Ca−Al-Rich Inclusions In Carbonaceous Chondrites: the Oldest Solar System Objects

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Abstract—This paper presents a review of recent available data on the first solid condensates of the Solar System, which include refractory CAIs (Ca−Al-rich Inclusions) mostly composed of Ca, Al, Mg, and Ti minerals. A theoretical condensation sequence calculated from thermodynamic data confirmed that CAIs formed as fine-grained aggregates in the protoplanetary disk from an ^{16}O-rich gas of solar composition at temperatures $>1300°$ K and pressures $<10^{-4}$ bar. Based on the diversity of CAI types, their mineralogical, bulk chemical, and isotopic compositions, it can be concluded that CAIs experienced melting and evaporation, possibly by shock waves, which may have occurred in the protoplanetary disk within a brief time interval. Some CAIs may have experienced multiple events such as melting, evaporation, and recycling back to the disk by means of a bipolar outflow. The CAIs having an absolute age of 4567.30 ± 0.16 Myr are the oldest objects in the Solar System. The study of CAIs revealed two distinct oxygen isotope reservoirs (^{16}O-rich and ^{16}O-poor) and established a chronology of the sequence of processes forming individual CAI components using Mg−Al, Cr−Mn and Pb−Pb isotopic systematics.

INTRODUCTION

According to star formation theories supported by direct observations of star-forming regions, the Solar System formed from a relatively small, about 10^3– 10^4 solar masses, dense cloud of gas and dust collapsing under its own gravity. Gravitational instability within the cloud may have been triggered by the expanding shock waves from nearby stellar explosions. Most of the collapsing mass collected in the center, forming the Sun, while the rest of the matter flattened into a revolving protoplanetary disk out of which the planets, asteroids and other Solar System bodies formed. The collapsing protoplanetary cloud began to heat up, evaporating the dust grains. Then as the heat dissipated the cloud re-cooled, first condensing gas into solid particles, which eventually stuck together forming even larger objects, which then grew by accretion into planetesimals. The exact timing or duration of the condensation processes in the solar protoplanetary disk and the processes that resulted in the formation of solids in our Solar system is not precisely known.

The most refractory grains which were among the first solids to condense in the protoplanetary disk have been found in the carbonaceous chondrites (MacPherson, 2014). Carbonaceous chondrites, the most primitive of all meteorite types, have solar-like compositions, and contain the following components: 1) refractory Ca−Al-rich inclusions (CAIs) considered to be formed from refractory Ca-, Al-, Mg-, and Ti-rich minerals, 2) amoeboid olivine aggregates (AOAs) composed of olivine, Al-diopside, anorthite, and spinel, and 3) chondrules that are ferromagnesian silicate embedded in a fine-grained matrix. These components are thought to preserve a record of the processes of isotope and chemical fractionation that occurred during the earliest formation of the Solar System from a cloud of gas and dust. Therefore, a clue to these processes can be provided by a detailed laboratory study of the presolar material such as carbonaceous chondrites, delivered to Earth.

The laboratory study of CAIs began 40 years ago while the advent of new, high precision analytical methods has offered new kinds of data, which have vastly improved our knowledge of their origin. The modern types of instrumentation available at present provide non-destructive analytical techniques for the analysis of such a rare material in order to derive the maximum information from increasingly smaller samples using a variety of analytical methods. Instrumental techniques and instruments used include optical microscopy, scanning electron microscopy, ion microprobe analysis, atomic absorption spectroscopy with

inductively coupled plasma mass spectrometry. A considerable advance in the study of CAIs has been brought about by a new type of ion microprobe, the NanoSIMS, used for isotopic imaging.

Several hypotheses have been proposed for the origin of CAIs. One recent suggestion was that they may have originated from outside the Solar system, in different geochemical environments, and have been ejected to our Solar System as a result of a nearby supernova explosion. However, the recent suggestions that CAIs formed originally within or outside the Solar System are untenable (Nittler, 2005). Carbonaceous chondrites are known to contain presolar grains of hibonite and spinel with non-solar oxygen isotope compositions, whereas CAIs are shown to contain ^{26}Al, ^{41}Ca, ^{10}Be, and ^{60}Fe, which (except for ^{10}Be) cannot be produced within our Solar System and thus may have been delivered in the ejecta of presolar supernova explosions (Ouellette et al., 2005).

The present paper provides a review of the most recent studies on the formation of refractory inclusions, combining our own observations with data from the literature on the formation of early Solar System materials.

TYPES OF REFRACTORY CALCIUM–ALUMINUM-RICH INCLUSIONS

CAIs are commonly found in carbonaceous chondrites (CV3), although a few specimens were reported from ordinary and enstatite chondrites. These inclusions were first described in detail from the Allende CV3 chondrite (classification of carbonaceous chondrites is given in Scott and Krot (2004)) and grouped according to their structure and mineral composition (Grossman, 1975; Wark 1987). In addition, CAIS in CV3 chondrites are among the largest ones and permit more information to be extracted from these objects based on their mineralogical–petrographic, chemical, and isotopic study. In this respect, the CV3 chondrites are the most attractive type of chondrites for the search and examination of CAIs, typical examples of which include the unique Efremovka meteorite in the Meteorite Collection of the Russian Academy of Sciences (Nazarov et al., 1984; Ulianov et al., 1989) and other meteorites, i.e., new CV3 chondrites from Northwest Africa, e.g., the North West Africa 3118 (NWA 3118) chondrite containing abundant large (>1 cm) refractory inclusions.

CAIs are complex objects, which have long been thought to be early aggregates of high-temperature condensates. However, it is now recognized that they formed by interactions with nebular gas as a result of repeated heating and evaporative partial or complete melting, shock transformation, secondary mineralization within the protoplanetary cloud and/or on parent asteroids (MacPherson, 2014). All these processes are recorded in their structure, different types of rim layers, and the assemblages of primary and secondary minerals. Because the same mineral phases in refractory inclusions can be the products of either primary or secondary processes, we must clarify their definition. Primary minerals are those that form first in a sequence of formation processes, i.e., condensation, melt crystallization, or recrystallization of a solid phase. Secondary minerals are defined as minerals that form by replacement reactions with gas or melt, usually at rims around the primary phases. For example, in fine-grained unmelted melilite inclusions, melilite is replaced by anorthite and Ca-pyroxene, which are the primary phases in inclusions unequivocally formed from melt droplets.

A typical melilite inclusion from the CV3 chondrite is shown schematically in Fig. 1. Its core is usually composed of primary melilite crystals with included smaller crystals of spinel, hibonite, and sometimes perovskite. Fine-grained secondary anorthite replaces melilite at grain boundaries. All inclusions are surrounded by Wark–Lovering rim layers that are typically monomineralic and composed of minerals similar to those of the inner part of inclusions, i.e., melilite, spinel, and pyroxene, but formed at different times during CAI formation. The Wark–Lovering rim layers are in turn surrounded by a fine-grained matrix-like olivine–pyroxenite accretionary rim, differing in structure from the chondrite.

CAIs can also be grouped as fine-grained and coarse-grained inclusions (Figs. 2a–2h). Fine-grained CAIs are classified into Fluffy Type A or FTAs (Fig. 2b) and spinel-rich inclusions (Brearly and Johns, 1986). Based on mineralogy, coarse-grained CAIs are classified into compact Type A (CTA) (Fig. 2a), B (Fig. 2c), and C (Fig. 2d) inclusions, as well as forsterite-rich Type B (*FoB*) inclusions (Fig. 2e) (Bullock et al. 2012). Type B is grouped into Types B1 and B2 differing in their structure: unlike B2, B1 CAIs have an outer melilite rim and a core composed of pyroxene, anorthite, melilite, and spinel (Fig. 2c).

This classification of CAIs is based on variations in the modal abundances of major inclusion components such as melilite, spinel, Al–Ti-rich pyroxene, anorthite, and forsterite. The remaining minerals, including hibonite, grossite, dmitrivanovite (or krotite), perovskite and others, are present as accessory phases in these types of CAIs. For example, Type A CAIs are mainly melilite- and spinel-rich; Type B are composed of melilite, Al–Ti-rich pyroxene, and spinel, with minor anorthite; Type C CAIs are either plagioclase-rich or consist of anorthite and Al,Ti-rich pyroxene; fine-grained spinel-bearing CAIs are composed mainly of spinel. However, relative to other carbonaceous chondrite groups, CAIs in the CH–CB chondrites (classification is given in Scott and Krot (2004)) and metal-rich chondrites (Weisberg et al., 1995; Krot et al., 2002a; Ivanova et al., 2008) are mostly grossite- and hibonite-rich due to the predominance of
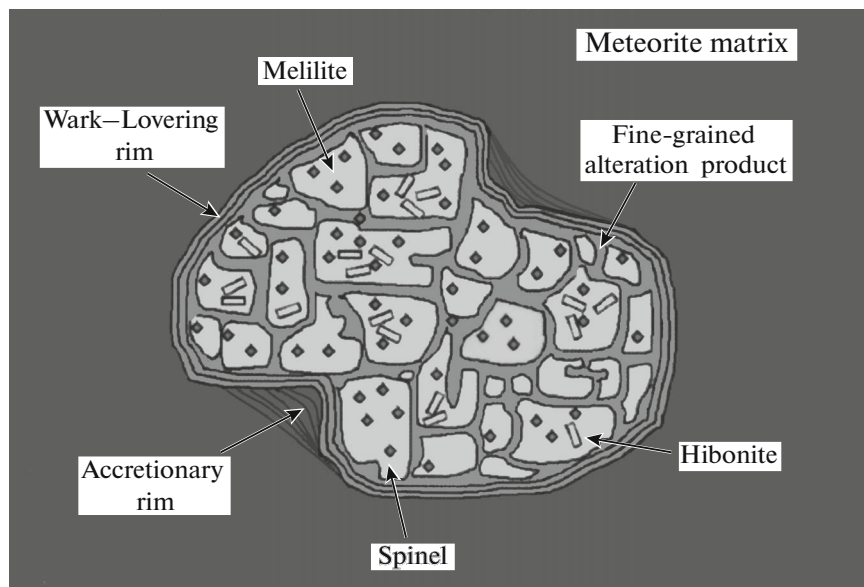
Fig. 1. Schematic representation of major structural components of a hypothetical CAI (MacPherson, 2014).

