



INFOREX-3.0: A DATABASE ON EXPERIMENTAL STUDIES OF PHASE EQUILIBRIA IN IGNEOUS ROCKS AND SYNTHETIC SYSTEMS: II. DATA DESCRIPTION AND PETROLOGICAL APPLICATIONS

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(Received 31 May 1995; revised 5 February 1996)

Abstract—The purpose of the paper is to provide details of the application of the INFOREX-3.0 database, a package designed to store, retrieve, and process phase equilibria information. This most recent release of the system accesses data of 162 experimental studies, conducted from 1962 to 1994, including a total of 6174 experiments with 5188 addressed to natural igneous rocks and 986 runs carried out in synthetic systems, mostly CMAS. The total database was divided into 3893 “dry” conditions experiments, and 2281 runs performed in the presence of H₂O and/or CO₂; 1618 of the “wet” runs represented are water saturated. The number of 1 atm experiments (3750) is greater than the number of high-pressure runs (2474). The INFOREX database contains 8311 coexisting phase compositions: 3197 for glasses, 1247—olivine, 1429—pyroxenes, 501—spinel, 842—plagioclase. One block of the INFOREX information includes 298 liquid compositions where the Fe³⁺/Fe²⁺ ratio was determined. Data for sulfur and water solubility experiments also have been systematized. The INFOREX data management system allows users to find and print out data on a specific set of mineral-melt or two mineral equilibrium experiments requested for a given range of temperatures, pressures, oxygen fugacities, and compositions in a matter of a few seconds. In addition, one can use subsets of the data to develop mineral-melt geothermometers for equilibria including olivine, plagioclase, pyroxenes, and spinels for any specific system type. Two examples illustrate the use of INFOREX for testing empirical equations proposed for the calculation of water solubility and Fe³⁺/Fe²⁺ ratio in basic to acid melts. Copyright © 1996 Elsevier Science Ltd

Key Words: Experimental data, Phase equilibria, Database, Management system.

INTRODUCTION

In a companion paper (Meshalkin and Ariskin, 1996) we presented the INFOREX-3.0 database, designed to store, retrieve, and process experimental data on phase equilibria of natural igneous rocks and synthetic silicates. The goal of the first paper was to describe the general structure of the INFOREX system with an emphasis on the organization of datafiles, their linkage to master records and the description of the user interface, including the most important options. The purpose of this second paper is to provide a more detailed treatment of the INFOREX information available to date, as well as to demonstrate several examples of the application of these data to petrologic problems. We have also included an Appendix providing a complete list of references to the experimental studies incorporated into INFOREX. This allows the interested reader to gain more insight into the database information, the prospects of its updating, and into possible applications.

At the date of manuscript submission, the INFOREX database contains information on 162 experimental studies carried out from 1962 to 1994 (Fig. 1A), including 3893 runs conducted in “dry” systems and 2281 experiments with volatile components. As much as 85% of the data are related to natural igneous rocks while others apply only to synthetic systems. The number of 1 atm experiments (3750) is greater than the number of high-pressure runs (2474). In total, the database contains 8311 coexisting phase compositions (Fig. 1B). A representative dataset for 127 sulfur and 165 water solubility experiments have been systematized also. In addition, a subset of the INFOREX information includes 298 liquid compositions in which Fe³⁺/Fe²⁺ ratio was determined.

It should be noted that a primary goal of the development of INFOREX was to provide fast access to published mineral-melt equilibria information. Therefore only a few experiments are currently available on solidus rock equilibria. Nevertheless, the general organization of the INFOREX system allows

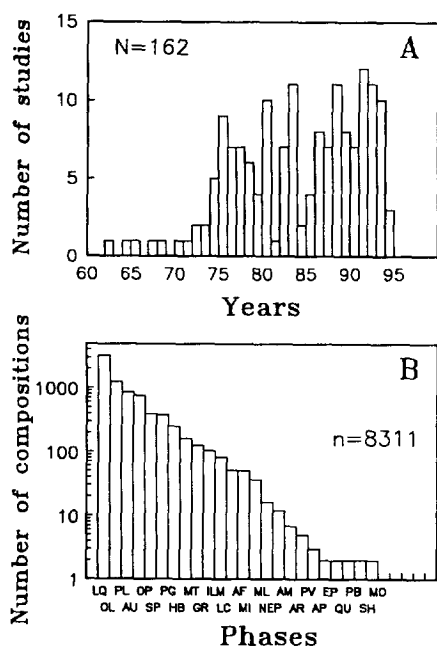


Figure 1. Distribution of number of experimental studies in terms of date of publication (A) and phase compositions (B) available in INFOREX-3.0 database.

users to update the database through a special *IMPORT* procedure (Meshalkin and Ariskin, 1996), inputting any desired phase equilibria information, accumulated from the literature or available in different laboratories as unpublished data.

