Stability and Water Solubility of Calcium Ferrite-type Aluminum-rich Phase: Implications for Deep Water Cycle Caused by Subducting Basaltic Crusts

Supporting Information

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### Introduction

This supporting information includes the figures and tables helping to understand the manuscript.



**Figure S1**. Total Na2O contents in the mineral assemblages in hydrous and dry MORB system (Ishii et al. 2019; Liu et al. 2019). The value is calculated by multiplying the Na2O content by the modal fractions of each mineral. The colored bands show the Na2O content in the starting materials.



**Figure S2**. An illustration of the cell assembly for high-pressure and high-temperature experiment of 1k3791. The solid line located at the central part and through the octahedral edges is a thermocouple.

**Figure S3**. A phase diagram of CF phase in MgO-Al2O3-5 wt% H2O systems. Solid circles: δ-AlOOH (δ) + periclase (Per) + corundum (Cor); solid squares: CF phase (CF) + δ+ Per; solid diamonds: CF + Cor + MgO rich melt (L); black solid line: a formation boundary of CF determined in this study; grey dashed line: a phase boundary between Per + Cor and CF in MgAl2O4 system from Irifune et al. (2002) with Anderson’s Au pressure scale (Anderson et al. 1989); black dotted line: phase boundaries between Per + Cor and CF from Irifune et al. (2002) with new Au scales (Tsuchiya 2003; Yokoo et al. 2009); black dotted line: a phase boundary between Per + Cor and CF in MgAl2O4 system from Kojitani et al. (2012); red dashed line: an expected boundary between δ + Per and Cor + L.



Figure S4. A representative FTIR spectrum of a single crystal synthesized at 1900 °C as an example of baseline subtraction process.



**Figure S5**. Representative unpolarized FTIR spectra of MgAl2O4 CF phase synthesized at 26 GPa and 1500-1900 °C. (a) 1500 °C; (b) 1700 °C; (c) 1900 °C. Each spectrum represents a different single crystal. The baseline has been subtracted and the spectra are normalized to the same thickness.



Figure S6. Unpolarized FTIR spectra of different areas within a MgAl2O4 CF phase single crystal synthesized at 26 GPa and 1900 °C. The baseline has been subtracted for each spectrum.



Figure S7. A representative unpolarized FTIR spectrum of corundum single crystal from recovered product synthesized at 26 GPa and 1700 °C. The baseline has been subtracted.

