter *et al.,* 1975; Eggert & Kerrick, 1981; Jacobs & Kerrick, 1981)
138) dol + 2q = di + $2CO_2$ (Eggler *et al.*, 1976)
139) dol + 2coe = di + $2CO_2$ (Luth, 1995)
140) di + 3dol = 2fo + 4cc + $2CO_2$ (Kase & Metz, 1980)
141) 2dol + ta + 4q = tr + $4CO_2$ (Eggert & Kerrick, 1981)
142) di + cc = ak + CO_2 (Walter, 1963)
143) ak + fo + cc = 3mont + CO_2 (Walter, 1963)
144) fo + di + 2cc = 3mont + $2CO_2$ (Walter, 1963)
145) 5dol + 4ta = 6fo + 5di + $4H_2O$ + $10CO_2$ (Skippen, 1971)
146) ta + 3cc + 2q = 3di + H_2O + $3CO_2$ (Skippen, 1971)
147) 5dol + 8q + H_2O = tr + 3cc + $7CO_2$ (Slaughter *et al.*, 1975; Eggert & Kerrick, 1981)
148) 5ta + 6cc + 4q = 3tr + $6CO_2$ + $2H_2O$ (Slaughter *et al.*, 1977)
149) 3dol + 4q + H_2O = ta + 3cc + $3CO_2$ (Eggert & Kerrick, 1981; Metz & Puhan, 1971; Gordon & Greenwood, 1970)
150) tr + 3cc + 2q = 5di + $3CO_2$ + H_2O (Slaughter *et al.*, 1975)
151) tr + 11dol = 8fo + 13cc + $9CO_2$ + H_2O (Metz, 1976)
152) 3tr + 5cc = 11di + 2fo + $5CO_2$ + $3H_2O$ (Chernosky & Berman, 1986a,b)
153) ky = and (Holdaway, 1971; Newton, 1966a; Richardson *et al.*, 1969; Bohlen *et al.*, 1991)
154) ky = sill (Newton, 1966b; Richardson *et al.*, 1968; Holdaway, 1971; Bohlen *et al.*, 1991)

155) and = sill (Pattison, personal communications)
156) and = sill (Holdaway, 1971; Bowman, 1975; Kerrick & Heninger, 1984)
157) and = sill (Richardson *et al.*, 1969)
158) ky = cor + q (Harlov & Newton, 1993; Harlov & Milke, 2002)
159) cor + q = sill (Harlov *et al.*, 2008)
160) cor + q = and (Harlov & Newton, 1993)
161) cor + stv = ky (Schmidt *et al.*, 1997)
162) 2dsp = cor + H_2O (Haas, 1972; Fockenberg *et al.*, 1996)
163) 2dsp = cor + H_2O (Vidal *et al.*, 1994)
164) prl + 6dsp = 4and + $4H_2O$ (Haas & Holdaway, 1973; Hemley *et al.*, 1980)
165) 2dsp + 4q = prl (Theye *et al.*, 1997)
166) 2dsp + 4coe = prl (Theye *et al.*, 1997)
167) prl = cor + 4q + H_2O (Chatterjee *et al.*, 1984)
168) prl = and + 3q + H_2O (Hemley *et al.*, 1980; Kerrick, 1968)
169) prl = and + 3q + H_2O (Haas & Holdaway, 1973)
170) kao + 2q = prl + H_2O (McPhail, 1985; Hemley *et al.*, 1980)
171) 2kao = 2dsp + prl + $2H_2O$ (Hemley *et al.*, 1980)
172) tpz = ky + H_2O (Wunder *et al.*, 1993)
173) gr + 2ky + q = 3an (Koziol & Newton, 1988; Goldsmith, 1980)
174) gr + 2ky + q = 3an (Gasparik, 1984; Hays, 1967)
175) gr + q = an + 2wo (Huckenholz *et al.*, 1975; Newton, 1966c; Hays, 1967; Windom & Boettcher, 1976)
176) gr + cor = geh + an (Boettcher, 1970; Huckenholz *et al.*, 1975)
177) 2gr = 3wo + geh + an (Huckenholz *et al.*, 1975; Hays, 1967)
178) gr + 2cor = 3cats (Gasparik, 1984)
179) 2cats + 2caes = 3an (Gasparik, 1984)
180) gr + 3ky = 3an + cor (Gasparik, 1984)
181) gr + 3cats = 2an + 2geh (Hays, 1967)
182) 3cats = an + geh + cor (Hays, 1967)
183) gr + 3ky = 3an + cor (Gasparik, 1984)
184) 3an + cc = me (Baker & Newton, 1994)
185) 3an + cc = me (Goldsmith & Newton, 1977)
186) gr + cc + 2ky + q = me (Baker & Newton, 1994)
187) 4zo + q = 5an + gr + $2H_2O$ (Boettcher, 1970; Newton, 1966; Chatterjee *et al.*, 1984)
188) 4zo + q = 5an + gr + $2H_2O$ (Newton, 1966)
189) 6zo = 6an + 2gr + cor + $3H_2O$ (Boettcher, 1970; Newton, 1965; Chatterjee *et al.*, 1984)
190) 2zo + ky + q = 4an + H_2O (Goldsmith, 1981; Jenkins *et al.*, 1983; Johannes, 1984)
191) 2zo + sill + q = 4an + H_2O (Newton, 1966; Newton & Kennedy, 1963)
192) ma = an + cor + H_2O (Chatterjee, 1974)
193) ma = an + cor + H_2O (Storre & Nitsch, 1974)
194) ma + q = an + and + H_2O (Storre & Nitsch, 1974)
195) ma + q = an + ky + H_2O (Storre & Nitsch, 1974)
196) 4ma + 3q = 2zo + 5ky + $3H_2O$ (Jenkins, 1984)
197) ma + q = an + and + H_2O (Nitsch *et al.*, 1981)
198) ma + q = an + ky + H_2O (Nitsch *et al.*, 1981)
199) 4ma = 2zo + 2ky + 3cor + $3H_2O$ (Chatterjee *et al.*, 1984)
200) law = an + $2H_2O$ (Crawford & Fyfe, 1965)
201) 4law + 2q = 2zo + prl + $6H_2O$ (Nitsch, 1972)
202) 12law = 6zo + 2ky + prl + $20H_2O$ (Nitsch, 1972)
203) 5law = 2zo + ma + 2q + $8H_2O$ (Nitsch, 1974)
204) 2law + dsp = zo + ky + $4H_2O$ (Schmidt & Poli, 1994)
205) 4law = 2zo + ky + q + $7H_2O$ (Schmidt & Poli, 1994; Chatterjee *et al.*, 1984)
206) 4law = 2zo + ky + q + $7H_2O$ (Newton & Kennedy, 1963)
207) 4law = 2zo + ky + q + $7H_2O$ (Skrok *et al.*, 1994)
208) pre = an + wo + H_2O (Chatterjee *et al.*, 1984)
209) 5pre = 2zo + 2gr + 3q + $4H_2O$ (Connolly & Kerrick, 1985)
210) wrk = an + 2q + $2H_2O$ (Liou, 1970)
211) lmt = an + 4q + $4H_2O$ (Thompson, 1970)
212) lmt = wrk + $2H_2O$ (Liou, 1971a,b,c)
213) law + 2q + $2H_2O$ = lmt (Liou, 1971a,b,c)
214) law + 2q = wrk (Liou, 1971a,b,c)
215) lmt + 3q + $2H_2O$ = heu (Cho *et al.*, 1987)
216) stlb = lmt + 3q + $3H_2O$ (Liou, 1971a,b,c)
217) 3cc + an + cor = 2geh + $3CO_2$ (Shmulovich, 1974)
218) 2cc + an = wo + geh + $2CO_2$ (Shmulovich, 1974)
219) wo + cc + an = gr + CO_2 (Hoschek, 1974)
220) an + cor + 3cc = 2geh + $3CO_2$ (Hoschek, 1974)
221) 2an + 3cc = geh + gr + $3CO_2$ (Hoschek, 1974)
222) an + 2cc = geh + wo + $2CO_2$ (Hoschek, 1974)
223) 2zo + CO_2 = 3an + cc + H_2O (Allen & Fawcett, 1982)
224) cc + q + and = an + CO_2 (Chernosky & Berman, 1991)
225) cc + q + and = an + CO_2 (Jacobs & Kerrick, 1981)
226) cc + q + ky = an + CO_2 (Jacobs & Kerrick, 1981)
227) per + cor = sp (Chamberlin *et al.*, 1995)

