

Calculation of Titanomagnetite Stability on the Liquidus of Basalts and Andesites with Special Reference to Tholeiitic Magma Differentiation

A. A. Ariskin

Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences,
ul. Kosygina 19, Moscow, 117975 Russia

Received November 12, 1996

Abstract—A detailed review of experimental data on magnetite–melt equilibria in systems ranging from basalts to dacites is presented. This information (99 experiments) was processed statistically to yield the following equation relating the crystallization temperature of magnetite to melt composition and oxygen fugacity:

$$10^4/T = (b_0 + b_1X_{\text{SiO}_2} + b_2X_{\text{TiO}_2} + b_3X_{\text{FeO}_{\text{tot}}}) \log f_{\text{O}_2} + c + d_1X_{\text{SiO}_2} + d_2X_{\text{TiO}_2} + d_3X_{\text{FeO}_{\text{tot}}} + d_4X_{\text{P}_2\text{O}_5}.$$

For 90% of the data, this equation reproduces experimental temperatures to a precision of $\pm 15^\circ\text{C}$; the average deviation of the calculated temperatures from experimental ones is 9.3°C . The crystallization temperature of magnetite shows a complex dependence on oxygen fugacity: for ferrobasic and andesitic melts with moderate contents of Fe (up to ~ 15 wt %) and TiO_2 (up to ~ 2 wt %), there is a fairly steep slope of the magnetite liquidus $\sim 20^\circ\text{C}/\log f_{\text{O}_2}$, whereas, for high-Ti (4–5 wt % TiO_2) and Fe-rich (17–18 wt %) basalts, liquidus temperatures are virtually independent of oxygen fugacity and are near 1100°C . The equation for the magnetite liquidus can be used as an empirical basis for improving computer models of magma crystallization involving the separation of magnetite-bearing mineral assemblages.

THE PROBLEM OF THOLEIITIC DIFFERENTIATION TREND

Titanomagnetite is one of the principal mineral phases that crystallize in the final evolutionary stages of basaltic magmas. This is indicated by its confinement to the most fractionated rocks of large layered complexes [1, 2] and differentiated sills [3, 4] and by the fact that the assemblages always contain phenocrysts, which represent the most evolved andesitic–dacitic members of tholeiitic [5, 6] and calc-alkaline [6–9] volcanic series. These observations attest to the important role played by magnetite crystallization in the formation of the main types of major-element trends; however, the validity of this inference for tholeiitic series has become the subject of debate.

The main distinguishing feature of the tholeiitic differentiation trend is a stepwise enrichment of residual melts in iron oxides during the early and middle stages of fractionation and a strong depletion during the final stages. At present, most petrologists agree that this accumulation of total FeO_{tot} ($\text{FeO} + 0.9\text{Fe}_2\text{O}_3$) is the result of low-pressure fractionation of basaltic magma when the crystallizing assemblages *Ol-Pl* and *Ol-Pl-Px* \pm *Mt*¹ are dominated by plagioclase [10, 11].

¹ The following abbreviations are used: *Ol* = olivine; *Pl* = plagioclase; *Px* = pyroxene (*Cpx* = clinopyroxene; *Aug* = augite; *Pig* = pigeonite; *Opx* = orthopyroxene); *Sp* = spinellid; *Mt* = titanomagnetite; and *Ilm* = ilmenite.

Controversial topics include the highest possible degree of Fe enrichment, the direction of the SiO_2 trend (enrichment or depletion), and the relative contributions of silicate phases and magnetite to these major-element signatures.

Differences of Tholeiitic Trends for Intrusive and Volcanic Rocks

Using data on the relative volumes and average compositions of cumulates of the Skaergaard intrusion, Wager and *et al.* [1, 2] calculated the compositions of residual melts approximating the compositional evolution of the primary tholeiitic magma during intrachamber differentiation. According to these data, while the mass fraction of solidification F ranges from 0 to 88%, the calculated compositional series demonstrates a monotonic increase in the sum of iron oxides (FeO_{tot}) from 9.6 to 18.2 wt %. The final crystallization stages $88 < F < 98\%$ are characterized by a small increase in FeO_{tot} to 21.7% and SiO_2 to 49.8% followed by a decrease in the concentration of iron oxides and formation of very unusual ferroandesitic compositions: at $F = 99.3\%$, the contents of FeO_{tot} and SiO_2 in the model differentiates are 18.5 and 55.0%, respectively (Fig. 1).

The trend thus calculated became for many years the standard for the evolution of tholeiitic magmas with the maximum enrichment in Fe (Fenner's trend), and

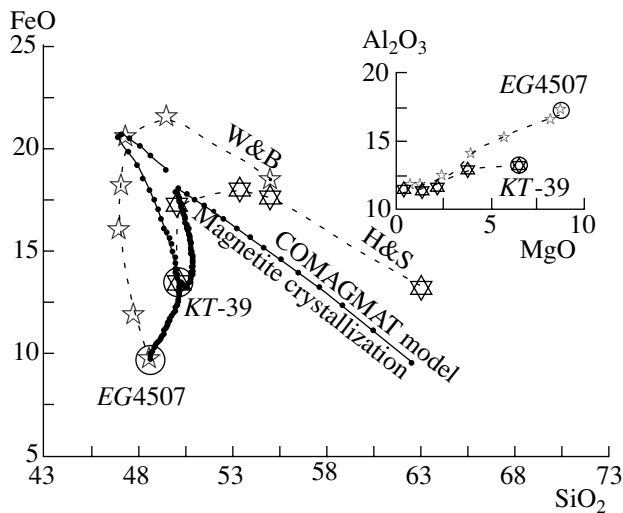


Fig. 1. Model trends of Skaergaard magma evolution.