GENERAL STATISTICS OF INFOREX EXPERIMENTAL DATA

The histogram in Figure 1A represents the distribution of the number of experimental studies included in INFOREX as a function of the year in which the experiments were conducted. Without claiming that this listing is exhaustive, we believe that the references (see Appendix) are sufficiently representative for a few preliminary conclusions. First, note that the total number of experimental studies per year rarely exceeds 10–12. This value is limited largely by the number of experimental laboratories that are active in any year. The distribution peaked in 1976, 1983, 1988, and 1992–1993 (the most recent studies, published in 1994–1995 are currently being incorporated). The first peak, 1975–76 was generated largely by the first batch of experiments on lunar basalts and related silicate systems. Other peaks are less obvious and may be due to periodicity in funding or publication.

The compositional data in INFOREX include 396 starting materials and 8311 run products analyzed by electron microprobe. From a frequency distribution of the numbers of experimentally observed phase compositions (Fig. 1B) it appears that the data for glasses (*LQ*—3197), olivine (*OL*—1247), plagioclase (*PL*—842), pyroxenes (*AU*, *OP*, *PG*—1429) and

spinel (chromian *SP* + *MT*—501) are strongly predominant over other phases. This provides a good basis for the development of thermodynamic and empirical models of igneous differentiation, where these rock-forming minerals control the chemical evolution of magmatic systems (Nielsen and Dungan, 1983; Ghiorso and Carmichael, 1985; Nielsen, 1990; Weaver and Langmuir, 1990; Ariskin and others, 1993). A representative dataset for garnets (*GR*—105), alkali feldspars (*AF*—50) and micas (*MI*—36) also deserves attention.

Phase equilibria experiments in dry and wet igneous systems

As already mentioned, most of the experiments available in INFOREX were performed sub-solidus and include information on both minerals and coexisting glass compositions. To specify the statistical parameters for the phase equilibria information, we have extracted them from INFOREX by excluding “water solubility” and “redox equilibria” experiments, and dividing the data into two subsets corresponding to “dry” and “wet” systems. The most important statistical parameters of the two experimental groups are shown in Figures 2 and 3.

The production of anhydrous experimental data has a relatively uniform distribution, with an average value of 100–200 experiments per year. The number of experiments in water-bearing systems peaked at almost 1000 runs/yr in 1975–1976 (NN 128–130 in Appendix). Since then, the total number of “wet” experiments has fluctuated around 100 runs/yr (Fig. 3). The distribution of run durations in both plots is similar, whereas, in general, “dry” systems investigations are characterized by experiments of longer duration. It should be noted that dry experiments encompass a wider range of pressures, up to 160 kbars, whereas hydrous experiments conducted at pressures more than 50 kbars are rare. The temperature histograms are markedly different: a peak of 1150–1250°C is peculiar to dry-system studies and a broad peak of 950–1050°C is observed for runs carried out in water-bearing systems. This is due primarily to the fact that wet experiments were conducted in water saturated conditions ($n = 1618$), where H_2O contents in melts could reach 4–15 wt.% at elevated and high pressures. The number of water undersaturated runs is only 663: many of them are related to runs carried out on natural amphibolites.

PETROLOGIC APPLICATIONS

The most obvious application of the INFOREX data is to obtain information on phase diagrams for different rock types and for systems in a restricted, specific range of temperatures, pressures or oxidation-reduction conditions. This information can be derived from INFOREX in a few seconds (Meshalkin and Ariskin, 1996). Phase assemblages and P - T - f_{O_2}