Equilibrium: opx cor py (Gasparik & Newton, 1984), involving next two reactions:
228) 3en + 2cor = 2py
229) en + mgts = py

Equilibrium: opx cor py (Fockenberg, 2008), involving next two reactions:
230) 3en + 2cor = 2py
231) en + mgts = py

Appendix 2. (*Continued*)

Equilibrium: py q opx sill (Perkins, 1983; Hensen & Essene, 1971), involving next two reactions:
232) 2py + 2q = 3en + 2sill
233) en + mgts = py

Equilibrium: py opx q ky (Hensen, 1972), involving next two reactions:
234) 2py + 2q = 3en + 2ky
235) en + mgts = py

Equilibrium: fo py sp opx (Danckwerth & Newton, 1978; Gasparik & Newton, 1984), involving next two reactions:
236) fo + py = sp + 2en
237) en + mgts = py
238) en + sp = mgts + fo (Gasparik & Newton, 1984)
239) en + mgts = py (Perkins et al., 1981)
240) hcrd = crd + H_2O (Mirwald et al., 1979)
241) hcrd = crd + H_2O (Schreyer & Yoder, 1964)
242) hcrd = crd + H_2O (Carey, 1995; Skippen & Gunter, 1996)
243) hcrd = crd + H_2O (Mukhopadhyay & Holdaway, 1994)

Equilibrium: opx sp fo crd (Hertzberg, 1983), involving next two reactions:
244) 5en + 2sp = 5fo + crd
245) en + sp = mgts + fo

Equilibrium: opx sp fo cd H_2O (Seifert, 1974; Fawcett & Yoder, 1966), involving next three reactions:
246) 5en + 2sp = 5fo + crd
247) en + sp = mgts + fo
248) hcrd = crd + H_2O

Equilibrium: opx sill q crd (Newton, personal communication), involving next three reactions:
249) en + 2sill + q = crd
250) 2mgts + 3q = crd
251) 3en + 6sill = 2mgts + 2crd

Equilibrium: opx sill cd cor H_2O (Newton, 1972), involving next four reactions:
252) 3en + 6sill = 2mgts + 2crd
253) en + 3sill = crd + cor
254) hcrd + cor = en + 3sill + H_2O
255) hcrd = crd + H_2O

Equilibrium: opx sa q crd (Newton, 1972; Perkins et al., 1981), involving next three reactions:
256) 2crd = spr4 + 8q
257) 5crd = 2spr5 + 2en + 19q
258) crd = 2mgts + 3q

Equilibrium: sa q crd sill (Newton, 1972; Perkins et al., 1981), involving next two reactions:
259) 2crd = spr4 + 8q
260) 3crd + 4sill = 2spr5 + 17q

Equilibrium: sa q opx sill (Newton, 1972; Hensen, 1972), involving next five reactions:
261) spr4 + 6q = 2en + 4sill
262) 2spr5 + 14q = 3en + 10sill
263) en + spr5 = mgts + spr4
264) spr4 + 2q = 4mgts
265) en + spr4 + 2sill = 6mgts

Equilibrium: py opx sa sill (Boyd & England, 1959; Arima & Onuma, 1977; Hensen, 1972), involving next three reactions:
266) 6py = spr4 + 7en + 2sill
267) 7py = spr5 + 9en + 2sill
268) py = en + mgts

Equilibrium: py opx sa ky (Fockenberg, 2008), involving next four reactions:
269) 6py = spr4 + 7en + 2ky
270) 7py = spr5 + 9en + 2ky
271) en + spr5 = mgts + spr4
272) py = en + mgts

Equilibrium: py sp cor sa (Ackermand et al., 1975; Doroshev & Malinovskiy, 1974), involving next two reactions:
273) 2py + 6sp + 4cor = 3spr4
274) py + 6sp + 8cor = 3spr5

Equilibrium: py cor sa sill (Malinovsky & Doroshev, 1975), involving next two reactions:
275) 4py + 14cor = 3spr4 + 6sill
276) py + 6cor = spr5 + 2sill

Equilibrium: opx cor sa sill (Malinovsky & Doroshev, 1975), involving next two reactions:
277) 2en + 6cor = spr4 + 2sill
278) 3en + 14cor = 2spr5 + 4sill

Equilibrium: sa opx cd sp H_2O (Seifert, 1974), involving next four reactions:
279) 2crd + 16sp = 5spr4
280) 5spr5 + 5en = 3crd + 19sp
281) hcrd = crd + H_2O
282) en + spr5 = mgts + spr4

Equilibrium: cor opx sp sa (Podlesskii, 1996), involving next three reactions:
283) en + 4sp + 6cor = 2spr5
284) en + 2sp + 2cor = spr4
285) en + 2cor = 2mgts

Equilibrium: chl cor cd sa H_2O (Seifert, 1974), involving:
286) 16clin + 64cor = 2crd + 19spr4 + 64H_2O

Equilibrium: chl cd opx sa H_2O (Seifert, 1974), involving next two reactions:
287) 16clin + 6crd = 32en + 7spr4 + 64H_2O
288) hcrd = crd + H_2O

Equilibrium: chl cor sp sa H_2O (Seifert, 1974; Ackermand et al., 1975), involving next two reactions:
289) 2clin + 8cor + 2sp = 3spr4 + 8H_2O
290) 2clin + 20cor + 8sp = 6spr5 + 8H_2O

Equilibrium: chl opx fo py H_2O (Pawley, 2003), involving:
291) clin + en = 2fo + py + 4H_2O

Equilibrium: chl opx fo sp H_2O (Baker & Holland, 1996), involving next two reactions:
292) clin = en + fo + sp + 4H_2O
293) ames = en + 2sp + 4H_2O