Mass-balance calculations involving compositions of cumulate rocks: W&B [1, 2]; H&S [18]. Computer modeling of all fractional crystallization of chilled margin gabbros EG4507 [1, 2] and KT-39 [22] was conducted with the COMAGMAT program [21] for WM buffer with a nominal crystallization step (ΔF) of 1 mol %.

analogous mass-balance calculations were conducted for some other intrusions (e.g. [12]). Paradoxically, although strongly Fe-enriched compositions (up to 18–19 wt % FeO_{tot} [13]) have been encountered in basalts and natural quenched glasses, no volcanic equivalents of the calculated ferroandesites (as the end products of magma differentiation at Skaergaard) have been found. It might also be noted that the majority of tholeiitic volcanic series display a moderate enrichment in FeO_{tot} in the field of basaltic compositions, usually up to 13–15% while exhibiting no decrease in SiO_2 concentration [5, 14].

Effect of Redox Conditions

Osborn [15] was the first to provide a physicochemical explanation for these facts. From experiments with the $\text{MgO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ system, he established that the different directions of the evolutionary trends for crystallizing melts are due to the different conditions of magnetite separation, which, in turn, are controlled by redox conditions. He found that upon closed-system crystallization (with the bulk composition and $\text{FeO/Fe}_2\text{O}_3$ ratio being constant) the separation of magnetite does not cause the melt to deplete in FeO_{tot} , and that in a system open with respect to oxygen ($P_{\text{O}_2} = \text{const}$), the content of Fe oxides in the melt rapidly drops after the onset of magnetite crystallization. An analysis of these chemical features led Osborn to infer that intrachamber differentiation of tholeiitic magmas, in particular at Skaergaard, can occur in a closed system, and that the fractionation of primary magmas of

volcanic series takes place at a certain oxygen pressure [15]. This conclusion was supported by additional experiments with the $\text{CaO-MgO-FeO-Fe}_2\text{O}_3\text{-SiO}_2$ system [16] and by experimental melting of natural basalts (e.g., [17]).

A new surge of interest in this problem was triggered by the British petrologists Hunter and Sparks [18], who offered a number of arguments that challenged the assumed evolutionary trend of Skaergaard magma composition [1, 2]. In their opinion, the principal contradiction of Wager's approach lies in the fact that the trend of Fe superenrichment accompanied by a monotonic decrease in the SiO_2 content (determined from mass-balance calculations) is inconsistent with the available estimates of the primary Skaergaard magma composition and experimental data on basaltic phase equilibria. This inconsistency applies both to Fe accumulation and to the trend of decreasing silica content, which is difficult (if not impossible) to correlate with the low SiO_2 content (44–46%) in the crystallization products of the "gabbroic assemblage" $\text{Ol-Pl-Px} \pm \text{Mt}$ [18]. Another discrepancy with experimental data is that the calculated point of inflection at which Fe enrichment is replaced by silica enrichment does not coincide with the onset of titanomagnetite crystallization, which is known to appear quite early in the cumulate sequence when model solutions are depleted in SiO_2 and enriched in FeO_{tot} [1, 2].

Thus, it was suggested that the differentiation of Skaergaard magma is in fact an example of the tholeiitic-magma evolutionary line ferrobasalt-andesite-dacite, which is common for volcanic series. During the early and middle stages, this process is characterized by the $\text{Ol-Pl} \pm \text{Px}$ assemblage, with the result that the melt is monotonously enriched in FeO_{tot} , while the silica content in the melt is roughly constant; the appearance of *Mt* in the final fractionation stages causes the melt to be strongly depleted in FeO_{tot} with a concomitant enrichment in SiO_2 [18]. This interpretation implies that the major difference of the real Skaergaard series of melts (inaccessible to determination by direct analytical methods) from the typical assemblages of tholeiitic volcanics [5] is an elevated, but not anomalous, enrichment in Fe oxides (apparently to 17–18 wt % FeO_{tot}), which is related to a relative delay in magnetite crystallization due to the more reducible conditions in the magma chamber.

It should be noted that the method of estimating the compositions of the differentiation products based on successive subtraction of specified amounts of the gabbroic constituent from the primary magma [18] has the same drawback as Wager's method [1, 2]: when using the compositions of real intrusive rocks in mass-balance calculations, no allowance is made for the possible presence of trapped melt in the cumulates and the potential existence of suspended crystalline phases in the magma. For this reason, both of the trends presented in Fig. 1 [2, 18] are rather imprecise. It was, therefore, very important that the new interpretation of

Skaergaard data [18] was further developed through numerical modeling of fractional crystallization of Skaergaard magma [11, 19] with the TOLEMAG program [20].

*Computer Simulation
of Skaergaard Magma Crystallization*

The TOLEMAG program was a precursor to the COMAGMAT software [20, 21]. COMAGMAT makes it possible to simulate the evolution of the phases (including their compositions) during the fractionation of basaltic magmas under specified pressure and oxygen fugacity. Figure 1 shows the results of COMAGMAT modeling of the fractional crystallization for two samples of chilled margin gabbro from Skaergaard; these samples (EG4507 [1, 2] and KT-39 [22]) were previously examined as possible analogues of the primary Skaergaard magma. Calculations were performed for 1 atm and oxygen fugacity defined by the wüstite–magnetite (WM) buffer; the nominal crystallization step was 1 mol %, with the most fractionated melts corresponding to 90% crystallization.

According to these calculations, both samples are anchitectic (*Ol + Pl*) compositions with liquidus temperatures of ~1240°C (EG4507) and 1170°C (KT-39). They are characterized by the appearance of high-Ca clinopyroxene as a third crystallizing phase, and, within a fairly wide crystallization range of the *Ol + Pl + Cpx* assemblage, there is indeed a trend of decreasing SiO₂ content with an increase in FeO in the melt (Fig. 1). However, in both cases, while the *Ol + Pl* cotectic crystallizes and before *Cpx* appears, there is a monotonic increase in the SiO₂ content in the model solutions; after titanomagnetite (enriched in the ulvospinel component) appears, this trend becomes irreversible.

The simulated phase equilibria of Skaergaard magma indicate that the compositional evolution of magmatic melt in the course of intrachamber differentiation can be of a much more complex nature than can be inferred from mass-balance recalculations based on cumulate compositions (Fig. 1). It should be kept in mind that the interpretation of the phases present in natural melts makes great demands on the accuracy of the crystallization models used. In particular, the COMAGMAT program was shown to be quite good in predicting the evolution of basaltic magmas where silica crystallization is concerned, but rather inadequate in simulating the separation of Fe-rich spinel [23]. In this paper, we will analyze the conditions for titanomagnetite stability on the liquidus of andesitic–basaltic systems—an important step in constructing an adequate computer model for crystallization of magnetite-bearing mineral assemblages.

