PHASE DIAGRAMS FOR CERAMISTS

VOLUME VIII

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Bjorn O. Mysen

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Volume VIII

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The Phase Diagrams published in this volume were collected and reviewed by the Phase Diagrams for Ceramists Data Center, located in the Institute for Materials Science and Engineering of the National Institute of Standards and Technology. Significant support from the American Ceramic Society was crucial in providing this important reference information to the ceramics community.

Malcolm W. Chase
Acting Director, Standard Reference Data
National Institute of Standards and Technology

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Preface

This volume is the eighth in the series *Phase Diagrams for Ceramists* and the third to appear since the National Institute of Standards and Technology (NIST) [formerly National Bureau of Standards] and the American Ceramic Society (ACerS) embarked on a jointly-sponsored Ceramic Phase Equilibria Program. The goal of the Program is to support growth and progress in the ceramics industry by providing relevant critically-evaluated phase diagrams. To achieve this, a multiyear program was established to improve currency with the archival literature and to provide critically-evaluated phase diagrams for oxides, salts, carbides, nitrides, borides, compound semiconductors, and chalcogenides. Computer graphics, database management, computer evaluation and predictive modeling are being used where possible to produce databases for distribution and generation of computer-typeset products. Program updates appear periodically in the American Ceramic Society Bulletin.

Program Origins: For over fifty years the National Bureau of Standards (now NIST) and ACerS have collaborated on the publication of evaluated phase diagrams of ceramic systems, best represented by the series *Phase Diagrams for Ceramists*, Volumes I-V. The joint Ceramic Phase Equilibria Program, representing a continuation and expansion of the effort to make ceramic phase information readily and comprehensively available, was initiated in December 1982.

Program Responsibility: To achieve the goals of the expanded program a multiyear effort was established with support from NIST and other federal agency programs and from a fund-raising effort managed by the ACerS. NIST provides overall coordination and technical guidance and ensures quality data coverage and evaluation. NIST has also developed a prototype PC graphics database. The ACerS is responsible for the production aspects and dissemination of the data in both printed and computer database forms.

Sponsorship: The fund-raising effort managed by ACerS is an ongoing activity. As of June 1989 a total of $2,486,410 has been contributed or pledged to the program. There are five basic categories of participation in the Ceramic Phase Equilibria Program: Primary Sponsors, $200,000 or more; Sponsors, $100,000 or more; Affiliate Sponsors, $25,000 or more; Contributors, $5,000 or more; and Members and Friends, any smaller amount. Contributions to the program, through June 1989, from individuals and the following organizations are gratefully acknowledged.

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INTRODUCTION

This volume, VIII, in the *Phase Diagrams for Ceramists* series includes 295 Figures containing 915 diagrams of systems collected from the literature between 1975 and 1983,[1] together with some overflow from earlier volumes.

The systems include oxide and salt systems with and without water, most at pressures above ambient atmospheric pressure. The following diagrams are at atmospheric pressure: 7887A, 7889, 7894A, 7897, 7898, 7900, 7904, 7917, 7919, 7920, 7931, 7948, 7952, 7958, 8126, 8127, 8134, 8135, 8136A, 8136B, 8146, 8147, and 8149.

A significant portion of the diagrams, in particular those from chemically complex systems, is from the earth science literature. Those diagrams, and diagrams obtained at pressures above ambient, are particularly relevant to earth science. Water and other volatile components (CO_2, CH_4, N_2) are of central interest and their influence on phase relations, particularly in alkali metal - alkaline earth - alumina - silica systems at high pressure (above ambient), is a principal focus among earth scientists using and generating phase diagrams. Diagrams for such systems were included because of their general relevance and because this expansion makes *Phase Diagrams for Ceramists* more attractive to a wider audience of phase diagram users.

Those diagrams and others in this compilation not only will aid a wide audience of phase diagram users, but also illustrate that the *Phase Diagrams for Ceramists* series is intended for all materials scientists, including those studying earth materials. The chemical compositions and physical conditions often vary from discipline to discipline, but the practical and principal use of phase diagrams is the same. Phase diagrams relevant to a particular problem may be published in literature not readily available or not viewed as relevant. The compilation in Volume VIII should assist in making the literature accessible to all users of phase diagrams.

The reader should note that the indexes in this volume are cumulative for Volumes VI, VII, and VIII. Cumulative indexes for Volumes I, II, and III were published in Volume III and a separate volume of indexes was published in 1984 covering Volumes I through V.

Individuals whose names do not appear on the title page who deserve acknowledgement and thanks for their contributions to the publication of this book are acknowledged here.

The software used for generating and editing the database and the commentaries, and for computer typesetting, is the series of programs written by Carla G. Messina. Thanks also go to Kimberly M. Kessell for assistance in running the computer-typesetting programs.

The graphics programs with which diagrams were digitized, edited, and plotted are those used for Volumes VI and VII, written by Peter K. Schenck with Jennifer R. Dennis Verkouteren. The following persons assisted in the phase diagram graphics data effort to produce Volume VIII: Michael Rodtang, Daniel Pennington, Raymond Yang, Thomas Green, Theresa Messina, and Barbara Lee.

For a fuller discussion of the procedures used in collecting, evaluating, and editing the diagram information, and a description of the computer graphics software used in digitizing, storing, retrieving, and plotting the phase diagrams, the reader is referred to the "General Guidelines" and "Graphics Program" sections in Volume VI.

The individuals listed below are the editors who contributed to Volume VIII. The commentaries submitted by each are identified in the book by the initials shown.

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1. C. G. Messina, M.A. Clevinger, L. P. Cook, and R.S. Roth, *Phase Diagrams for Ceramists Bibliographic Update for Oxides and Salts through January 1, 1984*, 182 pp (The American Ceramic Society, Inc., Westerville, Ohio, January 1986).

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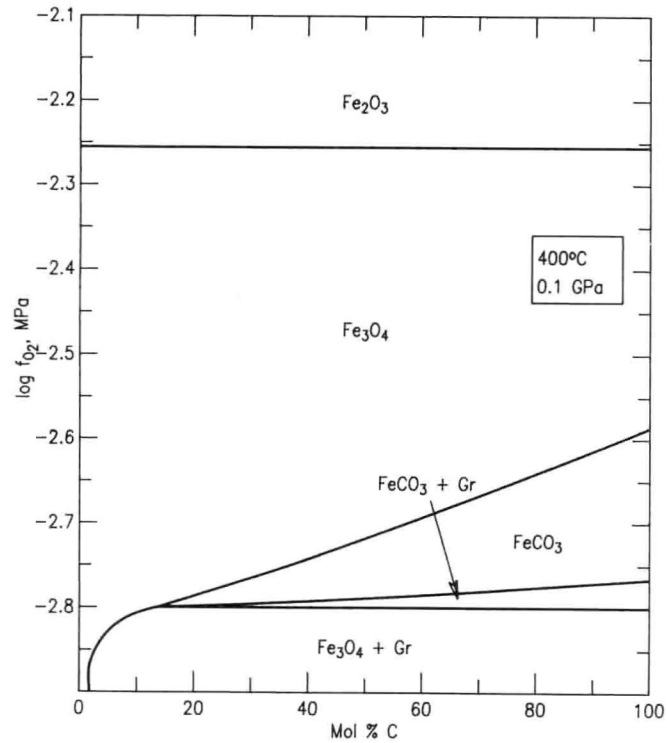
*Except for certain Figures as noted in the Introduction, all of the systems included in this volume were studied at pressures above ambient atmospheric pressure.

