A new titanium-bearing calcium aluminosilicate phase: I. Meteoritic occurrences and formation in synthetic systems

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Abstract—A new titanium-bearing calcium aluminosilicate mineral has been identified in coarse-grained calcium-aluminum-rich inclusions (CAIs) from carbonaceous chondrites. The formula for this phase, which we have temporarily termed "UNK," is Ca$_3$Ti(Al,Ti)$_2$(Si,Al)$_3$O$_{14}$, and it is present in at least 8 of the 20 coarse-grained CAIs from the Allende CV3 chondrite examined as part of this project. The phase occurs in Types A and B1 inclusions as small tabular crystals oriented along two mutually perpendicular planes in melilitite.

UNK crystallizes from melts in dynamic crystallization experiments conducted in air from four bulk compositions modeled after Types A, B1, B2 and C inclusions. Cooling rates resulting in crystallization of UNK ranged from 0.5 to 200 °C/h from maximum (initial) temperatures of 1375 to 1580 °C. Only below 1150 °C does UNK itself begin to crystallize. To first order, the presence or absence of UNK from individual experiments can be understood in terms of the compositions of residual melts and nucleation probabilities.

Compositions of synthetic and meteoritic UNK are very similar in terms of major oxides, differing only in the small amounts of trivalent Ti (7–15% of total Ti) in meteoritic samples. UNK crystallized from the Type A analog is similar texturally to that found in CAIs, although glass, which is typically associated with synthetic UNK, is not observed in meteoritic occurrences. A low Ti end-member of UNK ("Si-UNK") with a composition near that of Ca$_3$Al$_2$Si$_4$O$_{14}$ was produced in a few samples from the Type B1 analog. This phase has not been found in the meteoritic inclusions.

INTRODUCTION

Calcium-aluminum-rich inclusions (CAIs) from carbonaceous chondrites have been studied intensely to determine physical conditions during the early history of our Solar System (MacPherson et al., 1988; and references therein). Coarse-grained CAIs, those that can be studied by standard petrographic techniques, are host to minerals formed at different stages in the evolution of the inclusions so that each mineral constrains specific aspects of the history of CAIs. This is the first in a series of three papers dealing with a new mineral, which we term "UNK" following Paque et al. (1986). This work describes the characteristics of meteoritic UNK from coarse-grained inclusions in the Allende meteorite, the conditions under which it can be produced in dynamic crystallization experiments, and the relevance of melting to the origin of meteoritic UNK. The second paper deals with the crystallography and crystal chemistry of synthetic UNK crystallized during a cooling rate experiment on a CAI bulk composition and hypotheses relating to its formation and significance to the early history of the Solar System (Barber et al., 1994). In the third paper, the space group of UNK is constrained using crystals from a mixer furnace slab (Barber and Agrell, 1994).

UNK, with the chemical formula Ca$_3$Ti(Al,Ti)$_2$(Si,Al)$_3$O$_{14}$ (see Barber et al., 1994), was first noted in synthetic slab samples by Agrell (1945) and in a CAI from the meteorite Essebi by El Goresy et al. (1984). The phase has also been noted in synthetic samples produced in several experimental studies of CAIs (Paque and Stolper, 1984; Paque et al., 1985; Beckett and Stolper, 1994; this study). More recently, Floss et al. (1992) described an unusually Ti-rich, Al-poor phase probably related to UNK from an Allende Type A inclusion.

ANALYTICAL PROCEDURES

Phases were identified and textures observed by backscattered and secondary electron imaging on a JEOL 733 microprobe at the Smithsonian Astrophysical Observatory. Chemical analyses were also performed on this microprobe. Accelerating voltage was 15 kV and sample current 15 to 30 nA as measured on a Faraday cup placed in the path of the beam. Counting times for each element ranged from 15 to 30 s for the majority of analyses, and recalibration of the raw data followed the method of Albee and Ray (1970). A glass similar in composition to a Ti-fassaite was used as an internal standard.

EXPERIMENTAL PROCEDURES

Starting Materials

CAIs are classified according to textures and relative amounts of major phases (e.g., MacPherson et al., 1988). Type A inclusions are composed mainly of melilitie, with minor amounts of spinel, hibonite, perovskite, and Ti-fassaite. They can be subdivided into compact Type A inclusions (CTA) characterized by rounded shapes and axiolitic intergrowths of melilitie, and fluffy Type A inclusions (FTA) with irregular shapes. Type B2 inclusions have sub-equai amounts of melilitie, anorthite, pyroxene, and spinel, while Type B1 inclusions are characterized by a melilitie-rich mantle surrounding a core that is petrographically similar to Type B2a. Type C inclusions are similar to Type B2a but are unusually rich in anorthite and poor in melilitie. Compact Type As and Types B and C inclusions are generally thought to have crystallized from partially molten droplets. The role, if any, of melts in the evolution of fluffy Type As is still controversial (e.g., MacPherson et al., 1988). We synthesized four bulk compositions representing the different types of Allende CAIs as part of a larger study on the crystallization properties of CAIs. The compositions represent melilitie-rich Type A ("CA": SiO$_2$, 25.8; TiO$_2$, 1.5; Al$_2$O$_3$, 32.6; MgO, 6.65; CaO, 25.7); pyroxene-rich Type B1 ("CA": SiO$_2$, 31.4; TiO$_2$, 1.13; Al$_2$O$_3$, 28.3; MgO, 9.9; CaO, 29.1) and Type B2 ("B2C": SiO$_2$, 35.7; TiO$_2$, 1.39; Al$_2$O$_3$, 27.1; MgO, 12.9; CaO, 22.4) and anorthite-rich Type C ("TC": SiO$_2$, 38.8; TiO$_2$, 1.31; Al$_2$O$_3$, 29.0; MgO, 5.77; CaO, 24.9) inclusions.

Starting materials were prepared by mixing high purity oxides and carbonates under ethanol in an automated agate mortar for 5 h or more, followed by decarbonation at 1000 °C, melting in air for one day at either 1525 °C or 1530 °C, and quenching in deionized water after removing the crucible.
through the top of the furnace. Further details on preparation of the starting materials and the experimental techniques can be found in Stolper and Paque (1986).

Crystallization Experiments

A summary of isothermal crystallization sequences for the bulk compositions used in this study can be found in Paque and Stolper (1984) along with preliminary results on the controlled cooling experiments. Crystallization behavior of the CAI bulk composition has also been studied by Stolper (1982), MacPherson et al. (1984), Stolper and Paque (1986) and Beckett et al. (1990). UNK was synthesized for this study in dynamic crystallization experiments performed in air in a vertical tube Delphen VT-31 furnace. The sample temperature was monitored with a Pt/PtRh (Type S) thermocouple calibrated against the melting points of Au (1064 °C) and Fe (1554 °C) and placed in the hot spot adjacent to the samples. In each experiment, several powdered samples of the synthetic material were suspended in the hot spot using Pt loops. Samples were held for 3 h at the maximum temperature of the experiment (1430 °C) then cooled at a controlled, approximately linear rate. Individual samples were quenched in deoxygenated water at various temperatures along the cooling path in order to determine the temperature of appearance for individual phases and the liquid line of descent.

RESULTS

Meteoritic Occurrence of UNK

A survey of 20 coarse-grained Allende CAIs (four compact Type As, two fluffy Type As, eleven Bls, and three B2s) was conducted to determine the extent to which UNK occurs in natural materials and the variability in its composition and nature of occurrence. The search was carried out using a JEOL 733 electron microprobe. Initially, the sample was scanned using backscattered electron (BSE) imaging to locate potential grains of UNK, which has a lower BSE albedo than perovskite, but higher than melilitc, anorthite, spinel, and all but the most Ti-rich fassailes (>15 wt% TiO2) due to its high mean atomic number (2). Energy dispersive spectroscopy (EDS) was then used to confirm the identification of UNK. Final analyses were made by wavelength dispersive spectroscopic (WDS) analysis. UNK is a minor constituent of approximately half of the Type A and Type B1 inclusions examined. It was positively identified in one CTA (4691), one FTA (A-WPl), and six Type Bls (3529-30, 3529-33, 3529-41, 3655A, 3658, 3682). No likely candidates for UNK grains were observed in CTAs 3643 or 3898, FTA 3529-46, Bls 3529Y, 3529Z, 3529-21 or 3529-31, or B2s All-201, RB-B3I or 3529-32. For two inclusions, CTA 3529-45 and the Type B1 3732-1, the grain size (<1 μm) of phases tentatively identified as UNK was so small that it was not possible to demonstrate conclusively that the grains were UNK. In the Type A CAIs, UNK can be found in melilitc throughout the inclusion. In Type Bls, UNK occurs only in the melilitc mantle and is most commonly found in regions close to the rim (i.e., the outer quarter of the melilitc-rich mantle) of the inclusion. UNK was not observed in any of the Type B2 inclusions surveyed, although the sample set included only three inclusions. Type C inclusions were not studied as part of this project.

