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An empirical model for the calculation of spinel-melt equilibria in mafic igneous systems at atmospheric pressure: 1. Chromian spinels

Abstract In order to develop a model for simulating naturally occurring chromian spinel compositions, we have processed published experimental data on chromian spinel-melt equilibrium. Out of 259 co-existing spinel-melt experiments reported in the literature, we have selected 118 compositions on the basis of run time, melt composition and experimental technique. These data cover a range of temperatures 1150–1500°C, oxygen fugacities of $-13 < \log f_{O_2} < -0.7$, and bulk compositions ranging from basalt and norite, to komatiite. Six major spinel components with Cr^{3+}, Al^{3+}, Ti^{4+}, Mg^{2+}, Fe^{3+} and Fe^{2+}-bearing end-members were considered for the purpose of describing chromite saturation as a function of melt composition, temperature and oxygen fugacity at 1 atmosphere pressure (0.101 MPa). The empirically calibrated mineral-melt expression based on multiple linear regressions is:

$$\ln K_i^{Sp} = A/T(K) + B \log f_{O_2} + C \ln (Fe^{3+}/Fe^{2+})_L + D \ln R_L + E,$$

where K_i^{Sp} is an equilibrium constant and R_L is a melt structure-chemical parameter (*MSCP*). Twenty-eight forms of equilibrium constants were considered, including single distribution coefficients, exchange equilibrium constants, formation constants for AB_2O_4 components, as well as simple "spinel cation ratios". For each form of the equilibrium constants, a set of 16 combinations of the *MSCP*s have been investigated. The *MSCP* is present in the form of composite ratios [e.g., Si/O, NBO/T,(Al + Si)/Si, or (Na + K)/Al] or as simple cation ratios (e.g., Mg/Fe^{2+}). For the calculation of Fe^{3+} and Fe^{2+} species in silicate melts, we used existing equations, whereas the Fe^{3+}/Fe^{2+} ratio of spinels was calculated from the spinel stoichiometry. The regression parameters that best reproduce the experimental data were for the following constants: $(Fe^{3+}/Fe^{2+})_{Sp}$, $(Mg/Fe^{2+})_{Sp}/(Mg/Fe^{2+})_L$, $(Cr/Al)_{Sp}/(Cr/Al)_L$, $K_{FeCr_2O_4}$, and Ti_{Sp}/Ti_L. These expressions have been combined into a single program called SPINMELT, which calculates chromite crystallization temperature and composition at a given f_{O_2} with an average accuracy of $\sim 10°C$ and 1–2 mol%. An example of the use of SPINMELT is presented for a magma parental to the Bushveld Complex.

Introduction

Within the past decade, a significantly large number of new experimental data on chromium solubility and spinel compositions in a wide range of mafic magmas have been obtained (e.g., Barnes 1986; Murck and Campbell 1986; Roeder and Reynolds 1991). These new data led to several thermodynamic and empirical models developed for predicting spinel crystallization or describing activities of chrome spinel components as a function of temperature, oxygen fugacity and melt composition (Roeder and Reynolds 1991; Sack and Ghiorso 1991a, b; Poustovetov and Roeder 1994; Ariskin and Nikolaev 1995). Traditionally, chromian spinels have served petrologists as a source of information on the redox conditions of magmas and for deducing other parameters of magma evolution in different geological environments (e.g., Irvine 1967; Allan et al. 1988; Danyushevsky and Sobolev 1996). Interest in spinels as petrogenetic indicators has been amplified as a consequence of computer models that provide calculation of crystallization sequences and liquid lines of descent during magma crystallization (Nielsen and Dungan 1983; Nielsen 1990; Ghiorso 1985; Ariskin et al. 1987, 1993; Weaver and Langmuir 1990; Ghiorso and Sack 1995).

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Our purpose here is to present a system of empirically calibrated equations for spinel-melt equilibria that can be integrated into a single empirical model for use in computer simulations. This model would serve a useful tool for igneous petrologists investigating the effects of oxygen fugacity and chromium contents on equilibrium temperature and composition of chromian spinels crystallized from mafic magmas.

Another goal of this study is to integrate the spinel model into the current version of the COMAGMAT software (which is being used by many igneous petrologists, Ariskin et al. 1993) to calculate the composition of chrome spinel crystallizing simultaneously with silicate minerals.

Experimental data and criteria for equilibrium

This work began with a detailed systematization of experimental data on spinel-melt equilibria in natural systems available in the INFOREX-3.0 database (Ariskin et al. 1996; Meshalkin and Ariskin 1996). The current version of INFOREX is a computerized melting-experiment reference database containing 6,174 individual runs from 162 separate studies carried out between 1962 and 1994. The program can sort the data based on compositions, pressure, temperature, oxygen fugacity, experimental run duration, types of experimental containers, and resultant phase assemblages. The INFOREX-3.0 database can access 8,311 coexisting phase compositions; 3,197 represent experimental glass compositions. The main options in the program include: (1) the ability to update and edit the database files, (2) selection of experiments based on a given set of igneous system indicators or intensive parameters, (3) extraction of mineral-melt equilibria data for the selected set of experiments, (4) calculation of phase equilibria parameters (distribution coefficients, geothermometers) and (5) exchange of data files between different users. Using the INFOREX-3.0 database it takes only a few seconds to search and process data from the literature.

For the purpose of this paper, we conducted a global search of spinel-melt equilibria data in INFOREX and found 305 compositions produced in anhydrous silicate systems at 1 atm (0.101 MPa). The low-pressure spinels have been subdivided into two groups: 259 *chromian spinels* and 46 *titanomagnetites* based on Cr_2O_3 contents > 20 wt% and FeO (total) < 30 wt%. For further consideration, three experiments on synthetic melt systems and 34 runs on lunar basalts were excluded from the "chromian spinel" group because of the differences between these compositions and those obtained in experiments with terrestrial igneous rocks. Thus, the final experimental dataset includes only those data on terrestrial basalts (162), norites (41) and komatiites (19).

All the experimental runs were carried out using "Pt wire loop" technique with controlled oxygen fugacities ($10^{-13} < f_{O_2} < 10^{-0.7}$) for temperatures ranging from 1150 to 1500°C. A major problem in the use of these data for thermodynamic modeling is determining which experiments represent equilibrium compositions. There is a general consensus among experimentalists that run durations of ~ 100 hours are necessary to achieve equilibrium between spinel crystals and glass, especially at temperatures lower than 1250–1200°C (Barnes 1986; Murck and Campbell 1986; Roeder and Reynolds 1991). For the above reason, we selected a set of spinel-melt compositions that satisfy the constraints of run duration τ for three temperature ranges: $\tau \geq 96$ h at $1150 < T < 1200$°C, $\tau \geq 72$ h at $1201 < T < 1300$°C, $\tau \geq 48$ h at $1301 < T < 1500$°C. Only 137 experiments from 7 studies satisfy these constraints (Fisk and Bence 1980; Grove and Bryan 1983; Barnes 1986; Murck and Campbell 1986; Sack et al. 1987; Roeder and Reynolds 1991; Thy et al. 1991).

