# ZONED Ca-Al-RICH CHONDRULE IN BALI: NEW EVIDENCE AGAINST THE PRIMORDIAL CONDENSATION MODEL 

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## 1. Introduction

$\mathrm{Ca}-\mathrm{Al}$-rich inclusions and chondrules have recently been described from various Type-III carbonaceous chondrites [1-10]. Many of these inclusions are highly enriched in $\mathrm{Ca}, \mathrm{Al}, \mathrm{Ti}, \mathrm{Zr}, \mathrm{Y}, \mathrm{REE}, \mathrm{Ir}, \mathrm{Sc}$, and other elements as compared to chondritic composition [10-15]. Enrichments of both the major and trace elements are clearly related to the vapor pressures of the respective element, oxide or compound [10,11]. Also, the large enrichment factors of some elements as well as the apparent simultaneous enrichment of siderophile, e.g. Ir [13-15], and lithophile elements, e.g. $\mathrm{Ca}, \mathrm{Al}, \mathrm{Ti}, \mathrm{Sc}, \mathrm{Zr}, \mathrm{Y}, \mathrm{REE}$, seem to exclude an origin of these inclusions by magmatic differentiation

[^0]processes. Since the chemistry is obviously governed by gas-liquid and/or gas-solid differentiation processes only two models for the genesis of these materials have been suggested so far: enrichment of refractory elements by partial evaporation or by partial condensation. Theoretical calculations assuming thermal equilibrium show that the early condensates from a gas of solar composition should be free of Fe and depleted in Si $[16,17]$, with perovskite, spinel and anorthite as early phases. Since these are some of the phases observed in Ca -Al-rich inclusions, it has been widely believed that the $\mathrm{Ca}-\mathrm{Al}$-rich material represents early condensates from the primitive solar nebula (i.e., [9,11,17]). As pointed out before [10] this requires a rather complicated sequence; the $\mathrm{Ca}-\mathrm{Al}$-rich material has to condense, be removed from the system (to prevent further condensation) and be brought back and mixed with the products of the condensation of the main constituents, i.e. the bulk of the meteorites in which they occur. Furthermore, the products of a
condensation from a gas of solar composition can only be solids $[16,17]$ because the condensation temperatures of all the phases involved are far below the solidi of these phases and the respective systems. Petrological investigations of Ca -Al-rich materials, however, unambiguously point to a liquid origin (i.e., $[8,10,18]$ ). This is in contradiction with the condensation models and supports the partial evaporation-condensation hypotheses $[10,19,20]$ for the origin of the $\mathrm{Ca}-\mathrm{Al}$ rich inclusions as they occur now.

In the course of a study of the Bali carbonaceous chondrite we found a large rounded $\mathrm{Ca}-\mathrm{Al}$-rich particle, apparently a chondrule. We present here the results of a detailed petrologic investigation of this particular chondrule because it bears some new evidence for a non-condensation genesis.

The study is based on microscopic investigations and electron-microprobe analyses which were performed with an ARL EMX-SM and an ARL SEMQ at an accelleration potential of 15 kV with a sample current of $1-2 \cdot 10^{-8} \mathrm{~A}$. Wet chemically analyzed
minerals were used as standards. The measured X-ray intensities were corrected according to the procedure of Bence and Albee [21].

## 2. Description

The originally egg-shaped chondrule had a large diameter of 8.5 mm (Fig. 1). It is rather coarsegrained ( $0.5-2 \mathrm{~mm}$ ) and consists of approximately equal amounts of melilite and augite with some interstitial anorthite. All phases present incorporate varying amounts of small spinel crystals which range in size from about $1 \mu \mathrm{~m}$ to $50 \mu \mathrm{~m}$. All together this chondrule is very similar to a chondrule described by Clarke et al. [22] from the Allende chondrite. There is, however, a difference in the distribution of minerals within the chondrule. The Bali chondrule has a rim of on average 1.5 mm width which consists predominantly of melilite and scattered augite. The latter being present either as individual prismatic


Fig. 1. Ca -Al-rich chondrule from the Bali carbonaceous chondrite. Melilite and augite form large crystals (up to 2 mm ) and are undistinguishable in this photograph. Anorthite occurs as irregularly shaped interstitial grains within the main central portion. The mottled appearance of most of the crystals is due to tiny spinel crystals. Largest visible diameter of the chondrule is 7.5 mm . Plain transmitted light.
crystals or as interstitial grains in between the melilite grains. Both phases bear highly variable amounts of small spinel crystals. This surface zone is readily visible under crossed polarizers because the melilite there shows anomalous (blue) interference colors. This behaviour of the melilite changes gradually towards the inner portion of the chondrule. There also anorthite appears occasionally and fills some of the interstices between the melilites and/or augites. The augites too have a different optical appearance within the surface zone and the central portion. Near the surface they are pleochroic from light green to colorless whereas in the central portion they are non-pleochroic. These optical changes are due to changes in chemical composition as shown in Table 1 and discussed below.