Petrography of Meteoritic UNK—All of the meteoritic UNK crystals are enclosed in melilitc. The crystals are typically tabular in thin section (Fig. 1a), although occasionally they occur as anhedral crystals embedded in melilitc (Fig. 1b). Crystals of UNK are often found at the intersection of two perpendicular planes of cleavage ([001] and [110]; cf. Deer et al., 1992) in melilitc. There are usually several to many grains within different melilitc crystals in a given CAI, all less than 10 μm in maximum dimension. They are colorless in plane polarized light, and the larger crystals display third order interference colors under crossed nicols consistent with indices of refraction measured by Barber and Agrell (1994) on synthetic crystals of UNK from a mixed furnace slag. Extinction is parallel to the length of the crystals, and the reflectivity is slightly higher than that of fassaile.

Chemistry of Meteoritic UNK and Coexisting Melilitc—Table 1 shows representative analyses of UNK from meteorite samples. The phase contains subequal amounts of CaO (29–32 wt%), SiO2 (24–28%), and TiO2 (20–27%) with less Al2O3 (16–20%) and very low MgO (<1%). Calcium consistently represents one-third of the cations present, and deviations in analyses from Ca + Mg = 3.0 cations in a formula unit based on 9.0 cations can be attributed to contamination of the analyses by surrounding melilitc. Figure 2a shows cations of Si vs. cations of Ti for UNK analyses from Type B1 inclusions with 3.00 ± 0.05 cations of Ca in a formula unit based on 14 oxygens. All of the analyses plot close to, but slightly above, the Si + Ti = 4.0 line, probably a consequence of assuming that all Ti is tetravalent. If a stoichiometry of 9 cations and 14 oxygens is assumed and the valence state of Ti allowed to float, then analyses are consistent with the presence of small amounts, 7–13%, of trivalent Ti. Due to the limited spatial resolution of the electron microprobe, zoning can be characterized only in the largest crystals in Type B1 inclusions. These are consistent with slightly higher Ti in the core relative to the rim (Fig. 3a).

In Fig. 4, compositions of meteoritic UNK are cast in terms of the three components:

(Ca,Mg)3Ti4+Al5Si2O12, (Ca,Mg)3Al5Si2O12 and

![Fig. 1. Backscattered electron (BSE) images of UNK from Allende Type B1 inclusions. (a) NMNH 3682. Tabular crystals of UNK are oriented with long direction parallel to the c-axis in the melilitc (MEL). (b) NMNH 3529-41. This is the largest meteoritic grain of UNK found to date.](image-url)
Each open symbol represents the average of all UNK analyses obtained from an individual CAI, corrected for melilite contamination and variable TiO$_2$/Ti$^{IV}$ by requiring that the formula unit have 3.00 Ca + Mg cations, 9 total cations and 14 oxygens. The meteoritic UNKs are composed mostly of Ca$_3$TiO$_4$ with lesser amounts of (Ca,Mg)$_3$Al$_2$Si$_4$O$_{14}$ and Ca$_3$Ti$^{III}$Ti$_2$Si$_3$O$_{14}$. The calculated mole fraction of Ca$_3$Ti$^{III}$Ti$_2$Si$_3$O$_{14}$ is sensitive to the assumed composition of co-existing melilite and the MgO wt% in the analysis, leading to uncertainties on the order of ±5 mol%. There are no obvious compositional differences among UNKs from different classes of CAIs, but all are consistent with the presence of small amounts of trivalent Ti and, therefore, growth under reducing conditions.

Melilite in CAIs is essentially a binary solid solution between the end-member components gehlenite (Ge: Ca$_2$Al$_2$Si$_2$O$_7$) and åkermanite (Ak: Ca$_2$Mg$_2$Si$_2$O$_7$). When viewed in transmitted cross-polarized light, UNK crystals often appear to be surrounded by a halo of anomalously birefringent melilite relative to nearby portions of the host melilite crystal. This is borne out by measured melilite compositions at melilite-UNK contacts, which are highly variable (Ak$_{12}$ to Ak$_{56}$) but generally (Fig. 5b), though not always (Fig. 5a), more magnesian than expected based on regional zoning of the melilite. The zoning profile shown in Fig. 5b is for melilite in the vicinity of the UNK crystal depicted in Fig. 1b.

**Synthetic UNK**

Conditions of Formation and Chemistry—UNK is an occasional constituent of run products from cooling rate experiments from all four bulk compositions under conditions summarized in Fig. 6, but absent from all isothermal experiments. Typically, several samples were run under the same conditions of initial temperature ($T_{in}$) and cooling rate (CR), then quenched at various temperatures. UNK was noted as being present in Fig. 6 if any of the samples produced under the stated conditions of $T_{in}$ and CR contained the phase. To eliminate from consideration run sequences that did not include samples cooled to temperatures low

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**FIG. 2. Relationship between Ti and Si in UNK, based on a total of 9 cations, for all analyses with Ca = 3.00 ± 0.05 cations. The solid line indicates Si + Ti = 4.0.**

(a) Meteoritic Type B1 and (b) Synthetic.
The synthetic UNK is characterized by its textural and compositional variations. Ti-rich varieties (UNK) are similar to those found in meteoritic CAIs and are characterized by high Ti and low Si contents. Si-rich varieties (Si-UNK) are similar to Si-bearing meteoritic CAIs and are characterized by high Si and low Ti contents. The data for TCAN (Fig. 6d) is insufficient to characterize the crystallization behavior of UNK.

The natural UNK occurs in two distinct compositional varieties: a Ti-rich variety (UNK) similar to that found in meteoritic samples that can be described in terms of the two components $\text{Ca}_6\text{Al}_2\text{Si}_4\text{O}_{14}$ and $\text{Ca}_6\text{Ti}_2\text{Al}_2\text{Si}_4\text{O}_{14}$ and a Ti-poor, Si-rich variety (Si-UNK) on the same composition line, essentially $\text{Ca}_6\text{Al}_2\text{Si}_4\text{O}_{14}$. Like its meteoritic counterpart, synthetic UNK is characterized by high Ti and low Si contents, similar to that found in meteoritic CAIs with cores higher in Ti and lower in Si than rims (Fig. 3b). Mellitite surrounding larger UNK crystals is also a prominent feature in our samples, similar to that found surrounding UNK crystals in some Type B1 CAIs. In Fig. 2b, cations of Si are plotted vs. cations of Ti for synthetic UNK and Si-UNK analyses with $\text{Ca} = 3.0 \pm 0.05$. The analyses all fall near the $\text{Si} + \text{Ti} = 4.0$ line on the graph. These analyses plotting significantly above the line reflect contamination by intergrowths of mellitite, glass, anorthite, pyroxene, and a poorly characterized high Z phase. Compositions of meteoritic and synthetic UNKs are very similar with overlapping ranges in major oxides (Table 2; Fig. 2). Only in Ti$^{3+}$ contents are there significant differences (Fig. 4). The Si-UNKs crystallized in our experiments are compositionally distinct from both the Ti-rich meteoritic and synthetic UNK. This phase is characterized by 4 cations of Si in a formula unit based on a total of 9 cations and contains very little Mg or Ti (Table 2, Fig. 2b). It is possible that Si-UNK and UNK analyses shown in Fig. 4 lie on opposite limbs of a miscibility gap.

**Textural Relationships**—In an individual experimental charge, UNK occurs in one and only one of the four distinct petrographic associations illustrated in Fig. 7 and summarized by run conditions in Fig. 6. (1) UNK may occur as small (several $\mu$m) tabular crystals oriented along planes in melilitic or filling the acute ends of glass pockets (Fig. 7a). This type of occurrence is observed in experiments on the 98 bulk composition (Fig. 6c). The data base for TCAN (Fig. 6d) is insufficient to characterize the crystallization behavior of UNK.

(2) Synthetic UNK from the 98 bulk composition can also form thin ($5-10 \mu$m) rims on melilitic laths along with small prismatic crystals protruding from the ends of the melilitic laths (Fig. 7b). (3) In CAI experiments, UNK is typically part of an intergrowth containing anorthite, melilitic, pyroxene and UNK (Fig. 7c). One experiment on B2C also produced this texture. (4) UNK frequently crystallizes from the residual liquid between major phases in the sample (Fig. 7d). There is no obvious correlation between composition and textural type among the Ti-rich UNK.

The textural habit of Si-UNK is quite different from the Ti-bearing variety, appearing as a fibrous mass when viewed in...
Factors Controlling the Crystallization of UNK in Experiments—Based on our results, UNK crystallizes from residual melts derived from a variety of CAI bulk compositions analogous to those of meteoritic inclusions, but the factors controlling the appearance of UNK are subtle because several sets of samples from the CAI of meteoritic inclusions, but the factors controlling the appearance of UNK are subtle because several sets of samples from the CAI bulk composition with identical T<sub>max</sub>, cooling rate, and quench of UNK are comparable.