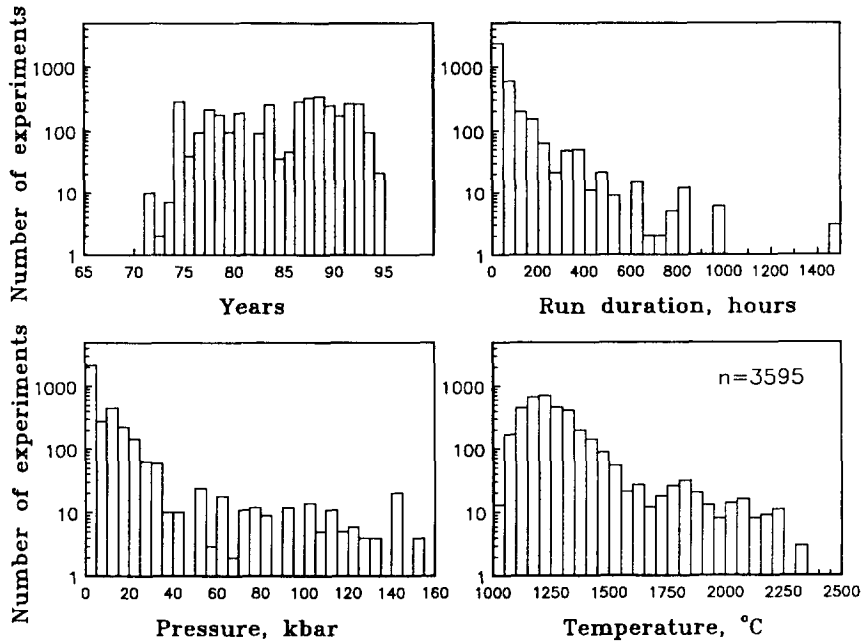


Figure 2. Distribution of number of "dry" experiments in terms of date of publication, run duration, total pressure, and experimental temperature.

conditions may be printed out in an easily read format. Another useful function allows users to analyze the effect of pressure or oxygen fugacity on experimental glass compositions (e.g. coexisting with minerals of mantle peridotites). Yet another is the ability to select experimental studies (based on rock types or starting material composition) for independent testing and modifying computer-based phase equilibria models (such an iterative procedure

is available in the COMAGMAT software—Ariskin and others, 1993). Several other INFOREX applications for processing phase equilibria data are described in this paper.

Calculation of mineral-melt geothermometers

As noted above, the INFOREX database has been designed primarily to provide access to published mineral-melt compositional information with the

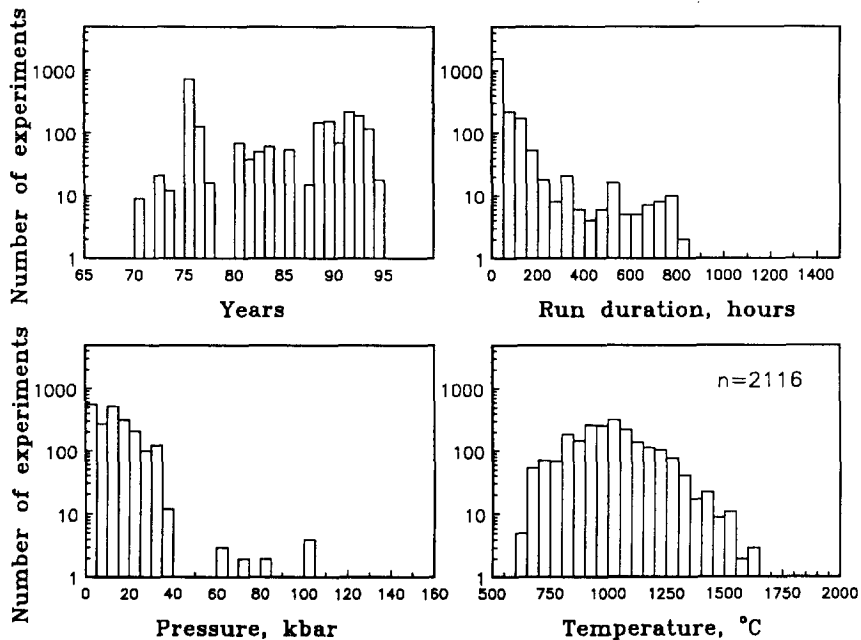


Figure 3. Distribution of number of "wet" experiments in terms of date of publication, run duration, total pressure, and experimental temperature.

goal of developing empirical geothermometers, which in turn can be applied to the modeling of natural igneous systems (Barmina, Ariskin, and Frenkel, 1989a; Barmina, Ariskin, and Frenkel, 1989b; Ariskin and Nielsen, 1993). To facilitate this function, the "Developing Geothermometers" (DG) option was incorporated into INFOREX which allows a system of equations to be created describing low pressure mineral-melt equilibria for rock-forming minerals such as olivine, plagioclase, high-Ca (augites from diopside to sub-calcium species) and low-Ca (pigeonite and orthopyroxene) pyroxenes as well as spinels (both chromian spinels and Ti-magnetite).