We also took into account the fact that in some chrome-doped experiments (e.g., Barnes 1986 – "B" series runs; Murck and Campbell 1986) "the chromite crystals typically do not equilibrate with the basaltic melt, so that their compositions are not reliable indicators of equilibrium" (Roeder and Reynolds 1991). In a previous study, we have processed data on the distribution of Fe^{3+} and Fe^{2+} between chrome spinels and mafic melts, and estimated the extent of possible non-equilibrium using data on chromite-doped experiments: most of the 19 low-temperature "B" series experiments of Barnes (1986) were found to have characteristics indicative of non-equilibrium (Ariskin and Nikolaev 1995). Therefore, in the present study the experiments by Barnes (1986) were also excluded from data representing "close to equilibrium" compositions (Table 1).

Calibration of spinel-melt geothermometers

General approach

The thermodynamic background for calculating mineral-melt equilibria from empirically calibrated geothermometers for olivine, plagioclase and pyroxenes has been described earlier (Ariskin et al. 1993). This approach is based on iterative solution of a system of equations, including temperature-compositional dependencies of equilibrium constants for end-member components and a stoichiometry equation for each mineral. A key aspect of the calibration is the use of values of equilibrium constants that are dependent upon the postulated solid and liquid activity models. Generally, it might seem that the more complex model one uses to describe spinel activities, the more accurate would be the calculated temperatures. However, regardless of whether a sub-ideal activity model (e.g., Nielsen 1990; Weaver and Langmuir 1990; Ariskin et al. 1987, 1993) or a regular solution model (e.g., Ghiorso 1985; Sack and Ghiorso 1991a, b) is used, the accuracy of calculated temperatures cannot be better than interlaboratory biases in experimental techniques and microprobe analytical uncertainties. Our experience in the field of mineral-melt equilibria leads us to conclude that if one uses data from ten or more melting experiments from different laboratories, experimentally determined temperatures can be reproduced with a precision of ~ 10°C for 70–80% of data (Ariskin et al. 1993). Achieving a precision of 10°C was the goal of the proposed spinel-melt geothermometers.

Six main spinel cations, Cr^{3+}, Al^{3+}, Ti^{4+}, Mg^{2+}, Fe^{3+} and Fe^{2+}, were selected for the development. This selection requires a set of at least five linearly independent equations describing the distribution of cations between spinels and melts in the form of equilibrium constants, which will be dependent upon temperature, oxygen fugacity and melt composition. To solve the equations, multiple regression calculations were performed to arrive at the following expression (Ariskin and Nikolaev 1995):

$$\ln(K_i^{Sp}) = A/T(K) + B\log f_{O_2} + C\ln(Fe^{3+}/Fe^{2+})_L + D\ln R_L + E,$$

(1)

where K_i is an equilibrium constant and R_L is a Melt Structure-Chemical Parameter (*MSCP*, e.g., Si/O, NBO/T; see next section). The use of the *MSCP*s as independent variables has proved efficient in the development of olivine-melt and plagioclase-melt geothermometers (Ariskin et al. 1993). This approach has also allowed us to distinguish the effects of oxygen fugacity and Fe^{3+}/Fe^{2+} ratio on spinel-forming reactions in mafic melts (Maurell and Maurell 1982). As shown below, all of the "spinel equilibrium constants" are dramatically dependent on the oxygen fugacity, even if the Fe^{3+}/Fe^{2+} ratios of the melts were not involved in the multiple regression.

Main empirical dependencies

In the process of searching for the spinel-melt geothermometers which best satisfy Eq. 1, 28 forms of the equilibrium constants were investigated. These included single distribution coefficients (e.g., Al_{Sp}/Al_L or Ti_{Sp}/Ti), exchange equilibria constants [e.g., $(Mg/Fe^{2+})_{Sp}/(Mg/Fe^{2+})_L$], formation constants for 8 components – $MgAl_2O_4$, $FeAl_2O_4$, Fe_2TiO_4, Fe_3O_4, $FeCr_2O_4$, $MgCr_2O_4$, $MgFe_2O_4$, $MgTi_2O_4$, and simple "spinel cation ratios" [e.g., $(Fe^{3+}/Fe^{2+})_{Sp}$ or $(Ti/Fe^{3+})_{Sp}$]. For each permutation of the 28 equilibrium constants, 16 combinations of melt structure-chemical parameters were investigated. These *MSCP*s include both commonly used ratios, such as Si/O, Al/Si, NBO/T, (Si + Al)/O, (Al + Si)/Si, (Na + K)/Al, Al/(Na + K + Al), and simple cation ratios, such as $(Mg/Fe^{2+})_L$ or $(Fe^{3+}/Fe^{2+})_L$. For the calculation of Fe^{3+} and Fe^{2+} species in silicate melts, we used the equations by Sack et al. (1980), wheras the Fe^{3+}/Fe^{2+} ratios in spinels were determined from spinel stoichiometry.

Using data from the sources listed in Table 1, up to 500 combinations of empirical dependencies were investigated. Mathematical processing for each of the combinations was performed in two stages. In the first stage, the regression parameters were calculated for the entire set of 118 coexisting spinel-melt compositions. Using the regression parameters, experimental phase compositions and f_{O_2} values, spinel-melt equilibrium temperatures were calculated. If the calculated temperatures are more than three times the average standard deviation of the experimental values, these temperatures are considered to present non-equilibrium experiments and excluded from the second stage processing of the data. As a rule, five to eight points with temperature deviations from $30°C$ to $60°C$ were excluded for each set of calculations, such that final processing was performed on a slightly reduced dataset. Moreover, we imposed an additional constraint in the case of "Cr-bearing" constants by considering only melts with chromium concentrations greater than 360 ppm (0.05 wt% Cr_2O_3). This constraint

Table 1 Dataset of coexisting spinel-melt compositions extracted from the INFOREX database, and used to calibrate new Spinel-Melt geothermometers (*ALB* alkalic basalt, *BAS* basalt, *KOM* komatiite, *NOR* norite). A complete list of the experimental conditions, including calculated spinel and melt molar concentrations, is available from the authors upon request

Reference	1150–1200°C	1201–1300°C	1301–1500°C
Fisk and Bence 1980	2 (BAS)	1 (BAS)	–
Grove and Bryan 1983	–	1 (BAS)	–
Barnes 1986	–	4 (NOR)	–
Murck and Campbell 1986	2 (BAS)	20 (BAS) 1 (KOM)	15 (BAS) 10 (KOM)
Sack et al. 1987	–	4 (ALB) 1 (BAS)	–
Roeder and Reynolds 1991	11 (BAS)	32 (BAS) 6 (KOM)	5 (BAS) 2 (KOM)
Thy et al. 1991	1 (BAS)	–	–
Total	16	70	32

is neccessary to minimizise the effect of possible analytical errors on the calculated constants. Multiple linear regression parameters for five spinel-melt equilibria equations, which are sufficient for a complete description of spinel compositions (including above six cations, see Appendix) and which best reproduce the available experimental data, are given in Table 2.