A. OXYGEN PLUS IRON PLUS CARBON PLUS HYDROGEN

O-Fe-C-H_2

(A)



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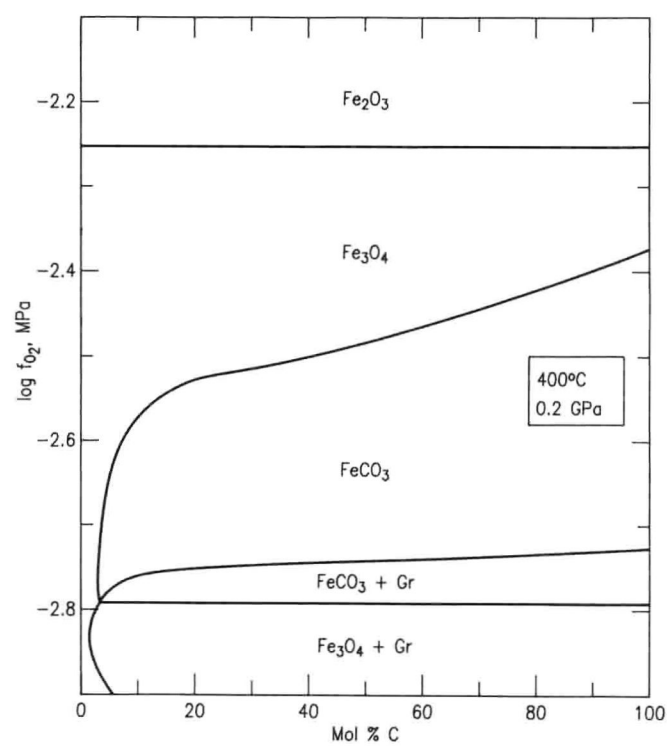

O-Fe-C-H_2 (cont.)

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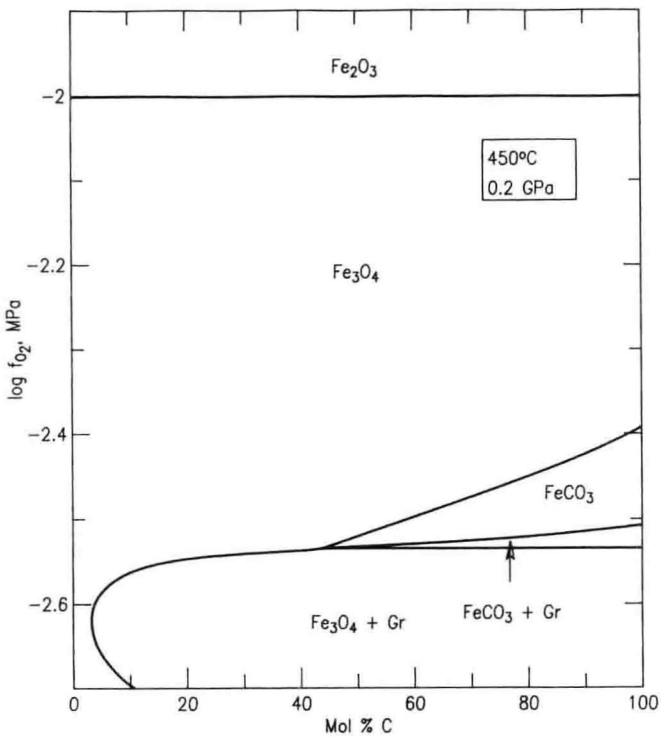

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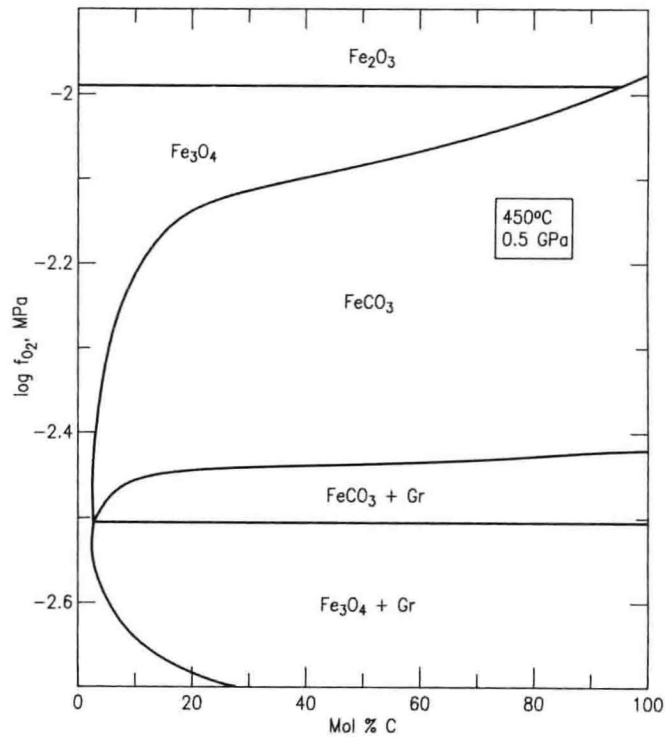

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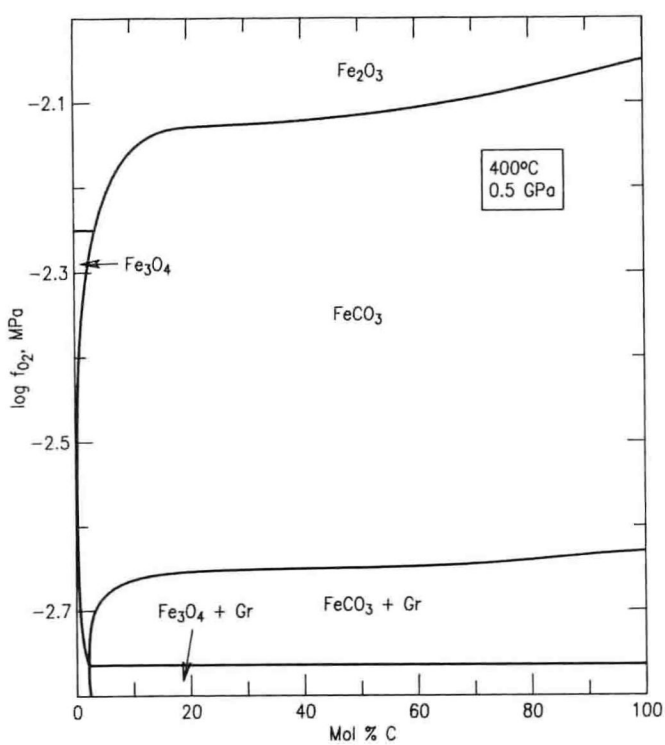

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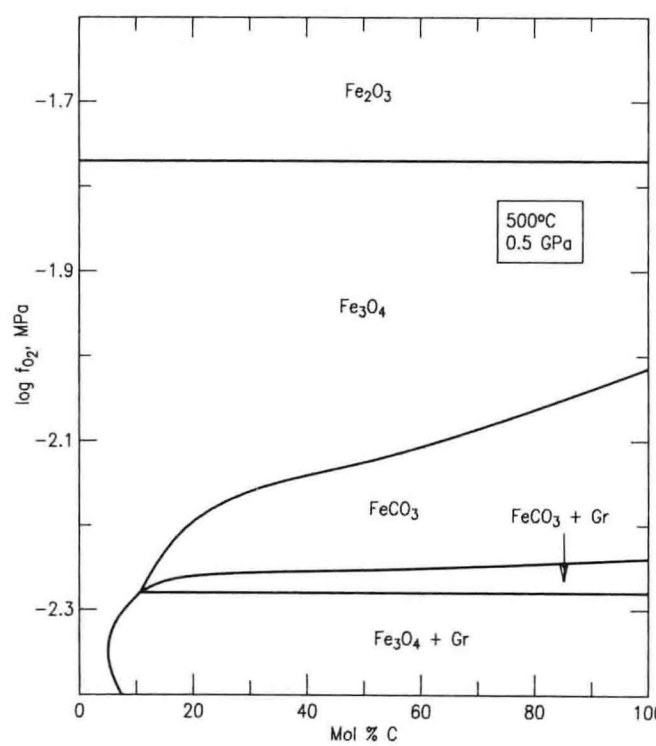


O-Fe-C-H_2 (concl.)