EXPERIMENTAL STUDIES OF MAGNETITE
STABILITY IN ANDESITIC–BASALTIC SYSTEMS

An attempt to revise traditional views on the evolutionary trend of Skaergaard magma could not but provoke a controversy among petrologists who, to this day, have not resolved the contradictions between geological arguments put forward by opponents of the new interpretation [24] and the data on phase equilibria on which Hunter and Sparks [18, 25] based their work. It is clear that the key to this problem is estimating the conditions under which magnetite crystallized from ferrobasaltic melts and assessing the effect of the separation of magnetite-bearing mineral assemblages on the evolution of residual liquids. During the last 15 years, a considerable amount of experimental petrological data on these equilibria has become available.

Using the INFOREX database [26, 27]², we searched for melting experiments conducted on samples of terrestrial igneous rocks and synthetic basaltic mixtures in which the quenched products include Fe- and Ti-rich spinel. The query was formulated as follows: among experiments conducted at atmospheric pressure in the absence of volatile components, we needed to find runs with available data on the compositions of melts in equilibrium with titanomagnetite³.

We retrieved 213 experiments from 22 studies (about half of the runs involved samples of alkaline basalts and nephelinites). For further analysis, this data set was narrowed to include only experiments in systems of low and moderate alkalinity by placing additional constraints on the compositions of quenched glasses ($\text{Na}_2\text{O} + \text{K}_2\text{O} < 7 \text{ wt } \%$) and the duration of melting (at least 48 h). The INFOREX database was found to contain 99 experiments that satisfy these criteria and represent 13 independent studies.

Most of these experiments portrayed systems of ferrobasaltic and ferroandesitic–basaltic composition (10–18 wt % FeO, Fig. 2a), with the TiO₂ content in residual melts varying from 1 to 5 wt %. All runs were performed in platinum capsules that controlled f_{O_2} at 10⁻⁶ to 10⁻¹³ bars, near values defined by the IW–NNO+2 buffer (Fig. 3). The crystallization temperatures of titanomagnetite range from 1040 to 1160°C (Figs. 2b, 3). The phase assemblages obtained in these experiments usually include four or five minerals plus a quenched glass, and, with a few exceptions, the fourth or fifth phase to crystallize was magnetite. Plagioclase is present on the liquidus of all 99 compositions; feric phases consist of *Ol*, *Aug*, *Pig*, and *Opx* in various combinations. In 49 runs, ilmenite was found to be present; this

² The most recent version of INFOREX (4.0, 1997) includes information from 235 works, in which the experimental conditions of 8660 runs and more than 11 370 glass compositions are reported.

³ When the spinel composition was present, we selected phases with a total content of Fe and Ti oxides of more than 85% and Cr₂O₃ concentration of less than 5%. When these data were not reported, spinel was classified as titanomagnetite based on descriptions provided by the authors.

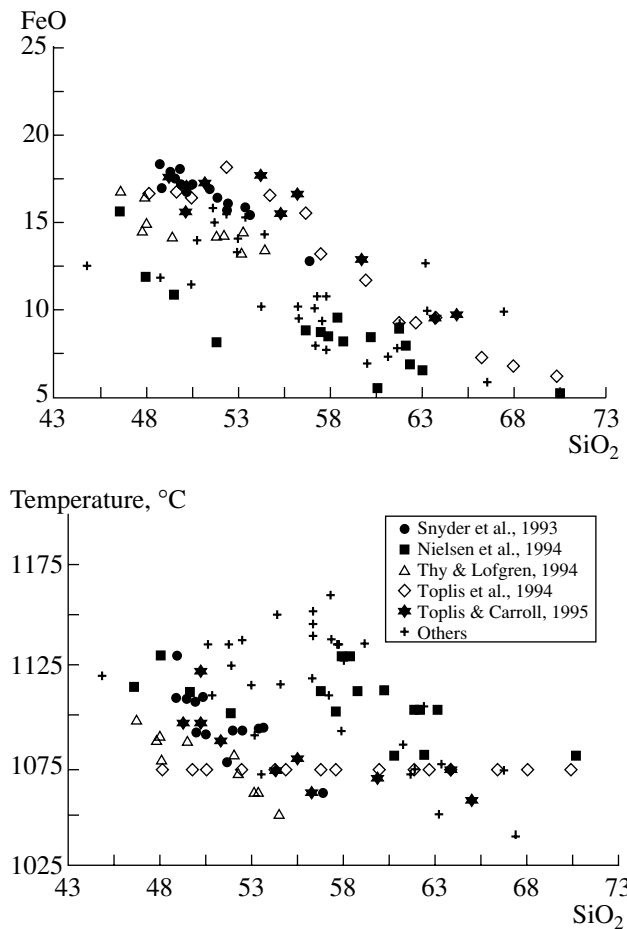


Fig. 2. Characteristics of the experimental data set of glasses corresponding to magnetite-melt equilibrium.

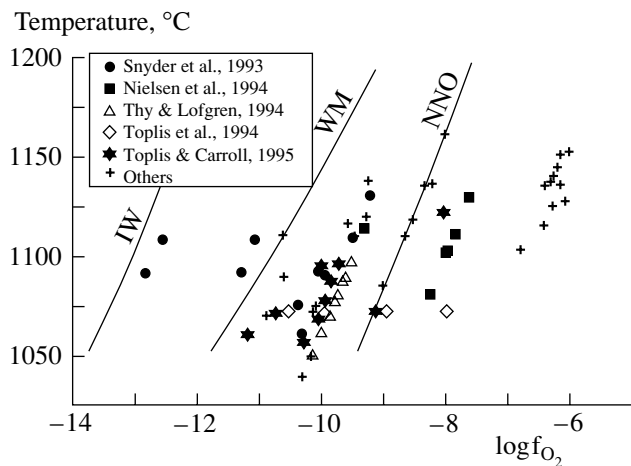


Fig. 3. Temperature of magnetite-melt equilibrium vs. oxygen fugacity for the experimental data set of 99 glasses (see Fig. 2).

phase appears in experiments conducted under reducing conditions ($f_{O_2} < 10^{-10}$). The most representative studies include five papers [28–32], which are worth discussing in greater detail.

