Physics and Chemistry of Minerals (2022) 49:44
https://doi.org/10.1007/s00269-022-01221-6

ORIGINAL PAPER

Stable compounds in the CaO-Al_2O_3 system at high pressures

Ekaterina I. Marchenko[1,2] · **Artem R. Oganov**[3] · **Efim A. Mazhnik**[3] · **Nikolay N. Eremin**[1]

Received: 14 June 2022 / Accepted: 8 October 2022

Abstract

Using the evolutionary crystal structure prediction algorithm USPEX, we showed that at pressures of the Earth's lower mantle (24-136 GPa) $CaAl_2O_4$ is the only stable calcium aluminate. At pressures above 7.0 GPa it has the $CaFe_2O_4$-type structure with space group *Pnma*. This phase is one of the prime candidate aluminous phases in the lower mantle of the Earth. We show that at low pressures $5CaO \bullet 3Al_2O_3$ (C_5A_3) with space group $Cmc2_1$, $CaAl_4O_7$ (with space group $C2/c$) and $CaAl_2O_4$ (space group $P2_1/m$) are stable at pressures of up to 2.1, 1.8 and 7.0 GPa, respectively. The previously unknown structure of the orthorhombic "CA-III" phase is also found in our calculations. This phase is metastable at 0 K and has a layered structure with space group $P2_12_12$.

Keywords CaO-Al_2O_3 system · Crystal structure prediction · High pressure · Evolutionary algorithm · USPEX · Earth's mantle

Introduction

Aluminum is the fifth most abundant element in the Earth's crust and mantle, the Al/Si ratio being 0.36 in the crust and 0.17 in the mantle (Anderson 1983). Today, it is thought that the lower mantle consists mainly of (Mg,Fe)SiO_3 bridgmanite with a perovskite-type (Pv) crystal structure (~ 70 vol.%), (Mg,Fe)O ferropericlase (~ 20 vol.%), and calcium perovskite $CaSiO_3$ (Ca-Pv) (6–12 vol.%) (Ringwood 1975; Irifune 1994; Pushcharovsky and Pushcharovsky 2010). It is known that in rocks of the composition of peridotite and pyrolite, Al is incorporated into bridgmanite and there is no separate aluminous phase at least up to the middle region of the Earth's lower mantle (Irifune et al., 1994; Kato et al. 1996; Liu et al. 2016). Several potential aluminous phases have been considered for the lower mantle. For example, a solid solution between $MgAl_2O_4$ and $CaAl_2O_4$ is known (Akaogi et al. 1999). It was also previously shown that Al-rich basalts contain $MgAl_2O_4$ with the $CaFe_2O_4$-type structure, which could coexist with aluminous bridgmanite in the Earth's lower mantle (Litasov and Ohtani 2005). Thus, the crystal chemistry of the CaO-MgO-Al_2O_3 system plays an important role for understand the chemistry of Al in the Earth's lower mantle.

All experimentally known polymorphic modifications of $CaAl_2O_4$ can be divided into low-pressure structures, where which aluminum atoms are in the tetrahedral coordination, and high-pressure phases, with aluminum in five or sixfold coordination. The well-known monoclinic modification with the space group $P2_1/n$ at normal conditions (Ito et al. 1980) consist of a framework of AlO_4 tetrahedra, topologically equivalent to the tridymite structure (SiO_2) (Fig. 1a). The voids of the framework are occupied by calcium atoms in three independent crystallographic sites with different coordination numbers: 6 (Ca1), 6 (Ca2) and 9 (Ca3). This modification was first observed in meteorites and the mineral was named crotite (Ma et al. 2011). Another monoclinic modification of $CaAl_2O_4$ with space group $P2_1/c$ (Fig. 1b) crystallizes in the *m*-$CaGa_2O_4$ structure type (Ito et al. 1980), where the AlO_4 distorted tetrahedra form a three-dimensional framework with the tridymite topology, and Ca atoms are seven-coordinate. This phase was also found in meteorites and was named dmitriivanovite (Mikouchi et al.