Following the extraction of a set of experimental data using INFOREX, including tables of coexisting mineral and glass compositions, the calibration of the equations is accomplished by multiple regression in the form of a modified Arrhenius relation:

$$\ln K_i = A/T + B \lg f_{O_2} + C \ln(Fe^{3+}/Fe^{2+})_L + D \ln R_L + E, \quad (1)$$

where K_i is an equilibrium constant of a formation reaction, distribution coefficient or exchange constant for component— i , T is the absolute temperature, f_{O_2} is oxygen fugacity, R_L is a melt structure-chemical parameter, such as Si/O , NBO/T , Al/Si , $(Na + K)/Al$, etc., while the parameters A , B , C , D and E are the regression constants.

To specify an end-member formation reaction equilibrium constant for a reaction of the formation (crystallization) of an end-member component, the degree to which K_i is compositionally dependent may be determined as a function of the melt component activities. The INFOREX DG-option enables the user to apply a single oxide, two-lattice (Nielsen and Dungan, 1983) or a modified two-lattice model (Ariskin and Barmina, 1990) for the melt component activities calculations. The use of melt structure chemical parameters as independent variables in Equation (1) is a method of fine-tuning the model. This approach assumes that the effects of nonideality on mineral-melt equilibria can be attributed primarily to the liquid phase.

The multiple linear regression calculations are built into the DG-option, allowing the user to study different combinations of equilibrium constants versus reciprocal temperature, oxygen fugacity or melt structure-chemical parameters numerically. Besides the regression parameters, the DG-option calculates the goodness of fit, comparing the calculated and experimental values, and permitting an independent estimate of the accuracy of the geothermometers. If the accuracy fails to satisfy the requirements for modeling, the calculations may be repeated for another combination of variables, until a good fit with the experimental data is obtained.

Olivine-melt and plagioclase-melt equilibria equations

Two examples of the use of the INFOREX DG-option are given in Figure 4. The results of the

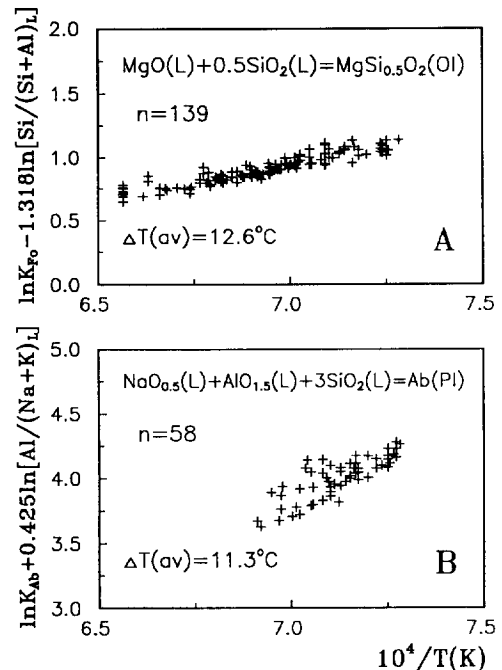


Figure 4. Correlation of mineral-melt $\ln K$ for forsterite (A) and albite (B) with reciprocal temperature, compensated for effect of melt composition. Dependencies were constructed based on two datasets extracted from INFOREX database in automatic mode, searching for mineral-melt equilibria (Meshalkin and Ariskin, 1996). Multiple regression constants describing dependencies as per linear model (Eq. 1) are given in Table 1. Values of $\Delta T(av)$ represent average deviations calculated-experimental temperatures.

processing of olivine-melt equilibria calculations (Fig. 4A) are based on a dataset of olivine and anhydrous glass compositions observed at 1 atm, 1100–1250°C. These glasses contain no more than 5 wt.% $Na_2O + K_2O$, and experimental run durations of no less than 48 h: 139 coexisting olivine and glass compositions were found to match these conditions. For the calculation of equilibrium constants of the forsterite (Fo) formation reaction, the two-lattice model by Nielsen and Dungan (1983) was used. We investigated five combinations of melt parameters with the $Si/(Si + Al)$ ratio found to be optimal (Table 1). The results are reproducible with an absolute accuracy of 12.6°C. The average deviation indicates that the model calculations reproduce experimental temperatures within 25°C for 92% of the data.