(G)

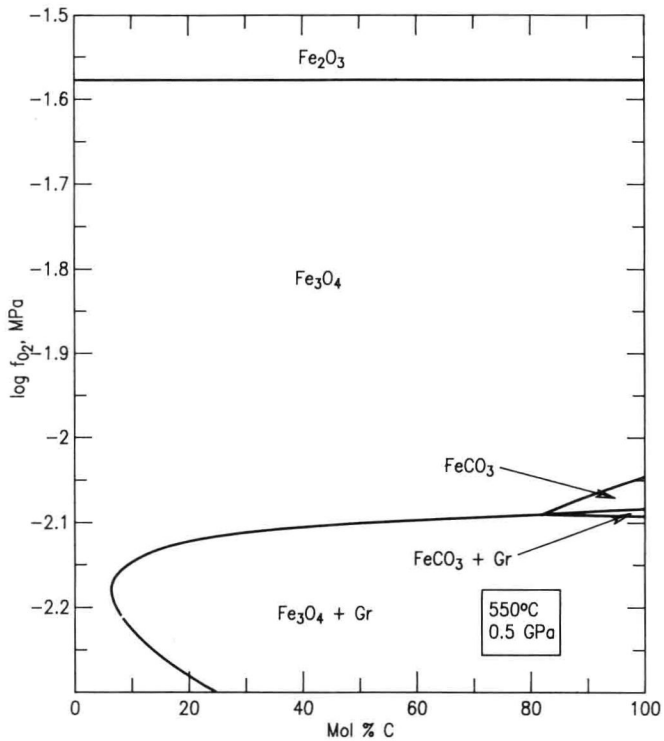


Fig. **7886**—System FeO-Fe_2O_3-$FeCO_3$-C. (*A-G*) log f_{O_2} vs mol% C as a function of temperature and pressure. Gr = graphite.
B. R. Frost, *Am. J. Sci.*, **279** [9] 1033-1059 (1979).

The stability of graphite in the presence of a C-O-H fluid has been calculated at pressures up to 1.0 GPa at temperatures above 400°C. In fluids not in equilibrium with graphite, fluid compositions have been calculated as a function of oxygen fugacity (f_{O_2}) at constant pressure and temperature. The system contains the species H_2O, CO_2, O_2, H_2, CO, and CH_4. The equilibrium constants used in the calculations, for the following reactions, are from the JANAF Tables.[1]

$$C + O_2 = CO_2, \quad K_1 = f_{CO_2}/f_{O_2} \tag{1}$$

$$C + 1/2O_2 = CO, \quad K_2 = f_{CO}/(f_{O_2})^{1/2} \tag{2}$$

$$H_2 + 1/2O_2 = H_2O, \quad K_3 = f_{H_2O}/[(f_{O_2})^{1/2}(f_{H_2})] \tag{3}$$

$$C + 2H_2 = CH_4, \quad K_4 = f_{CH_4}/(f_{H_2})^2 \tag{4}$$

$$CO_2 + 2H_2O = CH_4 + 2O_2, \quad K_5 = [f_{CH_4}(f_{O_2})^2]/[(f_{H_2O})^2 f_{CO_2}] \tag{5}$$

$$2CO_2 = 2CO + O_2, \quad K_6 = [f_{O_2}(f_{CO})^2]/(f_{CO_2})^2 \tag{6}$$

The standard states for the fluids are 0.1 MPa at any specified temperature and for the solids, any specified pressure and temperature. Fugacity coefficients of the fluids were determined from the expressions of Ref. 2 as modified by Refs. 3 and 4. For pure fluids, the calculated fugacity coefficients are within ±10% of measured values. Adjustments have been made for CO_2 + H_2O fluids to fit experimentally determined fugacity coefficients.[4] Relevant thermodynamic data are tabulated. For more complex fluids, no experimental data are available to check the accuracy of the calculated fugacity coefficients. In addition, the relationship given in Eq. 7 and the carbon content of the gas, X_C, are fixed.

$$P_{fluid} = P_{H_2O} + P_{CO_2} + P_{H_2} + P_{CO} \tag{7}$$

The X_C is the molar ratio of carbon to hydrogen in the system.

At low f_{O_2}, the equilibria in Eqs. 3 and 4 govern the equilibria shown in Eq. 8 and the carbon content of the fluid decreases with increasing oxygen fugacity.

$$C + 2H_2O = CH_4 + O_2 \tag{8}$$

The $X_{H_2O}^{max}$ is the maximum H_2O content for a fluid in equilibrium with graphite. This value increases rapidly with increasing pressure because the activity coefficient of CO_2 increases very rapidly with pressure,[5] whereas that of H_2O is nearly constant.

Relationships between redox equilibria of iron-bearing minerals and fluid compositions have been shown in the system Fe-C-O-H (*A-G*) as a function of X_C and f_{O_2} at a range of pressures and temperatures. Note in particular the extension of the siderite ($FeCO_3$) stability field to increasingly water-rich fluid compositions with increasing pressures.

The results have been applied to discussion of metamorphism in the crust of the earth.

1. D. R. Stull and H. Prophet, JANAF Thermochemical Tables, 2nd Ed., NSRDS–NBS–31, 1141 pp. U. S. Dept. of Commerce, Washington, D.C. 1971.
2. O. Redlich and J. N. S. Kwong, *Chem. Rev.*, **44**, 233 (1949).
3. R. deSantis, G. J. F. Breedveld, and J. M. Prausnitz, *Ind. Engl. Chem. Process, Des. Dev.*, **13** [4] 374 (1974).
4. J. R. Holloway, pp. 161–181 in Thermodynamics in Geology. Edited by D. G. Fraser. Boston, 1977.
5. G. B. Skippen, pp. 66–83 in Mineralogical Association of Canada Short Course in Application of Thermodynamics to Petrology and Ore Deposits. Edited by H. J. Greenwood. Mineralog. Assoc. Canada, Vancouver, 1977.