The melilite at the surface is rich in the gehlenite $\left(\mathrm{Ca}_{2} \mathrm{Al}_{2} \mathrm{SiO}_{7}\right)$ component. The akermanite component ( $\mathrm{Ca}_{2} \mathrm{MgSi}_{2} \mathrm{O}_{7}$, i.e. Mg content) of the melilites strongly increases towards the central portion of the chondrule. Positively correlated with this MgO increase are the alkali contents whereas the Al content decreases rapidly from the surface to the center. The compositional variation of melilites found here lies within the range of melilite compositions reported from Allende inclusions [ $1-7,9,22]$. It is noteworthy, however, that the akermanite contents of both the Bali and Allende melilites
are clearly higher than in melilites from Ca -Al-rich objects in Lancé [10,18]. The augites are typical aluminous titanaugites similar to those already described from $\mathrm{Ca}-\mathrm{Al}$-rich inclusions in other chondrites (i.e., $[1-7,9,22]$ ).

They are essentially Fe-free and also very low in alkalies. Again, the composition of these titanaugites changes with the distance from the chondrule surface: $\mathrm{TiO}_{2}$ and $\mathrm{Al}_{2} \mathrm{O}_{3}$ (and perhaps FeO and the alkalies) decrease, whereas $\mathrm{SiO}_{2}$ and MgO (and $\mathrm{Cr}_{2} \mathrm{O}_{3}$ ?) increase towards the central portion. The spinel composition changes similarily, with $\mathrm{TiO}_{2}$ and FeO decreasing, and $\mathrm{Cr}_{2} \mathrm{O}_{3}$ increasing towards the center. Anorthite is not present within the outermost zone. However, although subtle, some compositional change was observed with MgO (and $\mathrm{Na}_{2} \mathrm{O}$ ?) increasing and CaO decreasing towards the center.

## 3. Discussion

Some petrologic arguments have already been presented $[10,18]$ against the primordial condensation model for $\mathrm{Ca}-\mathrm{Al}$-rich objects with the shape (chondrules) and textures (igneous) of the majority of them. This study further enhances these arguments.

TABLE 1
Averaged electron-microprobe analyses of different phases in a $\mathrm{Ca}-\mathrm{Al}$-rich chondrule from the Bali carbonaceous chondrite. Analyses are arranged in the order of increasing distance from the chondrule surface (surface-intermediate zone-central portion).

|  | Melilite |  |  | Aluminous titanaugite |  |  | Spinel |  |  | Anorthite |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | surface | interme- <br> diate <br> zone | center | surface | interme- <br> diate <br> zone | center | suxiace | interme- <br> diate <br> zone | center | interme- <br> diate <br> zone | center |
| $\mathrm{SiO}_{2}$ | 31.1 | 34.5 | 38.9 | 38.4 | 40.5 | 42.1 | 0.77 | 0.42 | 0.46 | 43.9 | 44.3 |
| $\mathrm{TiO}_{2}$ | 0.03 | 0.02 | 0.05 | 7.5 | 5.5 | 4.2 | 0.33 | 0.26 | 0.15 | 0.06 | 0.08 |
| $\mathrm{Al}_{2} \mathrm{O}_{3}$ | 23.7 | 18.5 | 8.9 | 19.4 | 18.5 | 17.2 | 70.3 | 70.5 | 70.6 | 36.0 | 36.7 |
| $\mathrm{Cr}_{2} \mathrm{O}_{3}$ | 0.03 | 0.03 | 0.04 | 0.08 | 0.09 | 0.13 | 0.29 | 0.37 | 0.50 | 0.01 | 0.01 |
| FeO | 0.10 | 0.08 | 0.03 | 0.20 | 0.07 | 0.07 | 0.24 | 0.08 | 0.05 | 0.02 | 0.01 |
| MgO | 4.6 | 7.5 | 9.6 | 8.7 | 10.0 | 10.8 | 28.1 | 28.1 | 28.2 | 0.23 | 0.33 |
| CaO | 40.5 | 40.1 | 40.2 | 25.5 | 25.8 | 25.5 | 0.31 | 0.32 | 0.22 | 19.8 | 19.2 |
| $\mathrm{Na}_{2} \mathrm{O}$ | 0.06 | 0.15 | 0.25 | 0.02 | 0.02 | 0.01 | - | - | - | 0.09 | 0.11 |
| $\mathrm{K}_{2} \mathrm{O}$ | 0.06 | 0.06 | 0.08 | 0.02 | 0.06 | 0.03 | - | - | - | 0.04 | 0.05 |
| Total | 100.18 | 100.94 | 98.05 | 99.82 | 100.54 | 100.04 | 100.34 | 100.05 | 100.18 | 100.15 | 100.79 |
| Number of analyses | 19 | 7 | 4 | 4 | 12 | 8 | 14 | 12 | 15 | 8 | 5 |