Brief Review of Special Studies

Snyder *et al.* (1993) presented the results of 53 experiments on ferrobalt samples that are regarded, based on composition, as equivalents of the fractionation products of primary magmas for one of the layered complexes of Labrador and Skaergaard (Greenland) [28] (Table 1). With the exception of three cases, these runs were conducted at temperatures of 1060 to 1190°C and at oxygen fugacities $-12.9 < \log f_{O_2} < -8.5$. The quench products of 18 experiments were found to contain magnetite; for 15 of these runs, the compositions of coexisting glasses were determined (see solid circles in Figs. 2 and 3). Note that all magnetite-bearing assemblages ($Ol + Pl + Mt \pm Px \pm Ilm$) were obtained in experiments more than 100 hours in duration, suggesting that the conditions were close to equilibrium. The results indicate that the crystallization temperatures of titanomagnetite are no higher than 1130°C and, with f_{O_2} near the QFM buffer, strongly depend on the redox conditions (in Fig. 3, this range lies approximately midway between the IW and NNO lines). The separation of *Mt* causes the melts to be strongly depleted in FeO and enriched in SiO₂ (Fig. 2).

Nielsen *et al.* (1994) reported data from 16 experiments on 7 samples of basalts and andesites (the compositions of some of them are presented in Table 1). These runs were designed to study magnetite stability slightly above and below the NNO buffer; thus, *Mt* is present on the liquidus of all 16 compositions [29]. The experiments were conducted at temperatures of 1080 to 1129°C and at oxygen fugacities $-9.3 < \log f_{O_2} < -7.6$; run durations were at least 72 h. The data in Figs. 2 and 3 (solid squares) confirm that the crystallization temperature of *Mt* is a function of oxygen fugacity; both basaltic and andesitic melts display a depletion in FeO and enrichment in SiO₂.

Thy and Lofgren (1994) investigated the effect of melt composition on the crystallization temperature of magnetite along the QFM buffer (diamonds in Fig. 3). The starting materials in these runs were four samples of moderately alkaline ferrobalt containing 13.5–15.2 wt % FeO and 3.9–6.1 wt % Na₂O + K₂O (Table 1) [30]. For 15 out of the 46 runs, the end products contained magnetite (duration $\tau > 95$ h). The crystallization temperatures of *Mt* in these experiments varied from 1051 to 1098°C, and there was a very distinct trend for the melts to be depleted in FeO and enriched in SiO₂ (Fig. 2). An important conclusion that can be drawn from this study is that, irrespective of the initial composition, the temperatures at which *Mt* begins to appear in the crystallization sequence are $1105 \pm 5^\circ\text{C}$ —a fact that could greatly simplify the development of computer models involving the magnetite phase [30].

Toplis *et al.* (1994) reported the results of 34 isothermal experiments at $T = 1072^\circ\text{C}$ involving a sample of synthetic ferrobalt (Table 1, column 11) with varying

Table 1. Compositions of initial samples used in experimental studies of magnetite–melt equilibria

Reference	Snyder <i>et al.</i> , 1993			Nielsen <i>et al.</i> , 1994			Thy, Logfren, 1994				Toplis <i>et al.</i> , 1994–95		
	4-3	4-83C	SK	T85-77	121492	V-31	9005	7159V	8754	SAX2	SC4	SC1	SC4a
SiO ₂	48.63	47.07	50.28	45.87	50.64	63.83	48.31	48.37	47.50	46.18	50.47	48.75	49.45
TiO ₂	2.33	3.90	2.56	4.14	2.96	0.74	4.52	4.01	4.08	3.80	4.38	2.90	4.37
Al ₂ O ₃	14.57	13.65	13.69	15.16	15.05	15.09	13.11	13.80	12.59	15.23	11.73	14.89	11.68
FeO*	14.71	17.65	13.28	12.54	14.23	8.31	14.90	14.26	15.22	13.59	14.89	13.09	16.45
MnO	0.21	0.22	0.26	0.18	0.23	0.20	0.21	0.19	0.23	0.23	–	–	–
MgO	6.29	4.75	6.58	5.16	4.57	0.36	4.82	3.31	5.17	5.47	4.89	6.49	4.67
CaO	9.27	7.72	10.22	11.04	8.46	4.27	9.41	9.04	10.93	10.43	10.20	10.89	9.85
Na ₂ O	3.05	3.63	2.62	3.53	2.39	4.13	3.21	4.87	3.25	3.29	2.96	2.70	3.05
K ₂ O	0.72	1.05	0.51	1.87	0.95	2.87	0.89	1.28	0.65	1.06	0.49	0.30	0.50
P ₂ O ₅	0.23	0.36	0.00	0.50	0.52	0.19	0.60	0.88	0.38	0.72	–	–	–

Note: Compositions of samples are recalculated to 100 wt % dry substance; total Fe expressed as FeO.

amounts of P₂O₅. Although this study focused mainly on the effect of phosphorus on the phase equilibria of silicate phases, it includes the results from 15 experiments with magnetite as the liquidus phase (open diamonds in Figs. 2 and 3) [31]. These experiments were run for more than 149 hours, and the glass compositions encompassed a range from ferrobasalts to dacites. According to the experiments, magnetite crystallizes within the buffer range approximately from QFM–0.7 to QFM+1.9.

Toplis and Carrol (1995) supplemented the results of the previous study with ten new experiments in the field of magnetite–melt equilibria. These runs were performed on samples of three synthetic ferrobasalts (Table 1, columns 11–13) at temperatures of 1057 to 1122°C and oxygen fugacities $-11.2 < \log f_{\text{O}_2} < -8.1$ [32]. Run durations were more than 115 hours: in Figs. 2 and 3, these data are represented by six-point stars. As in the experiments described above, the glass compositions show a systematic decrease in FeO content from basalts to dacites; in the field of andesitic–dacitic compositions, the crystallization temperatures of *Mt* were near 1070°C.