The calculated regression parameters indicate a strong effect of temperature, f_{O_2} and melt structure-chemical parameters on the optimal equilibrium constants. For example, the standard deviations for the "*B*" parameter (1σ) average only 11.5 rel.% of the "*B*" values. This seems to be important, because the strong dependencies on oxygen fugacity indicate that ionic redox equilibria in melts (probably also in spinels), including Cr^{3+}/Cr^{2+} equilibrium, are likely to be more complex than that given by Sack et al. (1980) or the simple spinel stoichiometry calculations. We believe that these coefficients might be considered as an empirical reflection of the redox reactions (Roeder and Reynolds 1991; Poustovetov and Roeder 1994). In some respect, this conclusion applies to the calculated "*D*" regression coefficients as well. The effect of different *MSCP*s on the equilibrium constants might be interpreted as an efficient way to take into account the production of some unknown cation activity coefficients in melts which should be present to the right of Eq. 1 if we use molar fractions of cations in the left of the equation. We did not observe a strong dependence on $\ln(Fe^{3+}/Fe^{2+})_L$ for equilibrium constants involving Cr.

Using the geothermometers given in Table 2, one can invert the calculations to obtain spinel-melt equilibria temperatures for the initial database liquid compositions. Comparison of the calculated and

Table 2 Regression constants for expressions which best describe the distribution of spinel-forming cations between chromian spinels and melts at atmospheric pressure[a]

K_i	R_L	n	A	B	C	D	E	ΔT(av)
$(Fe^{3+}/Fe^{2+})_{Sp}$	$\dfrac{Al}{Al + Na + K}$	112	58107 (4887)	2.007 (0.151)	−3.026 (0.302)	−3.648 (0.466)	−30.623 (2.703)	8.5
$(Mg/Fe^{2+})_{Sp}/(Mg/Fe^{2+})_L$	$\dfrac{Si}{Si + Al}$	115	17996 (2008)	0.581 (0.057)	−1.192 (0.111)	−3.203 (0.397)	−10.832 (1.141)	11.1
$(Cr/Al)_{Sp}/(Cr/Al)_L$	$\dfrac{NBO}{T}$	92	22278 (831)	0.267 (0.013)	–	−1.115 (0.106)	−7.478 (0.462)	13.3
Ti_{Sp}/Ti_L	$\dfrac{Al}{Al + Na + K}$	110	29209 (5666)	0.840 (0.171)	−1.731 (0.345)	−2.442 (0.537)	−21.524 (3.136)	17.7
$(a_{FeCr_2O_4})_{Sp}/(a_{FeCr_2O_4})_L$	$\dfrac{Si}{Si + Al}$	93	43656 (1420)	0.457 (0.024)	–	−6.514 (1.227)	−14.598 (0.792)	11.2

[a] Five series of the regression constants correspond to 5 equilibrium constants K_i and 3 melt structure-chemical parameters R_L (molar ratios), included in the calculations as per linear model (1). Standard deviations (1σ) for the constants are given in parentheses. ΔT(av) – average deviations of the calculated temperatures from experimental values, if we use the regression constants to calculate temperature from spinel and melt compositions at given oxygen fugacities. NBO/T is from Mysen et al. (1982). Activity of $FeCr_2O_4$ in the melts was calculated using the two-lattice model of Nielsen and Dungan (1983), see Appendix, Eq. (13); for activity of $FeCr_2O_4$ in spinels see Appendix, Eq. (12)

Fig. 1 Comparison of chromian spinel saturation temperatures observed in experiments with those calculated using spinel-melt geothermometers given in Table 2. The values of ΔT(av) represent average deviations of the calculated temperatures from experimental values
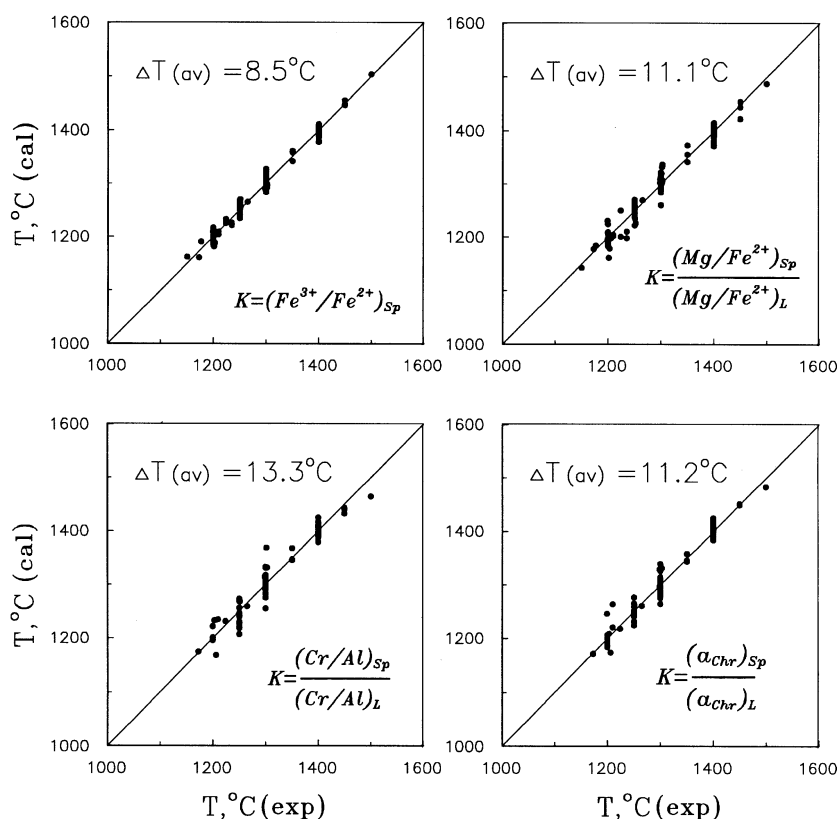
experimental temperatures indicate an accuracy of about 10°C (Fig. 1). The inverse calculations for equilibrium constants lead us to expect that the final spinel-melt equilibrium model based on the equations will also accurately reproduce spinel compositions (Fig. 2).