✉ Ekaterina I. Marchenko
marchenko-ekaterina@bk.ru

[1] Department of Geology, Lomonosov Moscow State University, GSP-1, 1 Leninskiye Gory, Moscow 119991, Russia

[2] Laboratory of New Materials for Solar Energetics, Faculty of Materials Science, Lomonosov Moscow State University, Moscow, Russia

[3] Skolkovo Institute of Science and Technology, Bolshoy Blvd 30, bld. 1, Moscow 121205, Russia

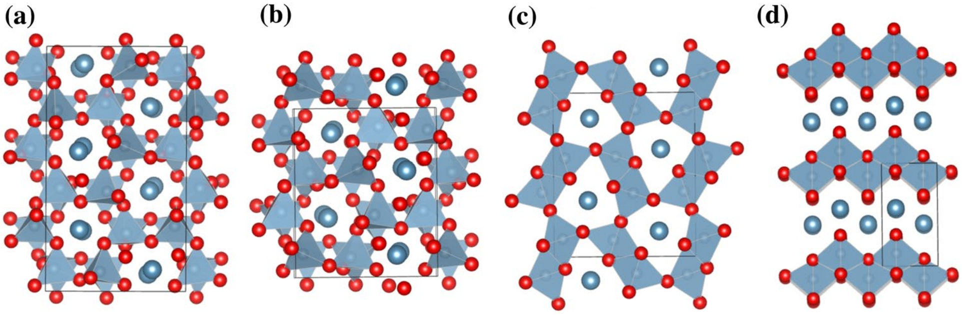


Fig. 1 Polyhedral representation of experimentally known $CaAl_2O_4$ structures with AlO_4 tetrahedra (gray color): $P2_1/n$ (*xz* projection) **a**, $P2_1/c$ (*yz* projection) **b**; and AlO_6 octahedra (gray color): *Pnma* modification (*xy* projection) **c** and "layered" $P2_1/m$ modification (*zy* projection) **d**. Ca^{2+} ions are shown as large balls

2009). The monoclinic $P2_1/c$ phase is slightly denser than $P2_1/n$, and the transition from $P2_1/n$ to $P2_1/c$ is observed at the pressure of 1 GPa and the temperature of 700 °C and at 2 GPa and 1300 °C (Ito et al. 1980). Among other low-pressure modifications of $CaAl_2O_4$ with AlO_4 tetrahedra, a crystal structure with space group $P6_3$ has been mentioned (Janáková et al. 2007). However, the authors have questioned the correctness of their structure refinement because of the high R-factor and highly distorted interatomic distances. Most likely, this phase is metastable at low pressures and does not have a stability field in the phase diagram.

With further increase in pressure, the coordination of Al atoms changes from tetrahedral to octahedral. Among the $CaAl_2O_4$ phases with the octahedral coordination of Al atoms the best-known orthorhombic *Pnma* modification was first described in 1957 (Decker and Kasper 1957) (Fig. 1c). This phase crystallizes in the $CaFe_2O_4$ structure type (space group *Pnma*) where edge-sharing AlO_6 octahedra forming channels along the c axis, filled with Ca^{2+} cations.

Another modification of $CaAl_2O_4$ is the monoclinic $P2_1/m$ phase with a layered structure, synthesized by (Lazić et al. 2006) (Fig. 1d). The layers of AlO_6 octahedra in this structure are separated by interlayer Ca cations. The phase transition $P2_1/m \rightarrow Pnma$ has been experimentally discovered at $P = 4–8$ GPa (Lazić et al. 2006). In the experimental study of the $CaAl_2O_4$-$CaGa_2O_4$ system (Ito et al. 1980), yet another modification of $CaAl_2O_4$, named "CA-III", and stable in the pressure range of 3–8 GPa, was described. Its crystal structure was not determined, but an orthorhombic cell was established with the parameters $a = 4.39$ Å, $b = 5.07$ Å, $c = 6.96$ Å.

In a recent theoretical paper (Eremin et al. 2016), it has been shown that the phase transition between $P2_1/m$ and *Pnma* is predicted by *ab initio* calculations at 7–8 GPa, which is in close agreement with the experiment (Lazić et al. 2006). Calculations based on semiclassical interatomic potentials overestimate the phase transition pressure, 18–19 GPa (Eremin et al. 2016). As calculations (Eremin et al. 2016) showed, when pressure increases, *Pnma*-$CaAl_2O_4$ becomes increasingly more favorable with increasing pressure in the entire range of mantle pressures and temperatures. The *Cmcm* phase of $CaAl_2O_4$ is always slightly (0.2–0.5 eV/f.u.) less stable than the *Pnma* phase.

Analyzing recent experimental and theoretical studies, one can conclude that under *P–T* conditions of the Earth's mantle, only two phases of $CaAl_2O_4$ may exist: monoclinic $P2_1/m$ and orthorhombic *Pnma*, both with the octahedral coordination of the Al atoms, and the stability field of the latter covers almost the entire *P-T* range of the Earth's mantle. So far, only the phases of stoichiometry $CaAl_2O_4$ have been investigated at conditions of the Earth's mantle, and even there some structures (such as Ca-III) remain experimentally unresolved.