However, some of the UNK-bearing glasses are not in equilibrium with spinel, based on the reaction

\[
4\text{MgAl}_2\text{O}_4(\text{sp}) + 7\text{Ca}_3\text{Al}_2\text{Si}_4\text{O}_{12}(\text{Si-UNK}) = 4\text{Ca}_2\text{MgSi}_2\text{O}_7(\text{Ak}) + 9\text{CaAl}_2\text{Si}_2\text{O}_{5}(\text{an}) + 2\text{Ca}_2\text{Al}_2\text{SiO}_5(\text{Oc})
\]

Equation (1) is, therefore, an inappropriate basis for interpreting our experiments. We can nevertheless crudely constrain the thermodynamic properties of the phase based on exchange equilibria involving components in the melt (liq). For the Ca<sub>3</sub>Al<sub>2</sub>Si<sub>4</sub>O<sub>14</sub> component (cf. Fig. 4), the reaction

\[
3\text{CaO}(\text{liq}) + 2\text{Al}_2\text{O}_3(\text{liq}) + 4\text{SiO}_2(\text{liq}) = \text{Ca}_3\text{Al}_2\text{Si}_4\text{O}_{14}(\text{UNK})
\]

Equation (2) is applicable. An equilibrium constant for reaction (2) can be written

\[
\ln K_2 = \ln \left( \frac{[\text{UNK}]}{[\text{CaO}]^3 [\text{Al}_2\text{O}_3] [\text{SiO}_2]^4} \right) = -\frac{\Delta G^0}{RT} - 20
\]

Equations (3).
or upon rearranging,

\[ \ln K^{(2)} = 3 \ln (a_{\text{CaSiO}_3}) + \ln (a_{\text{Al}_2\text{Si}_2\text{O}_7}) + 4 \ln (a_{\text{SiO}_2}) = \frac{\Delta_0^G}{RT} + \ln (a_{\text{UNK}_{\text{Si}}/\text{UNK}_{\text{UNK}}}). \tag{4} \]

**TABLE 2.** Selected analyses of UNK and Si-UNK from synthetic samples.

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Cations based on total = 9

\[
\begin{align*}
\text{Si} & = 2.29, 3.92, 2.57, 2.60, 2.54, 2.41, 2.35, 2.44 \\
\text{Ti} & = 1.77, 0.05, 1.40, 1.34, 1.33, 1.59, 1.57, 1.62 \\
\text{Al} & = 1.87, 1.96, 1.98, 2.05, 2.03, 1.89, 2.02, 1.86 \\
\text{Mg} & = 0.09, 0.08, 0.08, 0.01, 0.04, 0.05, 0.04, 0.09 \\
\text{Ca} & = 2.97, 3.00, 3.00, 3.03, 3.06, 3.05, 3.08, 2.99 \\
\text{Si + Ti} & = 4.06, 3.97, 3.97, 3.94, 3.87, 4.00, 3.92, 4.06
\end{align*}
\]

\* Cooling rate.

In Equations (3) and (4), \( a_j \) refers to the activity of component \( j \) in phase \( j \), \( \Delta_0^G \) to the standard state free energy of reaction for equilibrium (2), \( R \) to the gas constant and \( T \) to the temperature in degrees K. The activity-composition relationships for UNK solid solutions are not known so activity and standard state terms on the right hand of Eq. (4) cannot be separated. \( K_\alpha \) is that part of the equilibrium constant arising from activities of components in the melt. Given that the range in composition of the synthetic UNK is small (Fig. 4) and a \( \alpha_i \) may therefore be approximately constant, \( K_\alpha \) may in fact be approximately constant for a given temperature. Using Berman's (1983) activity model for silicate melts (assuming that all Margules parameters involving TiO_2 are zero), \( K_\alpha \) was evaluated for synthetic glasses and plotted against inverse temperature for glass compositions from UNK-bearing and UNK-absent run products in Fig. 9a. A linear regression line,

\[
\ln K_\alpha = 3 \ln (a_{\text{SiO}_2}) + \ln (a_{\text{Al}_2\text{Si}_2\text{O}_7}) + 4 \ln (a_{\text{SiO}_2}) = -12.5 - \frac{1.84 \times 10^4}{T}
\]

for the UNK-bearing experiments is also shown. We emphasize that this expression incorporates both standard state (free energy of formation from the solid oxides) and activity terms for the Ca_2Al_2SiO_5 component in UNK (cf. Eq. 4). This treatment also implicitly assumes that the composition of glass measured at some distance from crystals is the relevant measure of UNK stability.
COMPOSITION CRISTALLISÉ, THE RESIDUAL MELT MOVES TO THE RIGHT IN THE SEQUENCE. THE BASIS FOR OUR TREATMENT IS THAT AS A PARTICULAR BULK THE APPEARANCE SITION.

UNK COMPONENT FOR COEXISTING LINK AND MELT TOGETHER WITH FOUR UNK IS NOT OBSERVED IN THESE EXPERIMENTS UNK IS UNDERSATURATED WITH RESPECT TO Si-LINK, AND MOST OF THE COOLING RATE EXPERIMENTS PLOT BELOW THE LINE IN Fig. 9a (AT LOWER VALUES OF I/T) AND, THEREFORE, ARE PREDICTED TO BE UNK. KEEPING THESE CAVEATS IN MIND, CAI-LIKE MELTS WITH LN K&o_lock SATURATION MAY NOT BE POSSIBLE IN A SPECIFIC INSTANCE BECAUSE THE Ti-CONTENT OF THE MELT MAY BE INSUFFICIENT TO STABILIZE Ti-BEARING UNK WITH THE APPROPRIATE LN K&o_lock. THE PRESENT ANALYSIS, THEREFORE, SHOULD BE VIEWED AS PROVIDING NECESSARY BUT INSUFFICIENT CONDITIONS FOR THE STABILITY OF UNK. KEEPING THESE CAVEATS IN MIND, CAI-LIKE MELTS WITH LN K&o_lock PLOTTING BENEATH A PARTICULAR ISOACTIVITY LINE WILL TO FIRST ORDER BE UNDERSATURATED WITH RESPECT TO UNK OF A GIVEN ACTIVITY, AND HENCE OF SOME COMPOSITION, PROVIDED THAT A LN K&o_lock IS PHYSICALLY ACHIEVABLE. MELTS WITH LN K&o_lock PLOTTING ABOVE AN ISOACTIVITY LINE WILL BE SUPER-SATURATED WITH RESPECT TO UNK. ANY MELT WITH LN K&o_lock PLOTTING ABOVE THE A LN K&o_lock = 1 LINE WILL BE SUPER-SATURATED WITH RESPECT TO Si-RICH UNK REGARDLESS OF THE UNK COMPOSITION.

FOR ILLUSTRATIVE PURPOSES, WE CONSIDER A "ZONE", REPRESENTED BY THE UNK-SATURATED POINTS IN Fig. 9a AND BY THE ROUGHLY PARALLEL LINES OF CONSTANT A LN K&o_lock IN Fig. 9b, WHERE SATURATION WITH RESPECT TO UNK IS POSSIBLE. UPON COOLING OF A DROPLET OF CAI BULK COMPOSITION FROM ABOVE THE LIQUIDUS, FIRST SPINEL AND THEN MELILITE + SPINEL CRYSTALLIZE WITH DECREASING TEMPERATURE. THE MELT CHANGES COMPOSITION, BUT LN K&o_lock INCREASES ONLY SLIGHTLY BASED ON LIQUID LINES OF DESCENT DETERMINED EXPERIMENTALLY. IN PATH A, UNK SATURATION IS REACHED BEFORE ANY OTHER ADDITIONAL PHASES CRYSTALLIZE. UNK CRYSTALLIZES, AND LN K&o_lock CHANGES ALONG AN UNK-SATURATED PATH. IN DETAIL, A LN K&o_lock CHANGES AS THE COMPOSITION OF UNK AND OTHER PHASES CHANGE, BUT THE PRECISE PATH IS NOT QUANTIFIED BY OUR EXPERIMENTS. IN PATH B, PYROXENE CRYSTALLIZES BEFORE UNK, AND LN K&o_lock DECREASES RELATIVE TO A PYROXENE-ABSENT LIQUID LINE OF DESCENT. THIS HAS THE EFFECT OF DELAYING THE APPEARANCE OF UNK OF A GIVEN SATURATION.
a peak to lower temperatures. If pyroxene begins to crystallize early enough, UNK saturation may be delayed to such low temperatures that UNK never crystallizes (path C). It is possible that anorthite has an effect similar to that of pyroxene, although our data are insufficient to confirm this. In path D, no additional phases join melilite and spinel and eventually the melt becomes supersaturated with respect to UNK (as well as for other phases such as anorthite and pyroxene).