SPINMELT program simulating spinel-melt equilibrium

To develop a model for simulating naturally occurring chromian spinel compositions, it is necessary to link the empirical equations derived from Eq. 1 and the regression parameters given in Table 2, with some spinel

Fig. 2 Comparison of chromian spinel-melt equilibrium constants from experimental data with those calculated using spinel-melt geothermometers given in Table 2. The values of $\Delta \ln K$ (av) represent average deviations of the calcultated constants from experimental values
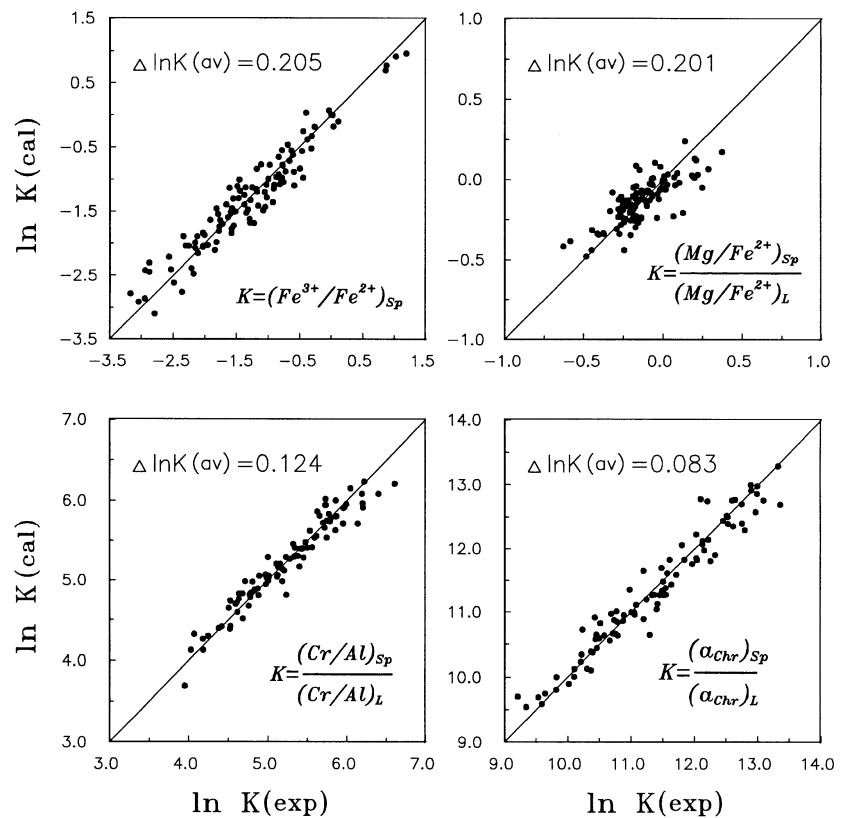
stoichiometry relationships such as bulk concentrations of Cr^{3+}, Al^{3+}, Ti^{4+}, Mg^{2+}, Fe^{3+}, Fe^{2+} and tetrahedral + octahedral occupancies of the cations. The occupancies contribute significantly to the values of activities for spinel components, including $FeCr_2O_4$ (Sack 1982; Sack and Ghiorso 1991b). The integration of the empirical equations and the stoichiometry relationships into a single algorithm can be used for calculating the saturation temperatures and spinel compositions as a function of magma composition at a given pressure and oxygen fugacity. A complete description of the formalization technique is presented in Appendix.

Based on the algorithm proposed, a special petrological program called SPINMELT has been developed. The program is written in Microsoft Fortran 5 for IBM-PC or compatibles and can be applied to a wide range of mafic igneous systems for the numerical investigations of the effect of oxygen fugacity and melt composition on the equilibrium temperature and composition of chromian spinels crystallized from magmas. Results of testing of the program on a coexisting spinel-melt composition dataset (Table 1), as well as an example of application of SPINMELT to a parental magma of the Bushveld Complex, are presented below.

Testing of SPINMELT options

The SPINMELT program provides three main options to be used in petrological calculations. The first is based on the algorithm described in the Appendix for the calculation of spinel temperature and composition in the equilibrium with a melt if oxygen fugacity is known. This subroutine can easily be integrated into the empirical phase equilibria models simulating crystallization of silicate minerals (Nielsen 1990; Ariskin et al. 1987, 1993).

The second option represents a slight modification of the basic algorithm. This option is based on the fact that the steps [1] and [2] (Fig. 6) could be changed if temperature for spinel-melt equilibrium is independently estimated. This could be temperature obtained experimentally for rehomogenized melt inclusions in natural crystals (e.g., a multiphase assemblage including a host mineral plus spinel and glass inclusions), or it could be temperature calculated from a well calibrated equilibrium such as the olivine-melt equilibrium. In both cases, the Fe^{3+}/Fe^{2+} ratios of the melt can be readily determined from the experimental or calculated temperatures using Eq. (17) (see Appendix) prior to the main iterative loop: this approach results in an