Equilibrium: chl opx fo H_2O (Baker & Holland, 1996), involving next two reactions:
294) clin = 2fo + mgts + 4H_2O
295) 2clin = ames + 2fo + en + 4H_2O

Equilibrium: chl cor sp H_2O (Baker & Holland, 1996), involving:
296) 3ames = 2clin + 2cor + 2sp + 4H_2O

Equilibrium: chl cor py sp H_2O (Ackermand et al., 1975), involving next two reactions:
297) clin + 2cor = py + 2sp + 4H_2O
298) 2py + 6sp + 12H_2O = 3ames + 2cor

Equilibrium: chl opx fo sp H_2O (Jenkins, 1981; Jenkins & Chernosky, 1986; Fawcett & Yoder, 1966), involving next two reactions:
299) clin = en + fo + sp + 4H_2O
300) ames = en + 2sp + 4H_2O

Equilibrium: chl opx fo sp H_2O (Jenkins, 1981; Jenkins & Chernosky, 1986; Fawcett & Yoder, 1966), involving next two reactions:
301) clin = en + fo + sp + 4H_2O
302) ames = en + 2sp + 4H_2O
303) 2mcar = sud + q (Vidal et al., 1992)

Equilibrium: chl py fo sp H_2O (Staudigel & Schreyer, 1977), involving:
304) 2clin = py + 3fo + sp + 8H_2O

Equilibrium: chl py fo sp H_2O (Fockenberg, 1995), involving:
305) 2clin = py + 3fo + sp + 8H_2O

Equilibrium: chl q ky tlc H_2O (Massonne et al., 1981), involving next two reactions:
306) 3clin + 14q = 3ky + 5ta + 7H_2O
307) 2clin + 4q = ames + 2ta + 2H_2O

Equilibrium: chl opx fo cd H_2O (Jenkins & Chernosky, 1986), involving:
308) 2clin + 3en = 7fo + crd + 8H_2O

Equilibrium: chl cd opx sp H_2O (Jenkins & Chernosky, 1986), involving next two reactions:
309) 5clin + crd = 10en + 7sp + 20H_2O
310) hcrd = crd + H_2O

Equilibrium: chl fo sp cd H_2O (Chernosky, 1974; McPhail et al., 1990), involving:
311) 5clin = 10fo + 3sp + crd + 20H_2O

Equilibrium: chl q tlc cd H_2O (Chernosky, 1978), involving:
312) 6clin + 29q = 8ta + 3crd + 16H_2O

Equilibrium: chl q tlc cd H_2O (Massonne, 1989), involving:
313) 6clin + 29q = 8ta + 3crd + 16H_2O

Equilibrium: tlc sill q cd H_2O (Newton, 1972), involving next four reactions:
314) 2ta + 6sill + q = 3crd + 2H_2O
315) hcrd = crd + H_2O
316) 2ta + 6sill + q + H_2O = 3hcrd
317) tap = sill + 3q + H_2O

Equilibrium: tlc ky q cd H_2O (Massonne & Schreyer, 1989), involving next two reactions:
318) 2ta + 6ky + q = 3crd + 2H_2O
319) hcrd = crd + H_2O

Equilibrium: chl ky q cd H_2O (Seifert & Schreyer, 1970), involving:
320) 2clin + 8ky + 11q = 5crd + 8H_2O

Equilibrium: chl and q cd H_2O (Seifert & Schreyer, 1970), involving next two reactions:
321) 2clin + 8and + 11q = 5crd + 8H_2O
322) hcrd = crd + H_2O

Equilibrium: chl and cd cor H_2O (Seifert, 1973), involving:
323) 2clin + 19and = 5crd + 11cor + 8H_2O

Equilibrium: chl sill cd cor H_2O (Seifert, 1973), involving:
324) 2clin + 19sill = 5crd + 11cor + 8H_2O

Equilibrium: chl ky cd cor H_2O (Seifert, 1973), involving:
325) 2clin + 19ky = 5crd + 11cor + 8H_2O

Equilibrium: chl cor cd sp H_2O (Seifert, 1974), involving:
326) 5clin + 20cor = 3crd + 19sp + 20H_2O
326) equil: chl cor cd sp H_2O (Seifert, 1974)
327) clin + 2mag = 3fo + sp + 2CO_2 + 4H_2O (Chernosky & Berman, 1986a,b)
328) 3mctd = py + 2cor + 3H_2O (Chopin & Schreyer, 1983)

Appendix 2. (*Continued*)

Equilibrium: mctd tlc chl ky H$_2$O (Koch-Müller & Wirth, 2001), involving:
329) 7mctd + ta = 2clin + 5ky
330) 8mctd + 3cor + 7ky = 2mst + 4H$_2$O (Schreyer, 1968)
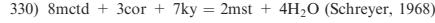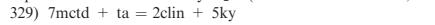
Equilibrium: chl ky cor mst H$_2$O (Massonne, 1995), involving:
331) 8clin + 51ky + 31cor = 10mst + 12H$_2$O
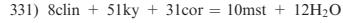
Equilibrium: chl ky cor mst H$_2$O (Fockenberg, 1998), involving:
332) 8clin + 51ky + 31cor = 10mst + 12H$_2$O
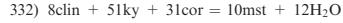
Equilibrium: mst ky cor opx H$_2$O (Fockenberg, 1998), involving:
333) 2mst = 7ky + 11cor + 4en + 4H$_2$O
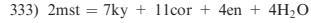
Equilibrium: mst tlc ky cor H$_2$O (Fockenberg, 1998), involving:
334) 6mst = 8ta + 13ky + 41cor + 4H$_2$O
335) 8mctd + 7ky + 6dsp = 2mst + 7H$_2$O (Fockenberg, 1998)
336) 6mst = 8py + 21ky + 25cor + 12H$_2$O (Fockenberg, 1998)
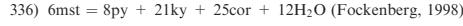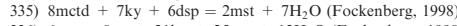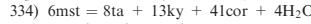
Equilibrium: tlc mst ky py H$_2$O (Chopin & Sobolev, 1995), involving:
337) 25ta + 12mst = 67ky + 41py + 49H$_2$O
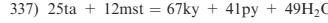
Equilibrium: tlc chl mst py H$_2$O (Fockenberg, 2008), involving next three reactions:
338) 67clin + 78ta = 16mst + 211py + 378H$_2$O
339) 2ames + 2ta = clin + 3py + 6H$_2$O
340) 67ames + 106ta + 8mst = 206py + 390H$_2$O
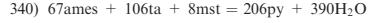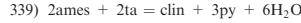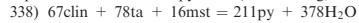
Equilibrium: mcar q tlc ky H$_2$O (Chopin & Schreyer, 1983), involving:
341) 3mcar + q = ta + 3ky + 5H$_2$O

Equilibrium: mcar chl ky tlc H$_2$O (Chopin & Schreyer, 1983), involving:
342) 14mcar + clin + 13ky + 3ta = 21H$_2$O
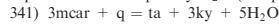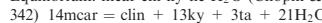
Equilibrium: mcar chl ky q H$_2$O (Chopin & Schreyer, 1983), involving:
343) 5mcar = clin + 4ky + 3q + 6H$_2$O