In addition to the structural modifications of $CaAl_2O_4$, literature describes experimentally investigated phases with different stoichiometric ratios where the aluminum atoms have tetrahedral coordination ($Ca_{12}Al_{14}O_{33}$ (Büssem and Eitel 1936), $CaAl_4O_7$ (Boyko and Wisnyl 1958), $Ca_3Al_2O_6$ (Mondal and Jeffery 1975), $Ca_5Al_6O_{14}$ (Vincent and Jeffery 1978), $Ca_4Al_6O_{13}$ (Ponomarev et al. 1970). The experimentally known phases in which aluminum atoms in mixed coordination have been described: $Ca_2Al_2O_5$ (Kahlenberg et al. 2000b; Lazic et al. 2008) with aluminum in tetrahedra and octahedra; $Ca_4Al_6O_{13}$ (Kahlenberg et al. 2000a), with aluminum in tetrahedra, octahedra and trigonal bipyramids; $Ca_3Al_2O_6$ (Steele and Davey 1929) with Al in octahedra and squares, and $CaAl_{12}O_{19}$ (Kato nd Saalfeld 1968) with aluminum in octahedra and trigonal bipyramids. The mineral mayenite (Hentschel G., 1964), which has a clathrate structure, has a rather complex composition $Ca_{12}Al_{14}O_{33}$ and the removal of one oxygen atom per formula unit leads to a peculiar metallic electride state (Matsuishi et al. 2003) (Figure S1). Overall, the tetrahedral coordination of aluminum is unstable at pressures above 2–8 GPa (Ito et al. 1980; Irifune and Tsuchiya, 2007; Eremin et al. 2016), therefore, phases with tetrahedral coordination of Al atoms in the CaO-Al_2O_3 system cannot exist in the deep mantle.

In this work, we theoretically predicted thermodynamically stable phases in the CaO-Al_2O_3 system at pressures in the range of 0–200 GPa using the Universal Structure Predictor: Evolutionary Xtallography (USPEX) algorithm (Oganov and Glass 2006; Oganov et al. 2011; Lyakhov et al. 2013).

Methods

Evolutionary searches for stable phases in the CaO-Al_2O_3 system were performed using the USPEX code (Oganov and Glass 2006; Oganov et al. 2011; Lyakhov et al. 2013) in its variable-composition mode. In our evolutionary searches, all structures and stoichiometries were allowed with up to 32 atoms in the primitive cell. The first generation contained 200 structures and was produced using symmetric (Lyakhov et al. 2013) and topological (Bushlanov et al. 2019) random structure generators. All subsequent generations had 120 structures. To determine stable compounds, USPEX builds convex hull diagrams (also known as Maxwell construction). Points lying on the hull indicate thermodynamically stable phases. Points lying above the hull are thermodynamically unstable phases. Evolutionary searches were performed at pressures of 25, 50, 100, and 200 GPa. All structures were relaxed using VASP (Kresse and Furthmüller 1996), using density functional theory at the level of generalized gradient approximation, with PBE exchange–correlation functional (Perdew et al. 1996) and PAW method (Blöchl 1994; Kresse and Joubert, 1999), with plane-wave cutoff of 600 eV. Brillouin zone was sampled using uniform k-meshes with reciprocal-space resolution $2\pi \times 0.05\ \text{Å}^{-1}$, which ensures that the errors in energy differences are below 1 meV/atom. Low-enthalpy structures predicted using USPEX and experimentally known structures of different stoichiometries were carefully relaxed at pressures ranging from 0 to 200 GPa. The full zero-temperature pressure-composition phase diagram of the CaO-Al_2O_3 system was constructed. It is worth noting that taking into account thermal contributions to the Gibbs free energy requires a lot of computing resources and is not required in this study, because the entropic factor ($T\Delta S$) at the temperatures of the Earth's mantle is estimated to be much less than k_BT (where k_B is the Boltzmann constant). Thus, the entropy contribution under such P–T conditions is negligibly small compared to ΔH and was not taken into account.

Thus, the phase stability is unlikely to be changed qualitatively by temperature at pressures of the lower mantle. Crystal structures were visualized using the VESTA program (Momma and Izumi 2011).

Results and discussion

Variable-composition USPEX searches allow for a detailed sweep of the entire compositional space in a single simulation. They recovered all known stable structures and phase transitions between them in CaO (Jerebtsov and Mikhailov 2001; Deng et al. 2007) and Al_2O_3 (Marton and Cohen 1994; Oganov and Ono 2005).