Toplis and Carrol [32] presented the most complete analysis of phase relations and mineral–melt equilibria during the crystallization of tholeiitic magmas with the participation of magnetite and ilmenite. Here we focus on three results of that analysis. First, mass-balance calculations involving the compositions and proportions of the run products were used to establish that the percentage of titanomagnetite in assemblages that crystallize in systems open with respect to oxygen can reach as high as 15–22 wt %; this appears to be the principal factor that causes the residual melts to be enriched in SiO₂ when magnetite-bearing assemblages separate. Second, within the buffer range from QFM–2 to QFM+1, the slope of the *Mt* liquidus temperature plot-

ted against f_{O_2} is about 30°C/log f_{O_2} . Third, a negative correlation between the inverse temperature and the content of Fe₂O₃ in the liquid was found to exist for magnetite-saturated melts (estimated from the equation of Kilinca *et al.* [33]), meaning that high temperatures of magnetite crystallization correspond to an elevated oxidation of Fe in magmatic melts. However, the authors [32] did not provide any consistent analysis of how the temperature of magnetite saturation depends on the melt composition and redox conditions.

LIQUIDUS EQUATION FOR TITANOMAGNETITE: DEVELOPMENT AND ANALYSIS

We set out to construct an internally consistent geothermometer with which the crystallization temperatures of titanomagnetite could be calculated within the widest possible range of melt compositions and oxygen fugacities. The aforementioned experimental data set of 99 compositions of glasses quenched at specified T and f_{O_2} provides a good empirical basis for this.

The experimental data were processed according to the following linear model:

$$10^4/T = b \log f_{\text{O}_2} + c + \sum X_i d_i, \quad (1)$$

where T is the temperature (K); X_i denotes the mole fractions of the melt components; and b , c , and d_i are regression coefficients. In these calculations, we intentionally excluded Fe₂O₃ as an independent component and used only the total Fe concentrations (FeO_{tot}). The intention was to minimize the errors in estimating the FeO/Fe₂O₃ ratio in melts; under the most reducing conditions, these relative errors may exceed 50% irrespective of the method adopted for the calculation [34]. Another motive was that the available equations for cal-

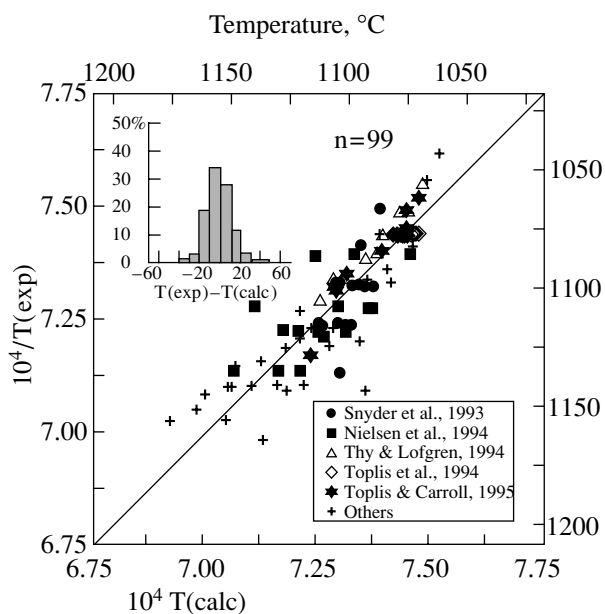


Fig. 4. Comparison of experimental and calculated (by equation (2)) values of inverse temperature for the experimental data set of 99 glasses. The histogram portrays the distribution of deviations $T(\text{exp}) - T(\text{calc})$.

culating the ferric–ferrous ratio ignore the effect of phosphorus, which can be very significant, according to recent data [35]. Another fundamental distinction of this calibration consists in that we studied the possibility of varying the regression coefficient b of oxygen fugacity depending on the composition of the liquid phase. Borisov and Shapkin [36] were the first to notice the importance of this factor when dealing with elements of variable valence; as will be shown below, this approach enabled us to considerably increase our accuracy in calculating the liquidus temperature of magnetite.

More than 30 variants of linear regression (1) involving varying sets and amounts of the melt components were analyzed. The criterion for finding the best

Table 2. Regression coefficients for equation (2) of magnetite liquidus

Parameter	Coefficient	Standard deviation (1σ)
b_0	−0.6232	0.0205
b_1	0.6826	0.0359
b_2	4.0438	0.9327
b_3	0.8251	0.2567
c	0.0159	0.0686
d_1	8.3626	0.2804
d_2	35.9674	8.0819
d_3	10.7347	2.1842
d_4	12.4418	2.3521

geothermometer was the accuracy in solving the inverse problem, i.e., the statistical estimate of the extent to which the calculated temperatures deviate from experimental ones for the specified melt composition and oxygen fugacity. It was established that the strongest influence on magnetite stability is exerted by the following four components: SiO_2 , TiO_2 , FeO_{tot} , and P_2O_5 ; the optimal equation that reproduces experimental temperature with an average accuracy of $\sim 10^\circ\text{C}$ has the form

$$10^4/T = (b_0 + b_1X_{\text{SiO}_2} + b_2X_{\text{TiO}_2} + b_3X_{\text{FeO}_{\text{tot}}})\log f_{\text{O}_2} + c + d_1X_{\text{SiO}_2} + d_2X_{\text{TiO}_2} + d_3X_{\text{FeO}_{\text{tot}}} + d_4X_{\text{P}_2\text{O}_5}. \quad (2)$$