The four paths illustrated schematically in Fig. 9b can also help to rationalize the association of UNK with particular ranges in experimental conditions (Fig. 6) because they are crudely correlated with \( T_{\text{max}} \) and cooling rate. For CAI experiments cooled at intermediate to rapid cooling rates from \( T_{\text{max}} \approx 1420 ^\circ \text{C} \), near melilite saturation for the CAI bulk composition (Stolper, 1982), the liquid line of descent intersects the temperature-liquid composition regime within which UNK can crystallize because the appearances of anorthite and fassaite are delayed so that UNK is stabilized at relatively high temperatures (e.g., path A in Fig. 9b) and, therefore, can crystallize provided appropriate nucleation sites are available. UNK crystallization for \( T_{\text{max}} \approx 1420 ^\circ \text{C} \) is unlikely at the highest cooling rates because, although the liquid compositions pass through an appropriate region of \( \ln K_{\text{CaO}} - 1/T \) for UNK crystallization, there is insufficient time for nucleation of UNK (or indeed of pyroxene or anorthite in many cases). At higher \( T_{\text{max}} \), crystallization of all of the silicates including UNK are greatly suppressed relative to their equilibrium appearance temperatures (Stolper and Paque, 1986) due to destruction of nuclei. Therefore, the probability that UNK will crystallize is

![TABLE 3. Comparison of glass analyses from CAI bulk composition samples with and without UNK, all other conditions equal.](image)

<table>
<thead>
<tr>
<th>Run #</th>
<th>263</th>
<th>264*</th>
<th>265*</th>
<th>288</th>
<th>287*</th>
<th>290</th>
<th>289*</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_{\text{max}} ) (ºC)</td>
<td>1420</td>
<td>1420</td>
<td>1420</td>
<td>1420</td>
<td>1420</td>
<td>1420</td>
<td>1420</td>
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<tr>
<td>CR (ºC)*</td>
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<td>2</td>
<td>2</td>
<td>50</td>
<td>50</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>( T_{\text{melit}} ) (ºC)</td>
<td>1048</td>
<td>1048</td>
<td>1048</td>
<td>1117</td>
<td>1117</td>
<td>1059</td>
<td>1059</td>
</tr>
<tr>
<td>UNK*</td>
<td>yes</td>
<td>no</td>
<td>no</td>
<td>yes</td>
<td>yes</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>

Oxide wt%:

- **SiO₂**: 42.7, 44.8, 44.9, 42.3, 43.3, 42.3, 45.9
- **TiO₂**: 1.37, 0.58, 0.55, 3.53, 1.53, 3.23, 1.75
- **Al₂O₃**: 18.2, 20.3, 21.9, 20.9, 19.2, 21.9, 14.0
- **MgO**: 10.8, 1.05, 0.71, 5.8, 3.93, 4.79, 1.30
- **CaO**: 27.0, 31.3, 29.7, 25.7, 30.7, 24.5, 34.3
- **Total**: 100.1, 98.0, 97.8, 98.2, 97.7, 96.7, 97.3

* Average of two analyses.
† Cooling rate.
** All samples containing UNK have the phase assemblage glass + spinel + melilite + Ti-fassaite + anorthite. Samples without UNK have the phase assemblage glass + spinel + melilite + Ti-fassaite. CAI-289 also contains anorthite.

**Fig. 8.** wt% CaO vs. wt% MgO in glass from CAI experiments. Lines join samples with and without UNK that were run under identical conditions at the same time.

**Fig. 9.** Stability of UNK. (a) Experimental results. Oxide activities in the melt were obtained using Berman's (1983) model and are relative to solid lines, corundum and cristobalite. Closed squares represent UNK-bearing controlled cooling rate experiments in which the phases spinel, melilite, pyroxene, anorthite, UNK and glass are all present. Isothermal experiments (open circles) and cooling rate experiments (open triangles) for which UNK was not observed, represent various phase assemblages. (b) Four schematic liquid lines of descent for an initially molten liquid of bulk CAI composition in terms of \( \ln K_{\text{CaO}} - 1/T \). Curve A: spinel + spinel + melilite + spinel + melilite + UNK (pyroxene fails to nucleate before UNK; intermediate to high \( T_{\text{max}} \), low to intermediate cooling rates). Curve B: spinel + spinel + melilite + spinel + melilite + pyroxene + spinel + melilite + pyroxene + UNK (pyroxene crystallizes before UNK and delays but does not prevent later UNK crystallization; intermediate \( T_{\text{max}} \) and cooling rate). Curve C: spinel + spinel + melilite + spinel + melilite + pyroxene (pyroxene appears at a high enough temperature to completely suppress UNK crystallization; low \( T_{\text{max}} \) and cooling rate). Curve D: spinel + spinel + melilite (pyroxene and UNK fail to nucleate; high \( T_{\text{max}} \) and cooling rate). Thermal histories in which one or both of melilite and spinel failed to nucleate (i.e., high \( T_{\text{max}} \) with very fast cooling rates) would lead to paths similar to D though with somewhat different slopes.
reduced at all cooling rates (path D in Fig. 9b). At lower \( T_{\text{max}} \) and cooling rates, pyroxene begins to crystallize at a higher temperature (paths B and C in Fig. 9b) so that the appearance of UNK is suppressed as discussed above. UNK may still crystallize (curve B) if cooling rates are not so slow that the early appearance of pyroxene leads to entirely suppressing UNK stability under igneous conditions (curve C). The probability of encountering UNK therefore decreases for both higher and lower \( T_{\text{max}} \) and for very high cooling rates. The data base is less complete for the B2C and 98 bulk compositions but the results are consistent with the same basic behavior.

**Origin of UNK**

There are several possible modes of origin for UNK in meteorites, including crystallization from a late-stage residual liquid, exsolution from the enclosing melilite, or alteration. It should be emphasized that different occurrences of meteoritic UNK may have different modes of origin. Here, we address the possibility that meteoritic UNK crystallized from a melt. A general discussion of other possibilities is given in Barber *et al.* (1994)

Based on Fig. 9a, UNK will not be stabilized as a near-liquidus phase for any of the Types A, B, or C inclusions described by Wark (1981), Wark and Lovering (1982), Beckett (1986), or Wark (1987) because the decomposition temperature is too low. The dynamic crystallization experiments demonstrate that UNK with composition very similar to meteoritic examples can crystallize from a range of bulk compositions representing these CAIs but only from very late-stage liquids after extensive crystallization of melilite and spinel + anorthite + fassaite, which drive the residual liquid near to UNK saturation. If meteoritic UNK crystallized from a melt, it, therefore, must have formed late in the crystallization sequence, but this poses potential problems for meteoritic occurrences of UNK described in this work. UNK is included in texturally early melilitic at least in Type B1 inclusions (i.e. it is preferentially in the outer portions of the melilite mantle), although it is possible that meteoritic UNK in the melilite mantle is actually a late-crystallizing phase analogous to fassaite inclusions in mantle melilitic (MacPherson *et al.*, 1984; Simon *et al.*, 1991) and the increase in \( X_{\text{AK}} \) near UNK inclusions (Fig. 5b) is consistent with this. If meteoritic UNK formed by such a mechanism, then extreme rare earth element (REE) enrichments would be expected whereas its REE content would be expected to be low if it had exsolved from the surrounding melilitic. The UNK described by El Goresy *et al.* (1984) is REE enriched and, therefore, consistent with crystallization from a melt, but the host inclusion is so unusual that it is not possible based on this occurrence to make general inferences about occurrences of UNK in the Allende CAIs described here. There are currently no REE analyses of UNK from these CAIs. Another problem with crystallization of meteoritic UNK from a melt is that glass is often associated with UNK included in melilitic in experimental samples, but this feature is not observed in CAIs. Floss *et al.* (1992) described a phase similar to UNK occurring as symplectic intergrowths in a Compact Type A inclusion apparently replacing perovskite. The phase is enriched in REE and although subsolidus reactions may be responsible, crystallization from near-solidus melts is a more likely origin for this type of texture.

Regardless of its origin the invariably low Mg and relatively high Al contents of UNK make it potentially useful for \( ^{26} \text{Al} \) studies analogous to those on corundum and anorthite (Podosek *et al.*, 1991; Virag *et al.*, 1991). The grains may yield useful information on the timing of whatever event produced them. Finally, it is worth noting that if a significant proportion of the Ti in meteoritic UNK coexisting with perovskite is trivalent (e.g., Floss *et al.*, 1992), then quantitative calibration of oxygen barometers such as

\[
3 \text{Ca}_3 \text{Ti}^{4+} \text{Al}_1 \text{Si}_3 \text{O}_{14} - 3 \text{CaTiO}_3 = \\
3 \text{Ca}_2 \text{Al}_2 \text{Si}_7 \text{O}_{22} + 2 \text{Ca}_3 \text{Ti}^{4+} \text{Al}_1 \text{Si}_3 \text{O}_{14} + \text{O}_2
\]

could provide useful insight into redox conditions.

**CONCLUSIONS**

UNK is found as small, tabular inclusions in melilite in approximately half of the Type A and B1 CAIs examined. It contains small amounts of \( \text{Ti}^{4+} \) (7-13\% of total Ti) suggesting growth under reducing conditions. UNK of similar composition is produced in dynamic crystallization experiments over a well-defined range of maximum temperatures and cooling rates. The crystallization of UNK from CAI-like bulk compositions requires residual melt compositions unlike those found under equilibrium conditions, thereby explaining its restriction to dynamic crystallization experiments, which generate a wider range of liquid compositions, some of which reach saturation with respect to UNK.