Interestingly, USPEX has also found (as stable or metastable at zero Kelvin) all previously known structures of $CaAl_2O_4$ with the octahedral coordination of aluminum atoms, including the marokite-type phase and the "layered" $P2_1/m$ modification. As we find, the $Pnma$ modification of $CaAl_2O_4$ with a marokite structure type turns out to be stable at pressures from 7.0 to at least 200 GPa (Figs. 2 and 3). It is worth noting that the previously theoretically predicted (Eremin et al. 2016) metastable $CaAl_2O_4$ phase with α-PbO_2–like structure is strongly inferior in energy to marokite-type phase in the studied pressure range.

At pressures below 7.0 GPa, the $P2_1/m$ structure is stable, and below 1.1 GPa the $P2_1/n$ structure is stable (Fig. 2). The $P2_1/c$ phase is unstable over the entire pressure range. At low pressures, we see yet another two phases as stable: 5CaO • $3Al_2O_3$ (C_5A_3) with space group $Cmc2_1$ (up to 2.1 GPa) and $CaAl_4O_7$ with space group $C2/c$ (up to 1.8 GPa) (Fig. 3a). However, the stability of C_5A_3 phase is marginal: if we include zero-point energy (we did its crude estimate with Debye model), C_5A_3 phase is no longer thermodynamically stable but is 0.009 eV/block above the convex hull. The convex hull of the CaO-Al_2O_3 system at pressures of 0 GPa and 100 GPa are shown in Fig. 4. It should be noted that the $Ca_3Al_2O_6$ (C_3A) and $CaAl_{12}O_{19}$ (CA_6) and $Ca_{12}Al_{14}O_{33}$ ($C_{12}A_7$) phases at low pressures are very close to the convex hull, being just 0.008, 0.027, and 0.008 eV/block, respectively, above it at a pressure of 0 GPa. The calculated fitness (the height above the convex hull, characterizing the degree of instability of a given structure) for these experimental structures as a function of pressure is shown in Figure S3. The calculated enthalpy of different polymorphs with CA composition is shown in Table S2.

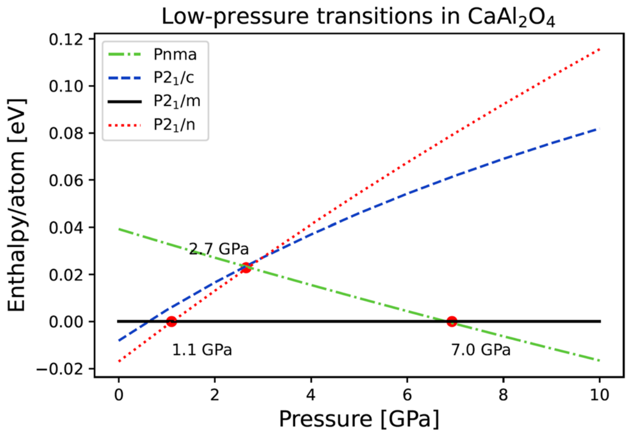
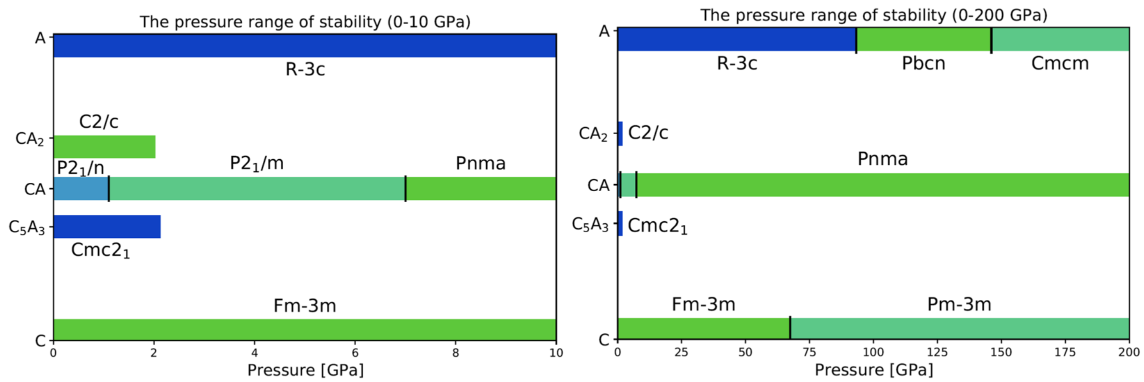
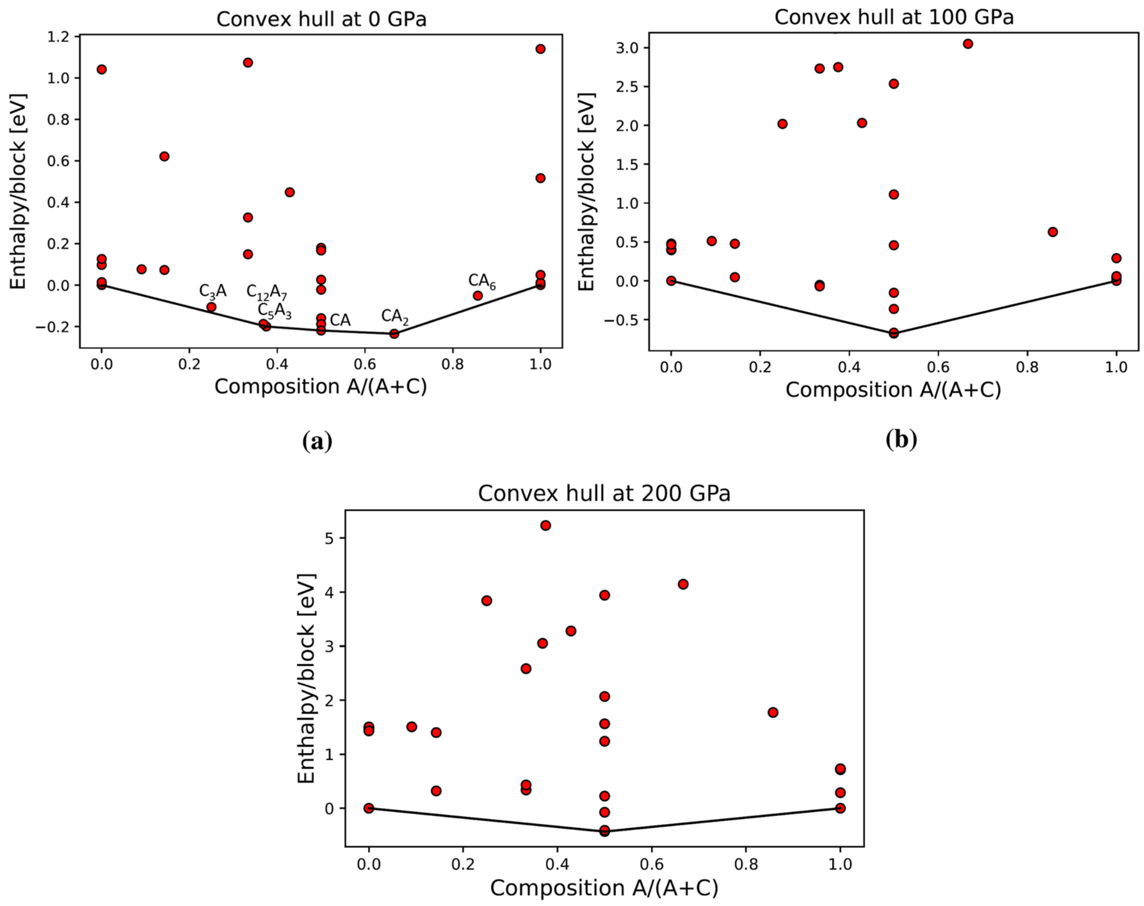