Fig. 3 Comparison of chromian spinel-melt compositions observed in experiments with those calculated at the same temperature and oxygen fugacity using the SPINMELT program. The values of ΔX (*av*) represent average deviations of the calcultated molar fractions from experimental values
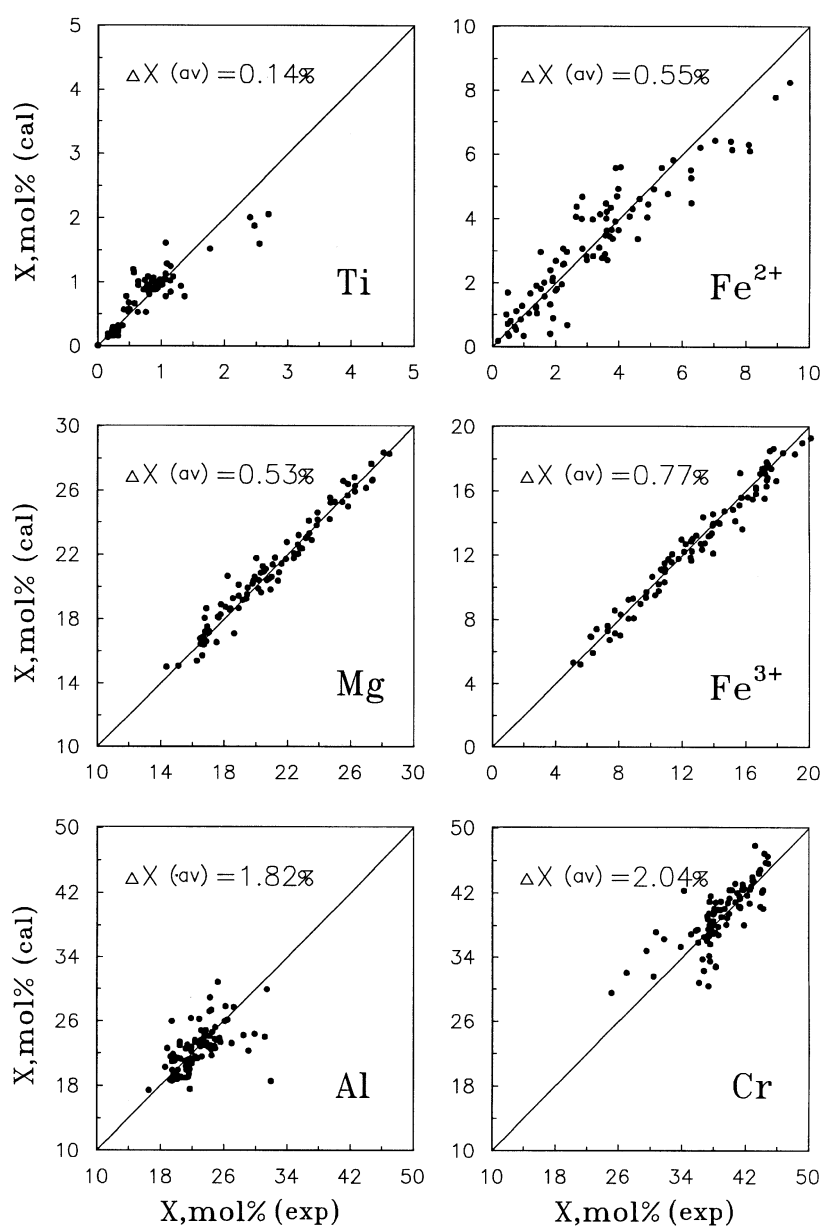
improved accuracy of the calculated spinel-melt equilibria. Using the second option of the SPINMELT program, we have calculated equilibrium temperatures and spinel compositions for 97 experimental melts (see Tables 1 and 2), which best satisfy the constraints of the of spinel-melt geothermometers. The experimental temperatures were reproduced with an average accuracy of $\pm 10°$ C: a comparison of the experimental spinel compositions with those calculated using the SPINMELT program (X_i, mol%) is shown in Fig. 3. These data indicate good absolute accuracy for Ti^{4+}, Mg^{2+}, Fe^{3+}, and Fe^{2+} concentrations with a slight scatter for Cr^{3+} and Al^{3+}. We believe that the 2% deviations for Cr^{3+} might also be considered as a good precision given

the range of chromium concentration (38–46 mol%; Table 3) used. The large deviations (in relative%) for Al^{3+}, especially in the field of high-Al spinels, indicate the compositional limit where the SPINMELT program does not provide a precise fit to the experimental data.

The third SPINMELT option includes the ability to calculate oxygen fugacities from natural spinel-glass compositions if temperature of equilibration is independently available. This option calculates f_{O_2} values using regression parameters in Table 2 with an accuracy of 0.1–0.2 log units (Ariskin and Nikolaev 1995). Examples of application of these options to natural basalts will be presented in a subsequent paper.

Table 3 Comparison of experimental temperatures and spinel compositions with those calculated for representative experimental glass compositions and oxygen fugacities using the SPINMELT program[a] (*GB* Grove and Bryan 1983, *MC* Murck and Campbell 1986, *RR* Roedes and Reynolds 1991)

| Ref	Sample	$\log f_{O_2}$	Temp	Phase	SiO_2	TiO_2	Al_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Cr_2O_3
RR	F2-1	−8.90	1173	Melt	51.23	1.41	13.49	10.11	0.27	7.76	13.91	1.73	0.01	0.08
				Spin	0.43	1.32	15.52	23.62	0.00	11.10	0.51	0.00	0.02	47.47
	Calc		*1167.6*	Spin	*0.00*	*0.97*	*15.45*	*21.61*	*0.00*	*11.55*	*0.00*	*0.00*	*0.00*	*50.42*
RR	C71	−9.04	1200	Melt	50.40	2.88	14.07	10.41	0.13	7.10	12.09	2.13	0.71	0.07
				Spin	0.53	3.38	19.92	23.31	0.35	11.48	0.52	0.00	0.01	40.50
	Calc		*1183.8*	Spin	*0.00*	*2.64*	*18.58*	*24.06*	*0.00*	*12.05*	*0.00*	*0.00*	*0.00*	*42.67*
GB	#5	−8.30	1224	Melt	48.98	0.84	15.75	11.18	0.16	9.44	11.89	1.57	0.12	0.07
				Spin	2.09	0.81	25.82	20.29	0.39	13.01	0.39	0.00	0.00	37.20
	Calc		*1221.2*	Spin	*0.00*	*0.71*	*25.40*	*19.26*	*0.00*	*14.59*	*0.00*	*0.00*	*0.00*	*40.04*
MC	J	−7.76	1250	Melt	50.43	0.50	14.28	11.73	0.20	9.79	11.38	1.50	0.10	0.09
				Spin	0.00	0.41	18.96	21.31	0.20	13.28	0.00	0.00	0.00	45.83
	Calc		*1239.0*	Spin	*0.00*	*0.42*	*20.52*	*21.34*	*0.00*	*13.71*	*0.00*	*0.00*	*0.00*	*44.00*
MC	J	−7.60	1265	Melt	49.82	0.50	13.70	12.45	0.20	11.21	10.82	0.99	0.20	0.12
				Spin	0.00	0.41	19.35	19.95	0.30	13.68	0.00	0.00	0.00	46.31
	Calc		*1263.6*	Spin	*0.00*	*0.38*	*20.04*	*19.67*	*0.00*	*14.00*	*0.00*	*0.00*	*0.00*	*45.92*
RR	K-30	−5.10	1298	Melt	50.01	0.59	12.18	11.89	0.24	11.41	12.05	1.39	0.13	0.10
				Spin	0.40	0.40	13.14	30.17	0.16	12.85	0.44	0.00	0.03	42.41
	Calc		*1293.0*	Spin	*0.00*	*0.36*	*14.11*	*26.95*	*0.00*	*13.61*	*0.00*	*0.00*	*0.00*	*44.98*
RR	401	−9.19	1300	Melt	54.17	1.96	16.46	7.86	0.17	7.22	9.88	1.27	0.73	0.27
				Spin	0.38	1.01	18.30	17.15	0.18	12.61	0.42	0.00	0.01	49.95
	Calc		*1303.0*	Spin	*0.00*	*1.08*	*17.34*	*17.28*	*0.00*	*12.96*	*0.00*	*0.00*	*0.00*	*51.34*
MC	J	−7.25	1300	Melt	49.49	0.30	13.10	13.26	0.20	12.50	10.18	0.71	0.10	0.16
				Spin	0.00	0.41	19.17	19.34	0.31	14.28	0.00	0.00	0.00	46.50
	Calc		*1300.4*	Spin	*0.00*	*0.21*	*19.59*	*18.93*	*0.00*	*14.22*	*0.00*	*0.00*	*0.00*	*47.05*
MC	401	−6.77	1350	Melt	50.88	1.90	16.06	12.81	0.20	6.88	9.18	1.30	0.60	0.19
				Spin	0.00	1.02	18.49	24.10	0.31	10.47	0.00	0.00	0.00	45.62
	Calc		*1351.2*	Spin	*0.00*	*1.03*	*19.02*	*24.72*	*0.00*	*10.67*	*0.00*	*0.00*	*0.00*	*44.58*
MC	J	−6.32	1400	Melt	49.50	0.50	13.20	12.47	0.20	13.10	10.10	0.50	0.10	0.33
				Spin	0.00	0.31	17.37	16.96	0.31	14.71	0.00	0.00	0.00	50.36
	Calc		*1400.3*	Spin	*0.00*	*0.27*	*18.57*	*17.29*	*0.00*	*14.35*	*0.00*	*0.00*	*0.00*	*49.53*
MC	K	−6.32	1400	Melt	48.33	0.40	10.81	10.82	0.20	20.31	8.31	0.40	0.10	0.32
				Spin	0.00	0.41	19.97	12.84	0.21	17.51	0.00	0.00	0.00	49.06
	Calc		*1396.0*	Spin	*0.00*	*0.33*	*19.49*	*13.12*	*0.00*	*17.96*	*0.00*	*0.00*	*0.00*	*49.11*
MC	K	−5.50	1500	Melt	46.27	0.39	9.53	10.43	0.20	25.15	6.88	0.49	0.10	0.56
				Spin	0.00	0.30	17.25	10.72	0.20	18.97	0.00	0.00	0.00	52.55
	Calc		*1495.9*	Spin	*0.00*	*0.35*	*20.03*	*12.24*	*0.00*	*19.11*	*0.00*	*0.00*	*0.00*	*48.28*