Figure 4B illustrates the development of an albite plagioclase-melt geothermometer for another group of previously selected experiments, including 58 "dry" runs conducted at 1 atm, 1000–1200°C, andesitic to dacitic glasses which contained 55–65% SiO_2 and 3–7% $Na_2O + K_2O$. Given the difficulty of obtaining equilibrium in plagioclase-melt experiments, the experimental dataset includes only those experiments with a run duration greater than 96 h. Activities of the albite melt components for each point (see the reaction shown Fig. 4B) were calculated

Table 1. Run conditions and regression constants for olivine-melt, plagioclase-melt, and chromian spinel-melt equilibria equations created using INFOREX "Developing Geothermometers"-option

| | Olivine-melt | Plagioclase-melt | Cr-spinel-melt |
|--------------------|--|---|--|
| | Run conditions | | |
| Pressure, bar | 1 | 1 | 1 |
| Temperature, °C | 1100 < T < 1250 | 1000 < T < 1200 | 1150 < T < 1500 |
| Composition, wt. % | Na ₂ O + K ₂ O < 5 | 55 < SiO ₂ < 6, 3 < Na ₂ O + K ₂ O < 7 | basalts and norites to komatiites |
| Duration, h | > 48 | > 96 | > 48 |
| | whole range | whole range | -13 < lg f _{O₂} < -3 |
| n | 139 | 58 | 112 |
| Solid component | Forsterite (Fo) | Equilibrium constants | — |
| Calculated K | aFo(OL)/aFo(L) | Albite (Ab) | (Fe ³⁺ / Fe ²⁺) _{Sp} |
| | | aAb(PL) / aAb(L) | |
| | | Regression constants | |
| A | 5685.7 (288.9) | 13659.2 (1462.9) | 58107 (4887) |
| B | — | — | 2.007 (0.151) |
| C | — | — | -3.026 (0.302) |
| D | -1.318 (0.205) | -0.425 (0.065) | -3.648 (0.466) |
| E | -3.033 (0.246) | -5.726 (1.062) | -30.623 (2.703) |

Notes: Regression constants were calculated as per linear model (Eq. 1). D values correspond to different melt-structure chemical parameters R_L (molar ratios): Si/(Si + Al) for Fo, (Na + K) / Al for Ab, and Al / (Al + Na + K) for spinel. Activities of Fo and Ab in melt were calculated using two-lattice models by Nielsen and Dungan (1983) and Ariskin and Barmina (1990), respectively. Standard deviation for each constant is given in parentheses.

using the two-lattice model proposed by Ariskin and Barmina (1990). Regression parameters for an optimal linear model are given in Table 1. These data point to a strong dependence of the calculated Ab-constant on the (Na + K)/Al ratio in the melts. Application of this ratio alone results in a reproducibility of 11.3°C.

Development of a chromian spinel-melt geothermometer

A global search for spinel-melt equilibria data found 386 coexisting anhydrous spinel-melt pairs, 305 of which are 1 atm runs, while 81 represent high-pressure experiments. The low-pressure spinels have been divided into two groups, consisting of 259 chromian spinels and 46 titanium magnetites using Cr₂O₃ > 20 wt.% and FeO (total) < 30 wt.% as the selection criteria. Three experiments in synthetic systems and 34 runs of lunar basalts have been excluded from the "chromian" group, leaving only data on terrestrial basalts (162 pairs), norites (41) and komatiites (19). These experiments were "Pt wire loop" experiments with controlled oxygen fugacities ($10^{-13} < f_{O_2} < 10^{-3}$) and a range of temperatures (1150–1500°C). Using the INFOREX SG-option (Meshalkin and Ariskin, 1996), an additional filtering of the selected experiments was conducted including run duration restrictions (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 seven studies satisfied the selection criteria (see NN 28, 31, 73, 74, 76, 81, 93 in Appendix). Thermodynamic processing has been performed on a slightly reduced dataset of the 112 coexisting spinel-melt compositions with the lowest analytical error, and longest run times. Five empirical equations including the distribution of six main spinel components, such as Cr³⁺, Al³⁺, Ti⁴⁺,

Mg²⁺, Fe³⁺, and Fe²⁺ were calculated from that data (Ariskin and Nikolaev, 1996).