Fig. 2 Enthalpy differences between low-pressure phases of $CaAl_2O_4$. Enthalpy for $P2_1/m$ phase was taken as a reference



(a) **(b)**

Fig. 3 Pressure-composition phase diagram of the CaO-Al_2O_3 system **a** in the 0–10 GPa pressure range, **b** in the 0–200 GPa pressure range

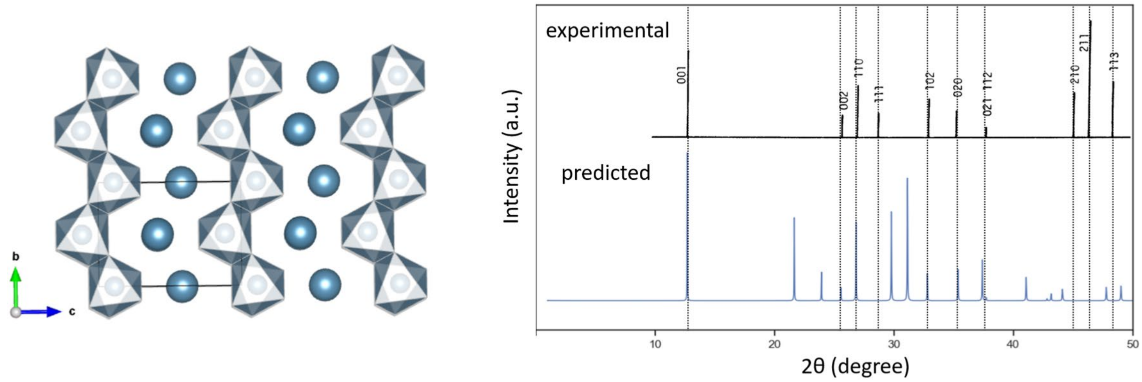


(a) **(b)**

(c)