these metals in modal compositions (Figs. 2g, 2h). These small size inclusions are the most refractory objects compared to the known types of inclusions in CV3 chondrites. Some of them are truly exotic and contain rare mineral phases such as calcium aluminates, dmitrivanovite or krotite (Ivanova et al., 2002; Ma et al., 2011).

Besides the above types of inclusions, there are compound refractory inclusions (Ivanova et al., 2012) that enclose several smaller CAIs (Fig. 2f). A unique 3N inclusion from the NWA 3118 chondrite contains 26 CAIs of different types, which were formed before they accreted to the host inclusion. Such inclusions usually contain an exceptionally rare type of ultrarefractory (UR) CAIs (Ivanova et al., 2012; Ivanova et al., 2013). The study of the *FoB* CAI 3N from the NWA 3118 (CV3) carbonaceous chondrite and FTA CAI 33E from the Efremovka (CV3) chondrite, containing UR CAIs 3N-24 and 33E-1, respectively, shows that these UR inclusions are composed of Zr-, Sc-, and Y-rich oxides (one of which is Zr-, Sc-, and Y-rich tazheranite), Y-rich perovskite, Zr-, Sc-, and Y-rich pyroxenes and a pure gehlenite (UR CAI 33E-1).

Among the great variety of CAIs, one special and very rare category of CAIs, called FUN inclusions (Fractionated and Unknown Nuclear Effect), is characterized by mass-dependent isotopic fraction of Mg, Si, and O, non-linear undifferentiated isotope anomalies of several elements (Ca, Ti, Sr, Ba, Nd, and Sm), and a low content of the short-lived ^{26}Al (half-life 0.72 Myr) (Wasserburg et al., 1977). Based on their structure and mineralogy, the FUN inclusions are similar to common types of CAIs. This type of CAIs was assumed to have formed before the injection of ^{26}Al and its homogenization (Lee et al., 1980; Sahijpal and Goswami, 1998) or after its decay. Thus, FUN CAIs may provide information on the composition of presolar dust aggregates in the protoplanetary disk and the earliest processes. However, the latest data show that compared to common CAIs, the FUN CAIs may have formed under different conditions, in a physico-chemical environment (at low or high pressures) leading to a number of unusual isotopic anomalies. The origin of these inclusions still remains enigmatic.

Most CAIs of various types contain metal grains of Fe–Ni and PGE metal alloys, called Fremdlinge (MacPherson, 2014). In addition, CAIs in the reduced CV3 chondrite subgroup (see classification of oxidized and reduced CV3 groups of Brearley and Jons (1998)) may contain Fremdlinge, an assemblage of different phases, including metals, sulfides, oxides, and phosphates (El Goresy et al., 1978). Fremdlinge are currently thought to result from secondary alteration, sulfidization of original metallic grains that are found in the reduced CV3 chondrite subgroup.

MORPHOLOGY OF REFRACTORY INCLUSIONS

Ca–Al-rich inclusions show highly variable morphologies, being often amoeboid (Fig. 3a), spherical, drop-shaped, elliptical, flattened disk or bowl-shaped aggregates (Fig. 3b). Spherical and disk-shaped inclusions commonly have a rounded cross-section while bowl-shaped inclusions appear as circles with center perforation when they are sectioned in the plane parallel to the base (Fig. 4a) or have a crescent shape when they are sectioned in the plane perpendicular to the base of the concave disk (Fig. 4b).
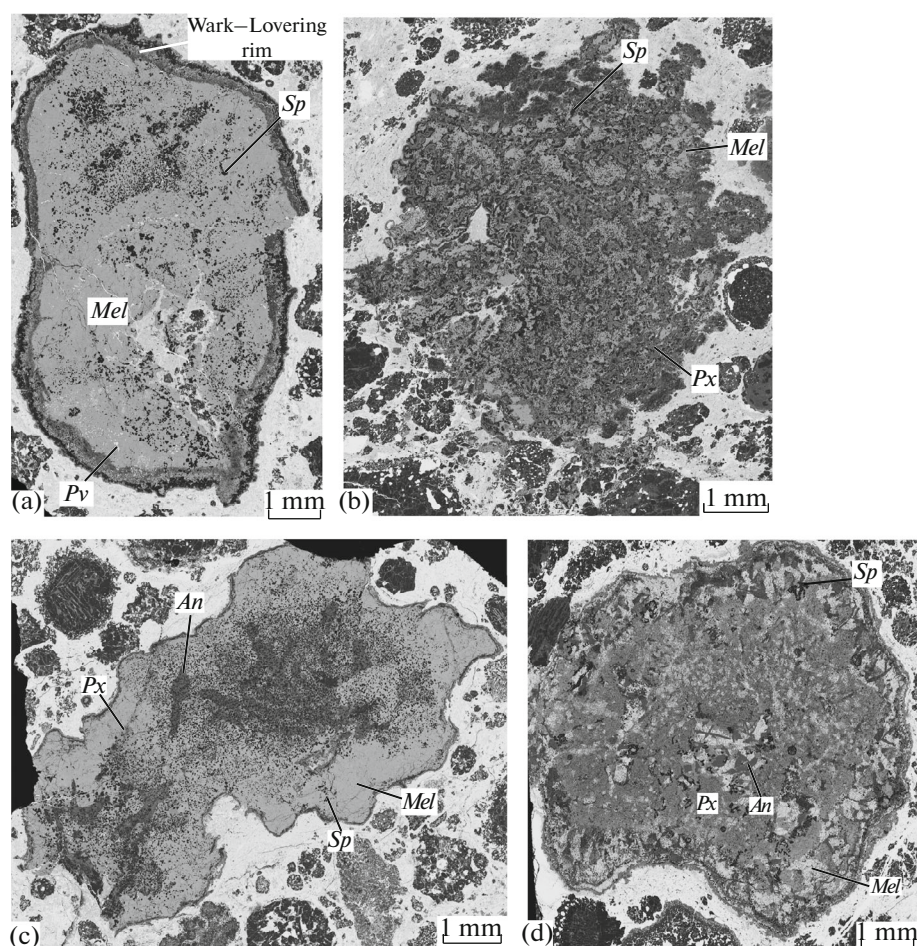
Fig. 2. Backscattered electron images of some CAI varieties: (a) compact type A (CTA) CAI 6aN from NWA 3118 (CV3) meteorite; (b) fluffy type A (FTA) CAI 33E from Efremovka (CV3) meteorite; (c) type B CAI 13N from NWA 3118 (CV3) meteorite; (d) type C CAI 27bE from Efremovka (CV3) meteorite; (e) type B, forsterite-bearing CAI 4N from NWA 3118 (CV3) meteorite; (f) compound CAI 3N from NWA 3118 (CV3) meteorite consisting of 26 CAIs of different types enclosed within the type B forsterite-bearing host CAI; (g) dmitrivanovite-bearing CAI E1-005 from NWA 470 (CH3) meteorite (Ivanova et al. 2002); (h) grossite-bearing CAI E1-354 from NWA 470 (CH3) meteorite (Ivanova, Petaev, 2015). Abbreviations: *Mel*-melilite, *Sp*-spinel, *Pv*-perovskite, *An*-anorthite, *Px*-pyroxene, *Fo*-forsterite, *Grs*-grossite, *Dm*-dmitrivanovite.

Nonspherical symmetric CAIs may have formed through aerodynamic plastic deformation of melted spherical droplets (Lorenz et al., 2012; Ivanova et al., 2014). Irregular shapes are typical of fine-grained fluffy type A inclusions, spinel-rich inclusions, and amoeboid olivine aggregates. Coarse-grained melted inclusions have compact rounded shapes. The flattened disk-like or bowl-like shapes of inclusions indicate that partial or complete melting played an important role in the evolution and transport of Solar System material.