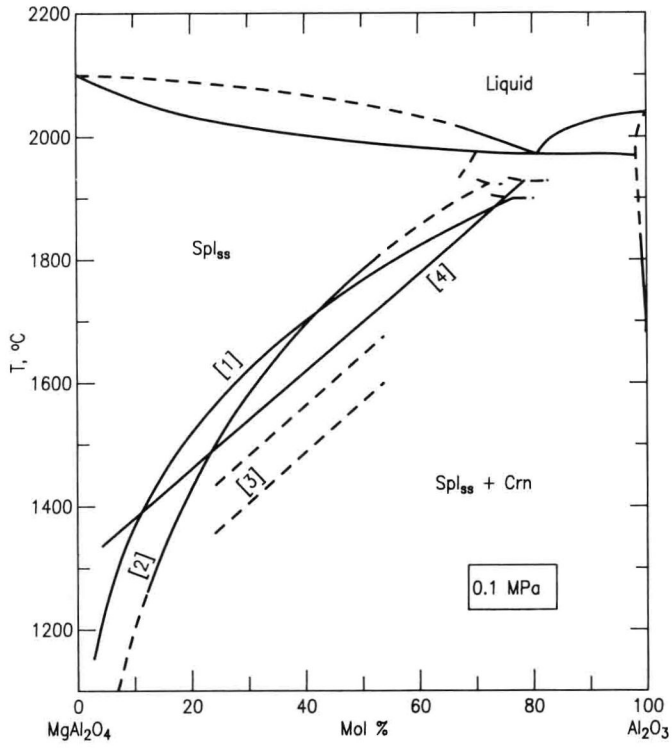
B.O.M.

B. OXIDES ONLY

I. Two Oxides

MgO-Al_2O_3

(A)



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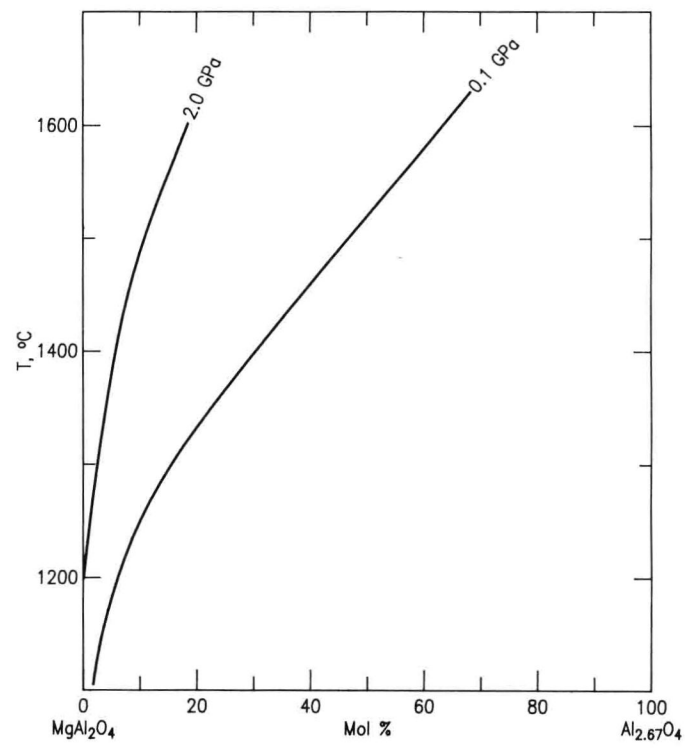
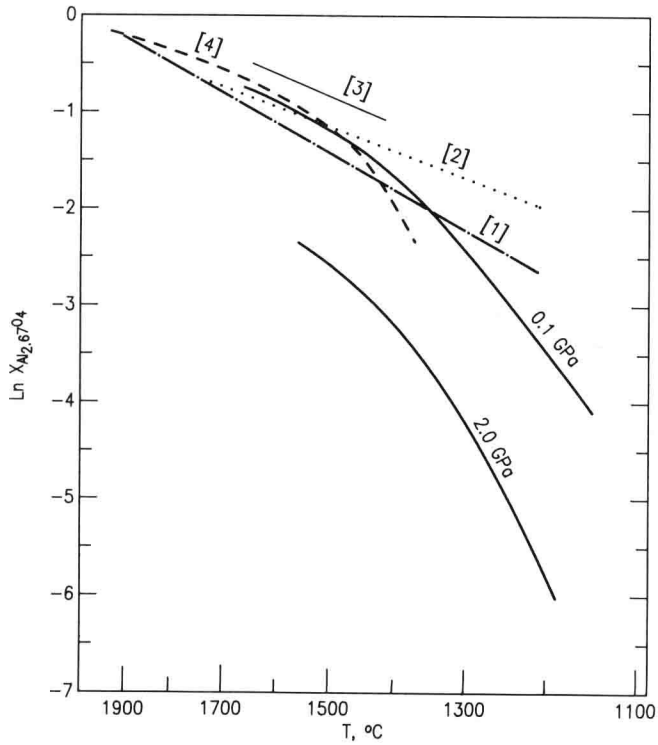


MgO-Al_2O_3 (concl.)

(C)



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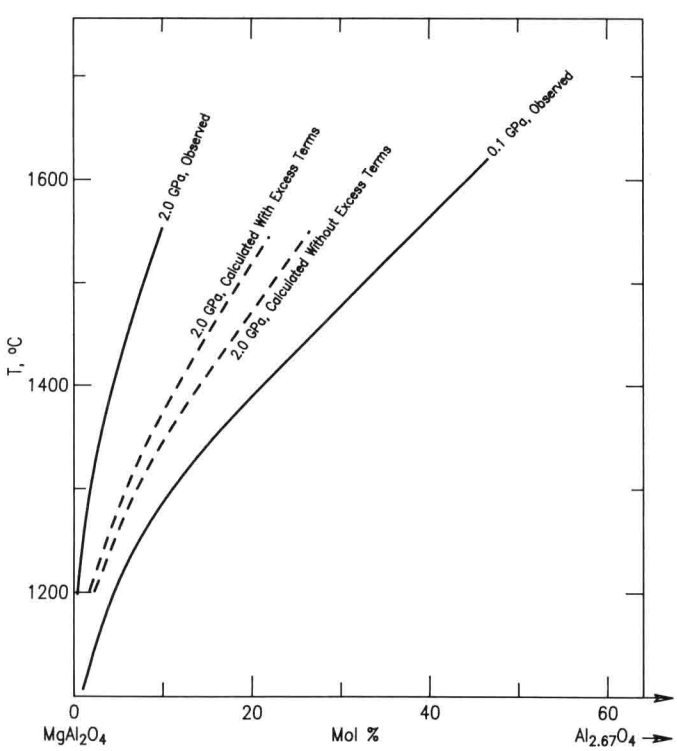


Fig. **7887**—System $MgAl_2O_4$-Al_2O_3. (*A*) Phase relations at 0.1 MPa (data from Refs. 1-4); (*B*) experimental results on defect spinel solid solution with Al_2O_3 at 0.1 and 2.0 GPa; (*C*) temperature-composition relations on the join $MgAl_2O_4$-$Al_{2.67}O_4$; (*D*) comparison of experimental results on defect spinel Al_2O_3 solid solubility and behavior predicted by models with and without consideration of excess mixing properties. Spl_{ss} = spinel solid solution ($MgAl_2O_4$); Crn = corundum (Al_2O_3). Numbers on lines refer to references.

H. U. Viertel and F. Seifert, *Neues Jahrb. Mineral., Abh.*, **140** [1] 89-101 (1980).

Stability relations were studied at 0.1 GPa (internally heated, gas-media apparatus) and at 2.0 GPa (solid-media, high-pressure apparatus) with mixtures of defect spinel[5] and Al_2O_3 as starting materials. A summary of previous data on this join, obtained at 0.1 MPa pressure, is shown in (*A*). The temperatures were measured with Pt-Pt90Rh10 thermocouples. Although no calibration methods are reported, the temperature uncertainties are reported as ±10° and ±20°C, respectively, at 1200° and 1600°C in the gas-media, high-pressure apparatus and as ±25°C at all temperatures in the solid-media, high-pressure apparatus. Pressure uncertainties (no calibration reported) are given as ±5.0 MPa and ±0.1 GPa in the gas-media, and solid-media, high-pressure apparatus, respectively. Experimental charges were examined by X-ray diffraction (with Si as internal standard), using the calibration methods of Ref. 5 to determine the spinel compositions.