Fig. 4 Convex hulls of the CaO(C) -Al_2O_3 (A) system at 0 GPa **a**, 100 GPa **b**, and 200 GPa **c**

We also calculated phase transition pressures for CaO and Al_2O_3. For CaO, the pressure of the phase transition from $Fm\bar{3}m$ to $Pm\bar{3}m$ is 67.4 GPa (Figure S2a). For Al_2O_3, the pressure of phase transitions from $R\bar{3}c$ to *Pbcn* is 93.2 GPa and further from *Pbcn* to *Cmcm* 146.1 GPa (Figure S2b). This compares well with the experiments (Jeanloz et al. 1979)(Funamori and Jeanloz 1997)



(a) **(b)**

Fig. 5 Predicted structure of "CA-III" metastable phase **a** and diffraction patterns of the "CA-III" phase according to the experimental data from Ito et al. (1980) and our predicted structure of "CA-III" phase **b**. The AlO_6 polyhedra are shown in gray color, Ca^{2+} ions are shown as large balls

and previous theoretical calculations (Oganov and Ono 2005; Deng et al. 2007; Liu et al. 2015).

To find the unknown crystal structure of the "CA-III" phase (Ito et al. 1980) with cell parameters a = 4.390 Å, b = 5.070 Å, c = 6.960 Å, we performed evolutionary USPEX searches with a fixed $CaAl_2O_4$ and fixed experimental cell parameters. The resulting structure has indeed the $P2_12_12$ symmetry, and features layers made of edge- and face-sharing AlO_6 octahedra (Fig. 5a), with Ca atoms located in the interlayer space. The coincidence of the main X-ray diffraction peaks ((001), (002), (110), (102), (020) and (112)) of our structural model and the experimental (Ito et al. 1980) diffraction patterns (see Fig. 5b) allows us to conclude that the structure was identified correctly. It should be noted that texturing of the sample in the experiment leads to a difference between the theoretical and experimental diffraction peak intensity ratios. The predicted crystal structure of the "CA-III" phase is metastable at 0 K, being 0.18 eV/atom higher in enthalpy than the monoclinic $P2_1/n$ phase.

Conclusions

Our systematic evolutionary searches for stable compounds in the CaO-Al_2O_3 system at pressures 0–200 GPa clearly establish that at pressures above 7.0 GPa (i.e. at all pressures of the Earth's transition zone and lower mantle) only one calcium aluminate, $CaAl_2O_4$ with $CaFe_2O_4$ structure (*Pnma*), is stable. This phase is one of the prime candidate aluminous phases in the lower mantle of the Earth. En route to this conclusion, we have also resolved the old puzzle of the low-pressure (3–8 GPa) metastable phase named "CA-III" – its crystal structure is now established as having the orthorhombic space group $P2_12_12$, and featuring layers of edge- and face-sharing AlO_6 octahedra. Our analysis also reveals that at low pressures 5CaO • $3Al_2O_3$ (C_5A_3) with space group $Cmc2_1$, $CaAl_4O_7$ (*C2/c*) and $CaAl_2O_4$ ($P2_1/m$) structures are stable up to 2.1, 1.8 and 7.0 GPa respectively.

$CaAl_2O_6$, $CaAl_{12}O_{19}$ and $Ca_{12}Al_{14}O_{33}$ phases are very close to thermodynamic stability at low pressures and are also known from the experiment. Very rich and complex at low pressures, the chemistry of the cement CaO-Al_2O_3 system becomes very simple at high pressures.

Competing interests

The authors declare that they have no competing interests.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s00269-022-01221-6.

Acknowledgements The research is carried out using the Oleg supercomputer of the Materials Discovery Lab of Skoltech and the shared research facilities of HPC computing resources at Lomonosov Moscow State University. Work of A.R.O. and E.A.M. is supported by Russian Science Foundation (grant 19-72-30043).

Author contributions EI. M: conceptualization, investigation, writing-original draft preparation; AR. O: data curation, writing—reviewing and editing; EA. M: investigation, methodology; NN. E: conceptualization, writing—reviewing and editing.

Declarations

Competing interests The authors declare no competing interests.