CHEMICAL COMPOSITION OF PRIMARY CAI MINERALS

As noted above, Ca–Al-rich inclusions in CM, CO, and CV3 chondrites (see classification of chondrite type in Scott and Krot (2004)) have only five primary minerals, including spinel, melilite, pyroxene, forsterite, and anorthite. Perovskite is an important accessory refractory mineral. In addition to the above minerals, Ca–Al-rich inclusions of the CH/CB chondrites may also contain calcium aluminates and highly refractory minerals such as hibonite and grossite.

Let us consider the chemical composition of the primary CAI minerals. Melilite in CAIs is a binary solid solution between the endmembers gehlenite ($Ca_2Al_2SiO_7$) and åkermanite ($Ca_2MgSi_2O_7$) and had a thermal minimum at the melilite with its åkermanite content of ~72 wt %. In high-temperature melts, the crystallizing melilite starts out aluminum-rich and becomes progressively more magnesium-rich with decreasing temperature. Such zoning (Al-rich core and Mg-rich rims) called "normal" develops in melilite during crystallization from a more aluminous melt (Stolper, 1982). Unlike normal zoning, the melilite
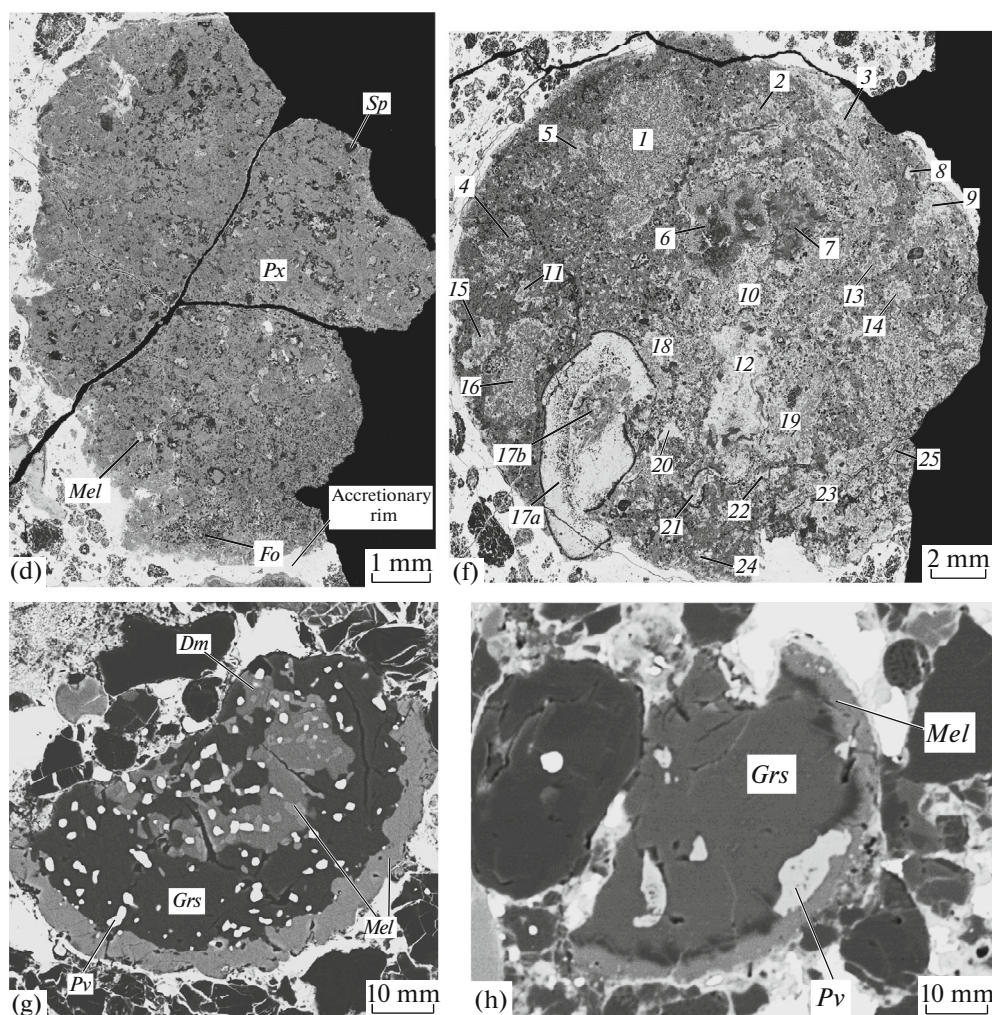
Fig. 2. (Contd.)

can be reversely zoned in some inclusions (Mg-rich core and Al-rich rims). The reversely zoned melilite with a more gehlenitic composition in type A CAIs may testify to a more complex history of CAI formation and also suggest that the inclusion was formed by condensation rather than melting and subsequently underwent thermal metamorphism (MacPherson, 2014).

Spinel ($MgAl_2O_4$) has a uniform composition in all types of CAIs that varies in iron content (Brearley and Jones, 1998). Spinel shows the largest variations in composition in Wark–Lovering rims and cores of CAIs. Spinel is the most stable mineral in terms of the initial isotopic compositions of oxygen, aluminum, and magnesium because high-temperature heating events did not reset the Al–Mg systematics or affect the oxygen isotopic composition (MacPherson, 2014).

The composition of pyroxene in CAIs is Ca-rich, with variable Al and Ti contents. Pyroxene commonly crystallized from melts, as is the case with type B CAIs. Pyroxene compositions vary considerably between cores and rims of CAIs, especially in type B

CAIs, and are characterized by markedly different Ti^{3+}/Ti^{4+} ratios associated with the redox conditions during crystallization. The outer layer of the Wark–Lovering rim sequence usually contains Al,Ti-diopside. Ti–Al-rich pyroxene (fassaite) may occur either in the center or at margins of the inclusion. Pyroxene in the central part of CAIs shows chemical zoning in terms of Al and Ti. Other pyroxene varieties include grossmanite $CaTi^{3+}AlSiO_6$, kushiroite $CaAl_2SiO_6$, and davisite $CaScAlSiO_6$ (Ma and Rossman, 2009).

Although equilibrium thermodynamic calculations predicted that corundum should condense first from a gas of solar composition, it is an extremely rare phase. The occurrence of hibonite ($CaAl_{12}O_{19}$) later replaced by $(Fe, Mg) Al_{12}O_{19}$ is much more common in CAIs. Perovskite can often be found in all type A and B CAIs and has a uniform composition of $CaTiO_3$. Grossite ($CaAl_4O_7$) and dmitrivanovite/krotite ($CaAl_2O_4$) are very rare phases (Ivanova et al., 2002; Ma et al., 2011) that can be found mainly in CAIs in CH and CB chon-
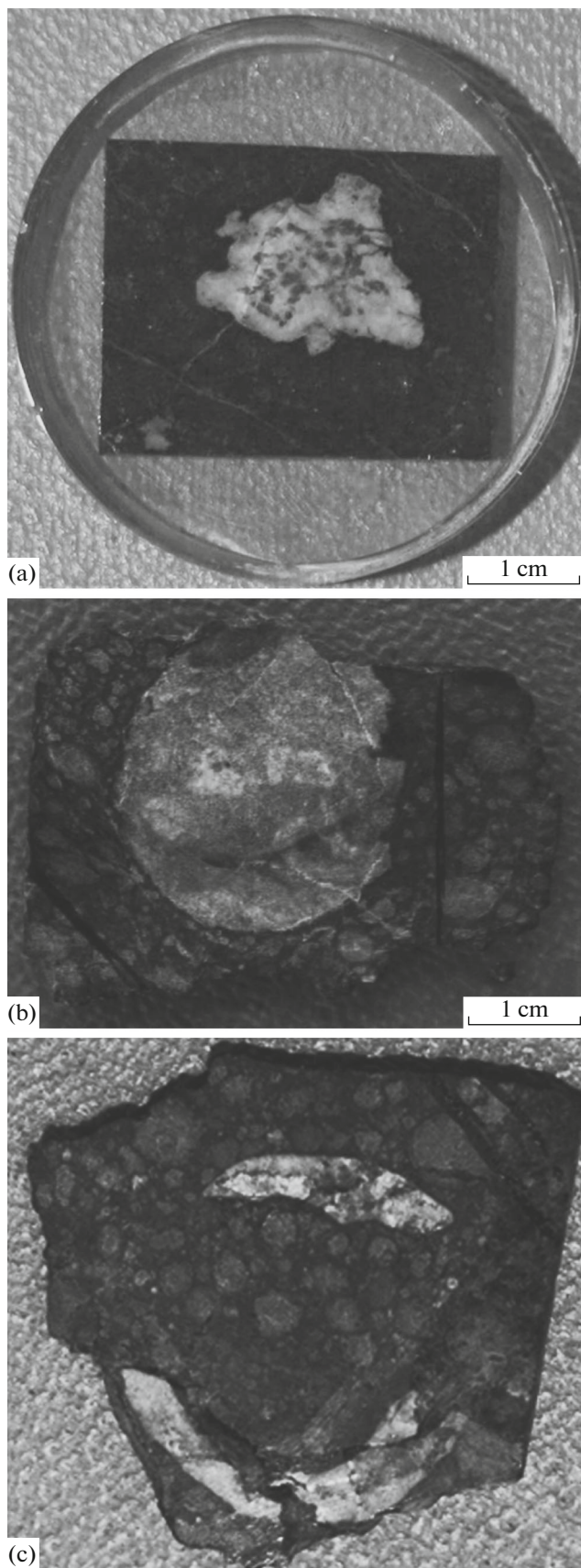
Fig. 3. Morphology of some CAI varieties: (a) polished thin section of an amoeboid inclusion, (b) thin section of a disk-shaped (or spherical) inclusion, (c) a bowl-shaped inclusion sectioned parallel to its base.

drites. Condensation of these minerals requires high dust/gas ratios in the protoplanetary disk.

