Phase Diagrams of Earth-Forming Minerals

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The purpose of this compilation is to present a selected and compact set of phase diagrams for the major Earthforming minerals and to show the present state of knowledge concerning the effect of pressure on the individual mineral stabilities and their high-pressure transformation products. The phase diagrams are arranged as follows:

The compilation has been compressed in three ways. (1)

For several of the mineral groups, only representative phase diagrams are shown. (2) The presentation of more complex phase diagrams that show mutual stability relationships among the various minerals and mineral groups has been minimized. (3) Many subsolidus phase diagrams important to metamorphic petrology and thermobarometry are excluded. Reviews of these subsolidus phase relationships and thermodynamic data for calculating the phase diagrams have been presented elsewhere [13, 50, 70, 122, 1541. Other useful reviews and compilations of phase diagrams are Lindsley [96] for oxides, Gilbert et al. [60] and Huckenholz et al. [74] for amphiboles, Liu and Bassett [104] for elements, oxides, and silicates at high pressures, and Phase Diagrams for Ceramists $[129-137]$. It will be noted that some diagrams are in weight percent and others are in mole percent; they have usually been left as originally published. Minor drafting errors and topological imperfections that were found on a few of the original diagrams have been corrected in the redrafted diagrams shown here.

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Fig. 1. Phase relationships for $SiO₂$. Numbers beside curves refer to the following sources: 1 - [178]; 2 - [168]; 3 - [160]; 4 - [4]. The melting curve is from Jackson [77] at pressures below 4 GPa, from Kanzaki [83] at pressures between 4 and 7 GPa, and from Zhang et al. [178] at pressures above 7 GPa. The temperature of the high quartz-low quartz-coesite invariant point is from Mirwald and Massonne [113]. The quartz-coesite transition is from Bohlen and Boettcher [24] but note that their curve lies toward the low-pressure side of the range of curves by others [5, 23, 31, 62, 89, 1131. The high quartz-low quartz curve is from Yoder [172]. Boundaries for the tridymite and cristobalite fields are from Tuttle and Bowen [164] and the contribution of $\frac{1}{2}$ and α , α and the ensignation shifted to accomodate the data of α point has been sinteed to σ . Si a to accomodate the data of $\frac{1}{2}$ $\frac{3}{2}$, $\$ structure at 35-40 GPa, $T>1000^{\circ}$ C by Liu *et al.* [105], and at 35 GPa, $500-1000$ °C by Togaya [162]. However, Tsuchida and Yagi [163] reported a reversible transition between stishovite and the CaCl₂ structure at 80-100 GPa and $T > 1000$ °C.

Fig. 3. Isopleth for the composition, $CaAl_2Si_2O_8$ [67, 94]. Cor, corundum; Gr, grossular; Ky, kyanite; Qz, quartz; Liq, liquid. Locations of dashed lines are inferred.

Fig. 2. Isopleth for the composition, $NaAlSi₃O₈$ [12, 16, 33]. The albite $=$ jadeite $+$ quartz reaction shown by Bell and Roseboom [12] and in this figure is about 0.1 GPa higher than the curve of Boettcher and Wyllie [22]. The ,latter passes through the "consensus" value of 1.63 GPa, 600°C for this reaction [81]. Also, the quartz-coesite curve shown by Bell and Roseboom [12] and in this figure is about 0.4 GPa higher at 1300°C than the pressure given by a linear extrapolation of the curve of Bohlen and Boettcher [24], which is shown in Figure 1. The curve of Bohlen and Boettcher would intersect the albite $=$ jadeite $+$ quartz curve at about 1300° C rather than the jadeite + quartz $(coesite) = liquid curve. At about 1000°C, Liu [101]$ synthesized NaAlSi₃O₈ in the hollandite structure at pressures from 21 to 24 GPa, and a mixture of NaAlSi04 $(CaFe₂O₄-type structure)$ + stishovite above 24 GPa. Jadeite, NaAl $Si₂O₆$; Coesite, $SiO₂$.