References

Anderson, D. L. (1983) ‘Chemical composition of the Mantle’, Proceeding of the fourteenth lunar and planetary science conference, 88(3): B41–B52

Akaogi M, Hamada Y, Suzuki T, Kobayashi M, Okada M (1999) High pressure transitions in the system MgAl2O4–CaAl2O4: a new hexagonal aluminous phase with implication for the lower mantle. Phys Earth Planet Inter 115(1):67–77. https://doi.org/10.1016/S0031-9201(99)00076-X

Blöchl PE (1994) Projector augmented-wave method. Phys Rev B 50(24):17953

Boyko E, Wisnyl LG (1958) The optical properties and structures of CaO.2Al 2 O 3 and SrO.2Al 2 O 3. Acta Crystallogr A 11(6):444–445. https://doi.org/10.1107/s0365110x58001183

Bushlanov PV, Blatov VA, Oganov AR (2019) Topology-based crystal structure generator. Comput Phys Commun 236:1–7. https://doi.org/10.1016/j.cpc.2018.09.016

Büssem VW, Eitel A (1936) Die Struktur des Pentacalciumtrialuminats. Z Kristallogr 95:175–178. https://doi.org/10.1515/9783112441107-005

Decker BF, Kasper JS (1957) The structure of calcium ferrite. Acta Crystallogr A 10(4):332–337. https://doi.org/10.1107/s0365110x5700095x

Deng Y et al (2007) Phase transition and elastic constants of CaO from first-principle calculations. Phys B 392(1–2):229–232. https://doi.org/10.1016/j.physb.2006.11.023

Eremin NN, Grechanovsky AE, Marchenko EI (2016) Atomistic and Ab initio modeling of CaAl2O4 high-pressure polymorphs under Earth’s mantle conditions. Crystallogr Rep 61(3):432–442. https://doi.org/10.1134/S1063774516030111

Funamori N, Jeanloz R (1997) High-pressure transformation of Al2O3. Science 278(7):1109–1111

Hentschel G. (1964) ‘Mayenit, 12CaO·7Al2O3, und Brownmillerit, 2CaO(Al,Fe)2O3, zwei neue Minerale in den Kalksteineinschlüssen der Lava des Ettringer Bellerberges’, N. Jb. Mineral. Mh., pp. 22–29. Available at: https://scholar.google.com/scholar?hl=ru&as_sdt=0%2C5&q=Hentschel+G.+Mayenit%2C+12CaO·7Al2O3%2C+und+Brownmillerit%2C+2CaO%28Al%2CFe%29203%2C+zwei+neue+Minerale+in+den+Kalksteineinschlüssen+der+Lava+des+Ettringer+Bellerberges.+N.+Jb.+Mineral.+Mh.%2C+1964%2C+22-29.&btnG.Accessed on 28 May 2022.

Irifune T (1994) Absence of an aluminous phase in the upper part of the Earth’s lower mantle. Nature. https://doi.org/10.1038/370131a0

Ito S et al (1980) High-pressure modifications of CaAl2O4 and CaGa2O4. Mater Res Bull 15(7):925–932. https://doi.org/10.1016/0025-5408(80)90217-2

Janáková S et al (2007) Preparation and structural investigations of sol-gel derived Eu3 +-doped CaAl2 O4. J Phys Chem Solids 68(5–6):1147–1151. https://doi.org/10.1016/j.jpcs.2006.12.034

Jeanloz R et al (1979) B1-B2 transition in calcium oxide from shock-wave and diamond-cell experiments. Science 206(4420):829–830. https://doi.org/10.1126/science.206.4420.829

Jerebtsov DA, Mikhailov GG (2001) Phase diagram of CaO–Al2O3 system. Ceram Int 27(1):25–28. https://doi.org/10.1016/S0272-8842(00)00037-7

Kahlenberg V, Fischer RX, Shaw CSJ (2000a) High-pressure Ca4Al6O13: an example of a calcium aluminate with three different types of coordination polyhedra for aluminum. Am Miner 85(10):1492–1496. https://doi.org/10.2138/am-2000-1019

Kahlenberg V, Fischer RX, Shaw CSJ (2000b) Rietveld analysis of dicalcium aluminate (Ca2Al2O5)-A new high pressure phase with the Brownmillerite-type structure. Am Miner 85(7–8):1061–1065. https://doi.org/10.2138/am-2000-0722

Kato T, Ohtani E, Ito Y, Onuma K (1996) Element partitioning between silicate perovskites and calcic ultrabasic melt. Phys Earth Planet Inter 96(2–3):201–207. https://doi.org/10.1016/0031-9201(96)03151-2

Kato, K. and Saalfeld, H. (1968) ‘Verfeinerung der Kristallstruktur von CaO (Al2O3)6’, Neues Jahrbuch für Mineralogie-Abhandlungen, 109, pp. 192–200. Available at: https://ci.nii.ac.jp/naid/10005739263/. Accessed on 28 May 2022.