[a] Experimental and modeled compositions were normalized to 100 wt% with total Fe as FeO

Calculation of chromite saturation surfaces and chromium solubility for a parental magma of Bushveld Complex

For a practical demonstration of the SPINMELT program, we have applied this code to a parental magma for the Bushveld Complex estimated from the compositions of micropyroxenite sills associated with the intrusion (Cawthorn et al. 1981). The proposed parental magma corresponds to a high-magnesium, high-Ti tholeiite that is saturated in silica. Simulation of the crystallization sequence for this magma using the COMAGMAT program (Ariskin et al. 1993) indicates that in spite of the high silica content of the magma, olivine is the first silicate liquidus phase at atmospheric pressure. The calculated olivine saturation temperatures range from 1360 to 1370° C (Fig. 4A), for oxygen fugacities ranging from $NNO + 2$ to iron-wüstite (*IW*) buffer. Based on the results, simulation of chromite saturation was carried out at temperatures slightly lower but considerably above the olivine liquidus.
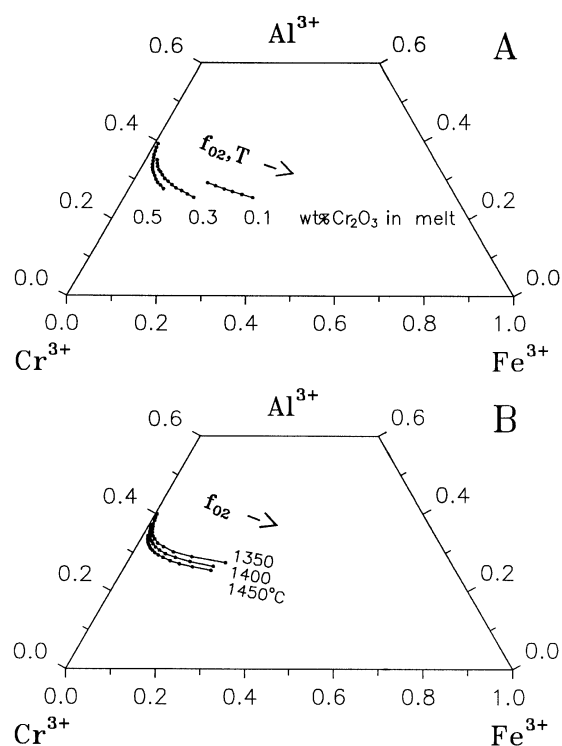
The first set of the calculations was performed with the goal of obtaining isopleths of chromium solubility in the mafic melt as a function of temperature and oxygen fugacity. The calculations were performed with Cr_2O_3 contents of 0.1, 0.3 and 0.5 wt%. For the modeling of chromite saturation temperatures and compositions at a given oxygen fugacity, we used the first option of SPINMELT with a f_{O_2} increment of 0.5 log units starting with −13. Results of the calculations are given in Figs. 4A and 5A. Figure 4A provides information on the conditions at which chromian
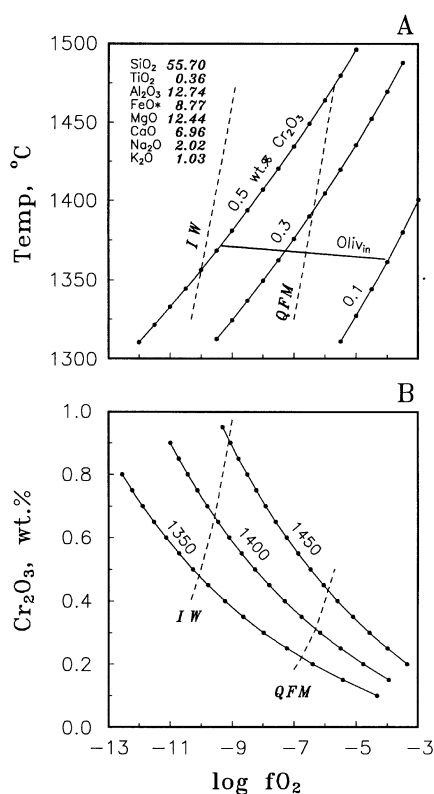
Fig. 4A, B Simulation of chromite saturation conditions in a parental magma to the Bushveld Complex (Cawthorn et al. 1981) using the SPINMELT program. **A** Isopleths of Cr_2O_3 solubility in melts were calculated assuming melt composition and oxygen fugacity. **B** Isotherms calculated for assumed melt composition and temperatures. The *dashed lines* represent iron-wüstite (*IW*) and quartz-fayalite-magnetite (*QFM*) oxygen buffers. The *solid line* represents olivine liquidus temperatures calculated for the Bushveld parent magma using the COMAGMAT program (Ariskin et al. 1993)

Fig. 5A, B Simulation of the compositions of chromites in equilibrium with a parental magma to the Bushveld Complex using the SPINMELT program. **A** Isopleths of Cr_2O_3 solubility in melts were calculated assuming melt composition and oxygen fugacity. **B** Isotherms calculated for assumed melt composition and temperatures. Relation between isopleths and isotherms used in Fig. 4

spinel could crystallize if the Cr_2O_3 content of Bushveld magma is known. For example, if we assume a Cr_2O_3 content of 0.2 wt%, the cotectic crystallization of chromite with olivine might proceed at $\sim$ 1 log units above the *QFM* buffer, whereas more reducing conditions imply that chromite could be produced at lower temperatures, perhaps during an intra-chamber (in situ) magma differentiation process. Figure 5A shows calculated compositions of chromite in equilibrium with the parental magma for selected Cr_2O_3 isopleths.