Equilibrium: tlc q ky H$_2$O (Hoschek, 1995), involving next two reactions:
344) 2ta + 3ky + H$_2$O = 3tats + 2q
345) tap = ky + 3q + H$_2$O
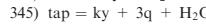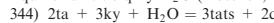
Equilibrium: zo tlc trts ky q H$_2$O (Hoschek, 1995), involving next three reactions:
346) 2ta + 3ky + H$_2$O = 3tats + 2q
347) 5ts + 7q = 3tr + 7ky + 2zo + H$_2$O
348) 12zo + 14ta = 3tr + 9ts + 14q + 8H$_2$O
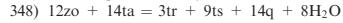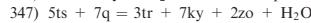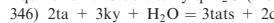
Equilibrium: phe tlc trts mbi zo q H$_2$O (Hoschek, 1990), involving next two reactions:
349) 9mu + 6tr = 9phl + 26q + ta + 6zo + 2H$_2$O
350) 33phl + 21ta + 22zo = 26east + 7mu + 22tr + 10H$_2$O
351) ts + 2di + 2q = tr + 2an (Jenkins, 1994)
352) ts + 2fo = tr + 2sp (Jenkins, 1994)
353) clin + 2dol = 3fo + 2cc + sp + 4H$_2$O + 2CO$_2$ (Chernosky & Berman, 1986a,b)
354) 3clin + 2cc = 2di + 5fo + 3sp + 2CO$_2$ + 12H$_2$O (Chernosky & Berman, 1986a,b)
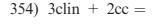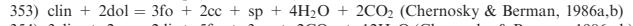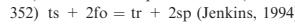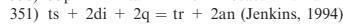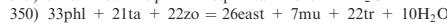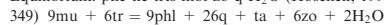
Equilibrium: mpm cz gr chl q H$_2$O (Schiffman & Liou, 1980), involving:
355) 25mpm = 29cz + 14gr + 5clin + 6q + 53H$_2$O
356) 2vsv + 6q = 11gr + 4di + wo + 9H$_2$O (Hochella et al., 1982)
357) cg = cgh (Bowen & Greig, 1925; Cohen & Klement, 1967)
358) ne = cgh (Greig & Barth, 1938)
359) jd + q = abh (Holland, 1980)
360) jd + q = ab (Newton & Smith, 1967; Holland, 1980)
361) jd + ky = abh + cor (Essene et al., 1972)
362) 2jd = ne + abh (Gasparik, 1985; Robertson et al., 1957; Boettcher & Wyllie, 1968)
363) 6ne + 2hlt = sdl (Sharp et al., 1989)
364) sdl = 6cgh + 2hltL (Sharp et al., 1989)
365) pa = jd + ky + H$_2$O (Holland, 1979)
366) pa = abh + cor + H$_2$O (Chatterjee, 1970)
367) pa + q = abh + and + H$_2$O (Chatterjee, 1972)
368) pa + q = abh + ky + H$_2$O (Chatterjee, 1972)
369) jd + H$_2$O = anl (Manghnani, 1970)
370) anl + q = abh + H$_2$O (Thompson, 1971; Liou, 1971)
371) mu = san + cor + H$_2$O (Chatterjee & Johannes, 1974)
372) mu + q = san + and + H$_2$O (Chatterjee & Johannes, 1974)
373) mu + q = san + sill + H$_2$O (Chatterjee & Johannes, 1974)

Equilibrium: mu q san mlt H$_2$O (Segnit & Kennedy, 1961), involving next three reactions:
374) mu + q = san + smul + H$_2$O
375) 5mu + 2q = 5san + 4amul + 5H$_2$O
376) 2smul + 3mu = 4amul + 3san + 3H$_2$O
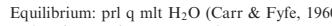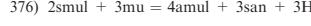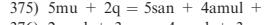
Equilibrium: prl q mlt H$_2$O (Carr & Fyfe, 1960), involving next two reactions:
377) prl = smul + 3q + H$_2$O
378) 5prl = 4amul + 18q + 5H$_2$O
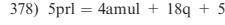
Equilibrium: crd cor mlt sa (Seifert, 1974), involving next four reactions:
379) 13smul = 2spr5 = 17cor + 3crd
380) 8smul + spr4 = 8cor + 2crd
381) 73smul + 6spr5 = 68amul + 9crd
382) 32amul + 6crd = 40smul + 3spr4
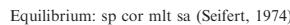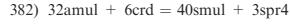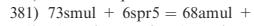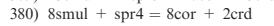
Equilibrium: sp cor mlt sa (Seifert, 1974), involving next four reactions:
383) 2smul + 3cor = 4amul
384) 26smul + 12spr5 = 40amul + 9spr4
385) 2smul + 4spr5 = 10cor + 3spr4
386) 4amul + 4spr5 = 13cor + 3spr4
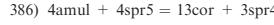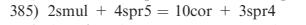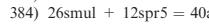
Equilibrium: mlt mqL (Klug et al., 1987), involving next two reactions:
387) smul = silL
388) 4amul + 3qL = 5silL

Equilibrium: mlt crst mqL (Klug et al., 1987), involving next three reactions:
389) crst = qL
390) smul = silL
391) 4amul + 3qL = 5silL

Equilibrium: mlt cor mqL (Klug et al., 1987), involving next three reactions:
392) cor = corL
393) smul = silL
394) 4amul + 3qL = 5silL
395) kcm = san + H$_2$O (Massonne 1999; Fasshauer et al., 1997; Thompson, 1994)
396) wa + ky + coe = 2san (Fasshauer et al., 1998; Yagi et al., 1994; Urakawa et al., 1994; Yong et al., 2008)
397) 2hol = wa + ky + coe (Yagi et al., 1994; Urakawa et al., 1994)
398) kls + san = 2lc (Scarfe et al., 1966; Lindsley, 1966; Fasshauer et al., 1998)
399) kls + 2coe = san + 2coe (Fasshauer et al., 1998)
400) san + fo = lc + en (Luth, 1967)
401) 2phl + 3en = 2san + 6fo + 2H$_2$O (Luth, 1967)
402) 2phl + san = 3lc + 3fo + 2H$_2$O (Luth, 1967)
403) 2phl + kls = lc + 3fo + 2H$_2$O (Luth, 1967)

Equilibrium: phe chl mbi ky q H$_2$O (Bird & Fawcett, 1973), involving next two reactions:
404) 5mu + 3clin = 5phl + 8ky + q + 12H$_2$O
405) cel + east = mu + phl
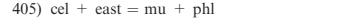
Equilibrium: phe chl mbi ky q H$_2$O (Massonne, unpublished), involving next two reactions:
406) 5mu + 3clin = 5phl + 8ky + q + 12H$_2$O
407) cel + east = mu + phl

Equilibrium: phe mbi q cd san H$_2$O (Seifert, 1976), involving next two reactions:
408) 6mu + 2phl + 15q = 3crd + 8san + 8H$_2$O
409) cel + east = mu + phl