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Run No. | T (°C) | P (GPa) | SM | Phase | MgO (wt%) | Al2O3 (wt%) | SiO2 (wt%) | Total (wt%) | Mg | Al | Si |
| 1k3791 | 1700 | 26 | 5 | CF | 29.3(2) | 71.4(4) | 0.3(1) | 101.0(5) | 1.025(7) | 1.972(4) | 0.007(2) |
|  |  |  |  | Cor | 0.85(4) | 98.3(2) | 0.13(9) | 99.3(2) | 0.021(1) | 1.982(2) | 0.002(2) |
|  |  |  |  | Per | 97.6(13) | 2.6(11) | 0.10(1) | 100.3(7) | 0.97(1) | 0.02(1) | 0.0006(1) |
|  |  |  |  | L | 31.3(16) | 14.1(7) | 0.42(7) | 45.9(14) |  |  |  |
|  |  |  | 10 | Cor | 0.85(7) | 97.9(3) | 0.16(2) | 98.9(4) | 0.022(2) | 1.981(1) | 0.0027(3) |
|  |  |  |  | Per | 98.8(7) | 0.96(4) | - | 99.8(7) | 0.9882(7) | 0.0076(4) | - |
|  |  |  |  | δ | 1.48(8) | 82.3(9) | 0.38(7) | 84.2(8) | 0.022(1) | 0.980(2) | 0.0039(7) |
|  |  |  |  | L | 35.1(25) | 13.8(7) | 0.28(3) | 49.2(32) |  |  |  |
| 1k3816 | 1900 | 26 | 5 | CF | 28.7(2) | 70.6(2) | 0.09(3) | 99.5(4) | 1.021(5) | 1.983(4) | 0.0020(7) |
|  |  |  |  | Cor | 0.88(1) | 97.39(4) | 0.05(3) | 98.329(5) | 0.0228(3) | 1.9826(5) | 0.0009(5) |
|  |  |  |  | Per | 97.8(11) | 2.0(4) | - | 99.8(6) | 0.975(6) | 0.016(3) | - |
|  |  |  |  | L | 32.3(10) | 6.4(4) | 0.10(2) | 38.8(7) |  |  |  |
| 1k3814 | 1500 | 26 | 5 | CF | 28.5(2) | 70.7(2) | 0.12(4) | 99.3(3) | 1.011(4) | 1.988(4) | 0.0029(9) |
|  |  |  |  | δ | 0.92(8) | 83.8(2) | 0.10(1) | 84.9(2) | 0.014(1) | 0.989(1) | 0.001(1) |
|  |  |  |  | Per | 96.8(9) | 2.9(4) | 0.4(6) | 100.2(7) | 0.960(8) | 0.023(3) | 0.003(4) |
| 1k3801 | 1400 | 26 | 5 | Cor | 0.5(1) | 98.5(1) | 0.2(1) | 99.12(7) | 0.012(3) | 1.988(4) | 0.003(2) |
|  |  |  |  | Per | 99.2(9) | 1.3(5) | - | 100.4(5) | 0.985(6) | 0.010(4) | - |
|  |  |  |  | δ | 0.67(3) | 82.7(3) | 0.09(2) | 83.4(3) | 0.010(1) | 0.992(1) | 0.0009(2) |
| 5k4195 | 1400 | 27 | 5 | CF | 28.5(13) | 70.6(14) | 0.04(4) | 99.1(7) | 1.01(5) | 1.99(3) | 0.0008(8) |
|  |  |  |  | Cor | 0.30(6) | 99.7(5) | 0.05(4) | 100.1(5) | 0.008(1) | 1.993(1) | 0.0009(7) |
|  |  |  |  | Per | 96.3(29) | 4.0(33) | - | 100.3(9) | 0.95(4) | 0.03(3) | - |
|  |  |  |  | δ | 1.1(9) | 83.4(9) | 0.07(5) | 84.6(10) | 0.02(1) | 0.987(9) | 0.0007(5) |
| 5k4199 | 1200 | 27 | 5 | Cor | 0.24(6) | 99.0(9) | 0.04(5) | 99.3(8) | 0.006(1) | 1.995(2) | 0.0006(9) |
|  |  |  |  | Per | 97.0(49) | 3.1(42) | - | 100.1(11) | 0.96(5) | 0.02(3) | - |
|  |  |  |  | δ\* | 3.2(10) | 82.4(9) | 0.06(4) | 85.7(10) | 0.05(1) | 0.97(1) | 0.0005(5) |
| 5k4209 | 1200 | 32 | 5 | CF | 29.4(10) | 68.9(9) | 0.15(7) | 98.5(4) | 1.06(4) | 1.96(2) | 0.004(2) |
|  |  |  |  | Per | 100.1(7) | 0.4(1) | - | 100.5(8) | 0.995(1) | 0.0032(9) | - |
|  |  |  |  | δ\* | 5.0(10) | 77.8(10) | 0.3(1) | 83.1(10) | 0.08(1) | 0.94(1) | 0.003(1) |

**Note:** The value displayed is the average value of 10 analytical points for CF phase and 2-5 analytical points for other phases.

\* The large Mg number observed in the δ-AlOOH phase quenched from 1200 °C is likely attributable to the small grain size of this phase (< 3 μm) in the experimental products.

Table S1. Chemical Compositions of Single Crystals of recovered products at Different Conditions.

|  |  |  |  |
| --- | --- | --- | --- |
| Temperature (℃) | Crystal Number | Thickness (μm) | Water content (ppm wt.) |
| 1500 | 1 | 30 | 97 |
| 2 | 50 | 74 |
| 3 | 30 | 99 |
| 4 | 50 | 80 |
| Average |  | 87(11) |
| 1700 | 1 | 40 | 78 |
| 2 | 35 | 74 |
| 3 | 40 | 96 |
| 4 | 40 | 98 |
| Average |  | 86(11) |
| 1900 | 1 | 65 | 65 |
| 2 | 90 | 71 |
| 3 | 50 | 77 |
| 4 | 40 | 77 |
| Average |  | 73(5) |

Table S2. Information of Single Crystals for FTIR Measurement at each Temperature.

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