Another attractive feature of the SPINMELT program is the ability to calculate equilibrium oxygen fugacity if temperature and chromium contents of melt are known (option 2). This option allows the user to determine the f_{O_2}– Cr_2O_3 concentration dependencies for different isothermal conditions and to specify the range of conditions controlling chromite saturation in mafic magmas. Previously, such isotherms were obtained experimentally and discussed for a few samples mostly at 1300° C (Murck and Campbell 1986; Roeder and Reynolds 1991). We have calculated isotherms for

the Bushveld magma at 1350, 1400, and 1450° C using the SPINMELT program. The calculations were performed stepwise with a Cr_2O_3 content increment of 0.05 wt% (Figs. 4B, 5B). In general, the forms of the modeled isotherms are similar to those of the experimental lines obtained by Roeder and Reynolds (1991), indicating a strong dependence of saturation temperatures on chromium content and f_{O_2}. The calculated spinel compositions were also sensitive to the redox conditions, whereas the influence of temperature is negligible (Fig. 5B).

Conclusions

In the paper we have presented a system of empirically calibrated spinel-melt equilibrium equations, which allows us to develop a model for calculating chromite crystallization temperatures in mafic melts with an accuracy of $\pm$ 10° C, and spinel compositions (including six cations – Ti^{4+}, Mg^{2+}, Fe^{3+}, Fe^{2+}, Cr^{3+} and Al^{3+}) with an accuracy of 0.5–2 mol%. The model called SPINMELT program can be successfully applied to a wide range of temperatures, oxygen fugacities and magma compositions for the purpose of

numerically studying the effects of temperature and oxygen fugacity on chromium solubility, and the timing for the onset of chromite precipitation. The model does not apply to natural spinels in equilibrium with high-Al basalt magmas in which the spinels have Al_2O_3 ranging from 25–30 wt%. Nevertheless, even at the current stage of its development the SPINMELT program represents a new powerful tool for igneous petrologic studies, because it can be used to investigate the problem of chromite precipitation and accumulation in both primitive high magnesian magmas and mafic layered intrusions.

Appendix

General stoichiometry description of spinel compositions

Using a spinel composition calculated from electron microprobe data and bulk molar fractions of five components:

$$X_{Al}^{Sp} + X_{Cr}^{Sp} + X_{Mg}^{Sp} + X_{Ti}^{Sp} + X_{FE}^{Sp} = 1, \tag{2}$$

where

$$X_{FE}^{Sp} = X_{Fe^{3+}}^{Sp} + X_{Fe^{2+}}^{Sp}, \tag{3}$$

one can calculate the bulk fractions of Fe^{2+} and Fe^{3+} from a general spinel formula $(A^{2+})(B^{3+})_2O_4$, taking into account the presence of Ti as ulvöspinel component $(Fe^{2+})_2(Ti^{4+})O_4$:

$$X_{Fe^{3+}}^{Sp} = 2/3 - X_{Al}^{Sp} - X_{Cr}^{Sp} - 2X_{Ti}^{Sp} \tag{4}$$

and

$$X_{Fe^{2+}}^{Sp} = 1/3 - X_{Mg}^{Sp} + X_{Ti}^{Sp}. \tag{5}$$

The six spinel cations (*i*) are distributed among tetrahedral (*tet*) and octahedral (*oct*) sites, with a mass balance for each:

$$X_i^{Sp} = X_i^{tet}/3 + 2X_i^{oct}/3. \tag{6}$$

Following the method of Sack (1982; see his Eq. 2–17),

$$X_{Fe^{2+}}^{oct} + X_{Fe^{3+}}^{oct} + X_{Al}^{oct} + X_{Cr}^{oct} + X_{Mg}^{oct} + X_{Ti}^{oct} = 1 \tag{7}$$

and

$$X_{Fe^{2+}}^{tet} + X_{Fe^{3+}}^{tet} + X_{Mg}^{tet} = 1. \tag{8}$$

If we assume a random distribution of Fe^{2+} and Mg^- between the octahedral and tetrahedral sites, i.e.

$$(X_{Fe^{2+}}/X_{Mg})^{tet} = (X_{Fe^{2+}}/X_{Mg})^{oct} = 1, \tag{9}$$

the individual cation occupancies X_i^{tet} and X_i^{oct} may be calculated from a set of fictive component concentrations, such as $X_2 = 3X_{Mg}^{Sp}$,

$X_3 = 1.5X_{Cr}^{Sp}$, $X_4 = 3X_{Ti}^{Sp}$, $X_5 = 1.5X_{Fe^{3+}}^{Sp}$ (Sack 1982). For example, in the case of chromite-forming components these occupancies are equal to

$$X_{Fe^{2+}}^{tet} = (1 - X_2 + X_4)(X_4 + X_5)/(1 + X_4), \tag{10}$$

$$X_{Cr}^{oct} = X_3. \tag{11}$$

From expressions 10 to 11, the activity of the chromite component in spinels may be defined as:

$$(a_{FeCr_2O_4})_{Sp} = X_{Fe^{2+}}^{tet}(X_{Cr}^{oct})^2, \tag{12}$$

if we further assume an ideal mixing of the divalent and trivalent cations in both tetrahedral and octahedral sites. Equation (12) should be considered as a first approximation, because it does not account for deviations from ideality observed in experimentally studied spinel systems (e.g., the join $FeCr_2O_4$–Fe_3O_4; Sack and Ghiorso 1991b). In spite of this, the approximation works well for natural spinel compositions over a wide range of temperature and oxygen fugacity (Figs. 1–2). Note that the activity of chromite in melts used for the calculations of $K_{FeCr_2O_4}$ was defined based on the two-lattice model of Nielsen and Dungan (1983):

$$(a_{FeCr_2O_4})_L = X_{Fe^{2+}}^{NM}(X_{Cr}^{NM})^2, \tag{13}$$

where *NM* is related to network-modifier components.