Equilibrium: phe chl q cd mbi H$_2$O (Seifert, 1970), involving:
410) mu + clin + 2q = crd + phl + 4H$_2$O
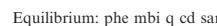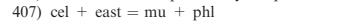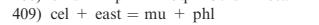
Equilibrium: cd phe mbi sill q H$_2$O (Seifert, 1970), involving next two reactions:
411) 2phl + 8sill + 7q = 3crd + 2mu
412) cel + east = mu + phl
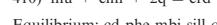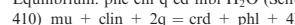
Equilibrium: tlc phe coe ky H$_2$O (Massonne & Schreyer, 1989), involving next two reactions:
413) 6cel + 6ky + 2H$_2$O = 2ta + 6mu + 4coe
414) 2ta + 3ky + H$_2$O = 3tats + 2coe

Equilibrium: tlc phe q ky H$_2$O (Massonne & Schreyer, 1989), involving:
415) 6cel + 6ky + 2H$_2$O = 2ta + 6mu + 4q

Equilibrium: phe ky py coe H$_2$O (Massonne & Szpurka, 1997), involving:
416) 3cel + 4ky = py + 3mu + 4coe
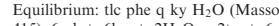
Equilibrium: fphe ky alm coe H$_2$O (Massonne & Szpurka, 1997), involving:
417) 3fcel + 4ky = alm + 3mu + 4coe
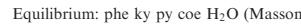
Equilibrium: fphe ky alm q H$_2$O (Massonne & Szpurka, 1997), involving:
418) 3fcel + 4ky = alm + 3mu + 4q
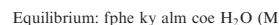
Equilibrium: phe mbi san q H$_2$O (Massonne & Schreyer, 1989), involving next four reactions:
419) 3mu + 2phl = 3east + 2san + 3q + 2H$_2$O
420) 3cel + 2phl = phl + 2san + 3q + 2H$_2$O
421) 3mu + 2phl = 3east + 2san + 3q + 2H$_2$O
422) cel + east = phl + mu
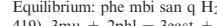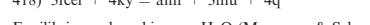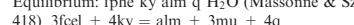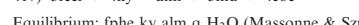
Equilibrium: tlc phe mbi ky q H$_2$O (Massonne & Schreyer, 1989), involving:
423) ta + mu = phl + ky + 3q + H$_2$O
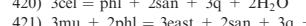
Equilibrium: chl mbi q phe tlc H$_2$O (Massonne & Schreyer, 1989), involving:
424) 3clin + 3phl + 23q = 3mu + 8ta + 4H$_2$O
425) 2phl + 6q = 3en + 2san + 2H$_2$O (Aranovich & Newton, 1998)
426) 2phl + 6q = 3en + 2san + 2H$_2$O (Berman et al., 1995)
427) 2phl + 6q = 3en + 2san + 2H$_2$O (Bohlen et al., 1983a,b,c)
428) 2phl + 6q = 3en + 2san + 2H$_2$O (Peterson & Newton, 1990)
429) 2phl + 6q = 3en + 2san + 2H$_2$O (Wood, 1976)
430) 2jd + ta = gl (Carman & Gilbert, 1983)
431) gl + 2q = ta + 2abh (Corona & Jenkins, 2007)
432) 2naph + 3en = 2abh + 6fo + 2H$_2$O (Carman & Gilbert, 1983)
433) 5phl + 6cc + 24q = 3tr + 5san + 6CO$_2$ + 2H$_2$O (Hewitt, 1975)
434) 3dol + san + H$_2$O = phl + 3cc + 3CO$_2$ (Puhan & Johannes, 1974; Puhan, 1978)
435) mu + cc + 2q = san + an + CO$_2$ + H$_2$O (Hewitt, 1973)
436) 2zo + mu + 2q = 4an + san + 2H$_2$O (Johannes, 1980)
437) 4law + ab = 2zo + pa + 2q + 6H$_2$O (Heinrich & Althaus, 1980)
438) 4law + jd = 2zo + pa + q + 6H$_2$O (Heinrich & Althaus, 1980)
439) 2parg = 3di + sp + an + 2fo + 2ne + 2H$_2$O (Westrich & Holloway, 1981; Lykins & Jenkins, 1992)
440) 2tr + 2fo = 4di + 5en + 2H$_2$O (Lykins & Jenkins, 1992)
441) 2ts = 2fo + 4an + en + 2H$_2$O (Lykins & Jenkins, 1992)
442) 2parg + 5en = 2di + 8fo + 2an + 2abh + 2H$_2$O (Lykins & Jenkins, 1992)
443) fs = fa + q (Bohlen et al., 1980)
444) 4mt + O$_2$ = 6hem (Myers & Eugster, 1983)
445) 4mt + O$_2$ = 6hem (Chou, 1978)
446) 3fa + O$_2$ = 3q + 2mt (Chou, 1978)

Appendix 2. (*Continued*)