Regression parameters for one of the equations describing the effect of temperature, oxygen fugacity, and liquid composition on the Fe³⁺/Fe²⁺ ratio in chromian spinels are given in Table 1. Applying the geothermometer, the internal precision of the geothermometer can be calculated by using the calibration dataset as unknowns and comparing the results to the experimental values. Such a comparison for temperature indicates an accuracy of 9°C (Fig. 5A). These parameters can be used for the calculation of log f_{O₂} also, if the spinel and melt compositions and temperature are known. Using the spinel parameters from Table 1, the experimental values of oxygen fugacity for 112 basic experiments were reproduced with an average accuracy of 0.1 log unit (Fig. 6B).

Testing empirical dependencies developed for the calculation of Fe³⁺ / Fe²⁺ ratio in melts

An important parameter for magmatic differentiation models is the Fe³⁺/Fe²⁺ ratio in the magma. Several equations for the calculations have been proposed, with the dependence of Sack and others (1980) being one of the most popular among igneous petrologists for the last fifteen years. Information on the redox equilibrium available in INFOREX includes over 300 experiments on which these calibrations were carried out (NN 147–153 in Appendix). This makes it possible to test the proposed equations for a given range of oxygen fugacities or melt compositions, or even to develop independently numerical constraints on the empirical dependencies.

For example, we have tested the Sack and others equation on two sets of redox experiments, including melts of a low alkalinity series (picrites, basalts, andesitic basalts—n = 56) and alkaline melts

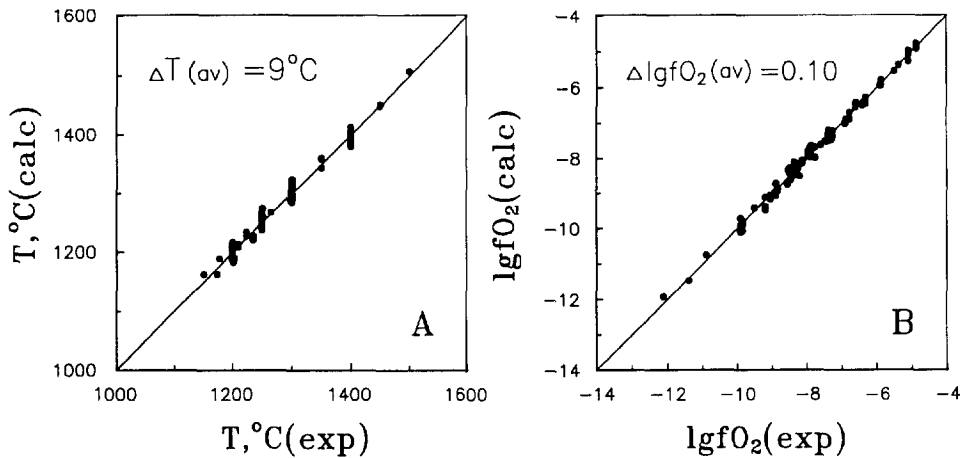


Figure 5. Comparison of chromian spinel saturation temperatures (A) and oxygen fugacities (B) observed in experiments with those calculated for same liquid compositions using spinel-melt geothermometer given in Table 1. Dependence was constructed based on dataset extracted from INFOREX database in automatic mode, searching for mineral-melt equilibria (Meshalkin and Ariskin, 1996). Multiple regression constants describing dependence as per linear model (1) are given in Table 1. Values of ΔT (av) and $\Delta \lg f_{O_2}$ (av) represent average calculated-observed deviations for temperatures and oxygen fugacities for calibration dataset.

($n = 50$). Those data include only runs conducted at temperatures lower than 1500°C and in the range of oxygen fugacities close to natural magma crystallization conditions: $IW < \lg f_{O_2} < NNO + 1$; a large dataset of experiments in air was excluded from consideration. The results (Fig. 6A,B—crosses) indicate an average internal precision for calculated $\text{Fe}^{3+}/\text{Fe}^{2+}$ melt ratio of 0.035 for the low alkalinity series and 0.043 for the alkaline melts. On first inspection, this seems adequate. However, note that these errors are of the same order as the absolute values obtained at the most reduced conditions, where the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios are lower than 0.1.