**REFERENCES**


A new titanium-bearing calcium aluminosilicate phase: II. Crystallography and crystal chemistry of grains formed in slowly cooled melts with bulk compositions of calcium–aluminum-rich inclusions

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Abstract—The crystallography and crystal chemistry of a new calcium-titanium-aluminosilicate mineral (UNK) observed in synthetic analogs to calcium-aluminum-rich inclusions (CAIs) from carbonaceous chondrites was studied by electron diffraction techniques. The unit cell is primitive hexagonal or trigonal, with $a = 0.790 \pm 0.002$ nm and $c = 0.492 \pm 0.002$ nm, similar to the lattice parameters of melilitic and consistent with cell dimensions for crystals in a mixer furnace slag described by Barber and Agrell (1994). The phase frequently displays an epitactic relationship in which melilite acts as the host, with $(001)_{\text{UNK}} \parallel (001)_{\text{host}}$ and $<100>_{\text{UNK}} \parallel <100>_{\text{host}}$. If one of the two space groups determined by Barber and Agrell (1994) for their sample of UNK is applicable (P3m1 or P31m), then the structure is probably characterized by puckered sheets of octahedra and tetrahedra perpendicular to the $c$-axis with successive sheets coordinated by planar arrays of Ca. In this likely structure, each unit cell contains three Ca sites located in mirror planes, one octahedrally coordinated cation located along a three-fold axis, and five tetrahedrally coordinated cations, three in mirrors and two along triads. The octahedron contains Ti but, because there are 1.3–1.9 cations of Ti/formula unit, some of the Ti must also be in tetrahedral coordination, an unusual but not unprecedented situation for a silicate. Tetrahedral sites in mirror planes would contain mostly Si, with lesser amounts of Al while those along the triads correspondingly contain mostly Al with subordinate Ti. The structural formula, therefore, can be expressed as

$\text{Ca}_7\text{Ti}_2\text{Al}_9\text{Si}_{11}\text{O}_{32}$

with Si + Ti = 4. Compositions of meteoritic and synthetic Ti-bearing samples of the phase can be described in terms of a binary solid solution between the end-members Ca$_4$TiAl$_3$Si$_4$O$_{14}$ and Ca$_4$Ti(Si$_4$O$_{14}$)$_2$Al$_2$. A Ti-free analog with a formula of Ca$_4$Al$_2$Si$_4$O$_{14}$ synthesized by Paque et al. (1994) is thought to be related structurally but with the octahedral site being occupied by Al, that is,

$\text{Ca}_7\text{Ti}_2\text{Al}_9\text{Si}_{11}\text{O}_{32}$

INTRODUCTION

Coarse-grained calcium-aluminum-rich inclusions (CAIs) in carbonaceous chondrites have chemical and isotopic signatures indicative of processes dating back to the origin and earliest evolution of the Solar System (see Grossman, 1980 and MacPherson et al., 1988 for reviews). The mineralogy is generally dominated by a combination of one or more of clinopyroxene, melilitic, spinel, anorthite, hibonite and perovskite. For each phase, the compositions and textures reflect the history of the host inclusion and can be used to impose constraints on physical conditions early in the Solar System. There are, in addition, various minor and trace minerals in CAIs including a new Ca-Ti-Al silicate described by El Goresy et al. (1984) and Paque et al. (1986). This phase could also contain genetic information about CAIs, but the crystal structure, phase relations, thermodynamic and kinetic properties that might allow such information to be extracted have not been characterized. In this study, we consider the crystal structure of the phase. The mineral remains unnamed because there are no X-ray diffraction (XRD) data currently available on the natural material, but for the purposes of this paper, we refer to the phase as UNK.

UNK is a ubiquitous, albeit minor, constituent of coarse-grained melilitic-rich (Type A: Grossman, 1975) and fassaitite-rich (Type B) CAIs. In occurrences of UNK reported thus far (El
Goresy et al., 1984; Paque et al., 1986, 1994), only small (<40 μm diameter) grains enclosed in melilitte have been observed. Larger (~100 μm) grains of a phase similar to UNK in a Type A inclusion from Allende were described by Floss et al. (1992), but these crystals have higher Ca contents than UNK and different cell dimensions (A. E. Goresy, pers. comm., 1992). Optically, UNK can be distinguished from fassaite, which has similar relief and reflectivity, by a lack of pleochroism, the presence of parallel extinction, and, in the largest grains, by indices of refraction determined by Barber and Agrell (1994). Colors, extinction and, in the largest grains, can be consistent with indices of refraction determined by Barber and Agrell (1994) on synthetic crystals from a mixer furnace slag. UNK is also chemically distinctive. The formula, based on 14 oxygens, can be represented by Ca₂₆Ti₂₂(Si₆₆Al₆₆)O₇₈, although neither the two sites occupied by Al + Ti nor the three sites occupied by Al + Si are necessarily crystallographically equivalent. With TiO₂ contents greater than 20 wt%, UNK is more titanium than all but the most Ti-rich of fassaites in CAIs, while MgO contents are quite low (<1 wt%), contrasting with the ~5–10 wt% MgO typical of the fassaites. Rhönite, another Ca-Al-Ti-rich phase occasionally encountered in CAIs (Fuchs, 1978) is strongly pleochroic and distinguishable chemically from UNK by its much higher MgO (~17 wt% vs. <1) and lower CaO (~18 wt% vs. ~31) contents.

Synthetic crystals with compositions and optical properties very similar to those of meteoritic UNK were produced as a late-crystallizing phase in cooling rate experiments on a variety of CA-like bulk compositions (Paque and Stolper, 1984; Stolper and Paque, 1986; Beckett and Stolper, 1994; Paque et al., 1994). In these experiments, a powdered glassy starting material was held at a maximum temperature, usually for 3 h, cooled at a constant rate and then quenched into deionized H₂O. UNK was produced over a wide range of maximum temperatures and cooling rates for these bulk compositions (Paque et al., 1994). Its occurrence in these experiments was controlled by the generation of residual melt compositions that intersect the UNK stability field and possibly by nucleation probabilities (Paque et al., 1994). Attempts to crystallize UNK from melts with bulk compositions approximating those of UNK failed due to the crystallization of large amounts of perovskite (i.e., UNK is unstable in a melt of its own composition).

This is the second of three papers describing the crystal chemistry and petrogenesis of UNK. In the first paper (Paque et al., 1994), the characteristics of meteoritic and synthetic UNK and the conditions under which they can be produced are described. In this paper, we report the results of chemical and structural characterization of UNK from the run product of a cooling rate experiment on bulk composition 98 (Paque and Stolper, 1984), an analog for Allende inclusion USNM 3898 and typical of compact Type A CAIs or unusually melilitite-rich Type B1s. The small grain sizes and great difficulty of obtaining reasonably pure separates of UNK precluded a structure determination by routine XRD methods. We, therefore, explored the crystal structure by using conventional electron diffraction and convergent beam electron diffraction (CBED) in conjunction with analytical transmission electron microscopy (ATEM). In the third paper of this series (Barber and Agrell, 1994), an occurrence of UNK from a furnace slag is described. Using CBED methods (Steeds, 1979; Williams, 1984; Champness, 1987), we establish that the space group of crystals from the slag is either P3m1 or P31m; therefore, we use four-digit Miller-Bravais indices and hexagonal axes throughout this paper in describing the crystallography of UNK.

**EXPERIMENTAL PROCEDURES**

**Synthesis**

Experimental procedures were similar to those described by Stolper and Paque (1986). Starting materials were synthesized by weighing out appropriate amounts of Na₂CO₃ and the oxides MgO, SiO₂, TiO₂ and Al₂O₃ (all ALFA Puratronic) for the bulk composition of interest, followed by grinding in an automatic agate mortar under ethanol for 5 h, decarbonation at ~1100 °C for 2 days and melting in a Pt crucible for 30 h in air at ~1585 °C. Experiments were conducted in air in a home-built MoSi₂ vertical tube furnace. Temperatures were measured using a bare Pt/Pt-10Rh thermocouple and were controlled by a Eurotherm Model 818 programmer. To produce sufficient quantities of UNK for characterization, by transmission electron microscopy (TEM), a large volume (~1 g, sample designated 86C-4) of the 98 bulk composition was held in a Pt crucible at 1500 °C for 3 h, cooled at 20 °C/h to 946 °C and quenched through the top of the furnace into deionized H₂O. Previous work (Paque et al., 1994) had shown that UNK would crystallize from the 98 bulk composition if subjected to such a thermal history, and indeed, the run product consisted mostly of melilitte, lesser amounts of fassaite and spinel, and trace UNK.

**Electron Microprobe Analysis and Scanning Electron Microscopy**

Wavelength dispersive analyses were carried out on an electron microprobe designed and constructed in the Department of Earth Sciences at the University of Cambridge with an Si(Li) detector and a 40° take-off angle linked to a Hewlett Packard 370D pulse processor and interfaced to a Nova 2 minicomputer. It was operated at 20kV and gives a relative precision of ~2% for major elements (i.e., those elements at >5 wt%).