447) $3fa + O_2 = 3q + 2mt$ (Myers & Eugster, 1983)
448) $3fa + O_2 = 3q + 2mt$ (Hewitt, 1978)
449) $3fa + O_2 = 3q + 2mt$ (O'Neill, 1987a)
450) $q + 2iron + O_2 = fa$ (O'Neill, 1987b)
451) $3iron + 2O_2 = mt$ (O'Neill, 1988)
452) $2gth = hem + H_2O$ (Voigt & Will, 1981)
453) $sid + hem = mt + CO_2$ (Koziol, 2004)
454) $2grun = 7fs + 2q + 2H_2O$ (Lattard & Evans, 1992)
455) $2grun = 7fa + 9q + 2H_2O$ (Lattard & Evans, 1992)
456) $2deer = 9fs + 6mt + 6q + 10H_2O$ (Lattard & Le Breton, 1994)
457) $deer + Ni = 6fs + 2mt + NiO + 5H_2O$ (Lattard & Le Breton, 1994)
458) $alm + 3hem = 3mt + ky + 2q$ (Harlov & Newton, 1992)
459) $alm + 2sill = 3herc + 5q$ (Bohlen et al., 1986)
460) $alm + 5cor = 3herc + 3sill$ (Shulters & Bohlen, 1989)
461) $2alm + 4sill + 5q = 3fcrd$ (Mukhopadhyay & Holdaway, 1994)
462) $6fst + 25q = 8alm + 46ky + 12H_2O$ (Rao & Johannes, 1979)
463) $6fst + 25q = 8alm + 46ky + 12H_2O$ (Ganguly, 1972)
464) $2fst + 15q = 4fcrd + 10sill + 4H_2O$ (Richardson, 1968)
465) $23fctd + 7q = 2fst + 5alm + 19H_2O$ (Rao & Johannes, 1979)
466) $8fctd + 10ky = 2fst + 3q + 4H_2O$ (Rao & Johannes, 1979)
467) $3fctd = alm + 2cor + 3H_2O$ (Ganguly, 1969; Vidal et al., 1994)
468) $3fctd = alm + 2cor + 3H_2O$ (Ganguly, 1969)
469) $3fctd = 4dsp + alm + H_2O$ (Vidal et al., 1994)
470) $6fst + 25q = 8alm + 46sill + 12H_2O$ (Richardson, 1968)
471) $6fst + 25q = 8alm + 46sill + 12H_2O$ (Dutrow & Holdaway, 1989)
472) $8fctd + 10sill = 2fst + 3q + 4H_2O$ (Richardson, 1968)
473) $5fctd = fcrd + 3herc + 5H_2O$ (Grieve & Fawcett, 1974)
474) $2fgl = 4abh + 3fa + q + 2H_2O$ (Hoffmann, 1972)
475) $rieb + 3hem = 2acm + 3mt + 4q + H_2O$ (Ernst, 1962)
476) $2ann + 6sill + 9q = 3fcrd + 2san + 2H_2O$ (Holdaway & Lee, 1977)
477) $2ann + 3q = 2san + 3fa + 2H_2O$ (Rutherford, 1973)
478) $2ann + 3q = 2san + 3fa + 2H_2O$ (Dachs & Benisek, 1995)
479) $2san + 2mt + 2H_2O = 2ann + O_2$ (Dachs, 1994)
480) $gr + 2alm = 3fa + 3an$ (Bohlen et al., 1983a,b,c)
481) $gr + 2alm = 3fa + 3an$ (Perkins & Vielzeuf, 1992)
482) $2hed = 2wo + fa + q$ (Lindsley & Munoz, 1969)
483) $2fact = 3fa + 5q + 4hed + 2H_2O$ (Jenkins & Bozhilov, 2003)
484) $2minn = 3fa + 5q + 2H_2O$ (Engi, 1986)
485) $glt + 2q = minn + H_2O$ (Rasmussen et al., 1998)
486) $2glt + 5minn = 3grun + 6H_2O$ (Rasmussen et al., 1998)
487) $3sid + minm = minn + 3mag$ (Klein, 1974)
488) $28fstp = 14ann + 5grun + 21alm + 79q + 156H_2O$ (Miyano & Klein, 1989)
489) $mstp + daph = fstp + clin$ (Miyano & Klein, 1989)
490) $andr = 3pswo + hem$ (Huckenholz & Yoder, 1971)
491) $6andr + 3fa = 6mt + 18wo + 3q$ (Gustafson, 1974)
492) $6andr + 2Ni = 4mt + 18wo + 2NiO$ (Gustafson, 1974)
493) $6andr = 4mt + 18wo + O_2$ (Moecher & Chou, 1990)
494) $3andr + mt + 9q = 9hed + 2O_2$ (Burton et al., 1982)
495) $2andr + q + 3fa = 4hed + 2wo + 2mt$ (Liou, 1974)
496) $3andr + 4q + 2Ni = 4hed + 2wo + 2NiO$ (Liou, 1974)
497) $3andr + mt + 9q = 9hed + 2O_2$ (Moecher & Chou, 1990)
498) $2andr + 4q = 4hed + 2wo + O_2$ (Moecher & Chou, 1990)
499) $3cc + hem + 3q = andr + 3CO_2$ (Taylor & Liou, 1978)
500) $cz = zo$ (Natural pairs, unpublished)
501) $2cz + ky + q = 4an + H_2O$ (Jenkins et al., 1983)

Equilibrium: epi an grd hem q H_2O (Holdaway, 1972; Liou, 1973), involving next five reactions:
502) $2fep = andr + an + hem + q + H_2O$
503) $2ep = gr + an + hem + q + H_2O$
504) $6ep = 2andr + 6an + hem + 3H_2O$
505) $4cz + q = 5an + gr + 2H_2O$
506) $6cz + hem + 3q = andr + 9an + 3H_2O$

Equilibrium: grd q an wo (Holdaway, 1972), involving:
507) $gr + q = an + 2wo$

Equilibrium: grd trd an wo (Holdaway, 1972), involving:
508) $gr + trd = an + 2wo$

Equilibrium: epi grd (Perchuk & Aranovich, 1979), involving:
509) $2cz + andr = 2ep + gr$
510) $12pmt + 6cup = 8gr + 4spss + 12ten + 6H_2O$ (Keskinen & Liou, 1979)
511) $osm1 = crd + san + 2q$ (Olesch & Seifert, 1981)
512) $4phl + 3crd + 2san + 33q = 6osm2 + 4H_2O$ (Olesch & Seifert, 1981)
513) $en + san + 2sill + 3q = osm1$ (Carrington & Harley, 1995)
514) $py + osm2 = osm1 + 2en$ (Carrington & Harley, 1995)
515) $osm1 + fs = fosm + en$ (Holland et al., 1996)
516) $fosm + crd = osm1 + fcrd$ (Holland et al., 1996)
517) $mag + ru = geik + CO_2$ (Haselton et al., 1978)
518) $mag + ru = geik + CO_2$ (Ferry et al., 2002)
519) $sph + ky = an + ru$ (Manning & Bohlen, 1991)
520) $ru + cc + q = sph + CO_2$ (Hunt & Kerrick, 1977)
521) $ru + cc + q = sph + CO_2$ (Jacobs & Kerrick, 1981)
522) $2ilm = 2iron + 2ru + O_2$ (O'Neill et al., 1988)
523) $2ilm = 2iron + 2ru + O_2$ (Anovitz et al., 1985)
524) $2usp = 2ilm + 2iron + O_2$ (O'Neill et al., 1988)
525) $2usp = 2ilm + 2iron + O_2$ (Anovitz et al., 1985)