To improve the calculations, two new equations were developed based on separate datasets. For the

low alkalinity series, the following equation was obtained:

$$\lg(\text{Fe}^{3+}/\text{Fe}^{2+})_L = \frac{3282.2}{T + 0.1396 \lg f_{O_2} - 1.424 \text{SiO}_2 - 4.359 \text{TiO}_2 - 9.449 \text{Al}_2\text{O}_3 - 0.755 \text{FeO} - 2.233 \text{MgO} + 0.340 \text{CaO} + 2.477 \text{Na}_2\text{O} + 4.453 \text{K}_2\text{O}}, \quad (2)$$

where indices of oxides denote mole fractions.

“Alkaline” data are described better by the following equation:

$$\lg(\text{Fe}^{3+}/\text{Fe}^{2+})_L = \frac{6447.3}{T + 0.2228 \lg f_{O_2} - 3.959 \text{SiO}_2 - 3.621 \text{TiO}_2 - 1.709 \text{Al}_2\text{O}_3 - 2.228 \text{FeO} - 2.594 \text{MgO} - 2.674 \text{CaO} - 2.856 \text{Na}_2\text{O} - 1.138 \text{K}_2\text{O}}. \quad (3)$$

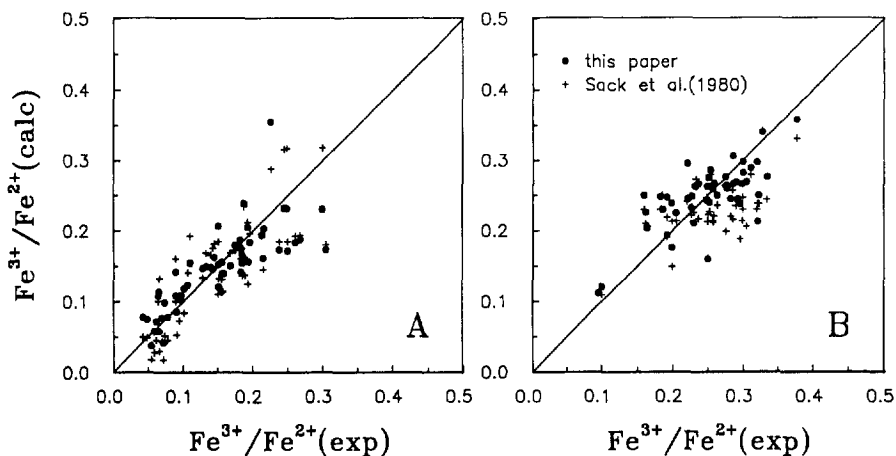


Figure 6. Comparison of experimentally determined $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios in low-alkali (A) and high-alkali (B) melts with those calculated using Sack and others (1980) and proposed in the paper Equations (2) and (3). Test was conducted based on two datasets extracted from INFOREX database in automatic mode searching for “redox equilibria” experiments in given range of melt compositions (Meshalkin and Ariskin, 1996), see NN 147–153 in Appendix.

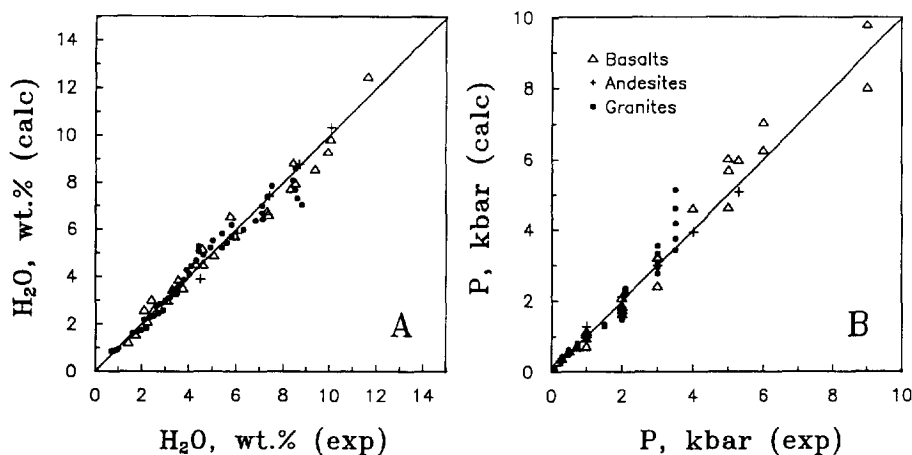


Figure 7. Comparison of experimentally determined water solubility (A) and pressure (B) with those calculated using regression constants of Equation (4). Test was conducted based on dataset extracted from INFOREX database in automatic mode, searching for "water solubility" experiments (Meshalkin and Ariskin, 1996), see NN 141–145 and 157 in Appendix.