Experimental results at 0.1 and 2.0 GPa (*B*) show that the solubility of Al_2O_3 increases isothermally with decreasing pressure and isobarically with increasing temperature. It is clear, however, from the representation in (*C*) that the solution cannot be considered ideal. The pressure effect is most likely due to the significant molar volume difference (12%) between ideal hercynite and defect spinel.[5] Modeling of the solubility behavior was also attempted using a regular solution model, but with no consideration of ΔV being pressure dependent (*D*). Although inclusion of an excess mixing term improves the calculated results, the model does not approach the experimental values. Most likely, this lack of agreement is due to ignoring the pressure dependence of the ΔV, as the molar volume of the defect spinel is pressure dependent.

1. A. M. Lejus and R. Collongues, *Bull. Soc. Chim. Fr.*, **1961**, 65 (1961).
2. D. M. Roy, R. Roy, and E. F. Osborn, *Am. J. Sci.*, **251** [5] 337 (1953).
3. H. Saalfeld and H. Jagodzinski, *Z. Kristallogr.*, **109** [2] 87 (1957).
4. K. Shirasuka and G. Yamaguchi, *Yogyo Kyokaishi*, **82** [12] 650 (1974).
5. H. U. Viertel and F. A. Seifert, *Neues Jahrb. Mineral. Abh.*, **134** [2] 167 (1979).

B.O.M.

II. Three Oxides

$NiO\text{-}Al_2O_3\text{-}SiO_2$

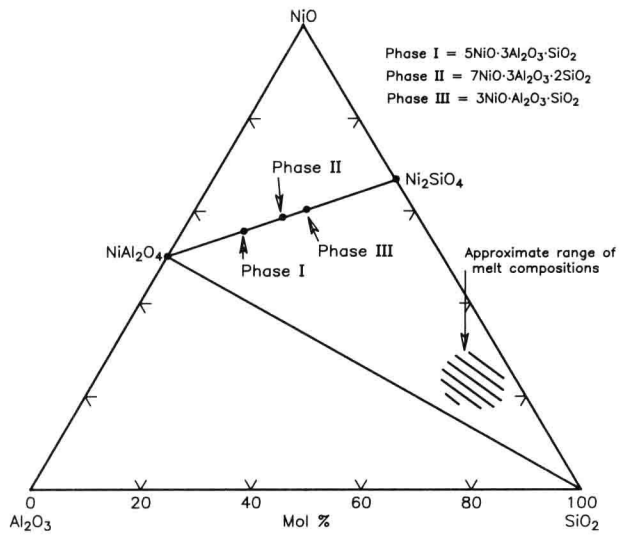


Fig. **7888**—System $NiO\text{-}Al_2O_3\text{-}SiO_2$. Composition triangle depicting location of three new phases (see text) and approximate composition of coexisting melt.

C. B. Ma, *Neues Jahrb. Mineral., Monatsh.*, No. 3-4, 113-126 (1974).

Solid-media, high-pressure apparatus[1] and Pt-wound vertical quench furnaces were used for the experiments. Temperatures were measured with Pt-Pt87Rh13 thermocouples. In these experiments, $\pm 10°C$ and $\pm 10\%$ uncertainties in temperature and pressure, respectively, were reported.[2] Starting materials were analytical grade $Al(OH)_3$, $NiCO_3$, and H_4SiO_4, sintered at 1400°C before use. These materials were loaded in crimped, but not sealed, Pt and Ag capsules. Optical, X-ray and electron microprobe methods were employed for sample identification and analysis.

Three new phases, grown in equilibrium with the melt, are reported. Their detailed crystallographic and chemical compositions are reported. Ideally formulated, these phases are I, $Ni_5Al_6SiO_{16}$, II, $Ni_7Al_6Si_2O_{20}$, and III, $Ni_3Al_2SiO_8$. These orthorhombic crystalline phases may be portions of a homologous series of the type $M_{2n}O_{n-1}T_nO_{3n+1}$ with M and T being octahedrally and tetrahedrally coordinated cations, respectively.[3]

1. F. R. Boyd and J. L. England, *JGR, J. Geophys. Res.*, **65** [2] 741 (1960).
2. C. B. Ma, Ph.D. Thesis, Harvard University, 1972.
3. P. B. Moore and J. V. Smith, *Phys. Earth Planet. Int.*, **3**, 166 (1970).

B.O.M.

III. Four Oxides

K_2O-FeO-Al_2O_3-SiO_2

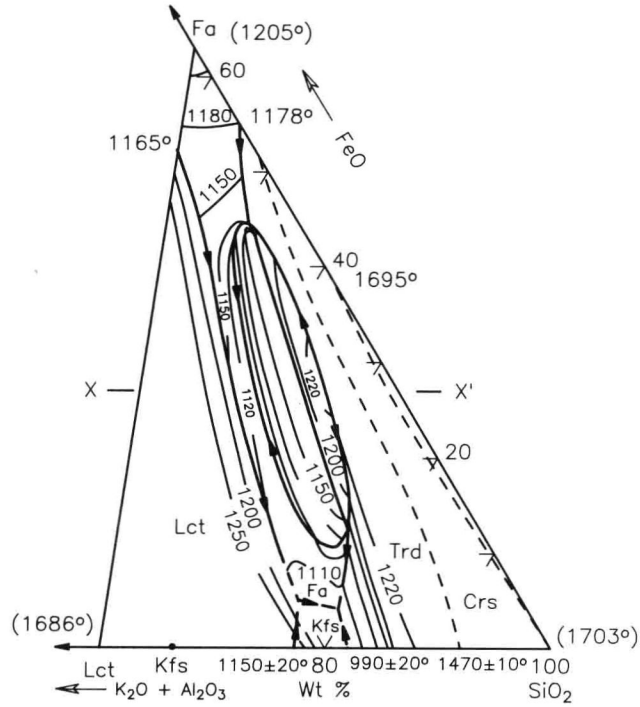


Fig. **7889**—System Fe_2SiO_4-$KAlSi_2O_6$-SiO_2. Liquidus relations. Trd = tridymite (SiO_2); Crs = cristobalite (SiO_2); Fa = fayalite (Fe_2SiO_4); Kfs = K-feldspar ($KAlSi_3O_8$); Lct = leucite ($KAlSi_2O_6$).