Anorthite in CAIs contains neither Na nor Ca. In type B CAIs, it can be either a primary magmatic phase in type B inclusions or secondary alteration phase replacing melilite in type A inclusions. Based on their chemical composition, both anorthite- and Ca-pyroxene-bearing CAIs appear to represent a link between aluminous chondrules with >10 wt % Al_2O_3 and forsterite- and pyroxene-bearing CAIs.

BULK CHEMICAL COMPOSITION OF CALCIUM–ALUMINUM-RICH INCLUSIONS

All CAIs can be grouped based on their chemical compositions on the Ca_2SiO_4–Al_2O_3–Mg_2SiO_4 diagram (MacPherson and Huss, 2005) (Fig. 5). This diagram is a projection of bulk chemical composition of inclusions from spinel onto the plane Al_2O_3–Mg_2SiO_4–Ca_2SiO_4–$MgAl_2O_4$ in which spinel ($MgAl_2O_4$) defines the apex of the tetrahedron. The fields defined by bulk chemical compositions of types A, B, and C inclusions are shown in Fig. 5, and forsterite-bearing type B inclusions are shown in Fig. 13 from Bullock et al. (2012) (the field of Al_2O_3-rich chondrules and amoeboid olivine aggregates (AOA) is shown for comparison). It is assumed that Al_2O_3-rich chondrules resulted from mixing between CAI material and olivine–pyroxene chondrules. The compositions of AOAs are similar to those of olivine–pyroxene chondrules.

Fine-grained spinel-bearing CAIs define a separate field between type C and forsterite-bearing type B (*Fo*B) inclusions (see Fig. 13 in Bullock et al., 2012).

Although different types of CAIs generally plot within respective compositional fields, the early crystallization behavior of the chemical elements remains poorly understood. For example, forsterite-bearing type B inclusions fall within the forsterite + spinel field (see Fig. 13 in Bullock et al., 2012), meaning that forsterite or spinel will be the first crystallizing phases from melts, followed by pyroxene, melilite or anorthite (Bullock et al., 2012). However, melilite from the inclusion interior has more magnesian compositions (greater than Ak72) and plots on one side from the minimum of the binary åkermanite–gehlenite system while melilite from the outer rim is more gehlenitic and more aluminous and plots on the other side from the minimum. Therefore, the compositions of melilite from the same inclusion plot on different sides from the liquidus minimum, which is inconsistent with simple fractional crystallization from a melt. It is thus
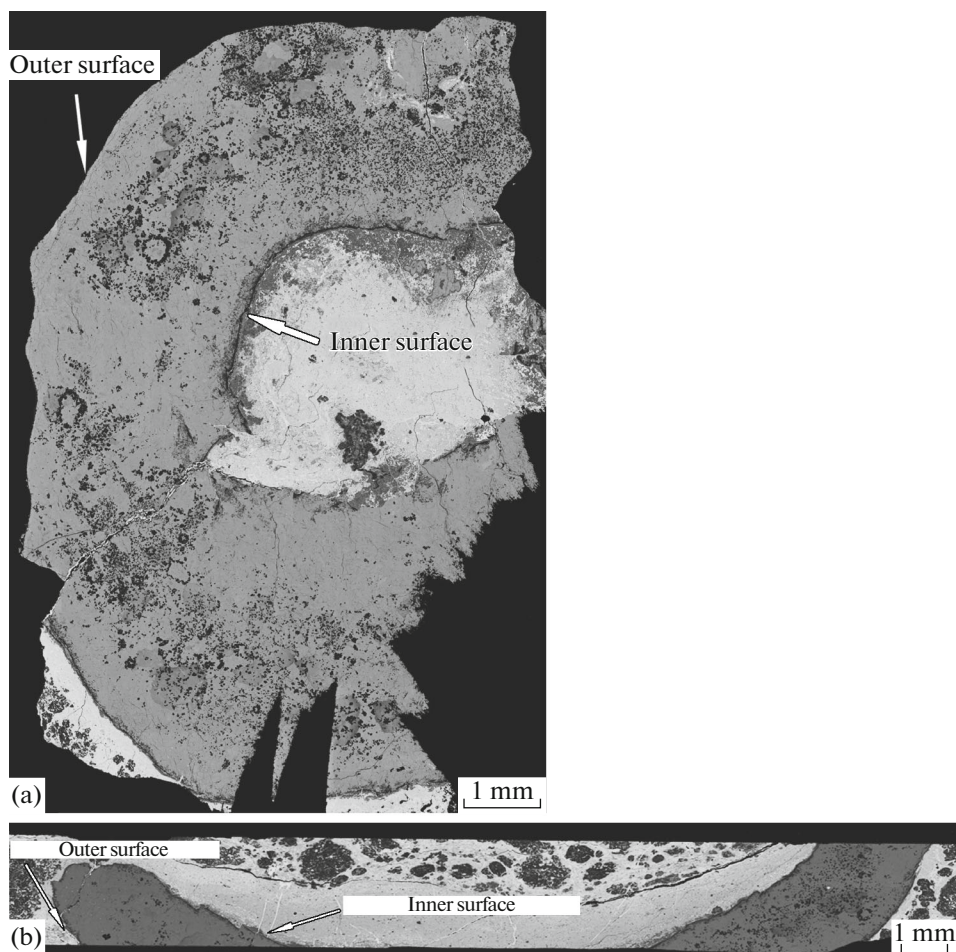
Fig. 4. Backscattered electron image of a bowl-shaped refractory CAI 1N from the NWA 3118 meteorite: (a) section parallel to its base, (b) section perpendicular to its base (Ivanova et al., 2014).

likely that forsterite-bearing type B inclusions experienced evaporation during melt crystallization under nebular conditions, which was reflected in the composition of melilite.

Recent studies showed that bulk compositions of most CAIs are transitional between different types, e.g., type A and B (Lin et al., 2006; Ivanova et al., 2015) and usually overlap each other. Therefore, these types are expected to form a continuum in bulk chemical compositions, which records either a gradual change in the composition of the original CAI material or a different degree of evaporation or recondensation during melting (Krot et al., 2007). For example, a transition from anorthite-free type A inclusions to anorthite-rich type B inclusions requires the involvement of an additional silica-rich component. This would be possible if secondary anorthite replaced melilite during interaction with gas before melting of the inclusion. The melting of altered inclusions produces compositions transitional between type A and B.

It is interesting to note that in most cases the compositions of the main CAIs, except for type A CAIs, do not follow the general equilibrium condensation trend calculated by Grossman et al. (1972) and their compositional fields lie far outside this trend on the Ca_2SiO_4–Al_2O_3–Mg_2SiO_4 diagram. However, some observations (Ivanova et al., 2015) show that many smaller inclusions that were injected in the host CAI (and subsequently formed a compound object) were not affected by evaporation and their original chemical compositions remained unchanged. For example, in the compound CAI 3N from the NWA 3118 chondrite, the compositions of its enclosed inclusions disperse along the equilibrium condensation trend, as opposed to most known types of CAIs that underwent melting, evaporation and thermal reprocessing in a solid state (Ivanova et al., 2015).