Algorithm for the calculation of chromite-melt equilibrium

Selection of the spinel stoichiometry equation is largely dependent upon the solid solution model assumed for spinels and the form of the empirical equilibrium constant equations. Using the expressions from Table 2 and Eqs. (2–11), we propose a basic octahedral site stoichiometry equation described below. Formulation of the equation is based on the assumption that only 1/2 of total ferric iron in spinels is distributed in the octahedral site, i.e., for a model solid solution:

$$X_{Fe^{3+}}^{tet} = 2X_{Fe^{3+}}^{oct}. \tag{14}$$

Combining Eq. (14) with Eqs (6–9), one can obtain an additional mass balance equation for the octahedral site:

$$X_{Fe^{3+}}^{oct} + X_{Ti}^{oct} = X_{Fe^{2+}}^{oct} + X_{Mg}^{oct}, \tag{15}$$

which results in *the basic octahedral site equation* in the form:

$$X_{Al}^{oct} + X_{Cr}^{oct} + 2(X_{Fe^{3+}}^{oct} + X_{Ti}^{oct}) = 1. \tag{16}$$

Note, that the Eq (16) is valid *only* for the "macroscopic" model formulated by Sack (1982) in his treatment of mixing relations between "fictive" end-member components of normal and inverse spinel types. This is the basis for the development of an iterative cycle for the calculation of crystallization temperatures and spinel compositions described in the following steps (Fig. 6).

[1] Assume an initial melt composition $X_L^j (I < j < n)$, oxygen fugacity f_{O_2}, and a spinel-melt equilibrium temperature $T_{pr} = T_o$.

[2] Calculate values of Fe^{3+}/Fe^{2+} ratio in the melt as a function of T_{pr}, oxygen fugacity and the melt composition (Sack et al. 1980):

$$(Fe^{3+}/Fe^{2+})_L^{pr} = F_{Sack}(T_{pr}, f_{O_2}, X_L^j). \tag{17}$$

[3] Calculate four values for equilibrium constants, using Eq. 1 and data in Table 2:

$$K_i = F_i[T_{pr}, f_{O_2}, X_L^j, (Fe^{3+}/Fe^{2+})_L^{pr}], \tag{18}$$
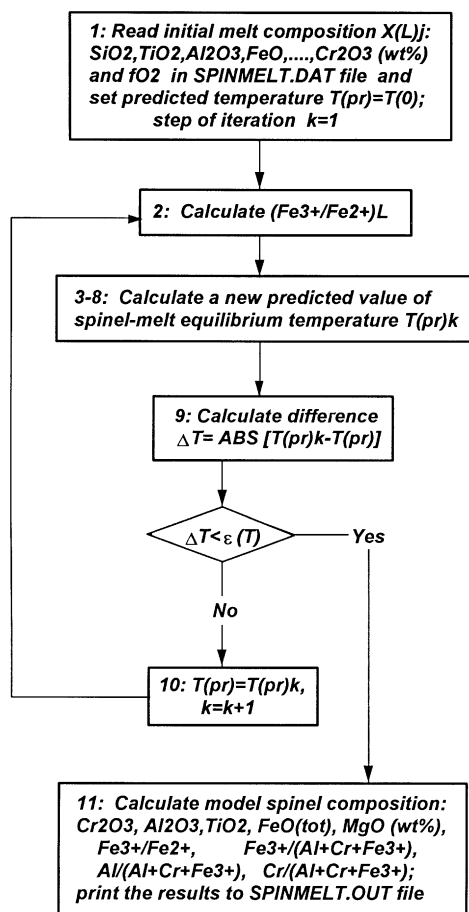
Fig. 6 General flowchart of SPINMELT for option 1: *calculation of spinel temperature and composition in the equilibrium with a melt if oxygen fugacity is known.* Numbers correspond to 11 steps of calculations of the crystallization temperature and spinel composition described in Appendix

where

$$K_1 = (Fe^{3+}/Fe^{2+})_{Sp}; \quad K_2 = (Mg/Fe^{2+})_{Sp}/(Mg/Fe^{2+})_L;$$

$$K_3 = (Cr/Al)_{Sp}/(Cr/Al)_L; \qquad K_4 = X^{Sp}_{Ti}/X^L_{Ti}. \tag{19}$$

[4] To account for the presence of Cr and Al in the octahedral site [Eqs. (5,9,19)], we define two values of octahedral cation ratios:

$$R_2 = (Mg/Fe^{2+})^{oct}_{Sp} = (Mg/Fe^{2+})_{Sp} = K_2(Mg/Fe^{2+})_L, \tag{20}$$

$$R_3 = (Al/Cr)^{oct}_{Sp} = (Al/Cr)_{Sp} = 1/[K_3(Cr/Al)_L], \tag{21}$$

and bulk Ti, Fe^{2+} and Fe^{3+} molar fractions:

$$X^{Sp}_{Ti} = K_4 X^L_{Ti}, \tag{22}$$

$$X^{Sp}_{Fe^{2+}} = (0.3333 - X^{Sp}_{Ti})/(R_2 + 1), \tag{23}$$

$$X^{Sp}_{Fe^{3+}} = K_1 X^{Sp}_{Fe^{2+}}. \tag{24}$$

[5] From Eqs (6,14) quantify Fe^{3+} molar fraction in the octahedral site:

$$X^{oct}_{Fe^{3+}} = 0.75 X^{Sp}_{Fe^{3+}}. \tag{25}$$

[6] Using R_3 from Eq (21), transform the basic stoichiometry of Eq (16) into the form:

$$X^{oct}_{Cr}(R_3 + 1) + 2X^{oct}_{Fe^{3+}} + 3X^{Sp}_{Ti} = 1. \tag{26}$$

Solve Eq. (26) for X^{oct}_{Cr}

$$X^{oct}_{Cr} = (1 - 2X^{oct}_{Fe^{3+}} - 3X^{Sp}_{Ti})/(R_3 + 1) \tag{27}$$

and using Eqs. (8, 9, 14, 20, 25) calculate

$$X^{tet}_{Fe^{2+}} = (1 - 2X^{oct}_{Fe^{3+}})/(R_2 + 1). \tag{28}$$

[7] Combining Eqs. (27, 28) with Eqs. (12, 13) one can calculate values of spinel-melt equilibrium constant for chromite component:

$$K_5 = [X^{tet}_{Fe^{2+}}(X^{oct}_{Cr})^2]/[X^{NM}_{Fe^{2+}}(X^{NM}_{Cr})^2]. \tag{29}$$

[8] The predicted value of K_5 may be used for the calculation of a new temperature T^k_{pr}:

$$T^k_{pr} = 43656/[\ln K_5 + 14.598 - 0.457\log f_{O_2} + 6.514(Si/Si + Al)_L], \tag{30}$$

where k is a step of the iteration loop and the regression parameters are from Table 2.

[9] Calculate differences between the current and previous temperatures. If the difference is less than a given iteration limit ε_T, go to step [11].

[10] Set $T_{pr} = T^k_{pr}$ and repeat the calculations starting with step [2].

[11] Calculate model spinel composition for the determined temperature and store or output the results.

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