Crystal structures of two oxygendeficient calcium aluminum silicate perovskites from NMR and powder X-ray diffraction

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Several high-pressure phases along the Ca₂Si₂O₆-Ca₂Al₂O₅ join have been reported to occur with oxygen-deficit perovskite structures [1], but their detailed crystal structures remained undetermined. We have successfully determined the crystal structures for two of these phases: a Ca₂AlSiO_{5.5} phase synthesized at 7 GPa and 1500 °C, and a Ca₂Al_{0.8}Si_{1.2}O_{5.6} phase synthesized at 11 GPa and 1500°C, both in a multi-anvil press. Here we report these results.

²⁹Si MAS NMR and ²⁷Al 3Q MAS NMR revealed one tetrahedral Si peak and one octahedral Al peak for the $Ca_2AlSiO_{5.5}$ phase, and two Si (one tetrahedral and one octahedral) peaks and one octahedral Al peak for the $Ca_2Al_{0.8}Si_{1.2}O_{5.6}$ phase.

The crystal structures were solved with an ab initio structural determination technique (using the program FOX) from synchrotron powder X-ray diffraction data (measured at BL19B2, SPring-8) using information from NMR as constraints, and were further refined using the Rietveld method (RIETAN-FP). The space groups for both phases were found to be C2/c. The crystal structure of the Ca₂AlSiO₅₅ phase consists of double-layers of perovskite-like AlO₆ octahedra and double-layers of SiO4 tetrahedra, stacked alternatively in the [111] direction of cubic perovskite, forming an 8-fold superstructure. That of the Ca₂Al_{0.8}Si_{1.2}O_{5.6} phase is made of triple-layers of perovskite-like AlO₆-SiO₆-AlO₆ octahedra and double-layers of SiO₄ tetrahedra, also stacked alternatively in the [111] direction, forming a 10-fold superstructure. The double-layers of SiO4 in both phases are similar, having deficient oxygens at the middle with one terminal oxygen (not bonded to other Si/Al) for each SiO₄ tetrahedron. These structures are related to the merwinite (Ca₃MgSi₂O₈) structure, which consists of alternating single layers of MgO₆ octahedra and double-layers of SiO₄ tetrahedra. This series of oxygen-deficit peroviskites provide additional insights into the local structural environments of Al- and Fe³⁺-containing CaSiO₃ perovskite.

[1] Bläß, UW et al. (2007) Phys. Chem. Mineral., **34**, 363-376.

Estimates of atmospheric CO₂ in the Neoarchean-Paleoproterozoic

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The weak luminosity of the younger Sun requires the early Earth to have more greenhouse effects than those today. The candidates for such greenhouse effect gases are CO_2 and CH_4 in the Neoarchean and the Paleoproterozoic. The quantification of CO_2 and CH_4 levels in the Neoarchean-Paleoproterozoic is a crucial issue, because the multiple glaciation events at ~2.9 Ga and ~2.4-2.2 Ga are considered to have been caused by the transitions of CO_2 and CH_4 levels.

Paleosols record vestiges of weathering by CO_2 and therefore have given estimates of atmospheric CO_2 levels. However, the CO_2 levels estimated from paleosols are less than those estimated by the climate model. Therefore, CH_4 is considered to have had a significant role as greenhouse effect gas. Because the CO_2 levels have been usually discussed indicating the contemporary CH_4 levels and vice versa, it is important to validate or assess the CO_2 levels extracted from paleosols so far. In this study, another method was developed to re-evaluate CO_2 levels from paleosols.

The new method estimates CO_2 levels operating in weathering profiles in 3 steps: (1) estimation of cation concentrations in porewater at the time of weathering from the loss amounts of cations in paleosol profiles, (2) estimation of pH in porewater at the time of weathering from likely secondary minerals in paleosols (kaolinite and smectite with no carbonates), and (3) CO_2 estimation from a charge-balance equation in porewater for dissolved CO_2 species (carbonic acid, bicarbonate ion and carbonate ion) and cations, using the estimated cation concentrations and pH. Application of the new method to modern weathering profiles has revealed that the new method reproduces modern soil CO_2 levels reasonabley well, confirming the validaty of the method.

Applyng the new method to the Neoarchean-Paleoproterozoic paleosols, the CO₂ levels were calculated to be > 100 PAL at ~2.8-2.4 Ga and < 100 PAL at ~2.3-1.8 Ga. The calculated levels of CO₂ throughout the above eras were sufficient to keep the average surface temperature of the Earth more than the freezing point of water. These results indicate (i) the general decreasing trend of CO₂ throughout the Neoarchean-Paleoproterozoic and (ii) that it would have been more difficult to make the Earth a Snowball than previously thought.