Kresse G, Furthmüller J (1996) Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. Comput Mater Sci 6(1):15–50. https://doi.org/10.1016/0927-0256(96)00008-0

Kresse G, Joubert D (1999) From ultrasoft pseudopotentials to the projector augmented-wave method. Phys RevB - Condensed Matter and Materials Phys 59(3):1758–1775. https://doi.org/10.1103/PhysRevB.59.1758

Lazić B et al (2006) On the polymorphism of CaAl2O4-structural investigations of two high pressure modifications. Solid State Sci 8(6):589–597. https://doi.org/10.1016/j.solidstatesciences.2005.12.010

Lazic B et al (2008) Incommensurate structure of Ca2Al2O5 at high temperatures - Structure investigation and Raman spectroscopy. Acta Crystallogr B 64(4):417–425. https://doi.org/10.1107/S0108768108016029

Litasov KD, Ohtani E (2005) Phase relations in hydrous MORB at 18–28 GPa: implications for heterogeneity of the lower mantle. Phys Earth Planet Inter 150:239–263. https://doi.org/10.1016/j.pepi.2004.10.010

Liu Y et al (2015) Prediction of new thermodynamically stable aluminum oxides. Sci Rep 5:14–18. https://doi.org/10.1038/srep09518

Liu Z, Irifune T, Nishi M, Tange Y, Arimoto T, Shinmei T (2016) Phase relations in the system $MgSiO_3$–Al_2O_3 up to 52GPa and 2000K. Phys Earth Planet Inter 257:18–27. https://doi.org/10.1016/j.pepi.2016.05.006

Lyakhov AO et al (2013) New developments in evolutionary structure prediction algorithm USPEX. Comput Phys Commun 184(4):1172–1182. https://doi.org/10.1016/j.cpc.2012.12.009

Ma C et al (2011) Krotite, CaAl2O4, a new refractory mineral from the NWA 1934 meteorite. Am Miner 96(5–6):709–715. https://doi.org/10.2138/am.2011.3693

Marton FC, Cohen RE (1994) Prediction of a high-pressure phase transition in Al2O3. Am Miner 79(7–8):789–792

Matsuishi S et al (2003) High-density electron anions in a nanoporous single crystal: [Ca24Al28O64]4+ (4e-). Science 301(5633):626–629. https://doi.org/10.1126/science.1083842

Mikouchi T et al (2009) Dmitryivanovite: A new high-pressure calcium aluminum oxide from the Northwest Africa 470 CH3 chondrite characterized using electron backscatter diffraction analysis. Am Miner 94(5–6):746–750. https://doi.org/10.2138/am.2009.3080

Momma K, Izumi F (2011) VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. J Appl Crystallogr 44(6):1272–1276. https://doi.org/10.1107/S0021889811038970

Mondal BP, Jeffery JW (1975) the crystal structure of triealeium aluminate, Ca3AI206*. Acta Cryst 31:689

Oganov AR, Glass CW (2006) Crystal structure prediction using ab initio evolutionary techniques: principles and applications. J Chem Phys. https://doi.org/10.1063/1.2210932

Oganov AR, Ono S (2005) The high-pressure phase of alumina and implications for Earth’s D″ layer. Proc Natl Acad Sci USA 102(31):10828–10831. https://doi.org/10.1073/pnas.0501800102

Oganov AR, Lyakhov AO, Valle M (2011) How evolutionary crystal structure prediction works-and why. Acc Chem Res 44(3):227–237. https://doi.org/10.1021/ar1001318

Perdew JP, Burke K, Ernzerhof M (1996) Generalized gradient approximation made simple. Phys Rev Lett 77:3865–3868

Ponomarev V.I., Kheiker D.M., Belov, N. V. (1970) 'Crystal structure of tetracalcium trialuminate - the aluminate analog of sodalite', *Kristallografiya*, pp. 917–921. Available at: https://scholar.google.com/scholar_lookup?title=Crystal structure of tetracalcium trialuminate — The aluminate analog of sodalite&journal=Sov Phys — Crystallogr&volume=15&pages=799–801&publication_year=1971&author=Ponomarev%2CVI&author=Kheiker%2CDM&author. Accessed on 28 May 2022.

Pushcharovsky YM, Pushcharovsky DY (2010) Geology of the Earth's mantle. GEOS, Moscow, p 140

Ringwood AE (1975) Composition and petrology of the Earth's mantle. McGraw-Hill Company, Newyork. https://doi.org/10.1016/0031-9201(77)90018-8

Steele FA, Davey WP (1929) The crystal structure of tricalcium aluminate. J Am Chem Soc 51:2283–2293. https://doi.org/10.1021/ja01944a001

Vincent MG, Jeffery JW (1978) The crystal structure of pentacalcium trialuminate, 5CaO. 3AI203. Acta Crystallogr b Struct Crystallogr Cryst Chem 34:1422–1428