The corresponding regression coefficients are presented in Table 2. Figure 4 compares the experimental and calculated values of the inverse temperature and a histogram of deviations $\Delta = T(\text{exp}) - T(\text{calc})$. In several cases, these deviations reach as high as $40\text{--}50^\circ\text{C}$, but, in general, about 90% of the data fall within the range $\pm 15^\circ\text{C}$; the absolute value of the average deviation Δ is 9.3°C . Note that, in the studies [28–32], these deviations do not fall outside 30°C and, for the 25 experiments of longest duration [31, 32], $\Delta = 3.6^\circ\text{C}$. The high reproducibility for the representative data set ($n = 99$) suggests that the form of the empirical relation obtained (2) reflects the real redox and structural-chemical equilibria in the liquid phase that involve the ions Fe^{3+} and Fe^{2+} and control stability on the titanomagnetite liquidus. The regression coefficients presented in Table 2 make it possible to specify the effect of each i th component selected. For this purpose, it is convenient to use partial derivatives of β_i (see equation (2)):

$$\beta_i = \partial(10^4/T)/\partial X_i = b_i \log f_{\text{O}_2} + d_i. \quad (3)$$

In the case of phosphorus, $\beta_{\text{P}_2\text{O}_5} = d_4 = 12.4418 > 0$ (Table 2), i.e., an increase in the P_2O_5 concentration in the melt raises the inverse temperature or decreases the crystallization temperature of magnetite. This effect is by no means insignificant, because the addition of 1 mol % P_2O_5 can cause the crystallization temperature of magnetite to decrease by about 20°C . The causes of the destabilizing effect of P on magnetite stability have already been analyzed in the literature; the principal cause is the possibility of some of the ferric iron being bound to phosphate complexes [31] and the decrease in the overall ferric–ferrous ratio in the melts with increasing P_2O_5 [35] concentration.

The increasing concentrations of SiO_2 and FeO_{tot} also have a destabilizing effect on magnetite: as can be inferred from Table 2 and equation (3), at $\log f_{\text{O}_2} > -12$, both derivatives of β_{SiO_2} and $\beta_{\text{FeO}_{\text{tot}}}$ are positive. With respect to SiO_2 , this result is quite natural, but it may appear somewhat surprising for FeO_{tot} . It seems strange that the stability of the iron-ore phase is inversely proportional to the total content of Fe in the melt. Nevertheless,

the low standard deviations for b_3 and d_3 (Table 2) indicate with certainty that this is a statistically based observation. An explanation for this fact should apparently be sought in structural-chemical and redox reactions involving Fe ions. For example, an analysis of experimental studies devoted to the dependence of the ferric-ferrous ratio on the composition of silica melts indicates that the percentage of ferric iron decreases with an increase in the total FeO concentration [36]. An analysis of equation (3) with parameters for TiO_2 shows that this component behaves ambivalently: at $\log f_{\text{O}_2} > -9$, the addition of Ti has a destabilizing effect and, under more reducing conditions, causes the crystallization temperature of titanomagnetite to increase, apparently owing to the enrichment of Ti-magnetite solution in the ulvospinel component.

Calculation of Isopleths of Magnetite Stability in the T - $\log f_{\text{O}_2}$ Coordinates

Consider the dependence of the crystallization temperature of *Mt* on $\log f_{\text{O}_2}$. It follows from equation (2) that systems of different compositions will react differently to a change in redox conditions. The strongest dependence on $\log f_{\text{O}_2}$ should be expected in ferrobasaltic compositions with low and moderate contents of TiO_2 and FeO (approximately up to 2 and 15 wt %, respectively). For compositions enriched in TiO_2 and FeO (such as Galapagos tholeiites [13]), this dependence may be fairly weak. This conclusion is illustrated by data shown in Fig. 5, in which the liquidus temperatures of titanomagnetite calculated for three model compositions (Table 3) are plotted against $\log f_{\text{O}_2}$. These compositions are approximate representations of low-Ti ferrobasalt (*BAS-1*), ferroandesite (*AND*), and high-Ti ferrobasalt (*BAS-2*).

For each of these compositions, the liquidus temperatures were preliminarily estimated with the COMAGMAT [21] program; for basalts, these temperatures correspond to *Ol-Pl* cotectics (~ 1165 and $\sim 1135^\circ\text{C}$); and for andesite, to a system slightly supersaturated in plagioclase with a liquidus temperature of about 1125°C (Table 3). Using equation (2) for the first two compositions *BAS-1* and *AND*, we calculated the temperatures of magnetite stability above the silica liquidus. These data indicate that, for both melts, the slope of magnetite liquidus is about $20^\circ\text{C}/\log f_{\text{O}_2}$ (Fig. 5). This value is about 1.5 times lower than that estimated in [32]; however, it should be borne in mind that, in contrast to the previous authors, our estimates were obtained for a constant composition of the melt. It is readily apparent that, according to calculations, the decrease in $\log f_{\text{O}_2}$ from -6 to -7 in going from ferrobasalt *BAS-1* to the ferroandesites is equivalent to a decrease of the magnetite liquidus by about 35°C (Fig. 5). Thus, our equation

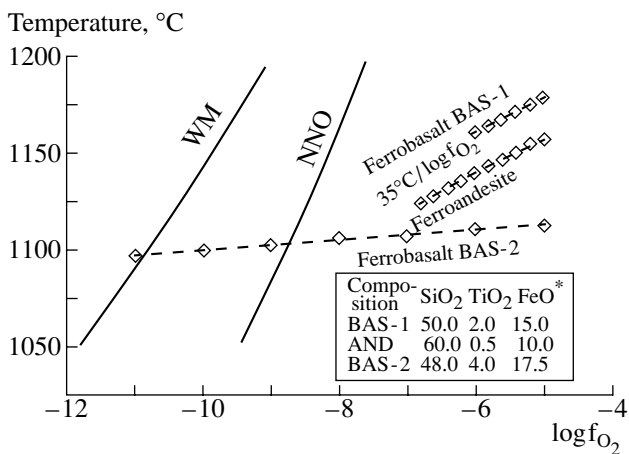


Fig. 5. Crystallization temperature of magnetite vs. oxygen fugacity according to equation (2) for two model compositions of ferrobasalts and ferroandesite (Table 3).

for magnetite stability realistically reproduces the pattern established with systems of variable compositions.