On the ternary diagram, the bulk chemical compositions of grossite-bearing and spinel–hibonite-rich inclusions plot far outside the known types of CAIs, within the grossite and hibonite field. They have a nonsolar Ca/Al ratio, as opposed to typical CAIs in the CV3 chondrites with solar Ca/Al ratios.
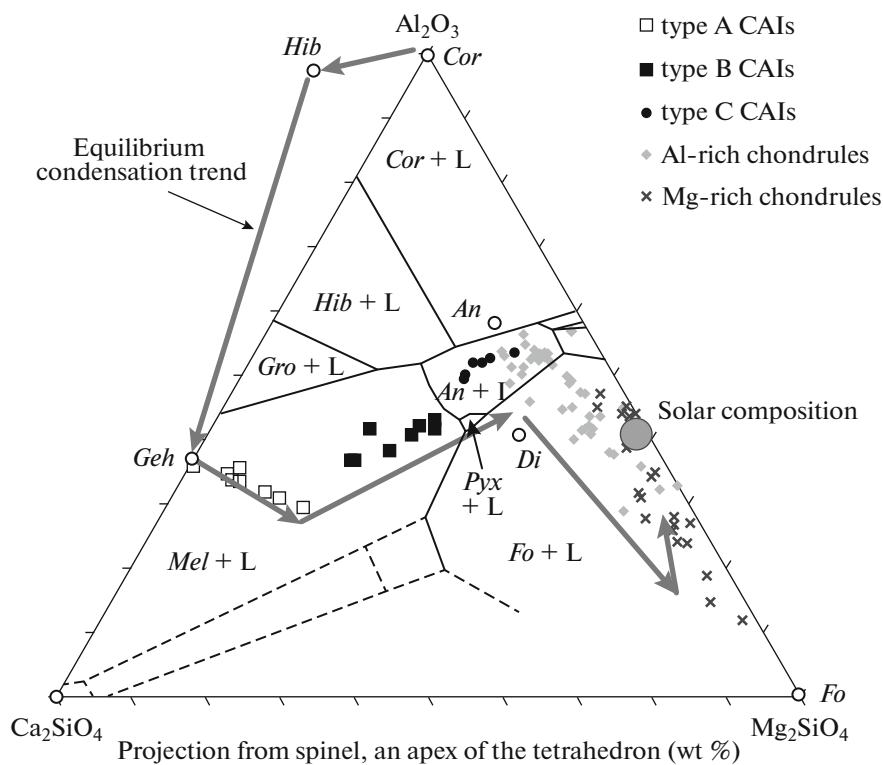
Fig. 5. Bulk compositions of major CAIs and Al-,Fe, Mg-rich chondrules from CV3 chondrites, equilibrium condensation trend for solid phases (Yoneda and Grossman, 1995), projected from spinel (MgAl$_2$O$_4$) onto the plane Al$_2$O$_3$–Mg$_2$SiO4–Ca$_2$SiO$_4$. The trend is depicted by lines with arrows. Data from MacPherson, 2014.

The bulk chemical compositions of ultrarefractory (UR) CAIs correspond to those of their host inclusions on the Ca$_2$SiO$_4$–Al$_2$O$_3$–Mg$_2$SiO$_4$ diagram (MacPherson and Huss, 2005). That is, if the host CAI is a forsterite-bearing type B inclusion, its enclosed UR inclusion would plot within the same field. However, unlike most of the host CAIs, the UR inclusions are considerably enriched in the less volatile elements such as Zr, Sc, Y, and Hf relative to both solar composition and bulk composition of all known refractory inclusions (Fig. 6).

An important feature of bulk chemical compositions of CAIs is their volatility-fractionated REE patterns, which exhibit enrichments in the most refractory REE relative to solar composition (average CI chondrite) and depletions in the most volatile REE. There are some specific REE patterns, notable for overall flat abundances with peaks reflecting either enrichments or depletions of Eu and Yb relative to the more volatile REE. It should be noted that CAIs have enriched REE patterns relative to CI chondrites and generally cosmic element abundance ratios.

One specific pattern, known as Group II (Mason and Martin, 1977), is notable for large depletions in the refractory REE (HREE) relative to the more volatile REE (except for Eu) (Fig. 7). Davis and Grossman (1979) suggested that this pattern can only be explained by fractional condensation from a gaseous reservoir in

which the most refractory REE were removed by prior condensation. Such patterns may come from perovskite or hibonite phases. Group II REE patterns are typical of unmelted fine-grained spinel-rich CAIs from the CV3 chondrites and hibonite-rich CAIs from the CM chondrites. CAIs with the complementary ultrarefractory REE patterns (Simon et al., 1996, El Goresy et al., 2002, Ivanova et al., 2012) are notable for enrichments in the most refractory REE relative to the more volatile REE and could represent high-temperature condensates that were removed by the solar wind from the source region to a lower-temperature prior to their condensation (Fig. 7).

OXYGEN ISOTOPIC COMPOSITIONS OF CALCIUM–ALUMINUM-RICH INCLUSIONS

On an oxygen three–isotope diagram (Clayton et al., 1977), most if not all CAIs in the CV3 chondrites plot on the slope ~0.95 CCAM line (Carbonaceous Chondrites Anhydrous Minerals), possibly relating to the enrichment in ^{16}O relative to ^{17}O and ^{18}O (Fig. 8) by the self-shielding effect (Clayton et al., 1977). For example, some minerals such as spinel, hibonite and forsterite are enriched in ^{16}O (δ^{18}O = −40‰), while the compositions of pyroxene and melilite may vary
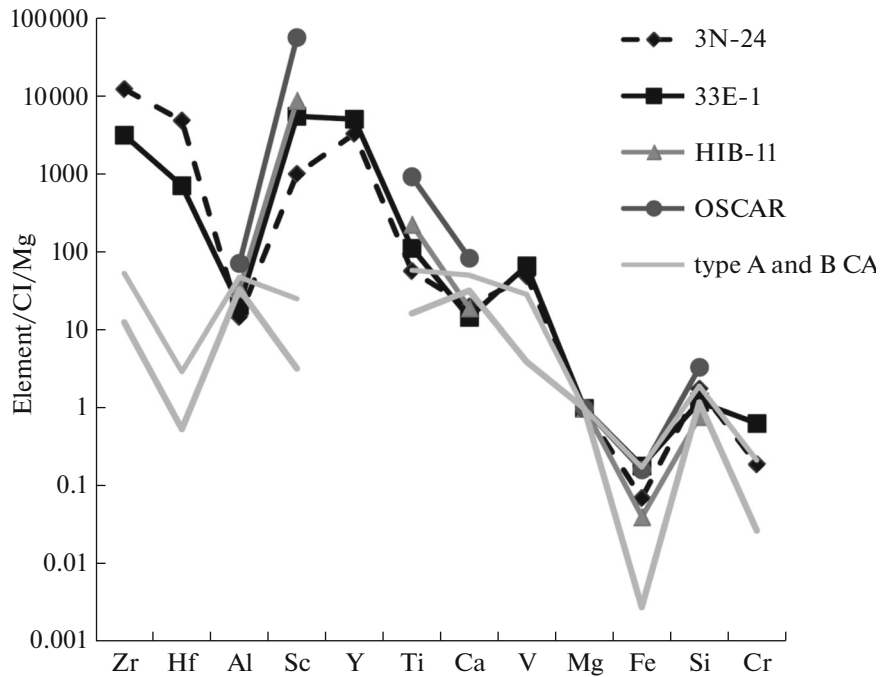
Fig. 6. Chemical composition of ultrarefractory CAIs 3N-24 and 33E-1 compared with common CAI varieties and other ultrarefractory (HIB-11 and OSCAR) inclusions. Data from Ivanova et al., 2012.

widely along this trend due to the isotopic exchange processes in CAIs. Secondary minerals of CAIs such as nepheline, sodalite, hedenbergite, and andradite are generally depleted in ^{16}O and plot close to the end of the CCAM line, below the terrestrial mass fractionation line with a slope of 0.5. These isotopic compositions are the result of low-temperature fluid metasomatism or aqueous alteration processes within the parent body (Cosarinsky et al., 2003).

However, some CAIs from other groups of chondrites, e.g., CH–CB chondrites, are consistently depleted in ^{16}O, as is the case for pyroxene- and melilite-rich CAIs, whereas the most refractory CAIs (hibonite-, grossite-, and spinel-bearing) show enrichments in ^{16}O. At the same time, ^{16}O-poor CAIs exhibit no effects of aqueous alteration, as is the case for CAIs from the CV3 chondrites. The depletion of ^{16}O CAIs in CH-CB chondrites was probably produced either by remelting of pre-existing ^{16}O-rich CAIs during chondule formation within an ^{16}O-poor nebular region or by a late-stage, highly energetic event in an impact-generated vapor cloud (Krot et al., 2012).

All minerals of ultrarefractory CAIs (except spinel) are consistently ^{16}O-depleted compared with minerals of the host CAI inclusions, which are enriched in ^{16}O similar to the common CAIs (Ivanova et al., 2012) (Fig. 8). It was shown that the precursor material of ultrarefractory CAIs was originally generated in a ^{16}O-rich reservoir, but later it became more depleted in ^{16}O during melting in an ^{16}O-poor nebular region due to

isotopic exchange in a gas–melt system (Ivanova et al., 2012).