Fig. 4. Isopleth for the composition, $KAISi₃O₈$ [93, 149]. At 12 GPa, 900°C, Ringwood et al. [144] synthesized KAlSi₃O₈ in the hollandite structure. In experiments from 8-10 GPa and 700°-1000°C, Kinomura et al. [88] synthesized the assemblage $K_2Si_4O_9$ (wadeite-type structure) + kyanite (A_2SiO_5) + coesite (SiO_2) from the composition KAlSi₃O₈; and they synthesized the hollandite structure of KAlSi₃O₈ at 900^oC, 12 GPa, and at 700°C 11 and 11.5 GPa.

Fig. 5. Compositions of coexisting alkan feldspar and plagfociase at 0.1 GPa and temperatures from 800 to 900° C, as indicated [49]. Note that the phase boundary is essentially isothermal except in the Ab-rich portion of the diagram. Many others have discussed ternary feldspar geothermometry [10, 39, 54, 58, 63, 66, 75, 80, 139, 142, 151-153, 165] and ternary feldspar phase relationships [68, 121, 156, 164, 175]. An, anorthite; Ab, albite; Or, orthoclase.

Fig. 6. Temperature-composition sections for the join NaAlSi₃O₈ (albite) - CaAl₂Si₂O₈ (anorthite) under anhydrous conditions at 1 atm [26, 117], 1 GPa, 2 GPa [33, 94], and under H_2O -saturated conditions at 0.5 GPa [79, 175].

Fig. ℓ . Temperature-composition sections for the join NaAlS13O8 (and ϵ) - KAIS13O8 (orthocrase) under anhydrous conditions at 1 atm [148], and under H_2O -saturated conditions at 0.2 GPa [29] and 0.5 GPa [119, 175]. Ab, albite; Liq, liquid; V, vapor. Locations of dashed lines are inferred.

Fig. 8. Isopleth for the composition $MgSiO₃$ [7, 9, 35, 45, 56, 57, 65, 76, 92, 127, 140, 169]. For additional data at pressures above 15 GPa, see also Sawamoto [147]. Not shown is a singular point at about 0.13 GPa below which enstatite melts incongruently to forsterite + liquid [45]. Position of dashed curve is inferred. For additional data on melting temperatures up to 58 GPa, see Zerr and Boehler [1771.

Fig. 9. Melting curve for diopside, $CaMgSi₂O₆$. Curve 1 is from Williams and Kennedy [166] uncorrected for the effect of pressure on thermocouple emf, and curve 2 is from Boyd and England [33]. See also Yoder [173] for data below 0.5 GPa. For CaMgSi₂O₆ composition, Mao et al. [110] found a mixture of perovskite ($MgSiO₃$) and glass at 21.7 and 42.1 GPa and lOOO"-1200°C. They interpreted the glass to be a second perovskite phase of $CaSiO₃$ composition which inverted to glass on quenching [see also 1021.

Fig. 10. The join $Mg_2Si_2O_6$ (enstatite) - CaMgSi₂O₆ (diopside) at 1 atm [43]. Many others have also discussed phase relationships on this join [9, 14, 36, 41, 42, 56, 78, 91, 106, 170, 1711. Forstering; Mgazing; Mgazing; Liquid; Liquid; Liquid; Liquid; Liquid; Liquid; Liquid; Liqu $P₁$, 100, 170, 171]. To, ioisierite; $M_{2.004}$, Eig, hydro; Pen, protoenstatite; Opx, orthopyroxene; Pig, pigeonite; Di, diopside; Oen, orthoenstatite.

Fig. 12. Pressure-composition section for the system $MgSiO₃-CaSiO₃$ at 1650°C [55, 57]. Garnet and clinopyroxene, when they are free of Ca on the left-hand margin of this diagram, are the same phases, respectively, as majorite and high-P clinoenstatite on Figure 7. 11, ilmenite; Gt, garnet; Pv, perovskite; Cpx, clinopyroxene; Opx, orthopyroxene; Di, diopside; CM, a high-pressure phase of unknown structure.

Fig. 11. Thermodynamically modeled subsolidus phase relationships for the system $Mg_2Si_2O_6$ (enstatite) - $CaMgSi₂O₆$ (diopside) from 1.5 to 10 GPa [56, 44]. The thermodynamic models are based on data from other sources [37, 98, 118, 123, 128, 150]. See also data of Biggar [15] from 1 atm to 0.95 GPa.