W. Visser and A. F. Koster van Groos, *Am. J. Sci.*, **279** [8] 970-988 (1979).

W. Visser and A. F. Koster van Groos, *Am. J. Sci.*, **279** [10] 1160-1175 (1979).

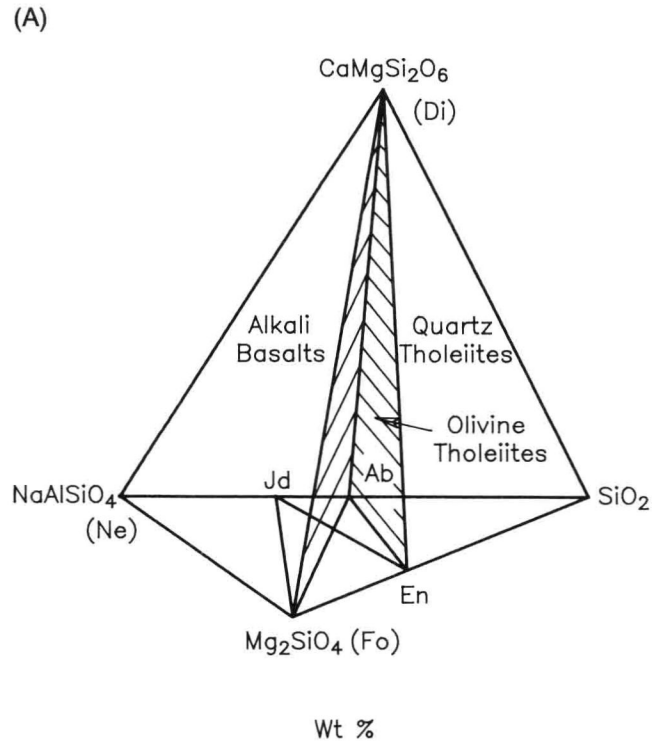
Starting materials for experiments in Mo-heated, vertical 0.1 MPa quench furnaces were leucite gel, SiO_2, Fe_2O_3, and Fe metal powder. The experiments were conducted with controlled oxygen fugacity (f_{O_2}) between that of the Fe-FeO and Mo-MoO_2 oxygen buffers. Temperature measurement and control were not discussed. Experimental charges were examined with optical microscopy and with the electron microprobe. No iron-loss, but up to 17% K-loss (relative), was reported.

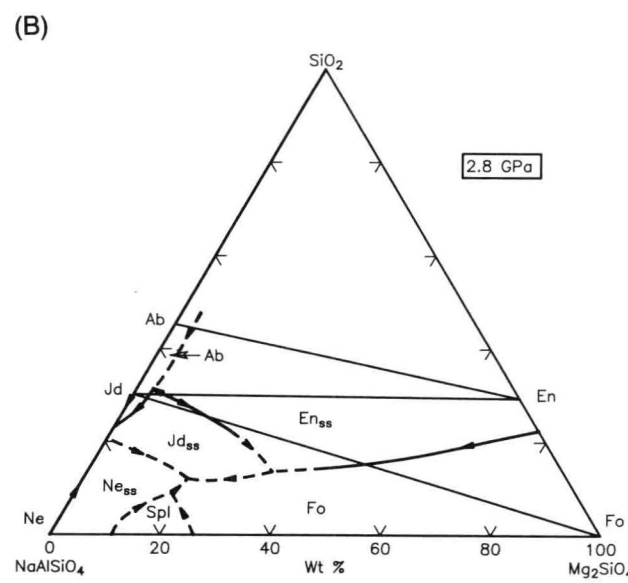
The diagram shows the liquid-liquid phase relations revised after that of Fig. 801, and represents the information reported by Ref. 1. The original source does not discuss why a revision of the original phase diagram was necessary, but it probably results from suggested problems with Fe- and K-loss in the original experiments. In that case, this diagram should be used, since it is the result of more carefully executed and monitored experiments.

1. W. Visser and A. F. Koster van Groos, *Trans., Am. Geophys. Union*, **59** [4] 401 (1978).

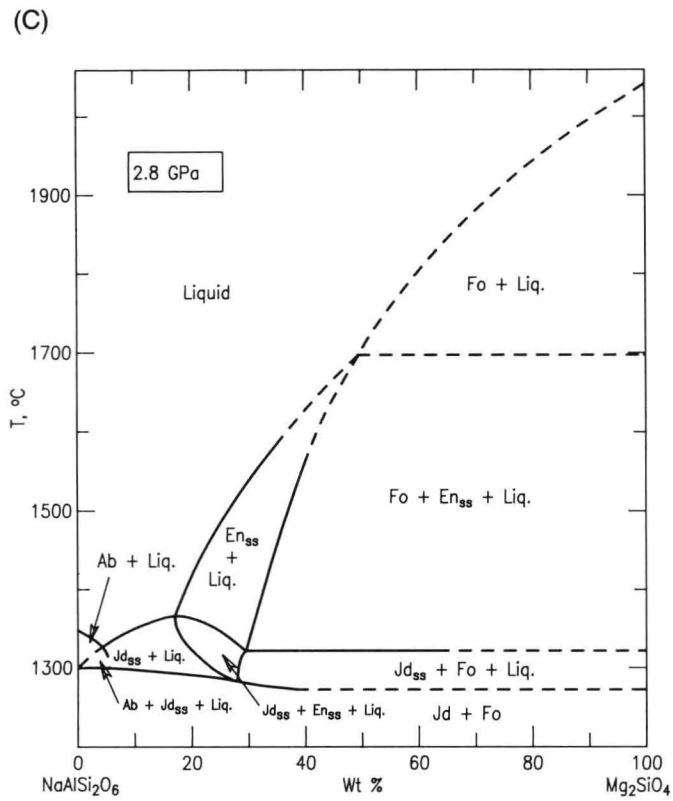
B.O.M.

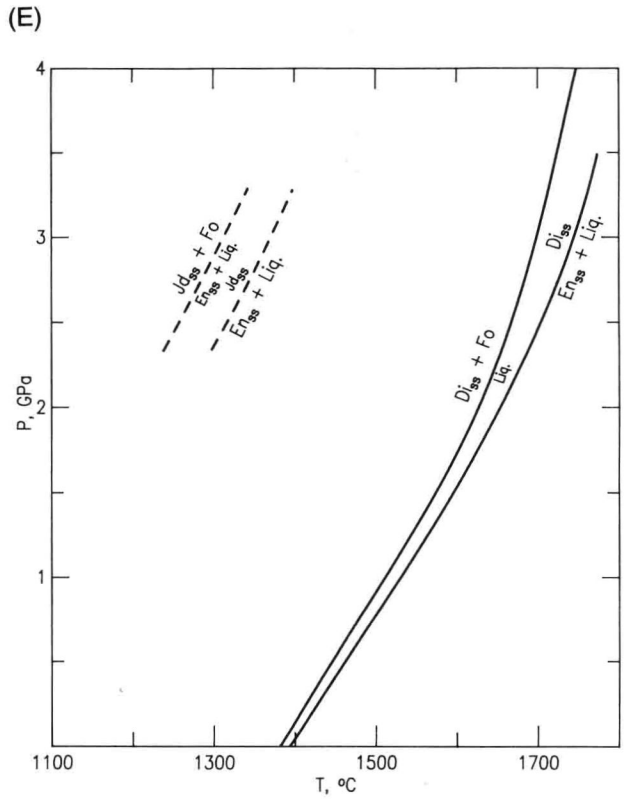
Na_2O-MgO-Al_2O_3-SiO_2





Na_2O-MgO-Al_2O_3-SiO_2 (cont.)