FUN (fractionation and unknown nuclear anomalies) CAIs have also ^{16}O-enriched compositions ($\delta^{18}O = -41‰$), which exhibit an evolutionary trend along a line of slope 0.5 (Fig. 8) on the oxygen three–isotope diagram. Davis et al. (2000) and Krot et al. (2008a) show that this line intersects the CCAM trend
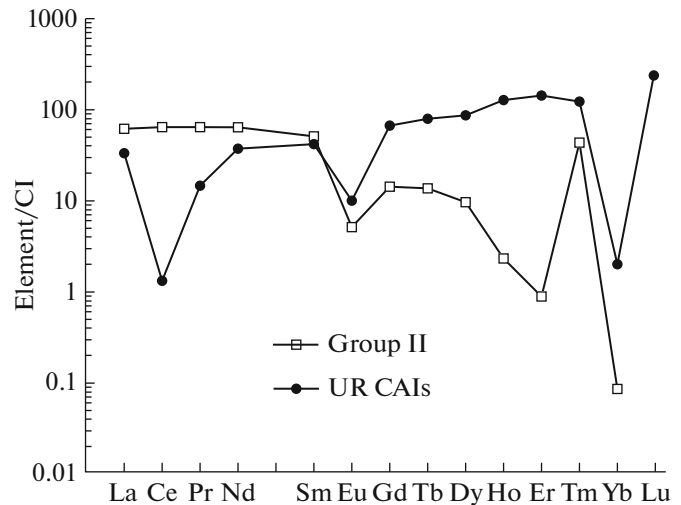
Fig. 7. REE patterns for the most abundant Group II and typical CAIs and the complementary REE pattern for ultrarefractory CAIs, data from MacPherson, 2014. Data for element abundances in CI chondrites are from Anders and Grevesse, 1982.
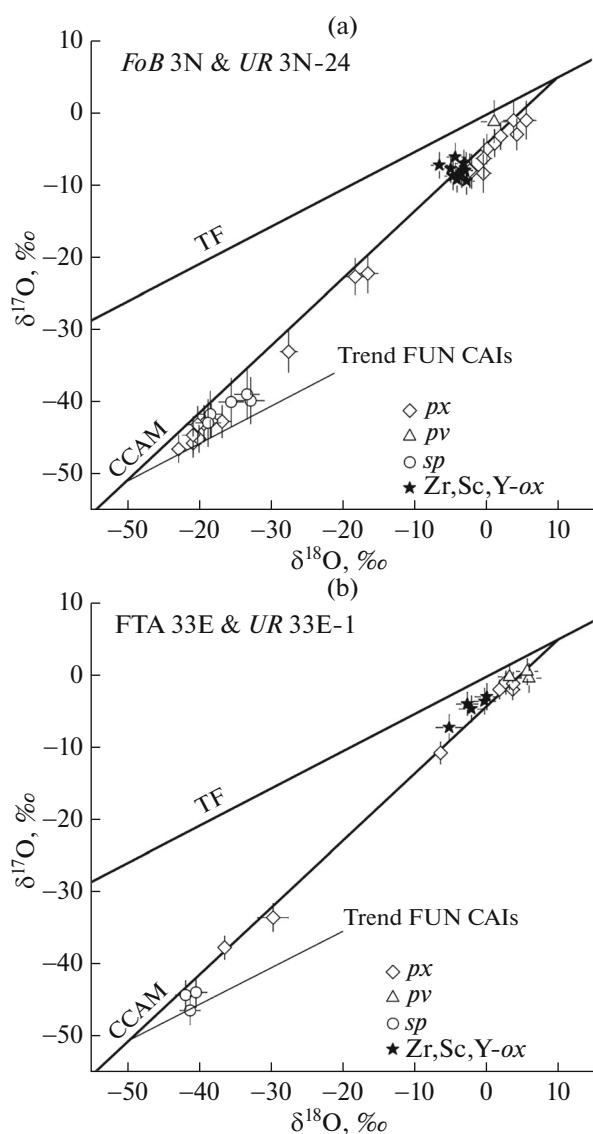
Fig. 8. Oxygen isotopic composition of minerals from ultrarefractory CAIs: a) *UR* CAI 3N-24 and its host forsterite-bearing type B (*FoB*) CAI from the NWA 3118 (CV3) meteorite; b) *UR* CAI 33E-1 and its host fluffy type A (FTA) CAI from the Efremovka (CV3) meteorite, data from Ivanova et al., 2012; FUN CAIs trend (MacPherson et al., 2014). Symbols are the same as in Fig. 2, Zr,Sc,Y-ox is Zr,Sc,Y-oxide.

and reflects a degree of ^{16}O enrichment slightly different from that reported for other CAIs.

Recent data from NASA's Genesis mission (McKeegan et al., 2011) demonstrated that the Sun is ^{16}O-rich (δ^{18}O ~ −50 ‰). Although the existence of ^{16}O-enriched and ^{16}O-poor gaseous reservoirs has been confirmed by many recent studies of CAIs, it still remains a matter of debate. Krot et al. (2010) proposed a scenario that readily explains the existence of two isotopically distinct reservoirs in the Solar system, which invokes ^{16}O-rich nebular gas and ^{16}O-poor dust dominating in dust-rich nebular regions. Recent supernova ejecta were substantially enriched in ^{17}O and ^{18}O relative to the interstellar medium and Galactic chemical evolution should result in the formation of ^{16}O-poor solids and ^{16}O-rich gaseous reservoir (Krot et al., 2010).

It has been shown that the oxygen isotopic compositions of Al,Ti-pyroxenes in some CAIs are clearly correlated with pyroxene bulk compositions (MacPherson et al., 2012a). The available data indicate that the oxygen isotopic variations may have resulted from oxygen isotopic exchange during crystallization of a zoned pyroxene such that the most Al- and Ti-enriched pyroxene in the interior of CAIs has a ^{16}O-poor isotopic signature, whereas low-Al and low-Ti pyroxene in the rims of zoned crystals are mostly ^{16}O-rich. One explanation for such a correlation between chemical and isotopic zoning is that Al, Ti-pyroxene may have been crystallized from perovskite (^{16}O-poor) by reaction with melilite and inherited the ^{16}O-poor isotopic signature of perovskite.

FORMATION CONDITIONS AND AGES OF THE OLDEST SOLAR SYSTEM SOLIDS

Based on the theoretical condensation sequence (Grossman et al., 1972), CAIs in the CV3 chondrites are considered as the earliest fine-grained condensates formed from a ^{16}O-rich gas of approximately solar composition in a region with high ambient temperature (>1300° K) and low pressure (<10^{-4} bar) and thus represent the oldest solids in the protoplanetary disk near the proto-Sun (Krot et al., 2005; MacPherson, 2014). The mineral, chemical, and isotopic compositions suggest that they may have been formed by evaporation, condensation, and accretion, the earliest events in the Sun and Solar System evolution. Many CAIs may have experienced melting and partial evaporation by shockwaves over a relatively short period of time while some CAIs may have undergone multiple recycling back to the disk by means of a bipolar outflow (the x-wind of Shu et al. (1996)). Solid particles can be sprayed to greater or smaller heliocentric distances by a turbulent flow of material inside the protoplanetary disk. CAIs forming closer to the Sun may have been affected by high-energy events from a supernova explosion, which were themselves a source of heating or produced transient heating in the nebula by shock waves.

Ultrarefractory (UR) CAIs are thought to have originated from precursor material differing from the main populations of CAIs by composition and formation conditions. The accumulation of rare elements such as Zr, Y, Hf, and Sc in CAI material to concentrations high enough to form oxides would require either repeated evaporation of a precursor of solar composition or condensation of a gas of nonsolar composition enriched in these elements. The chemical

composition of the UR CAIs is indicative of a high degree of fractionation of ultrarefractory elements at high temperatures. It is assumed that the precursors of the UR CAIs 3N-24 from NWA 3118 and 33E-1 from Efremovka were generated by evaporation and/or condensation at very high temperatures ($>1600°C$), as opposed to the precursors of their host CAIs 3N and 33E that were generated at a temperature $<1600°C$ (Ivanova et al., 2012). The precursor of the UR CAI 3N-24 and its host CAI 3N, subsequently forming a compound aggregate, experienced partial melting and annealing, as opposed to the precursor of the UR CAI 33E-1 and its host CAI 33E, which was probably not subjected to melting of the whole, like many fluffy type A CAIs (Ivanova et al., 2012).

The most recent geochemical, isotope, and thermodynamic data on CAIs in the CH–CB chondrites are indicative of their formation conditions different from those of CAIs from the most common CV3 carbonaceous chondrites (Ivanova and Petaev, 2015). It was shown that the formation of CAIs in the CH–CB chondrites can be readily explained by the condensation with partial isolation model (Petaev and Wood, 1998) rather than equilibrium condensation model (Grossman 1972). Alternative models invoke an origin by condensation from a gas–dust cloud of impact ejecta from the parent body (Wasson and Kallemeyn, 1990) or by a collision between planetesimals before dissipation of H_2-rich gas (Krot et al., 2005). The latter hypothesis argued that chondrules in CB chondrites are younger than chondrules in CV3 carbonaceous chondrites (Connelly et al., 2012), because there have yet been no attempts to date CAIs in CH–CB chondrites.

The colliding planetesimals hypothesis postulates that condensation took place in a gas–dust reservoir with a nonsolar chemical composition and a dust/gas ratio different from the canonical ratio of the system. This is supported by several populations of refractory inclusions in CH–CB chondrites, including the most refractory, grossite- and hibonite-bearing inclusions, containing rare aluminates such as dmitrivanovite and krotite, as well as common inclusions (types A, B, and C, fine-grained, fluffy and forsterite-bearing CAIs in CV3 chondrites) (Krot et al., 2008b; Ivanova et al., 2008). On the other hand hibonite- and grossite-bearing CAIs can be produced by evaporation of previously formed refractory material (Ryazantsev, 2015).

The current perception of the relative timing of the formation of Solar System materials largely depends on the precise chronology of the early Solar System processes, including the timing and rate of transformation of a protoplanetary disk of interstellar dust and gas into solid objects such as CAIs, chondrules, and their parent asteroids. Numerous data on the isotopic composition of heavy elements revealed an anomalous enrichment of refractory inclusions in some daughter nuclides of short-lived radioactive isotopes. Because

the Sun does not synthesize heavy elements and all elements heavier than helium have been produced by the first generation stars, such isotopic anomalies suggest that the protosolar nebula was enriched in elements nucleosynthesized at the inner edge of the solar accretion disk by at least two supernova explosions before the collapse of the solar nebula, and CAIs are the witness of this time (McKeegan et al., 2000).