526) $alm + 3ru = 3ilm + sill + 2q$ (Bohlen et al., 1983a,b,c)
527) $2alm + gr + 6ru = 6ilm + 3an + 3q$ (Bohlen & Liotta, 1986)
528) $zrc = bdy + crst$ (Butterman & Foster, 1967)
529) $zrc + 2mag = bdy + fo + 2CO_2$ (Ferry et al., 2002)
530) $2NiO = 2Ni + O_2$ (O'Neill, 1987)
531) $2mag + fa = fo + 2sid$ (Dalton & Wood, 1993)
532) $2dol + fa = fo + 2ank$ (Dalton & Wood, 1993)
533) $dol = ank + mag$ (Anovitz & Essene, 1987)
534) $dol + sid = ank + mag$ (Rosenberg, 1967)
535) $dol + sid = ank + mag$ (Klein, 1978)
536) $dol + sid = ank + mag$ (Klein, 1978)
537) $py + ann = alm + phl$ (Ferry & Spear, 1978)
538) $py + ann = alm + phl$ (Perchuk & Lavrent'eva, 1983)
539) $3fcrd + 2py = 3crd + 2alm$ (Perchuk & Lavrent'eva, 1983)
540) $alm + 3cel = py + 3fcel$ (Green & Hellman, 1982)
541) $alm + 3cel = py + 3fcel$ (Hynes & Forest, 1988)
542) $alm + phl = py + ann$ (Hynes & Forest, 1988)
543) $phl + mu = cel + east$ (Hodges & spear, 1988)
544) $2phl + mu + 2sill = 3east + 5q$ (Hodges & spear, 1988)
545) $2phl + mu + 2ky = 3east + 5q$ (Pigage & Greenwood, 1982)
546) $2mu + phl + py = 3east + 6q$ (Natural)
547) $2mu + phl + py = 3east + 6q$ (Hynes & Forest)
548) $5cel + daph = 5fcel + clin$ (Currie & Van Staal99)
549) $ames + cel = mu + clin$ (Currie & Van Staal99)
550) $2hed + en = fs + 2di$ (Lindsley, 1983)
551) $2hed + fo = fa + 2di$ (Perkins & Vielzeuf, 1992)
552) $fs + fo = en + fa$ (Matsui & Nishizawa, 1974)
553) $fs + fo = en + fa$ (von Seckendorff & O'Neill, 1993)
554) $2py + 3fa = 2alm + 3fo$ (O'Neill & Wood, 1979)
555) $2py + 3fa = 2alm + 3fo$ (Hackler & Wood, 1989)
556) $2py + 3fs = 2alm + 3en$ (Lee & Ganguly, 1988)
557) $2py + 3fs = 2alm + 3en$ (Kawasaki & Matsui, 1983)
558) $2py + 3fs = 2alm + 3en$ (Harley, 1984)
559) $alm + 3di = 3hed + py$ (Wood, 1976)
560) $2herc + fo = 2sp + fa$ (Jamieson & Roeder, 1984)
561) $2herc + fo = 2sp + fa$ (Engi, 1983)
562) $fa + 2mft = 2mt + fo$ (Jamieson & Roeder, 1984)
563) $3en + 2ann = 2phl + 3fs$ (Fonarev & Konilov, 1986)
564) $fact + 5di = tr + 5hed$ (Natural Kd)
565) $7en + 2fanth = 2anth + 7fs$ (Natural Kd)
566) $3tr + 5fgl = 5gl + 3fact$ (Natural Kd)
567) $spr4 + 2fcrd = fspr + 2crd$ (Waters, 1986)
568) $spr4 + 2fs = fspr + 2en$ (Natural Collected)
569) $2acm + pa + 2q = 3ab + hem + H_2O$ (Holland & Ray, 1985)
570) $jd + ep = acm + cz$ (Holland & Ray, 1985)
571) $5alm + 3clin = 5py + 3daph$ (Dickenson & Hewitt, 1986; Laird, 1989)
572) $5phl + 3daph = 5ann + 3clin$ (Laird, 1989)
573) $clin + fact = tr + daph$ (Laird, 1982)
574) $pre + ep = fpre + cz$ (Cho et al., 1986)
575) $5mpm + daph = 5fpm + clin$ (Evans, 1990)
576) $fpm + 5ep = jgd + 5cz$ (Cho et al., 1986)
577) $alm + 3mctd = py + 3fctd$ (Chinner & Dixon, 1974; Miller, 1986)
578) $3fctd + ta = 3mctd + fta$ (Chinner & Dixon, 1974; Chopin & Monie, 1984; Miller, 1986)
579) $5fctd + clin = 5mctd + daph$ (Vidal et al., 1999)
580) $mcar + fctd = fcar + mctd$ (Natural, Seidel & Okrusch, 1977; Theye et al., 1992)
581) $5mcar + daph = 5fcar + clin$ (Natural, Theye et al., 1992)
582) $5sud + 2daph = 5fsud + 2clin$ (Theye et al., 1992)
583) $pxmn = rhod$ (Maresch & Mottana, 1976)
584) $rhc + q = pxmn + CO_2$ (Peters, 1971)
585) $rhc = mang + CO_2$ (Huebner, 1969)
586) $pxmn + rhc = teph + CO_2$ (Huebner & Eugster, 1968)
587) $fo + 2mang = teph + 2per$ (Wood et al., 1994)
588) $2spss + 3fo = 2py + 3teph$ (Wood et al., 1994)
589) $spss + 3ilm = alm + 3pnt$ (Pownceby et al., 1987)
590) $phl + 3mnctd = mnbi + 3mctd$ (Mahar et al., 1997)
591) $4phl + 3mnst = 4mnbi + 3mst$ (Mahar et al., 1997)
592) $2phl + 3mncrd = 2mnbi + 3crd$ (Mahar et al., 1997)
593) $5phl + 3mnchl = 5mnbi + 3clin$ (Mahar et al., 1997)
594) $phl + spss = mnbi + py$ (Mahar et al., 1997)
595) $syv = syvL$ (Clark, 1966)
596) $hlt = hltL$ (Clark, 1966)
597) $di = diL$ (Clark, 1966)
598) $san = kspL$ (Lindsley, 1966)
599) $en = enL$ (Clark, 1966)
600) $pswo = woL$ (Yoder, 1966)
601) $cor = corL$ (Shen & Lazor, 1995 omitting UHP)
602) $crst = qL$ (Jackson, 1976)
603) $crst = qL$ (Jackson, 1976)
604) $q = qL$ (Jackson, 1976)
605) $q = qL$ (Hudon et al., 2002)
606) $q = qL$ (Kanzaki, 1990)
607) $coe = qL$ (Kanzaki, 1990)
608) $coe = qL$ (Zhang et al., 1993)
609) $an = anL$ (Clark, 1966; Goldsmith, 1980)

Appendix 2. (*Continued*)

Equilibrium: an H$_2$O anwL (Clark, 1966), involving next two reactions:
610)	H$_2$OL = H$_2$O
611)	an = anL
612)	lc = lcL (Lindsley 1967; (approx.))
613)	per = perL (Bowen & Anderson, 1914)
614)	lime = limL (Rankin & Wright, 1915)
615)	fo = foL (Davis & England, 1964)
616)	fo = foL (subset of Ohtani & Kumazawa, 1981)
617)	fo = foL (low temperature exp's)
618)	fa = faL (Clark, 1966)
619)	sill = silL (Cameron, 1977; Holland & Carpenter, 1986)
620)	cgh = neL (Bowen, 1912)
621)	ne = neL (Smith, 2003)
622)	abh = abL (Schairer & Bowen, 1956)
623)	abh = abL (Boyd & England, 1963)
624)	abh = abL (Nekvasil & Carroll, 1996)

Equilibrium: abh H$_2$O abwL (Goldsmith & Jenkins, 1985), involving next two reactions:
625)	H$_2$OL = H$_2$O
626)	abh = abL
627)	abh = abL (Goldsmith & Jenkins, 1985)
628)	h$_2$OL = H$_2$O (Goldsmith & Jenkins, 1985)

Equilibrium: san H$_2$O kspwL (Lambert *et al.*, 1969; Goldsmith & Peterson, 1990), involving next two reactions:
629)	h$_2$OL = H$_2$O
630)	san = kspL

Equilibrium: trd H$_2$O qwL (Kennedy *et al.*, 1962), involving next two reactions:
631)	h$_2$OL = H$_2$O
632)	trd = qL

Equilibrium: q H$_2$O qwL (Kennedy *et al.*, 1962), involving next two reactions:
633)	h$_2$OL = H$_2$O
634)	q = qL
635)	h$_2$OL = H$_2$O (Johannes & Holtz, 1996)
636)	h$_2$OL = H$_2$O (Goranson, 1936)
637)	h$_2$OL = H$_2$O (Behrens, 1995)
638)	h$_2$OL = H$_2$O (Behrens, 1995)