**Transmission Electron Microscopy**

The run product from 86C-4 was coarsely crushed, chunks were mounted in epoxy resin, ground flat and then polished. The polished surfaces were examined by reflected light microscopy, and the positions of UNK crystals as judged by relief and contrast were noted and photographed. Each mount was then coated with Pt-Au and examined in an SEM equipped with an energy dispersive analyzer in order to confirm the identity of UNK in the polished face. Hereafter called face A. A typical example is shown in Fig. 1. Mounts that contained the UNK phase were then cemented, face A downwards, onto glass slides by means of "Crystabond" resin and reduced in thickness to about 40 μm by grinding and polishing. The resulting thin sections were demounted, and all traces of the resin removed with acetone. Finally, aperture-type Cu electron microscope grids, with hole diameters of either 0.4 or 0.6 mm, were resin-bonded to the A-faces of pieces of the thin sections, thereby positioning an UNK crystal centrally within each aperture.

Ion-beam-milling from opposite the A-face was used to erode the specimen surface until the material was very thin in the proximity of the UNK phase. Both ion beam sources were then used for final milling to electron transparency. This process was not straightforward because UNK is usually surrounded by melilitte, which spatters away faster than any other phase in the sample and also tends to crack during ion milling. As a result, UNK crystals were often lost.

![Fig. 1. Back-scattered electron SEM image of prismatic UNK grain together with spinel (SP) and Ti-fassaite (TPX) in melilitte (MEL). Scale bar is 100 μm.](image-url)
from the mounts before they were thin enough for investigation by ATEM. Surviving specimens were coated with a thin layer of C prior to insertion in the electron microscope, in order to prevent electrical charging.

The ATEM work was carried out on two instruments: a JEOL 200-CX instrument fitted with free-lens controls and scanning-type objective pole pieces, and a Phillips CM12 microscope. Both microscopes were equipped with B-window energy dispersive X-ray analysis (EDX) systems and spectrum-processing routines based on the Cliff and Lorimer (1975) ratio method for determining element concentrations. Cliff-Lorimer k-factors were available for each microscope, determined experimentally from material standards. For electron diffraction, the 200-CX was operated at 200 kV and the CM12 at 120 kV. For electron analysis by EDX, the 200-CX was operated at 120 kV using the "free lens" controls to form small electron probes. Specimens were examined in both the 200-CX and the CM12 modes by means of eucentric double-tilting goniometer holders, giving maximum rotations of ±45°, ±60°, and ±15°, respectively, where the first figure in each pair corresponds to the tilt axis and the second to rotation about the axis of the "pencil"-type holder. All accurate orientating of UNK crystals to characterize the reciprocal cell was carried out with the 200-CX. The "pencil" (roll) axis of this instrument has a vernier scale and is, in principle, capable of giving angles accurate to ±0.2°. Both goniometer scales were calibrated by recording the angular readings when the electron beam was successively set parallel to the <100> and <110> zone axes of single crystal MgO. Settings of the tilt axis (i.e., the axis orthogonal to the "pencil" axis) were found to be irreproducible and, therefore, unreliable because of slippage in the tilt-drive mechanism; this limited the ways in which the crystallographic investigations could be carried out.

For maximum precision in microanalysis, grid-mounted specimens were placed in a graphite insert of the single-axis-tilt sample holder of the 200-CX. At a late stage in the study, selected area electron diffraction (SAD) patterns from UNK were accurately calibrated by evaporating a thin (<30 nm) film of Au onto uncoated specimens to give superposed ring patterns from the metal. Measurements of distances in zone axis SADs were made directly from the negatives with the aid of a Joyce Loebel recording microdensitometer.

As explained earlier, we attempted to determine the full symmetry of the UNK crystals by means of the CBED method. Experiments were first carried out by operating the 200-CX instrument in the "free lens control mode" with the objective lens focussed (Goodman, 1980), but later work mostly involved the CM12. In practice, the CAI-melt-derived crystals gave CBED patterns that lacked detail, even after specimens were further lightly spot-thinned at low accelerating voltages and at glancing angles to reduce the thickness of radiation-damaged surface layers. A double-tilt goniometer stage cooled by liquid-nitrogen was also used in an attempt to obtain better convergent beam diffraction, but this too failed to yield any significant improvements.

RESULTS

General Observations by ATEM

The synthetic crystals of UNK have no unusual or distinctive microstructural characteristics when viewed by TEM, in contrast to most phases in CAIs (Barber et al., 1984). This most likely reflects the simple thermal histories of the synthetic material. Dislocation densities are extremely low except at the crystal peripheries where the phase is sometimes intergrown with other minerals. Nor is there any evidence for ordered domains in TEM images or for superstructure reflections in the diffraction patterns. Microanalyses by ATEM show a modest spread in composition in general agreement with the results of Paque et al. (1986; 1994). The slight core-to-rim chemical zonation reported by Paque et al. was also apparent in some crystals, but no other chemical heterogeneities were found.

The most interesting morphological finding is the existence of an epitaxial relationship between UNK and adjacent melilite. Several instances of this epitaxial contact were observed. Figure 2 shows the SAD most commonly obtained from interface regions. The square grid of diffraction spots, of which the center is marked by white lines, is the <001> zone axis pattern from melilite. The hexagonal pattern (first order spots denoted with arrows) is from UNK and corresponds to the <0001> zone axis pattern of the reciprocal lattice determined later. On the basis of the unit cell proposed below for UNK, the epitaxial relationship between

![Fig. 2. Electron diffraction pattern from coherent interface between UNK and melilite, illustrating the epitaxial relationship (0001)UNK || (001)mel and <1010>UNK ||<100>mel. White lines indicate the 100-type reciprocal lattice spots from the melilite and arrows point to the 1010 spots from the UNK phase. Note the three-fold symmetry.](image-url)
It was evident that at least two zone axes of high symmetry had been encountered. One of these gave a diffraction pattern with three-fold rotational symmetry, which was, in fact, the three-fold pattern from the UNK phase already illustrated in Fig. 2. We inferred from this observation that there should be another major zone axis at 90° to the triad.

The next step was to obtain a CBED pattern corresponding to the three-fold axis in order to measure the radius of the first order Laue zone (FOLZ) ring. Its radius gives approximately the spacing of crystal planes in the direction of the zone axis along which the electron beam is directed according to the equation (e.g., Champness, 1987)

\[ R = \frac{2H}{\lambda} \]

where \( \lambda \) is the appropriate electron wavelength and \( H \) is the spacing of the crystallographic planes. The measured radius was calibrated in terms of the distance in reciprocal space from the undiffracted electron beam to a first order diffraction spot and converted via an appropriate instrumental camera factor. As mentioned earlier, CBED patterns from UNK were generally of poor quality, and although the FOLZ ring appeared weakly and without useful detail, its radius was still measurable. The result indicated that spacing of the lattice planes in the direction of the three-fold axis was about 0.5 nm. An interplanar spacing of about 0.5 nm was present in the list of observed spacings, but it had been obtained from another UNK specimen and could not immediately be established as fundamental to the diffraction pattern from a zone axis orthogonal to the assumed c-axis. However, in due course, an additional UNK crystal was obtained with a fortuitous positioning of the hypothesized c-axis with respect to the plane of the specimen. By suitably orienting this specimen in the goniometer stage with respect to the tilt axes, it was arranged that the three-fold diffraction pattern was obtained when the specimen was rolled by \(-45°\) about the "pencil" axis of the goniometer. By then rolling in the opposite sense and making only small adjustments \((<5°)\) to the other tilt axis (as already mentioned, this tilt axis did not give reproducible scale readings), the three-fold diffraction pattern could be related to another zone axis SAD of two-fold symmetry, which clearly corresponded to an axis at 90° to the triad.

During the operations just described, it was a simple matter to record other zone axis patterns \textit{en route} and the settings of the goniometer stage at which they occurred. Subsequent direct use of the settings of the stage tilt angles at which the zone axis patterns occurred made possible the provisional indexing of all the low index reflections in the diffraction patterns. A reasonably accurate provisional stereographic projection was generated in this way and the approximate dimensions of the hexagonal prism-shaped reciprocal lattice cell were calculated. The latter gave provisional values for the lengths of the c and a axes of a tentative unit cell for UNK. These values and the assumption of a hexagonal-structured crystal were used as input for a computer program that calculates the spacings of lattice planes, interplanar angles, and reciprocal lattice vectors in all possible zones for a selected microscope camera constant. The data thus generated gave reasonable agreement with values derived directly from the SADs. The good agreement established that the unit cell of the reciprocal lattice could be referred to hexagonal axes with \( c \approx 0.5 \) nm and \( a \approx 0.8 \) nm. Figure 4 shows several SADs indexed according to this cell. It remained to measure the cell parameters more accurately and, if possible, to ascertain the full symmetry of UNK, which could be either hexagonal or trigonal based on the above data.