Chondrules represent coalesced dust aggregates that were subsequently rapidly melted and cooled in lower-temperature regions (<1000 K) and higher ambient vapor pressure ($\geqslant 10^{-3}$ bar) than refractory inclusions, which resulted in the formation of their magmatic porphyritic textures. Another hypothesis of chondrule origin suggests that they formed in an impact-generated vapor cloud during collision between planetesimals. Although refractory inclusions and chondrules formed by different processes (condensation or dust accretion) under different physicochemical conditions, both types of solid objects of the early Solar System subsequently experienced the same highly energetic impact and heating events.

Al-Mg-isotope systematics of Ca–Al-rich inclusions. Dating of early Solar System processes is based on measurements of refractory inclusions and chondrules using the $^{26}Al–^{26}Mg$ chronometer. The method is based on the decay of the short-lived ^{26}Al to ^{26}Mg (half-life ~0.72 Myr). The age gap is an artifact of different initial $^{26}Al/^{27}Al$ ratios defined by the differences in slopes of the isochrons of various inclusions. Al and Mg are refractory elements in CAI minerals and their isotope systematics provide a clear record of high-temperature events in the protoplanetary disk rather than low-temperature parent-body asteroidal processes. At the same time, initial Al/Mg fractionation by condensation and solidification between the different mineral phases produces internal (mineral) isochrons with insignificant slopes and a large spread in Al/Mg values.

The $^{26}Al–^{26}Mg$ dating method was severely criticized for the disputed distribution of radiogenic ^{26}Al in space and time within the protoplanetary disk (Larsen et al., 2011) and the problem of a homogeneous distribution of ^{26}Al still remains a matter of debate, although recent data confirm ^{26}Al homogeneity in the CAI-forming region. Earlier studies on Al–Mg systematics showed that chondrules formed 1–2 Myr after CAIs (Kita et al., 2005), while the most recent data revealed that the formation of CAIs occurred within a time period of 200000 years (Fig. 9). Based on these data, it was assumed that different heat sources were involved in the formation of chondrules and refractory inclusions. However, some objects, e.g., FUN CAIs, containing isotopic anomalies, are characterized by the near-lack of excess ^{26}Mg and, thus, the lack of ^{26}Al during their formation.
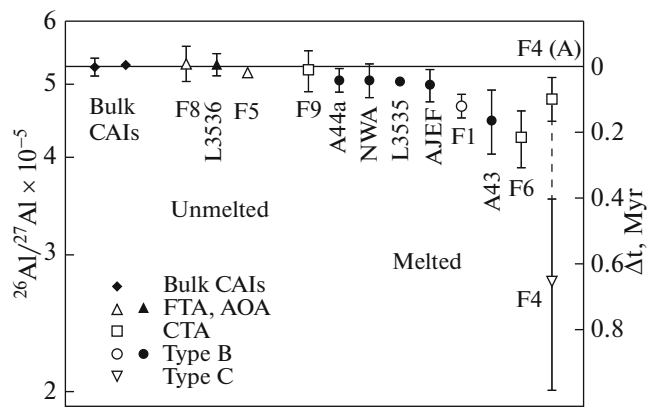
Fig. 9. Al−Mg isotopic age of CAI formation, data from MacPherson, 2014. Unmelted, fluffy type A (FTA) CAIs and amoeboid olivine aggregates (AOAs) are generally older than melted coarse-grained CAIs. Most CAIs formed within ~0.2 Myr except one type C CAI F4, which experienced remelting ~0.7 Myr after CAI formation. Bulk CAIs is the bulk average value for CAIs. F8, L3536, F5, F9, A44a, NWA, L3535, AJEF, F1, A43, F6, F4(A), F4 are numbers of CAIs. White symbols are from MacPherson et al., 2012b; black symbols are from references in MacPherson et al., 2014.

MacPherson et al. (1995) reviewed all available data for the initial $^{26}\mathrm{Al}/^{27}\mathrm{Al}$ ratio, denoted as $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0$, in CAIs, that confirmed its bimodal distribution (Fig. 10). Most CAIs give values approximating $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0$ of ~ 4.5×10^{-5}, while the remaining CAIs, including FUN CAIs, have initial $^{26}\mathrm{Al}/^{27}\mathrm{Al}$ ratios slightly above zero. The most important observation that has been made since 1995 in the study of CAIs indicates that the inclusions that never experienced melting have $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0$ values of $(5.2 \pm 0.1) \times 10^{-5}$ (in FTA and spinel-bearing fine-grained CAIs), which represent the initial, so-called canonical $^{26}\mathrm{Al}/^{27}\mathrm{Al}$ ratio in the Solar System (MacPherson et al., 2012b). The melted CAIs show a scattering of $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0$ values of $(4.2-5.2) \times 10^{-5}$ (Fig. 10), while the reprocessed inclusions that experienced multiple remelting have $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0$ ratios different from the canonical value. This suggests that reprocessing of CAIs or their precursors in the protoplanetary disk lasted 200000 years and the canonical $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0$ ratio of $(5.2 \pm 0.1) \times 10^{-5}$ represents the timing of initial Al/Mg fractionation, probably by condensation. This fractionation occurred within a very short time period of 20000 years in all primary CAI minerals and subsequent transformation (repeated melting and crystallization) may have resulted in resetting of $^{26}\mathrm{Al}$ (MacPherson et al., 2012b). For example, the formation of the CAI 4N, a forsterite-bearing type B inclusion from the NWA 3118 chondrite (Ivanova et al., 2014) falls within the same time interval as all known refractory inclusions found in carbonaceous chon-
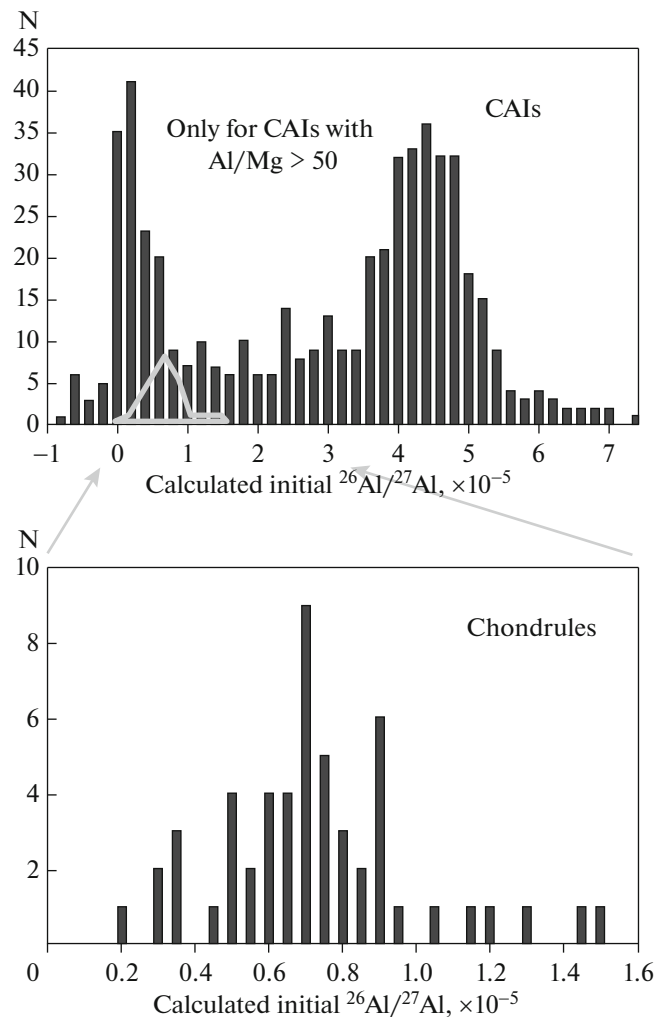
Fig. 10. Histogram showing the calculated initial $^{26}\mathrm{Al}/^{27}\mathrm{Al}$ ratios for CAIs and chondrules. The data show a bimodal distribution with $^{26}\mathrm{Al}/^{27}\mathrm{Al}$ values of ~ 0 and 5×10^{-5}. The values near zero include data for FUN CAIs but generally record the effect of late alteration processes (heating events and secondary aqueous alteration) after decay of $^{26}\mathrm{Al}$. The grey solid line in the topmost diagram depicts the distribution of values for chondrules shown in the lower diagram for comparison with CAIs. Data from MacPherson, 2014.

drites, although it has a complex, multistage formation history.

Therefore, the isotopic heterogeneity of inclusions may be associated with transformation of primary inclusions with $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0 = (5.2 \pm 0.1) \times 10^{-5}$ during successive melting, evaporation and crystallization, which resulted in loss of the daughter $^{26}\mathrm{Mg}$ and shift in $(^{26}\mathrm{Al}/^{27}\mathrm{Al})_0$ toward zero. The second mode of the CAI distribution near zero corresponds to the CAIs formed either after $^{26}\mathrm{Al}$ decay or before its injection into the solar system.