Fig. 13. Orthopyroxene + augite, orthopyroxene + augite + pigeonite, and pigeonite + augite equilibria at 1 atm and 500-1300°C [95]. Phase relationships to the right of the forbidden zone boundary are metastable relative to augite + olivine + silica. Lindsley [95] has presented three other similar diagrams at 0.5, 1, and 1.5 GPa. Lindsley and Andersen [97] should be consulted for correction procedures required before plotting pyroxenes on these diagrams for geothermometry. En, enstatite (MgSiO₃); Fs, ferrosilite (FeSiO₃); Di, diopside (CaMgSi₂O₆); Hd, hedenbergite (CaFeSi₂O₆).

Fig. 14. Isopleth for the composition Mg_2 SiO₄ [48, 57, 141]. Additional studies of the meiting relations **red.**

Fig. 15. Phase relationships for the system Mg_2SiO_4 (forsterite) - $Fe₂SiO₄$ (fayalite) in equilibrium with Fe at 1 atm [27]. Locations of dashed lines are inferred.

 Γ g. To. Pressure-composition sections for the join Mg_2SiO_4 -Fe₂ SiO_4 at various temperatures. Phase relationships above 21 GPa are from Ito and Takahashi [76] and those below 21 GPa are from Akaogi *et al.* [3]. Other references $[51, 87, 157]$ give additional data and discussion of these phase relationships. Pv, perovskite $(MgSiO₃-FeSiO₃$ solid solution); Mw, magnesiowistite (MgO-FeO solid solution); St, stishovite $(SiO₂)$; Sp, spinel; Mod Sp, modified spinel; Ol, olivine.

Fig. 17. Isopleth for $Mg_3Al_2Si_3O_{12}$, pyrope garnet. Phase relationships at pressures less than 5 GPa are from Boyd and England [32]. The melting curve at 5 GPa and above is from Ohtani et al. [125]. Liu [99] reported that pyrope transforms to perovskite + corundum at about 30 GPa, 200- 800°C. Liu [100] subsequently revised this result and found that pyrope transforms to the ilmenite structure at about 24-25 GPa, 1000° -1400°C, and that ilmenite then transforms to perovskite at about 30 GPa. Locations of dashed lines are inferred.

 $\frac{1}{2}$. To. 1 ressure-composition section for the join $\frac{1}{2}$ Al₂O₃ at 1000 and 1650°C [57, 82]. For additional data along the boundary between the garnet and clinopyroxene + garnet fields at 1000 $^{\circ}$ C, see Akaogi and Akimoto [2]. At 1100 and 1600° C for pressures between 2 and 6.5 GPa, the Al_2O_3 content of pyroxene in equilibrium with garnet increases with decreasing pressure to at least 15 mole percent [30, 34].

Fig. 19. The system CaSiO₃-MgSiO₃-Al₂O₃ at 1200°C, 3 GPa [30]. Co, corundum; Di, diopside; Ca-Gt, Cagarnet; Mg-Gt, Mg-garnet; Wo, wollastonite; En, enstatite; CaAl2SiO₆, Ca-Tschermak's molecule.

Fig. 20. Compositions (unsmoothed) or coexisting garnet (Gt), Ca-rich pyroxene (Cpx), and Ca-poor pyroxene (Opx or Cpx) at various pressures and temperatures [69]. Labels of the type, 9, 2000, indicate pressure (GPa) followed by temperature (°C). Pyrope, $Mg_3Al_2Si_3O_{12}$; Grossular, Ca3Al₂Si3O₁₂.

Fig. 21. Temperature-composition section for the system Fe-O at 1 atm [46,47, 64, 120, 1381. Light dash-dot lines are oxygen isobars in atm.

Fig. 22. The system TiO₂-FeO-Fe₂O₃ at 1300°C, 1 atm [161]. Light dashed lines are oxygen isobars labeled in log oxygen fugacity units (atm). Psb, pseudobrookite (Fe₂TiO₅); Fpb, ferropseudobrookite (FeTi₂O₅); Ilm, ilmenite (FeTiO₃); Hem, hematite (Fe₂O₃); Usp, ulvospinel (Fe₂TiO₄); Mt, magnetite (Fe₃O₄); Wüs, wüstite $(Fe_{1-x}O).$

Fig. 23. Temperature-oxygen fugacity (f_{O_2}) grid for coexisting magnetite-ulvospinel solid solution and ilmenite-hematite solid solution pairs [1551. Lines with labels of the type, I-70, indicate mole % ilmenite in the ilmenite (FeTiO₃) - hematite (Fe₂O₃) solid solution. Lines with labels of the type, U-70, indicate mole % ulvospinel in the ulvospinel (Fe₂TiO₄) - magnetite (Fe₃O₄) solid solution. Mt, magnetite; Usp, ulvospinel; Ilm, ilmenite; Hem, hematite.