Each diffraction disk in a CBED pattern should ideally exhibit a rich pattern of lines caused by high order Laue zone reflections (HOLZ). Such fine structure is missing in the diffraction disks from the melt-derived UNK, which could imply the presence of strain, or high defect densities, or some disorder. Although CBED studies of CAI-type UNK were not generally satisfactory, acceptable diffraction patterns containing reflections from both the zeroth order Laue zone (ZOLZ) and HOLZ were obtainable with the electron beam parallel to several major zone axes. Diffraction spots in the HOLZ for the three-fold axis, and for axes orthogonal to it, occurred in positions that superposed when the ZOLZ reciprocal lattice layer was extended to meet the HOLZ. This implies that points of the reciprocal lattice in successive lattice layers lie immediately above one another and that no points occur at intermediate (fractional) positions with respect to lattice points in the zeroth layer. These patterns give important confirmation of the simple primitive nature of the UNK unit cell. Moreover, since the spacings of the spots in the two Laue zones were the same, there was no masking of forbidden reflections in the diffraction patterns by double diffraction effects, thereby making interpretation of the diffraction data in terms of a unit cell of the reciprocal lattice very straightforward.

**Determination of Accurate Unit Cell Parameters**

To overcome hysteresis in the tilt axis of the goniometer stage mentioned earlier, it was necessary to use crystals of UNK in which
at least two major zone axes could be accessed merely by rotation about the "pencil" axis. In principle, this would be sufficient to establish the three-dimensional geometry of the reciprocal cell with reasonable accuracy. The approach, however, required suitable crystals to be found and mounted in the stage in just the right orientation for the chosen single roll axis to be effective, a tedious and exacting procedure.

The reciprocal lattice vectors in SADs for the <0001> and <1120> zone axes, recorded from the same area of an UNK crystal, were provided with a built-in calibration by coating the specimen with a thin layer of Au and then finding a small area that had previously been X-ray microanalyzed (Fig. 5). The lattice parameters that follow apply to UNK with a wt% oxide composition of MgO = 0.4, Al₂O₃ = 19.7, SiO₂ = 28.7, CaO = 30.8, TiO₂ = 20.4. Care was taken to ensure that the diffraction patterns were recorded with the electron beam exactly parallel to a <1120> zone axis, since failure to do this would have affected the accuracy of the results. The 200 interplanar spacing of Au (0.2039 nm) was used as an internal calibration standard via the spacings of diffraction spots in the <0001> and <1010> reciprocal lattice directions because the 111AU ring is very close to the UNK 3030 reflections. This causes the Au peaks to partially superpose on those of the 3030 and 3030 diffraction spots in microdensitometer recordings. The lattice parameters thus determined are c = 0.492 nm and a = 0.790 nm, both with an estimated accuracy of ±0.002 nm. The cell parameters are within error of values determined by
Barber and Agrell (1994) for UNK in a mixer furnace slag (a = 0.791 nm, c = 0.492 nm) and very similar to those of melilit e (tetragonal with c = 0.50 nm and a = 0.78 nm for Akso melilit e; Kimata, 1980) though the crystal systems are different. The c/a ratio is 0.624, and the cell volume is 0.267 nm³. For UNK of the composition given above and a unit cell containing 14 oxygens, the density is 3.34 g/cm³, comparable to that of CAI fassaites.

Table 1 gives the list of measured electron diffraction spacings for low index planes together with calculated values based on the calibrated d-spacings for the (0001) and (10T0) planes.

Lattice Images

Although the atom-milled UNK grains did not give particularly good high resolution images, it was possible to obtain lattice images with the electron beam parallel to both the <0001> and <1120> directions. Typical examples are illustrated in Fig. 6. The spacing of lattice fringes in these images is consistent with the interplanar spacings (Table 1) derived from diffraction patterns for the zone axis orientations and supports the conclusions concerning the primitive nature of the unit cell and its dimensions. No defects are visible in the lattice images (conventional SADs are not sensitive to a low density of crystal defects). Nor are there other features that explain the lack of fine structure in HOLZ patterns, which might therefore be due partly to preparation procedures.

DISCUSSION

Structure of UNK

Each mineral in a CAI carries within it information that can be used to constrain the origin and evolution of the host inclusion and, hence, of the early history of the Solar System. While it is certainly possible to obtain useful information on the nebular environment in a strictly empirical fashion, an understanding of the stability of solid solutions such as UNK or of trace element partitioning between UNK and melt ± vapor ± other crystals requires some understanding of the crystal structure and crystal chemistry of the phase (e.g., Beckett, et al., 1990; Beckett and Stolper, 1994). In this section, we explore constraints on the crystal structure of UNK imposed by stoichiometry, chemical variability, cell parameters, and allowable space groups. We then consider implications of the UNK structure for equilibria involving other minerals.

Paque et al. (1994) describe the composition of synthetic and meteoritic UNK in some detail. The UNK has 3.0 cations of Ca in a formula unit based on 14 oxygens. Choosing an alternative formula unit leads either to a non-integer number of Ca or to anomalously high densities (e.g., a formula unit based on 28 oxygens results in a theoretical density of 6.7 g/cm³). Provided there are 14 oxygens and three Ca cations in the formula unit, the Ti, Al and Si must (for available analyses) be distributed among six

TABLE 1. Interplanar spacings (averaged) measured from electron diffraction patterns and calculated spacings for hexagonal unit cell

<table>
<thead>
<tr>
<th>Plane</th>
<th>Interplanar spacing (measured: nm)</th>
<th>Reciprocal spacing (calculated: nm)</th>
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<tbody>
<tr>
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<td>5.374</td>
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<tr>
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<td>30.336</td>
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* Calibrated in terms of the Au(200) spacing and used to determine the UNK lattice parameters from which the data in column 3 are calculated.
sites with 2.2–2.5 cations of Si, 1.8–2.1 cations of Al and 1.3–1.9 cations of Ti. Silicon is almost certainly located exclusively in tetrahedral sites, so there must be at least three tetrahedra/formula unit in order to accommodate the >2 cations of Si. Paque et al. (1994) were able to synthesize a Ti-free analog of UNK with a formula of Ca$_3$Al$_2$Si$_4$O$_{14}$. There is a large gap in composition between this phase and the Ti-bearing UNK crystals described here and in Barber and Agrell (1994) so the structures may also be different. Nevertheless, the existence of Ca$_3$Al$_2$Si$_4$O$_{14}$, which must contain at least four tetrahedral sites, suggests that there may also be four or more tetrahedral sites in the unit cell of UNK. Based solely on chemistry, the substitution mechanism for Ti is unclear as either direct substitutions for Si or coupled substitutions involving Si and Al are possible. Moreover, Al and Ti are known to substitute into four-, five- or six-coordinated sites (Moore and Louisnathan, 1967; Waychunas, 1987; Kerrick, 1990; Della Ventura et al., 1991) although Ti prefers octahedral coordination, so all three possibilities must be considered.

The striking similarity of the cell parameters of UNK and melilitie together with the tendency for UNK to grow epitaxially on the (001) and (100) faces of melilitie suggests that there are also similarities in the two structures even though they crystallize in different systems. The structure of melilitie can be described as a puckered sheet of tetrahedra perpendicular to the c-direction coordinated by near-planar layers of Ca (Louisnathan, 1971). In general, crystals with primitive space groups tend to be layer structures so it is reasonable to hypothesize that the structure of UNK, which has no center of symmetry (Barber and Agrell, 1994), involves sheets of Al-, Si-, Ti-centered polyhedra coordinated by sheets of Ca.

Barber and Agrell (1994) were able to constrain the space group of UNK from a mixer furnace slag to being either P31m or P3m1. In both space groups, a general position has a multiplicity of six. Special positions in mirror planes generate three equivalent positions/unit cell, and those along three-fold axes have a multiplicity of one or two. Each of the 14 oxygens in the unit cell must be coordinated to one or more polyhedra containing Al, Si, and/or Ti and all of the oxygens in the structure can be accounted for in terms of six of these polyhedra/unit cell. At least three of the polyhedra are tetrahedra, but the remaining three Al + Ti + Si sites may, in principle, be four-, five- or six-coordinated with O. The combination of stoichiometry constraints and the two allowable space groups, however, greatly restricts the possible structure of UNK. For example, if the structure contained four tetrahedra and two octahedra, three of the tetrahedra would have to be centered in mirror planes while the two octahedrally and one of the tetrahedrally coordinated cations would lie along three-fold axes. Unless shared tetrahedral edges are allowed, there would be at least one unshared vertex corresponding to the apical O of the unique tetrahedron. However, four tetrahedra and two octahedra have a total of $4 \times 4 + 2 \times 6 = 28$ vertices and, upon introducing the stoichiometric constraint of 14 oxygens/unit cell, there must be $28-14 = 14$ shared vertices (i.e., all vertices are shared). This contradicts the requirement that there be at least one unshared vertex, so the class of structures involving four tetrahedra and two octahedra can be rejected. Similar arguments can be used to reject all classes of possible UNK structures except those that place Ca and three of the tetrahedrally coordinated cations in mirror planes and one octahedrally and two tetrahedrally coordinated cations along the three-fold axes.