The recent results of $^{26}\mathrm{Al}$-$^{26}\mathrm{Mg}$ dating of Wark–Lovering rims around refractory inclusions (Mane

et al., 2015) show that the age difference between the inner cores and Wark–Lovering rims around refractory inclusions is 590000–690000 years, suggesting that CAIs had not yet been accreted to their parent body.

^{53}Mn–^{53}Cr systematics of Ca–Al-rich inclusions. Of particular interest is the study of ^{53}Mn–^{53}Cr systematics of secondary minerals (hedenbergite and kirschsteinite) from accretionary rims within a layered Wark–Lovering rim sequence surrounding refractory inclusions (MacPherson et al., 2015). The ^{53}Mn–^{53}Cr isotope system (^{53}Mn half-life ~3.7 Myr) has proved very useful for unraveling the chronology of fluid-assisted parent-body processes on chondritic asteroids. All of the secondary minerals analyzed give an age of 3.37 ± 0.7 Ma after formation of refractory CV3 CAIs (Connelly et al., 2012). Therefore, the formation of secondary minerals in the accretionary rims occurred after accretion of parent chondritic asteroids

^{41}Ca and ^{10}Be in Ca–Al-rich inclusions. Srinivasan et al. (1994, 1996) presented evidence for the presence of the now-extinct ^{41}Ca in the early Solar System, which constrains the time interval between the injection of freshly synthesized nuclides to the solar nebula from suitable stellar sources and the formation of CAIs, since this isotope has a very short half-life of ~0.1 Myr. Correlation between ^{26}Al and ^{41}Ca indicates that both isotopes have a similar source. However, our inability to confirm the presence of ^{41}Ca in the early Solar System, which is delayed by the technical difficulties, requires further investigation.

McKeegan et al. (2000) reported evidence for the existence of the short-lived radionuclide, ^{10}Be (half-life 1.39 Myr), in CAIs. This isotope is thought to be produced by spallation rather than nucleosynthesis and the available data are insufficient to conclude whether it was produced in the protosolar nebula under the effect of cosmic rays or before collapse of the molecular cloud by reaction between galactic irradiation and the interstellar medium.

Absolute Pb-Pb age of refractory inclusions and chondrules. As opposed to the above dating techniques, this geochronological method relies on the knowledge of the present-day abundances of long-lived parent and daughter isotopes in a sample and is free from assumptions on parent nuclide homogeneity. Of the various long-lived radioisotope systems, the Pb-Pb dating method is the most powerful tool to establish a high-resolution chronology of the first 10 Myr of the Solar System.

This chronometer is based on two isotopes, ^{238}U and ^{235}U, that decay to ^{206}Pb and ^{207}Pb, respectively and was used to determine the absolute age of several CAIs and chondrules in the primitive CV3 chondrites (Connelly et al., 2012). These CAIs yield an age of 4567.30 ± 0.16 Ma, suggesting that the timescale of the CAI-forming event may be as short as 160000 years,

whereas the chondrule ages range from 4567.31 ± 0.40 to 4564.70 ± 0.27 Ma. These data indicate that chondrule formation started nearly contemporaneously with CAIs and lasted ~3 Myr (Connelly et al., 2012), which is inconsistent with the long-held view that chondrules formed 1–2 Myr after CAIs.

These new data allow a revision of the chronology of the early Solar System processes. This timescale is similar to protoplanetary disk lifetimes inferred from astronomical observations (Fig. 11). These data suggest that the composition and structure of CAIs and chondrules reflect the processes in the evolution of the solar nebula and protoplanetary disk. For example, the brief formation interval for the CAI-forming event (condensation and melting) is similar to the average lifetimes of class 0 protostars of ~0.1–0.2 Myr inferred from astronomical observations of star-forming regions. Therefore, the thermal regime required for CAI condensation may only have existed during the earliest stages of disk evolution and condensation occurred within a brief time interval.

In contrast to CAIs, chondrule formation continued during the lifetime of the protoplanetary disk (~3 Myr), which is comparable with the lifetime of a Solar-type protostar (or a young stellar object) inferred from astronomical observations. The formation of chondrules by melting of disk dust under the effect of shock waves (the favored mechanism) requires, according to the latest chronological data, different and stable sources of shock waves during the lifetime of the protoplanetary disk.

CONCLUSIONS

CAIs, the oldest known objects in the Solar System, have complex structure and composition. Studies of these unique objects during the last 40 years resulted in the discovery of new types and varieties of CAIs and allowed determination of their morphology, mineralogy, bulk chemical and isotopic composition, age, and CAI-forming processes such as condensation (equilibrium and fractional), evaporation, melting, crystallization, metasomatic and thermal alteration, and accretion. Studies of CAIs also resulted in the discovery of two distinct types of oxygen isotope reservoirs, ^{16}O-rich and ^{16}O-poor, provided explanations for the possible mechanisms of formation of isotopic anomalies in CAIs, with normal and unknown isotope fractionation (FUN CAIs), allowed determination of the canonical ^{26}Al/^{27}Al ratios of the Solar System using Al–Mg and Cr–Mn isotopic systematics, revealed the sequence of processes forming the inner cores of CAIs, Wark–Lovering rim layers, and accretionary rims around inclusions.

The time interval of formation of chondrules was much longer than that of CAIs, although their absolute age indicates that chondrule formation started
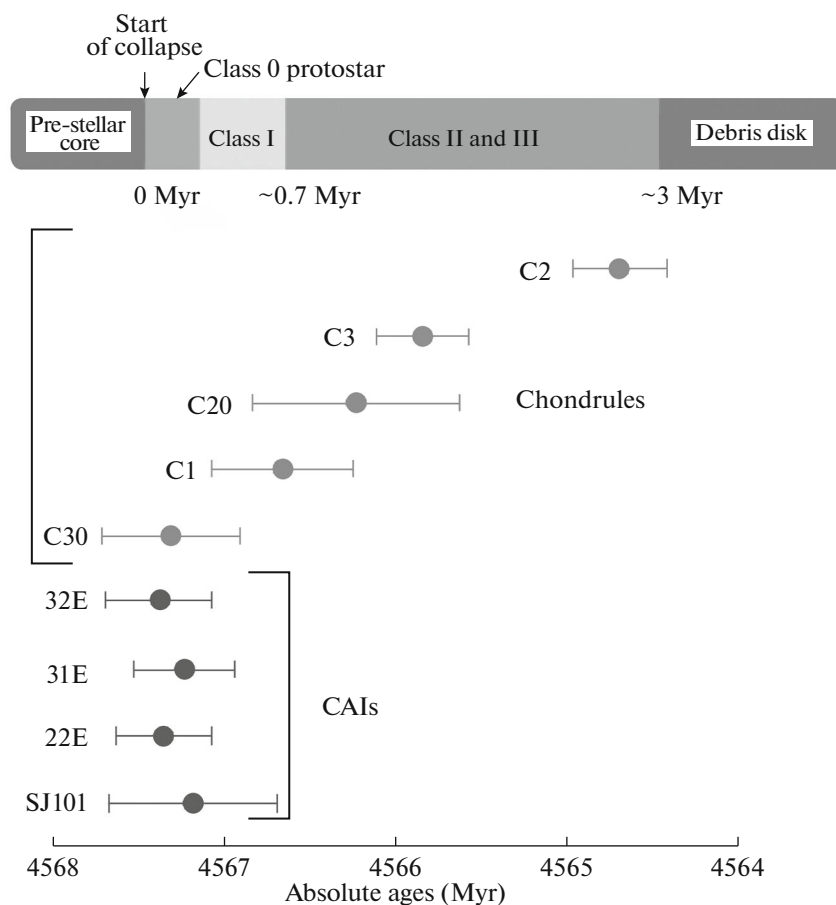
Fig. 11. Time scales of solid formation and disk evolution (Connelly et al., 2012). The brief formation interval corresponding to an age of 4567.30 ± 0.16 Myr of refractory CAIs is similar to the median lifetimes of class 0 protostars of ~0.1 to 0.2 Myr inferred from astronomical observation of star-forming regions (Evans et al., 2009). Therefore, the thermal regime required for CAI condensation may only have existed during the earliest stages of disk evolution typified by high mass accretion rates (~10^{-5} $M_\odot$ year^{-1}) to the central star. As opposed to refracrory CAIs, the events responsible for melting of chondrules occurred during the lifetime of the protoplanetary disk (~3 Myr), which is consistent with the median lifetime of solar-mass stars inferred from astronomical observations. Protostar classes (Larson, 2003): class 0—corresponds to early accretion phase, submillimeter range; class I—main accretion phase, far-infrared range; class II—classical T Tauri star, near-infrared range; class III—weak-lined T Tauri star, visible range. C30, C1, C29, C3, and C2 are chondrule numbers; 32E, 31E, 22E, SJ101 are CAI numbers.

contemporaneously with CAIs. The results of the studies provided a chronology of Solar System formation from class 0 protostar until the Sun became a main-sequence star.

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