TRANSMISSION ELECTRON MICROSCOPY STUDIES OF RUTILE AND CAO INCLUSIONS FROM CARBONACEOUS CHONDRITES

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Transmission electron microscopy (TEM) studies were performed on four Ca-Al-rich inclusions (two Type A, one Type B, and a spinel-perovskite spherule) from the carbonaceous chondrites Allende (CV3), Acfer 082 (CV3), Acfer 086 (CV3), and Acfer 094 (unique). Two Type A and one Type B inclusion contain the pure oxide phases rutile (TiO2) and CaO. Within a spinel-perovskite spherule from Acfer 094 periclase (MgO) and corundum (Al2O3) were found coexisting with rutile and CaO. The oxides were found as tiny single grains (50-200 nm) of rounded morphologies inside and at grain boundaries of constituent minerals of the CAIs. We suggest that these oxides are primary condensation products which did not react during the condensation process with the remaining nebular gas to form other oxides or silicates.

INTRODUCTION. Calcium-aluminum-rich inclusions (CAIs) are common constituents of carbonaceous and rare in ordinary chondrites. They consist of refractory minerals like spinel, perovskite, melilite, hibonite, fassaite and grossite which are predicted to be the first solids to have condensed from a cooling gas of solar composition [1] and have, therefore, been subject of numerous studies. Among the phases in CAIs primary oxides are extremely rare. Only very few Al2O3-bearing inclusions have been found [e.g. 2-5]. However, no other pure oxides were found so far. One reason for not finding single element oxides could be their small grain size (below the resolution of a scanning electron microscope). In this study we performed a transmission electron microscope (TEM) study on four CAIs from four carbonaceous chondrites.

METHODS AND SAMPLES. Two coarse-grained Type A inclusions, one Type B inclusion and one spinel-perovskite spherule from Acfer 082 (CV3), Acfer 086 (CV3), Acfer 094 (unique), and Allende (CV3; A37) [4] were studied in thin sections using a scanning electron microscope. After detailed petrographic studies slotted Cu grids were glued on the CAIs. After immersion in acetone for 2-3 hours the thin sections glued to the grids were removed and ion thinned using a GATAN duo ion beam mill. Detailed studies were carried out using a Philips CM20 analytical TEM operating at 200 kV equipped with a Tracor energy dispersive X-ray detector and a JEOL JEM 100CX TEM operating at 100 kV.

RESULTS. Besides the mineral phases, which are typical for Ca-Al-rich inclusions like e.g. melilite, fassaite, spinel, and perovskite four different oxides were found in the CAIs: TiO2 (rutile), CaO, MgO (periclase), and Al2O3 (corundum). The nature of these inclusions was verified from electron diffraction patterns and chemical analyses. Inclusions of rutile (TiO2) were identified in all CAIs studied. These oxides are in the size range of 50-100 nm and typically occur as rounded grains mostly located at grain boundaries between spinels and between spinel and perovskite. The second oxide found in all CAIs is CaO. The oxide grains show perfect rounded morphologies and do not contain any detectable lattice defects. In contrast to the rutile-inclusions CaO grains are somewhat larger (100-200 nm) and were found exclusively embedded within the host mineral and not along grain boundaries. Host minerals for the CaO-inclusions are spinel, perovskite, and melilite. The spinel-perovskite spherule from Acfer 094 is the richest in oxide phases of all inclusions studied and contains periclase (MgO) and corundum (Al2O3) coexisting with rutile and CaO. In sharp contrast to the Type A and Type B inclusions, spinel is the only host phase of the oxide phases in the spinel-perovskite spherule. Rutile mostly occurs at grain boundaries, whereas CaO is enclosed within the spinels. Periclase is rare and all of the MgO-inclusions found were located at the grain boundaries between spinel grains. The rounded grains are 100-150 nm in
PURE CaO, MgO, TiO₂, AND Al₂O₃ in CAIs  
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size and pure MgO in composition. Inclusions of corundum are also 100-150 nm in size, but sometimes found enclosed within spinel grains; however, most of them are located at the spinel grain boundaries.

**DISCUSSION.** Thermodynamic calculations by Grossman [1] predict corundum to be the first solid oxide phase condensing from a hot gas of solar composition. However, under equilibrium conditions it will react with the remaining gas forming melilite and spinel. Unfortunately, no stability conditions for the oxides TiO₂, CaO, and MgO have been discussed in the literature. We suggest that these phases have been formed at high temperatures prior to the formation of more complex oxides and silicates. Since most of these phases were found within spinels, it is suggested that the oxides were protected from being consumed by reactions with the remaining gas to form silicates during further condensation processes or survived within spinels during partial melting of certain types of Ca,Al-rich inclusions. Clayton [6] addressed ²⁶Mg excess and O isotopic anomalies to the presence of isotopically anomalous submicron-sized grains. The oxide phases described in this study might be these grains.


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**Fig. 1-4.** Dark field TEM micrographs of the different inclusions imaged with reflections from the particles only. (1) Rutile (TiO₂)-, corundum (Al₂O₃)- and CaO-inclusions in spinel from Acfer 094. (2) Large Perovskite (Pv) grain and small CaO-inclusions in melilite from Acfer 082. (3) Periclase (MgO)-inclusions in spinel from Acfer 094. (4) Rutile (TiO₂)-inclusion in spinel from Allende (A37).

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