![Fig. 6. Lattice images of UNK recorded with the electron beam parallel to (a) <0001> and (b) <1120>.](image-url)
Based on the above discussion, the structural formula of UNK has the form
\[ \text{Ca}_{y}^{3+} \text{X}^{2+} \text{Y}^{2+} \text{Z}^{2+} \text{O}_{14}. \]

The X-site is most likely occupied almost completely by Ti because there is always more than one Ti\(^{4+}/\text{formula unit in UNK analyzed by Paque et al. (1994)}, and Ti generally greatly prefers octahedral coordination in silicates. Constraints on site assignments for the remaining cations are ambiguous. We assume that the Y sites are occupied mostly by Al and Ti and the Z sites mostly by Si because this places Ti and Si on different crystallographic sites; we also recognize that alternative site assignments are possible. To a good approximation, the compositions of meteoritic and synthetic Ti-bearing UNK (Paque et al., 1994) can then be described as a binary solid solution between the end-members
\[ \text{Ca}_{y}^{3+} \text{Ti}_{x}^{3+} \text{Al}_{y-x}^{3+} \text{Si}_{x}^{4+} \text{O}_{14} \text{ and Ca}_{z}^{3+} \text{Ti}_{z-x}^{3+} \text{Al}_{z-x}^{3+} \text{Si}_{x}^{4+} \text{O}_{14}. \]

Small amounts of Ti\(^{3+}\) that may be present in meteoritic UNK (Paque et al., 1994) probably substitute into the octahedral site, again due to the strong preference of Ti for octahedral coordination. Paque et al. (1994) also analyzed a Ti-free phase for which we infer a formula based on 14 oxygens of
\[ \text{Ca}_{y}^{3+} \text{Al}_{x}^{3+} (\text{AlSi}_{3})_{y}^{4+} \text{O}_{14}. \]

This phase is plausibly related structurally to Ti-bearing UNK with the octahedral site being completely occupied by Al.

**Origin of UNK in Calcium-Aluminum-rich Inclusions**

Meteoritic UNK occurs exclusively within melilite as monomineralic inclusions. There are three classes of models for the origin of UNK (Allen et al., 1978; Paque et al., 1986, 1994) all of which we consider below. These involve alteration, exsolution, and crystallization from a melt.

Titanium does not appear to have been very mobile during low-temperature alteration of CAIs. Most of the Ti occurs in phases such as fassaite, perovskite and hibonite that are quite resistant to the process (e.g., Allen et al., 1978; Barber et al., 1984) although ilmenite lining margins of, and cracks within, perovskite and fassaite is occasionally observed (Kornacki and Wood, 1985; Hashimoto and Grossman, 1987). Thus, if UNK formed either as an exsolution or alteration product of melilithe, then melilithe itself was probably the source of the Ti. The precise nature of such an UNK-forming reaction would depend, however, on the mechanism of Ti substitution into melilite, for which there are few constraints. For illustrative purposes, we assume that the ~100 ppm Ti in CAI melilithe (Johnson et al., 1988) substitutes either into the Ca-site accomodated by a defect molecule of the form CaTi\(^{2+}\)O\(_{7}\), where \(\Box\) refers to a vacant Mg-Al site, or into interstitial sites, interstitial
\[ \text{Ti}^{2+} \text{ (mel) ,} \]

charge-balanced by Si vacancies. Simple reactions between melilithe and UNK can then be written
\[ \text{CaTi}^{2+}\text{Si}_{2}^{4+}\text{O}_{7} \text{(mel)} + \text{Ca}_{2}\text{Al}_{2}\text{SiO}_{7} \text{(mel)} = \text{Ca}_{3}\text{Ti}_{2}\text{Al}_{2}\text{Si}_{2}\text{O}_{14} \text{(UNK),} \]

or
\[ \text{Ti}^{2+} \text{ (mel) + Ca}_{3}\text{Ti}_{2}\text{Al}_{2}\text{Si}_{2}\text{O}_{14} \text{(UNK)} = \text{Si}^{2+} \text{ (mel) + Ca}_{3}\text{Ti}_{2}\text{Al}_{2}\text{Si}_{2}\text{O}_{14} \text{(UNK),} \]

Equ. (1)

Reaction (1) could involve either exsolution from the melilithe lattice or, perhaps more likely, nucleation on the abundant dislocations (Barber et al., 1984) that characterize CAI melilithe. Note that gelitic melilithe is consumed in reaction (1) and that UNK is nearly Mg-free. This could account for observed enrichments of Mg near the interface between meteoritic UNK and host melilithe (Paque et al., 1994). Alternatively, since Si, Mg and Ca were all mobile, probably as hydroxide species, during low temperature alteration of CAIs (Hashimoto, 1992), reactions to form UNK may have been balanced by various combinations of Mg, Ca and/or Si species in the vapor. It is expected that if UNK formed by either exsolution from melilithe or alteration processes, then trace element abundances would be relatively low, consistent with abundances in the host melilithe.

UNK is readily produced in cooling rate experiments on partially molten samples with bulk compositions corresponding to those of CAIs so we know that crystallization of meteoritic UNK from a melt is at least possible. Moreover, UNK in the unique Essel inclusion described by El Goresy et al. (1984) is enriched in Hf and the rare earth elements (REE) consistent with crystallization from a late-stage residual melt. There are, however, two difficulties with such a model for most UNK from CAIs. First, in experiments discussed by Paque et al. (1994), UNK is a very late-stage crystallization product, whereas in CAIs, UNK usually occurs in texturally early melilithe. Second, although it is possible to find in the experimental run products examples of UNK+ melilithe with no other associated phases, other phases are often present. In meteoritic occurrences, such additional phases are not found, which argues against, for example, the possibility that UNK crystallized from melt inclusions trapped within early crystallizing melilithe. Neither of these two major objections necessarily rules out crystallization from a melt. Small pyroxene inclusions that have trace element abundances consistent with very late stage crystallization from a melt are often observed in texturally early CAI melilithe from the mantles of B1 inclusions (Simon et al., 1991) and texturally similar occurrences are observed in experimental products (MacPherson et al., 1984). It is also worth noting that Mg is often enriched in the melilithe adjacent to the natural pyroxene inclusions and adjacent to UNK formed experimentally by crystallization of CAI-like bulk compositions. This feature is also observed in the vicinity of meteoritic UNK.

At present, we can not reject any of the three proposed models for the origin of UNK in CAIs. However, trace element abundances should provide less ambiguous constraints. If meteoritic UNK exsolved from melilithe or formed during the alteration process, then many trace elements will not be strongly enriched because the host melilithe has relatively low abundances. On the other hand, UNK that crystallized from a late stage melt should be strongly enriched even in very incompatible trace elements, a reflection of trace element abundances in the melt. As noted above, one meteoritic occurrence of UNK is known to exhibit such trace element enrichments (El Goresy et al., 1984) but the host inclusion is so unusual that it is not possible to make inferences based on it about the UNK occurrences described here.

**CONCLUSIONS**

UNK has a primitive hexagonal or trigonal unit cell with cell parameters, \(a = 0.790 \pm 0.002 \text{ nm}\) and \(c = 0.492 \pm 0.002 \text{ nm}\), similar to those of melilithe (tetragonal with \(a = 0.78 \pm 0.02 \text{ nm}\), \(c = 0.50 \pm 0.02 \text{ nm}\) for \(\text{Al}_{5}^{2+}\); Kimata, 1980). It frequently displays an epitactic
relationship in which melilitic acts as the host, with (0001)UNK \parallel (001)_{mel} and <10T0>UNK \parallel <100>_{mel}}. The observed epitaxial relationship and the similarity of the cell parameters to those of melilitic suggest that the structure may be related to that of intermediate melilitic on the kermanite-glehnite join, but that the presence of Ti and absence of Mg induces a different symmetry. The results presented in Barber and Agrell (1994) show that the space group of UNK is restricted to one of \textit{P}3\textit{m}1 or \textit{P}3\textit{1}\textit{rm}. It is suggested that the presence of Ti and absence of Mg induces a relationship and the similarity of the cell parameters to those of melilitic. The proposed structural formula is

\[ \text{Ca}^{2+}(\text{Ti},\text{Al})^{3+}(\text{Al},\text{Si})^{5+}(\text{Si})^{4+}O_{14}^{2-} \]

where Si + Ti = 4, and the compositions of meteoritic and synthetic Ti-bearing examples can be described mostly as a binary solid solution between the end-members \text{Ca}_3\text{Ti}_2\text{Si}_3\text{O}_{14} and \text{Ca}_3\text{Ti}(\text{Al},\text{Si})_2\text{O}_{14} with small amounts of trivalent Ti substituting in some cases for Al\textsuperscript{3+}. A Ti-free analog synthesized by Paque et al. (1994) is probably related structurally to Ti-bearing UNK with the octahedral site being completely occupied by Al; that is

\[ \text{Ca}^{2+}(\text{Al})^{3+}(\text{Si})^{4+}O_{14}^{2-} \]

Meteoritic UNK may have crystallized from melts, exsolved from melilitic or formed during alteration of the host CAI. Measurement of trace element abundances of UNK should provide strong constraints on the mode of origin for this phase.

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REFERENCES