Fig. 24. Pressure-temperature projection of pargasite, (Pa) $NaCa₂Mg₄Al₃Si₆O₂₂(OH,F)₂$, stability limits. The univariant curves labeled Pa-out (1.0) , Pa-out (0.5) , and Paout (0.3) are from Gilbert [59], Holloway [71], and Oba [124], and give the maximum stability of pargasite during melting in the presence of a pure H_2O or H_2O -CO₂ vapor with $H₂O$ mole fractions of 1.0, 0.5, and 0.3. Small concentrations of other constituents in the vapor are ignored. The dashed curve labeled $OH₁₀₀$, and the patterned areas labeled $F_{43}OH_{57}$ and F_{100} are from Holloway and Ford [72] and Foley [52], and show the breakdown of pargasite during vapor-absent melting for different proportions of fluorine and hydroxyl in the pargasite.

Fig. 25. Pressure-temperature projection showing the upper temperature stability limits for serpentine, $Mg_3Si_2O_5(OH)_4$ (curves 1 and 2), and phlogopite, $KMg_3AlSi_3O_{10}(OH)_2$ (curves 3-6). Numbers beside curves refer to the following sources: 1 - [28]; 2 - [90]; 3-6 - [115]. Curves 5 and 6 give the maximum stability of phlogopite in the presence (curve 5) and absence (curve 6) of vapor. Curves 3 and 4 give the corresponding maximum stability of phlogopite in the presence of forsterite and enstatite, and represent more closely the stability of phlogopite in the mantle. Curves 3- 6 are not univariant [114]. See Yoder and Kushiro [174] for an earlier study of the stability of phlogopite. Montana and Brearley [116] speculated that a singular point exists at about 1.5 GPa on curve 4, so that the curve above this pressure is metastable.

Fig. 26. Low pressure phase relationships for iron. Numbers beside curves refer to the following sources: 1 - [159]; 2 - [109]; 3 - [112]; 4 - [103]; 5 - [6]; 6 - [20,40]; 7 - [107]; 8 - [73]; 9 - [17, 21]. Several additional references [61, 108, 179] also discuss the α - ϵ transition,.

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Fig. 27. High pressure melting curves for iron. For reference to Figure 26 at low pressures, the curves of Mirwald and Kennedy [112], Bundy [40], and Boehler [17] are used for the α - ε - γ phase relationships. Numbers beside melting curves and brackets refer to the following sources: 1 - [I]; 2 - [II]; 3 - [167]; 4 - [25, 381; 5 - [17-19, 21, 103, 143, 1531. Gallagher and Ahrens [54] found that earlier shock data from their laboratory $[11]$ are 1000° K too high, which brings the data of Bass et al. [11] and Brown and McQueen [38] into agreement. The shock data of Yoo et al. [176] (not plotted but located at 6350 K, 235 GPa and 6720 K, 300 GPa) are at slightly higher temperatures than the data of Brown and McQueen. (Ross et al. [145] and Anderson [8] have proposed the existence of a new phase, $\frac{1}{100}$ and $\frac{1}{100}$ and $\frac{1}{100}$ is stable along the limit at pressures at pressures above $\frac{1}{100}$ α hold the state and α and α is defined as α and α and α is defined as α about 170 GPa. On the basis of molecular dynamics calculations, Matsui [111] has also proposed the existence calculations, maisur [111] has also proposed the existence α a new phase at 500 ST a and temperatures above 5000 K. baxcha ci al. $[170]$ have suggested that α -hold is the μ quidas phase down to a pressure of oo-70 GPa. CM, core-mantle boundary (136 GPa); IOC, inner-outer core boundary (329 GPa); C, center of Earth (364 GPa).

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