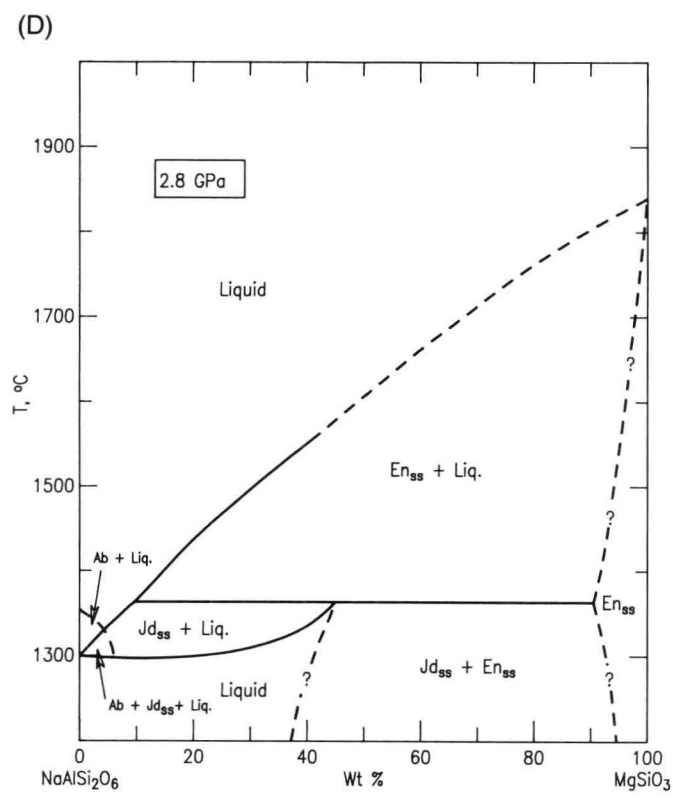


Fig. **7890**—System Na_2O-MgO-Al_2O_3-SiO_2. (*A*) Location of the jadeite-forsterite and jadeite-enstatite joins relative to other petrologically relevant joins and planes in the basalt tetrahedron (Ref. 1); (*B*) liquidus diagram for the subsystem $NaAlSiO_4$-Mg_2SiO_4-SiO_2 at 2.8 GPa (data from Refs. 2 and 3); (*C*) temperature-composition section (at 2.8 GPa) for the join $NaAlSi_2O_6$-Mg_2SiO_4; (*D*) temperature-composition section (at 2.8 GPa) for the join $NaAlSi_2O_6$-$MgSiO_3$; (*E*) comparison of the pressure-dependence of the solidus temperatures of jadeite + enstatite and jadeite + forsterite with diopside + enstatite and diopside + forsterite (Ref. 4). Di = diopside ($CaMgSi_2O_6$); Fo = forsterite (Mg_2SiO_4); En = enstatite ($MgSiO_3$); Ne = nepheline ($NaAlSiO_4$); Ab = albite ($NaAlSi_3O_8$); Jd = jadeite ($NaAlSi_2O_6$); Spl = spinel ($MgAl_2O_4$); Liq = liquid; ss = solid solution.

K. E. Windom and A. L. Boettcher, *Am. J. Sci.*, **281** [3] 335-351 (1981).

Starting materials were synthetic forsterite and enstatite prepared with the gel method described by Ref. 5 and natural jadeite from New Idra, California.[6] The starting materials were contained in sealed Pt containers and subjected to pressure and temperature in the solid-media, high-pressure apparatus with Pt-Pt90Rh10 thermocouples for temperature measurement. Calibration methods for pressure and temperature are reported by Ref. 7 and given as ±5% and ±10°C, respectively. Experimental durations ranged from 0.5 to 8 h, and the experimental conditions were reversed. Experimental charges were examined with optical microscopy and with X-ray powder diffraction.

The liquidus phase relations in the system Mg_2SiO_4-$NaAlSiO_4$-SiO_2 characteristically exhibit a large enstatite liquidus field at 2.8 GPa. On the join enstatite-jadeite, the principal topological features resemble those for the join enstatite-diopside,[4] but the melting temperatures are about 400°C lower. This temperature difference presumably at

Na_2O-MgO-Al_2O_3-SiO_2 (concl.)

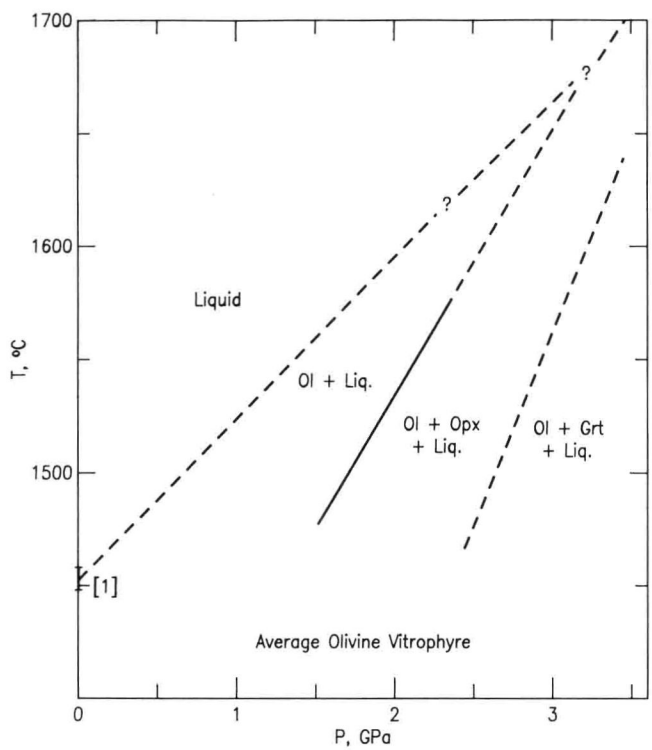
least partly is controlled by extensive solubility of the $MgSiO_3$ component in jadeite. The liquidus phase relations on the join forsterite-jadeite exhibit few similarities to the analogous join, forsterite-diopside.[4] Whereas, in the forsterite-jadeite join, forsterite, enstatite$_{ss}$, jadeite, and albite are liquidus phases, only forsterite and diopside occur on the liquidus on the forsterite-diopside join.

1. H. S. Yoder, Jr. and C. E. Tilley, *J. Petrol.*, **3**, 342 (1962).
2. P. M. Bell and E. H. Roseboom, Jr., *Mineral. Soc. Am. Spec. Pap.*, **2**, 151 (1969).
3. C. H. Chen and D. C. Presnall, *Am. Mineral.*, **60** [5-6] 398 (1975).
4. I. Kushiro, *Am. J. Sci.*, **267A**, 269-294 (1969).
5. W. C. Luth and C. O. Ingamells, *Am. Mineral.*, **50** [1-2] 255 (1965).
6. R. G. Coleman, *J. Petrol.*, **2**, 209 (1961).
7. K. E. Windom and A. L. Boettcher, *Am. Mineral.*, **61** [9-10] 889 (1976).

B.O.M.

CaO-FeO-MgO-SiO_2

(A)



(B)

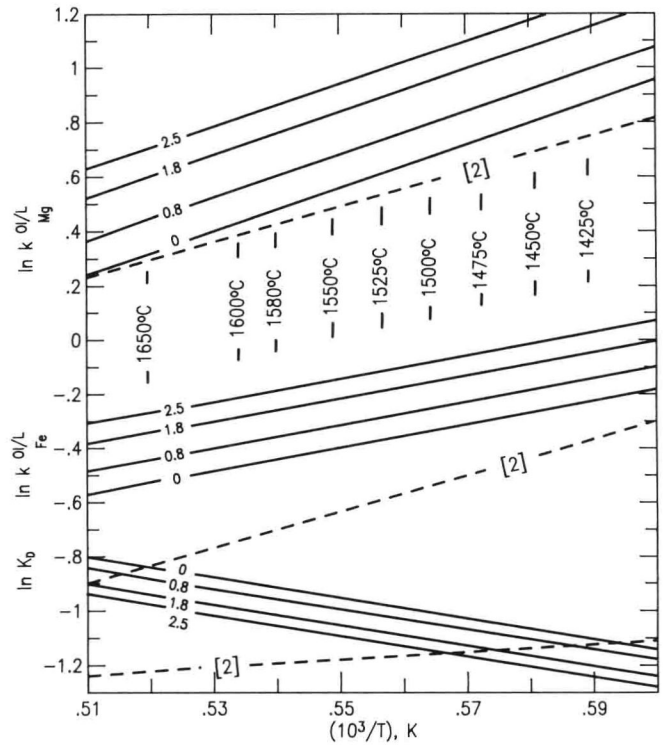


Fig. **7891**—System CaO-FeO-MgO-SiO_2. (*A*) Pressure-temperature stability relations of average lunar olivine vitrophyre. The 100 kPa (1 atm) liquidus temperature is from that computed by Ref. 1; (*B*) iron-magnesium partition coefficients between olivine and liquid (see text) at temperatures and pressures indicated (GPa). Dashed lines are from Ref. 2 for low-Ti mare basalt. Ol = olivine [$(Mg,Fe)_2SiO_4$]; Opx = orthopyroxene [$(Fe,Mg)SiO_3$]; Grt = garnet [$(Ca,Fe,Mg)_3Fe_2Si_3O_{12}$]; Liq = liquid.

