INCONGRUENT EVAPORATION OF DIOPSIDE TO AKERMANITE:
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Diopside is a major constituent mineral of CAIs, of which oxygen isotopic compositions show large anomalies. We have conducted evaporation experiments of diopside to investigate vapor pressure, mode of evaporation, and isotopic fractionation during evaporation.

Experiments were in a tungsten-wound high-temperature furnace constructed in a vacuum chamber, which was described by [1]. Vapor pressure was measured with the Knudsen method. Several mg of the powder was contained in a Mo Knudsen cell with small orifices. Solid and vapor are in equilibrium in a Knudsen cell, and the equilibrium vapor pressure can be calculated from the weight loss of the solid that was lost as vapor through orifices of the capsule. The weight loss was calculated against vapor pressure by an equation $P_v = \frac{1}{Ac} \cdot \frac{\partial w}{\partial t} \cdot \frac{\sqrt{2\pi R T}}{M}$, where $P_v$ is the vapor pressure of a substance, $Ac$ is factors dependent on the orifice of the capsule which was measured by [1], $\partial w$ is weight loss, $t$ is experimental duration, $M$ is molecular weight of the effusing vapor, $T$ is an absolute temperature, and $R$ is the gas constant. The pressure inside the chamber was kept at 2-4x10$^{-10}$ bar during experiments. The $f_{O_2}$ was buffered at the Mo-MoO$_2$ curve, which is between the MW and IW buffers. A Mo capsule can be an oxygen fugacity buffer in the present study because an oxide has higher vapor pressures than a metal and it evaporates quickly.

Starting material is a fragment or powder from a single crystal of diopside (about 1x1.5x5 cm) synthesized with the Czochralski pulling method by M. Morioka of University of Tokyo. Run #559 was at 1250°C for 28800 min (20 days) in a Mo capsule with the starting material of a crystal fragment (1-2mm). Run #564 was at 1350°C for 33825 min (about 23 days) in a Mo capsule with the starting material of a crystal fragment. Run #592 was at 1300°C for 7260 min (4 days) in a Mo capsule with powdered sample. Run #593 was at 1300°C for 7200 min (4 days) in a graphite capsule with powdered sample for the comparison with #592. Residues were made into polished sections and observed with an SEM, and the isotopic compositions were measured with a SIMS at the Woods Hole Oceanographic Institution.

Diopside yielded akermanite as a partial evaporation residue. Figure 1 is a BSE photograph showing heavier (Ak) crystals (10-20 μm) grow the surface of diopside (D). An example of an EDS analysis is shown in Table 1; the crystal is nearly stoichiometric Ca$_2$MgSi$_2$O$_7$. The reaction is CaMgSi$_2$O$_6$ → Ca$_2$MgSi$_2$O$_7$ + MgSi$_2$O$_5$ (gas). The gas composition of MgSi$_2$O$_5$ is a bulk composition, and it does not represent a gas species. We found akermanite crystals in experiments with starting materials of single crystals regardless of temperature (runs #559 and #564), but we could not find akermanite in experiments with the starting material of powder (runs #592 and #593). Since the temperature of the runs #592 and #593 was between those of #559 and #564, temperature has no relationship to the mode of evaporation. This apparent discrepancy is probably because of the thin layer of akermanite. We see a very thin bright layer (< 1μm) on the surface of diopside grains, but EDS analyses did not give a composition of akermanite. The layer is thinner than the spot size of EPMA (2-3 μm).

Figure 2 shows vapor pressures calculated from the weight loss. Since it evaporates incongruently, molecular weight of gas was assumed to be MgSi$_2$O$_5$ (160,403 g). This assumption does not depend on gas species. Single crystal and powder gave a consistent results, which is not always the case in evaporation. When diffusion in solid is slow and is a rate limiting factor of evaporation, single crystal should give a smaller vapor pressure than powder which has infinite surface area. In the present experiments, however, the two different samples give a consistent result, which means that solid state diffusion did not play a role. Furthermore, it supports the above discussion that akermanite should be present in the residue of powder sample. In other word, solid state diffusion does not play a role on the crystallization of akermanite. The difference between the Mo capsule and graphite capsule is due to difference in the $f_{O_2}$. 

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Experimental results on various minerals and oxides show that evaporation is faster when the $f_{O_2}$ is low [2]. It implies that evaporated gas decomposes into multiple species including an oxygen gas species ($O_2$). The temperature-vapor pressure relationship at the Mo-MoO$_2$ buffer is shown by an equation $\ln P_v = \Delta S_v + (\Delta H_v/RT)$, where $\Delta S_v$ and $\Delta H_v$ are entropy and enthalpy of evaporation, respectively. $\Delta S_v$ and $\Delta H_v$ obtained are 190$\pm$10 (10) J/mol*K and 571$\pm$14 kJ/mol, respectively, which are close to those of forsterite [3].

Preliminary SIMS analyses show that akermanite has the same Mg, Si, and Ca isotopic compositions with diopside; that is, there seems to be no fractionation during evaporation. This results, however, requires further investigation, specifically oxygen isotopic analyses will be required.

The present results suggest a possible explanation for the genetic relationship between clinopyroxene and melilite in CAIs. Although diopside used in the present study is pure and Al is not contained, we can say that gehlenitic melilite should be a residue of partial evaporation of fassaity clinopyroxene. Al is highly refractory and will stay in crystals during partial evaporation unless $f_{O_2}$ is high enough to form Ca or Al hydroxide [4]. Some Type B I and compact Type A CAIs in Allende have melilite which includes clinopyroxene and the texture is interpreted to be replacement during planetary metamorphism [5,6]. The mineral compositions that the Ak mol increases from contact with pyroxene to outer rim, however, is suggestive of the origin of melilite as an evaporative residue from clinopyroxene. If it is the case, some CAIs are evaporative residues which primarily had at least clinopyroxene and spinel. Since many CAIs are thought to have been formed through melting of precursor materials [e.g., 7,8], most CAIs prefer secondary origin from precursor minerals through evaporation or melting. The difference between evaporation and melting is the partial pressure of the CAI component, which corresponds to the dust/gas ratio. When the ratio was high (dust is enriched), the dust should have melted when heated. When the ratio is small (dust is not enriched), they have just evaporated.


Table 1 Representative chemical composition of akermanite.

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<th>SiO$_2$</th>
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<th>CaO</th>
<th>Tot</th>
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<th>Mg</th>
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</table>

Fig. 1 BEI photograph showing occurrence of akermanite (Ak) on the surface of diopside [Di].

Fig. 2 Vapor pressure of diopside. A: crystal in a Mo capsule, B: powder in a Mo capsule, C: powder in a graphite capsule, D: powder in a Mo capsule in the presence of hydrogen gas in the chamber (unpub. data).