Equilibrium: abh q abqL (Luth, 1969), involving next two reactions:
639)	abh = abL
640)	q = qL

Equilibrium: abh trd abqL (Schairer & Bowen, 1956), involving next two reactions:
641)	abh = abL
642)	trd = qL

Equilibrium: an anqL (Schairer & Bowen, 1947), involving:
643)	an = anL

Equilibrium: trd anqL (Schairer & Bowen, 1947), involving:
644)	trd = qL

Equilibrium: an trd anqL (Schairer & Bowen, 1947), involving next two reactions:
645)	an = anL
646)	trd = qL

Equilibrium: ol olL (Bowen & Schairer, 1935), involving next two reactions:
647)	fo = foL
648)	fa = faL

Univariant and divariant solid-solution equilibria start with the keyword 'equilibrium' and are followed by one or more equilibrium relations involving end-members in solid solutions. Solid-solution names: crpx, Cr-cpx; crsp, Cr-spinel; po, pyrrhotite; tro, troilite; ol, Fe–Mg olivine; wd, Fe–Mg wadsleyite; rg, Fe–Mg ringwoodite; pv, Fe–Mg perovskite; aki, Fe–Mg akimotoite; mwu, Fe–Mg periclase; crn, Mg–Al corundum; cum, Fe–Mg cummingtonite; opx, Mg–Al opx; cd, hydrous cordierite; sa, Mg–Al sapphirine; chl, Mg–Al chlorite; tlc, Mg–Al talc; trts, Al–tremolite; phe, Mg-phengite; mbi, Al-phlogopite; mlt, mullite; mqL, Al–Si liquid; epi, Fe–Al epidote; grd, grandite garnet; anwL, an-H$_2$O liquid; abwL, ab-H$_2$O liquid; kspwL, ksp-H$_2$O liquid; qwL, q-H$_2$O liquid; abqL, ab-q liquid; anqL, an-q liquid; olL, fo-fa liquid.

APPENDIX 3: OTHER DATA SET CHANGES

A list of some of the more important changes to thermodynamic data since HP98 follows. Further detailed information may be found on the website at: http://www.esc.cam.ac.uk/people/academic-staff/tim-holland.

1. New experiments by Aranovich & Newton (1998) on the reactions cc + q = wo + CO$_2$ and 2ta = 3en + 2q + 2H$_2$O, and by Koziol & Newton (1998) on 2mag + en = 2fo + 2CO$_2$ at higher pressures and temperatures than before have led to improved thermodynamic data not only on these end-members but also on the mixing parameters for H$_2$O–CO$_2$ mixtures.

2. The data for clinohumite has been updated to incorporate the experimental results of Pawley (2000) on the reactions chum = 4fo + per + H$_2$O and Pawley (2000) and Wunder (1998) on chum = 4fo + br. Compressibility data for chum are from Ross & Crichton (2001), thermal expansion is assumed as for forsterite.

3. Phlogopite data have been updated using the experiments of Aranovich & Newton (1998) on the reaction 2phl + 6q = 3en + 2san + 2H$_2$O. There has been some controversy over the molar volume to use, as the synthetic phlogopites have a larger volume (14.964 J^{-1} bar; Robie & Hemingway, 1995; Aranovich & Newton, 1998) than natural phlogopites (14.687 J^{-1} bar; Smyth & McCormick, 1995; Pavese *et al.*, 2003). Until this is resolved we will use the synthetic volumes as they presumably reflect the synthetic material used in the experiments.

4. The double carbonate reaction equilibrium reactions (arag + mag = dol and arag + sid = ank) are characterized by small free energy changes and are difficult to calculate with accuracy from thermodynamic data gained from a variety of mixed carbonate-silicate equilibria. The recent experimental study of Morlidge *et al.* (2006) means that these equilibria may now be fitted and refined, such that the small differences in free energy are made consistent with the experimental pressures. In addition, the experimental data for cc = arag is now known to much higher pressures and temperatures, and the experiments of Suito *et al.* (2002) may now also be fitted satisfactorily.

5. Data for chlorite have been updated using experiments of Pawley (2003) and Fockenberg (1995). The new heat capacity and entropy data for chlorite are from Bertoldi *et al.* (2007).

6. Compressibility data for pyrophyllite is taken from Pawley (2003). The thermal expansion has been increased somewhat higher than the measurements of Symmes (1986) to satisfy experiments.

7. The data for phengite and aluminous biotite are updated as discussed in Coggon & Holland (2002).

8. New experimental data on cor + q = ky from Harlov & Milke (2002) and Harlov *et al.* (2008) are now incorporated in the data fitting.

9. Heat capacity and entropy for carpholite are taken from Bertoldi *et al.* (2006).

10. New measurements are used for heat capacity and entropy for cordierite (Paukov *et al.*, 2006; Dachs & Geiger, 2008).

11. Ferroactinolite enthalpy is fitted to the experiments of Jenkins & Bozhilov (2003).

12. Experimental data of Koziol (2004) on sid + hem = mt + CO$_2$ are now used to derive enthalpy data for siderite.

13. Measurements of entropy of hercynite are taken from Klemme & Van Miltenburg (2003).
14. Chloritoid–chlorite Fe–Mg natural partitioning data are taken from Vidal *et al.* (1999) and used as low temperature constraints. Heat capacity and entropy for chloritoid and carpholite end-members have been modified using data of Koch-Müller *et al.* (2002) and Bertoldi *et al.* (2006).
15. Glaucophane data have been augmented by experiments of Corona & Jenkins (2007) for gl + q = ab + ta; new thermal expansion data for glaucophane are taken from Jenkins & Corona (2006).
16. Thermal expansion data for staurolite are now taken from Gibbons *et al.* (1981) and compressibility from Grevel *et al.* (1998).
17. Pargasite data are now fitted to the experiments of Westrich & Holloway (1981) and Lykins & Jenkins (1992) using a higher entropy than before. The derived enthalpy agrees well with measured values of Kahl *et al.* (2003). The amphibole mixing terms are from page 264 of Diener *et al.* (2007) except that, for good agreement with temperatures and amphibole compositions in the two experimental studies above, $W_{ts,parg}$ is now set at 2 kJ rather than -40 kJ.
18. Added high pressure experiments on antigorite and phase A from Wunder & Schreyer (1997) and Bose & Navrotsky (1998).
19. Added experiments of Aranovich & Newton (1999) on cc + q = wo + CO_2, mag + en = fo + CO_2 and ta = en + q + H_2O, and phl + q = san + en + H_2O. Also, those of Koziol & Newton (1998) for mag + en = fo + CO_2.
20. Sphene thermodynamic data have been updated using heat capacities and entropy of Manon *et al.* (2008), thermal expansion from Malcherek (2001) and compressibility from Angel *et al.* (1999a,b).
21. Thermodynamic data for zircon and baddeleyite have been updated through the experimental data in Butterman & Foster (1967), Ferry *et al.* (2002) and are in excellent agreement with the Gibbs energies retrieved by Newton *et al* (2010).
22. Geikelite enthalpy has been improved via the additional experiments of Ferry *et al.* (2002) on mag + ru = geik + CO_2.