J. E. Grover, D. H. Lindsley, and A. E. Bence, *Geochim. Cosmochim. Acta, Suppl.*, **14**, 179-196 (1980).

High-pressure and high-temperature experiments were conducted with a synthetic analog of average lunar vitrophyre 14321.[1] Starting materials were oxide mixtures reacted at 920°C at 0.1 MPa in Ag-lined, evacuated silica glass tubes (to form olivine, plagioclase, and clinopyroxene) and run as such, and also with known amounts of forsterite added for reversal experiments. High-pressure experiments were conducted in the solid-media, high-pressure apparatus with Fe containers with a tight-fitting lid. Temperatures were measured with W-Re thermocouples (exact alloy composition is not reported) with no report on thermocouple calibration methods. Temperature probably was uncertain to about ±10°C. No pressure calibration was reported either, but most likely is near 0.1-0.2 GPa. Experimental charges were examined with the electron microprobe and with optical microscopy. Detailed analytical results are tabulated in the text.

Pressure-temperature phase relations (*A*) show olivine on the liquidus to pressures above 2.5 GPa from which observation the authors conclude that olivine vitrophyre is not likely to have been formed by partial melting of the lunar mantle.

Partition coefficients, $K_{Mg}^{ol\text{-}liq} = X_{MgO}^{ol}/X_{MgO}^{liq}$, $K_{Fe}^{ol\text{-}liq} = X_{FeO}^{ol}/X_{FeO}^{liq}$, and $K_D^{ol\text{-}liq} = X_{FeO}^{ol}X_{MgO}^{liq}/X_{FeO}^{liq}X_{MgO}^{ol}$, were calculated from the analytical data (*B*) and compared with other 0.1 MPa data from Ref. 2 as well as

$CaO\text{-}FeO\text{-}MgO\text{-}SiO_2$ (concl.)

results from high-pressure experiments.[3] Distinct pressure and temperature dependence are noted. Both the $K_{Fe}^{pl\text{-}liq}$ and $K_{Mg}^{pl\text{-}liq}$ increased with increasing pressure, whereas K_D decreased. These relationships were expressed with the empirical expression in Eq. 1.

$$\ln K_D = aP(\text{GPa}) + 1000b/T(\text{K}) + C \quad (1)$$

The major difference between the present data and those of other published information has been assigned to bulk compositional differences in both liquid and olivine compositions.

The data were used to constrain conditions of formation of high-Mg lunar basalts.

1. F. M. Allen, A. E. Bence, and T. Grove, *Geochim. Cosmochim. Acta, Suppl.*, **11**, 695 (1975).
2. J. Longhi, D. Walker, and J. F. Hays, *Geochim. Cosmochim. Acta*, **42** [10] 1545 (1978).
3. J. F. Bender, F. N. Hodges, and A. E. Bence, *Earth Planet. Sci. Lett.*, **41** [3] 277 (1978).

B.O.M.

$CaO\text{-}FeO\text{-}Al_2O_3\text{-}SiO_2$

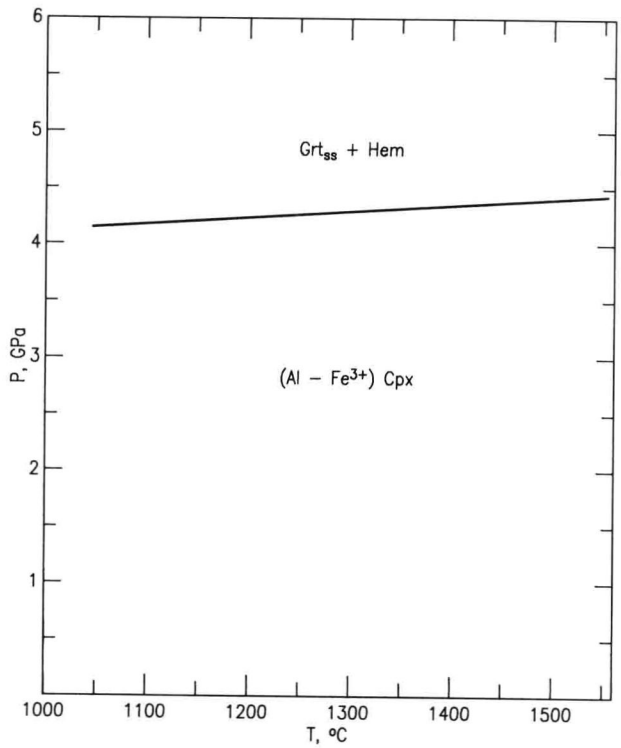


Fig. **7892**—System $CaAlFeSiO_6$ pyroxene. Pressure-temperature relations at the oxygen fugacity defined by the PtO_2-Pt buffer. Grt_{ss} = garnet solid solution $[(Ca,Fe)_3Al_2Si_3O_{12}]$; Hem = hematite ($Fe_2O_3$); Cpx = clinopyroxene ($CaAlFeSiO_6$).

H. Ohashi and Yu. Hariya, *Ganseki Kobutsu Kosho Gakkaishi*, **70** [3] 93-95 (1975).

High-pressure experiments were conducted in the solid-media, high-pressure, and the belt apparatus with no comments on pressure calibration or uncertainties. Typically, the pressure uncertainties are less than 10% in these types of apparatus. Temperatures were monitored with Pt-Pt87Rh13 thermocouples resulting in ±10°C uncertainty. Starting materials were mechanical mixtures of hematite (Fe_2O_3), wollastonite ($CaSiO_3$), gehlenite ($Ca_2Al_2SiO_7$), anorthite ($CaAl_2Si_2O_8$), and hedenbergite ($CaFeSi_2O_6$), which were sealed in Pt capsules together with PtO_2 in order to maintain high oxygen fugacity. There is no comment on steps used to eliminate H_2O from the hygroscopic PtO_2. Run durations were from 15 to 40 h, and the experiments were reversed. Although there is no comment on methods of identification, optical and X-ray techniques are commonly used in this type of study, and may have been employed here.

The experimental results for the univariant reaction

$$\text{Al-Fe-clinopyroxene} \leftrightarrow \text{garnet}_{ss} + \text{hematite}$$

show essentially no temperature dependence. The garnet solid solution is on the join grossularite-andradite. Because of the temperature insensitivity, the authors suggest its use as a geobarometer. However, due to the presence of iron, oxygen fugacity also plays an important role that is not considered in the present experiments.

B.O.M.