In the case of high-Ti ferrobasalt *BAS-2*, the system is not saturated in titanomagnetite over a wide f_{O_2} range because the calculated temperatures are near 1100°C , which is 25 – 30°C lower than the liquidus temperature of olivine and plagioclase. Apparently, when this type of crystallization takes place, the temperature at which Fe-spinellid begins to appear is buffered by the composition and will not deviate far from 1100°C if the melt is not substantially enriched in SiO_2 or depleted in Ti.

Table 3. Compositions of model melts

Sample	<i>BAS-1</i>	<i>AND</i>	<i>BAS-2</i>
SiO ₂	50.0	60.0	48.0
TiO ₂	2.0	0.5	4.0
Al ₂ O ₃	15.0	16.0	13.5
FeO*	15.0	10.0	17.5
MnO	–	–	–
MgO	6.0	3.0	5.0
CaO	9.0	5.5	9.0
Na ₂ O	2.5	3.5	2.5
K ₂ O	0.5	1.5	0.5
P ₂ O ₅	–	–	–
T_{Pl} , °C	1164	1126	1142
T_{Ol} , °C	1164	1094	1133

Note: *BAS-1* is low-Ti ferrobasalt; *AND* is ferroandesite; and *BAS-2* is high-Ti ferrobasalt. Compositions of samples are recalculated to 100 wt % dry substance; total Fe expressed as FeO. The temperatures of *Pl* and *Ol* liquidus are calculated with the COMAGMAT model [21].

CONCLUSIONS

Statistical processing of data on magnetite–melt equilibria from 99 experiments in systems ranging from basalts to dacites was used to obtain an equation relating the crystallization temperature of magnetite to melt composition and oxygen fugacity. For 90% of the data, this equation (2) reproduces experimental temperatures to a precision of $\pm 15^\circ\text{C}$. SiO_2 , TiO_2 , FeO_{tot} , and P_2O_5 are the components that have the strongest effect on the stability of magnetite.

The crystallization temperature of *Mt* shows a complex dependence on oxygen fugacity: for ferrobasaltic and andesitic melts with a moderate Fe content (up to ~15 wt %) and TiO_2 (up to ~2 wt %), there is a fairly steep slope of the magnetite liquidus $\sim 20^\circ\text{C}/\log f_{\text{O}_2}$, whereas, for high-Ti (4–5 wt % TiO_2) and Fe-rich (17–18 wt %) basalts, these temperatures are virtually independent of oxygen fugacity and are near 1100°C .

This equation for the magnetite liquidus can be used as an empirical basis for improving computer models of magma crystallization involving the separation of magnetite-bearing mineral assemblages.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, projects nos. 96-05-64231 and the 96-07-89054.

REFERENCES

- Wager, L.R. and Deer, W.A., Geological Investigations in East Greenland: Part III. The Petrology of the Skaergaard Intrusion, Kangerdlugssuaq, East Greenland, *Meddelelser om Gronland*, 1939, vol. 105, no. 4, pp. 1–352.
- Wager, L.R. and Braun, G.M., *Layered Igneous Rocks*, San Francisco: Freeman, 1967. Translated under the title *Rassloennye izverzhennye porody*, Moscow: Mir, 1970.
- Frenkel', M.Ya., Yaroshevskii, A.A., Ariskin, A.A., et al., *Dinamika vnutrikamernoi differentsiatsii bazitovykh magm* (Dynamics of Intrachamber Differentiation of Basic Magmas), Moscow: Nauka, 1988.
- Barmina, G.S., Ariskin, A.A., and Frenkel', M.Ya., Magmatic Types and Crystallization Conditions of Plagioclaserites of the Kronoki Peninsula, Eastern Kamchatka, *Geokhimiya*, 1989, no. 2, pp. 192–206.
- Carmichael, I.S.E., The Petrology of Thingmuli, a Tertiary Volcano in Eastern Island, *J. Pet. Sci. Eng.*, 1964, vol. 5, pp. 435–460.
- Grove, T.L. and Kinzler, R.J., Petrogenesis of Andesites, *Annu. Rev. Earth Planet. Sci.*, 1986, vol. 14, pp. 417–454.
- Grove, T.L., Gerlach, D.C., and Sando, T.W., Origin of Calc-alkaline Series Lavas at Medicine Lake Volcano by Fractionation, Assimilation, and Mixing, *Contrib. Mineral. Petrol.*, 1982, vol. 80, pp. 160–182.
- Babanskii, A.D., Ryabchikov, I.D., and Bogatikov, O.A., *Evolutsiya shchelochno-zemel'nykh magm* (Evolution of Alkaline-Earth Magmas), Moscow: Nauka, 1983.
- Kadik, A.A., Maksimov, A.P., and Ivanov, B.V., *Fiziko-khimicheskie usloviya kristallizatsii i genezis andezitov* (Physicochemical Conditions of Crystallization and Origin of Andesites), Moscow: Nauka, 1986.
- Grove, T.L. and Baker, M.B., Phase Equilibrium Controls on the Tholeiitic Versus Calcalkaline Differentiation Trends, *J. Geophys. Res. B*, 1984, vol. 89, pp. 3253–3274.
- Ariskin, A.A., Barmina, G.S., Frenkel', M.Ya., and Yaroshevskii, A.A., Computer Modeling of Fractional Crystallization of Tholeiitic Magmas at Low Pressure, *Geokhimiya*, 1987, no. 9, pp. 1240–1259.
- Morse, S.A., Kiglapait Geochemistry: IV. The Major Elements, *Geochim. Cosmochim. Acta*, 1981, vol. 45, pp. 461–479.
- Brooks, C.K., Larsen, L.M., and Nielsen, T.F.D., Importance of Iron-Rich Tholeiitic Magmas at Divergent Plate Margins: A Reappraisal, *Geology*, 1991, vol. 19, pp. 269–272.
- Osborn, E.F., *Reactor Principles, The Evolution of the Igneous Rocks: Fiftieth Anniversary Perspectives*, Yoder, H.S., Jr., Ed., Princeton: Princeton Univ. Press, 1979. Translated under the title *Evolutsiya izverzhennykh porod*, Moscow: Mir, 1982.
- Osborn, E.F., Role of Oxygen Pressure in the Crystallization and Differentiation of Basaltic Magma, *Am. J. Sci.*, 1959, vol. 257, pp. 609–647.
- Presnall, D.C., The Joint Forsterite-Diopside Oxide and Its Bearing on the Crystallization of Basaltic and Ultramafic Magmas, *Am. J. Sci.*, 1966, vol. 264, pp. 753–809.
- Lapin, I.V., Lukanin, O.A., and Kadik, A.A., Effect of Redox Conditions on the Crystallization and Differentiation of Icelandic Basalts at Shallow Depths, *Geokhimiya*, 1985, no. 6, pp. 747–760.
- Hunter, R.H. and Sparks, R.S.J., The Differentiation of the Scaergaard Intrusion, *Contrib. Mineral. Petrol.*, 1987, vol. 95, pp. 451–461.
- Ariskin, A.A., Barmina, G.S., and Frenkel', M.Ya., Crystallization Mechanism for Formation of the Tholeiitic Series, *Izv. Akad. Nauk SSSR, Ser. Geol.*, 1988, no. 4, pp. 11–19.
- Ariskin, A.A., Barmina, G.S., and Frenkel', M.Ya., Computer Modeling of Crystallization of Basaltic Melts at a Specified Oxygen Fugacity, *Geokhimiya*, 1986, no. 11, pp. 1614–1628.
- Ariskin, A.A., Frenkel, M.Ya., Barmina, G.S., and Nielsen, R.L., COMAGMAT: a Fortran Program to Model Magma Differentiation Processes, *Comput. Geosci.*, 1993, vol. 19, pp. 1155–1170.
- Hoover, J.D., Melting Relations of a New Chilled Margin Sample from the Scaergaard Intrusion, *Year Book Carnegie Inst. Washington*, 1978, vol. 77, pp. 739–743.
- Yang, H.-J., Kinzler, R.J., and Grove, T.L., Experiments and Models of Anhydrous, Basaltic Olivine–Plagioclase–Augite Saturated Melts from 0.001 to 10 Kbar, *Contrib. Mineral. Petrol.*, 1997, vol. 124, pp. 1–18.
- McBirney, A.R., Naslund, H.R., Morse, S.A., et al., The Differentiation of the Scaergaard Intrusion: A Discussion of Hunter and Sparks (Contrib. Mineral. Petrol. 95:

- 451–461), *Contrib. Mineral. Petrol.*, 1990, vol. 104, pp. 235–247.
25. Hunter, R.H. and Sparks, R.S.J., The Differentiation of the Scaergaard Intrusion: Reply to A.R. McBirney, H.R. Naslund, S.A. Morse, C.K. Brooks and T.F.D. Nielsen, *Contrib. Mineral. Petrol.*, 1990, vol. 104, pp. 248–254.
26. Meshalkin, S.S., Ariskin, A.A., Barmina, G.S., *et al.*, Development of an Experimental Database on Crystal–Melt Equilibria in Igneous Rocks: INFOREX System (Version 3.0), *Geokhimiya*, 1996, no. 2, pp. 99–105.
27. Ariskin, A.A., Meshalkin, S.S., Al'meev, R.R., *et al.*, INFOREX Information Retrieval System: Analysis and Processing of Experimental Data on Phase Equilibria in Igneous Rocks, *Petrologiya*, 1997, vol. 5, no.1, pp. 32–41.
28. Snyder, D., Carmichael, I.S.E., and Wiebe, R.A., Experimental Study of Liquid Evolution in a Fe-rich, Layered Mafic Intrusion: Constraints of the Fe–Ti Oxide Precipitation on the $T-f_{O_2}$ and $T-p$ Paths of Tholeiitic Magmas, *Contrib. Mineral. Petrol.*, 1993, vol. 113, pp. 73–86.
29. Nielsen, R.L., Forsythe, L.M., Gallahan, W.E., and Fisk, M.R., Major- and Trace-Element Magnetite–Melt Equilibria, *Chem. Geol.*, 1994, vol. 117, pp. 167–191.
30. Thy, P. and Lofgren, G.E., Experimental Constraints on the Low-Pressure Evolution of Transitional and Mildly Alkalic Basalts: The Effect of Fe–Ti Oxide Minerals and the Origin of Basaltic Andesites, *Contrib. Mineral. Petrol.*, 1994, vol. 116, pp. 340–351.
31. Toplis, M.J., Libourel, G., and Carroll, M.R., The Role of Phosphorus in Crystallization Processes of Basalt: An Experimental Study, *Geochim. Cosmochim. Acta*, 1994, vol. 58, pp. 797–810.
32. Toplis, M.J. and Carroll, M.R., An Experimental Study of the Influence of Oxygen Fugacity on Fe–Ti Oxide Stability, Phase Relations, and Mineral–Melt Equilibria in Ferro-Basaltic Systems, *J. Pet. Sci. Eng.*, 1995, vol. 36, pp. 1137–1170.
33. Kilinc, A., Carmichael, I.S.E., Rivers, M.L., and Sack, R.O., The Ferric–Ferrous Ratio of Natural Silicate Liquids Equilibrated in Air, *Contrib. Mineral. Petrol.*, 1983, vol. 83, pp. 136–140.
34. Nikolaev, G.S., Borisov, A.A., and Ariskin, A.A., Calculation of the Ferric–Ferrous Ratio in Magmatic Melts: Testing and Additional Calibration of Empirical Equations for Various Magmatic Series, *Geokhimiya*, 1996, no. 8, pp. 713–722.
35. Topis, M.J., Dingwell, D.B., and Libourel, G., The Effect of Phosphorus on the Iron Redox Ratio, Viscosity, and Density of an Evolved Ferro-Basalt, *Contrib. Mineral. Petrol.*, 1994, vol. 117, pp. 293–304.
36. Borisov, A.A., Shapkin, A.I., New Empirical Equation Relating the Fe^{3+}/Fe^{2+} Ratio in Natural Melts to Composition, Oxygen Fugacity, and Temperature, *Geokhimiya*, 1989, no. 6, pp. 892–898.