Comparison of the experimental $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios with those calculated using Equations (2) and (3) is shown on Figure 6A,B by solid circles. These data indicate an average accuracy of 0.029 for the normal alkalinity series and 0.031 for the alkaline melts. In absolute terms this is slightly better, but close to the model of Sack and others (1980). Nevertheless, the new equations markedly improve calculations at low values of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio in the first case (Fig. 6A) and to eliminate a large number of systematic errors observed in the second group (Fig. 6B). This example illustrates the importance of examining the $\text{Fe}^{3+}/\text{Fe}^{2+}$ calculations for a better understanding of possible uncertainties in the practical use of computer-based petrologic models.

Calculating water solubility in basaltic to granite melts

Another useful application of the INFOREX system is its ability to calculate water solubility in magmas. In the last decade, many investigations have been undertaken to develop thermodynamic models of water solubility. Each, to different extents, do so by accounting for the changes in the partial molar volume of H₂O and for the relations between H₂O species in silicate melts, see the review by Lange and Carmichael (1990). One problem that we encounter in applying this information to natural systems is that few experimental data on water solubility exist for natural systems, particularly for basalts and andesites. Therefore, a classic thermodynamic approach based on the use of independent constraints, such as the effect of temperature on the partial molar volume of H₂O, may generate additional errors to calculations of water solubility.

The water solubility experiments were extracted from the INFOREX database to develop a purely empirical equation, which can be applied to a wide

range of systems and conditions (NN 141–145 and 157 in Appendix). Processing of the data was carried out by multiple linear regression calculations with the melt structure-chemical parameters used as independent variables. A set of seventeen parameter combinations were investigated. The best internal precision was obtained using the expression:

$$\ln(C_{\text{H}_2\text{O}})_L = [-14709.66 + 38437.04(\text{Si}/\text{O})_L](1/T) + 0.5868 \ln P - 21.455(\text{Si}/\text{O})_L + 3.894(\text{Al}/\text{Si})_L + 4.393, \quad (4)$$

where $(C_{\text{H}_2\text{O}})_L$ is water content in silicate liquid (wt.%), P is total pressure (bars), and Si/O and Al/Si are atomic ratios. Comparison of the experimental values with those calculated using Equation (4) indicates an average accuracy of 0.3 wt.% H₂O (Fig. 7A). Solving the inverse problem for pressure (if water content in a saturated melt is given) also indicates a good average accuracy of 250 bars. This is consistent with our current understanding of the strong effect of pressure on water solubility.

Derivation of the equation for the calculation of water solubility in magmatic melts shows how the information in the INFOREX database can be developed further. There is a large existing dataset of water-saturated experiments, but direct analytical information on the water content of the experimental glasses is absent for almost all of them. Utilizing Equation (4), the water contents can now be calculated, potentially extrapolating up to 12–15 kbars as a prelude to a numerical study of the effect of water on mineral-melt equilibria. Taking this into account, a representative dataset of hornblende compositions ($n = 162$) has allowed us to develop hornblende-melt geothermometers for water-bearing systems. This branch of the INFOREX DG-option is now under development.

CONCLUSIONS

The INFOREX-3.0 package represents the most complete and sophisticated experimental database presently available to petrologists. This system of programs is designed to help petrologists and geochemists both in sorting data, and in manipulating subsets of the database. The thousands of phase equilibria experiments stored in INFOREX can now be accessed readily, examined and exchanged. Detailed examination of the information will enable petrologists to make better use of the existing data, and to examine the experimental systems that need further work.

Subsequent maintenance of the database, both adding new data and modifying the interface as the petrologic community's needs evolve, will be continued. We hope the job of maintaining the database will rotate annually amongst the major users. To request the INFOREX-3.0 package, including detailed instructions, please contact Dr. Alexei A. Ariskin in the Vernadsky Institute, Moscow, Russia (*e-mail*: ariskin@glas.apc.org).

Acknowledgments—The authors are grateful to Roger L. Nielsen for critically reading and correcting the manuscript. Financial support of the Russian Foundation of Fundamental Research (Grant N 94-05-16098) and the International Science Foundation (Grant N M1N000) is gratefully acknowledged.

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APPENDIX

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