The $\mathrm{Ca}-\mathrm{Al}$-rich is zoned - mineral of this zoning is ex expected from the i.e. all refractories surface whereas th Na ) are concentrat This distribution, cally different elen the apparent corre and vapor pressure indicate an elemen between liquid ant Bali chondrule ant to be conclusive e tion from a liquid tion might have 0 the solar nebula $h$ this chondrule an of carbonaceous "primordial" con tively old or "prit high ${ }^{26} \mathrm{Mg}$ [24]). the element and r plained by rapid of an overheated fast enough to pr unequilibrium $m$ i.e. heated substs perature (which $[8,18]$ ) is necess be the most plau

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The Ca -Al-rich chondrule from the Bali chondrite is zoned - mineralogically and chemically. The nature of this zoning is exactly opposite to what could be expected from the primordial condensation model: i.e. all refractories (e.g. $\mathrm{Ti}, \mathrm{Al}$ ) are enriched near the surface whereas the more volatile elements ( $\mathrm{Mg}, \mathrm{Cr}, \mathrm{Si}$, Na ) are concentrated in the center of the chondrule. This distribution, the equal enrichments of geochemically different elements, e.g. Ir and Sc [11,13-15] and the apparent correlation between enrichment factors and vapor pressures [10] (elements and/or compounds) indicate an elemental fractionation via an interaction between liquid and/or solid and gas. The shape of the Bali chondrule and its mineralogy and texture seem to be conclusive evidence for an original crystallization from a liquid although some mild recrystallization might have occurred. Since condensation from the solar nebula would not produce a liquid $[16,17]$ this chondrule and many similar objects from a variety of carbonaceous chondrites cannot be unaltered "primordial" condensates although they may be relatively old or "primitive" (e.g. low $\left.{ }^{87} \mathrm{Sr}\right){ }^{86} \mathrm{Sr}[23]$ and high ${ }^{26} \mathrm{Mg}$ [24]). Rather, the overall composition and the element and mineral distribution seem easiest explained by rapid loss of volatiles from the surface of an overheated melt which subsequently cooled fast enough to preserve a diffusion gradient (and/or unequilibrium mineral assemblages). If overheating, i.e. heated substantially beyond the liquidus temperature (which also may be very high $\sim 2,000^{\circ} \mathrm{K}$ $[8,18]$ ) is necessary, hypervelocity impacts seem to be the most plausible heat source.

Such events could cause substantial volatilization of target and projectile material, generating dense gas clouds from which dsariety of compounds and elements could condense. Thus, two geochemically indistinguishable mechanisms could account for the observed enrichments of refractory elements: fractional condensation of low-vapor-pressure elements or compounds from an impact gas cloud and fractional evaporation of high-vapor-pressure elements or compounds from overheated target and/or projectile material [ $10,19,20]$. Gas-liquid interactions have already been found to be the most plausible cause of zonal element distributions in meteoritic chondrules and their lunar counterparts, glass spheres [18,25].

Both models, fractional condensation and fractional evaporation can also account for the large variations
in composition between different "white" fragments. Although only some fragments from the Allende chondrite have been studied so far, the measured Ir contents vary by a factor of $\sim 70$ [11] or $\sim 400$ [27], if Ir depleted Na -rich fragments are included. This is not easily explained by the equilibrium condensation model. Furthermore, inclusions in Lancé seem to be much more highly enriched (at least ten times) in refractory elements than those from Allende. Unfortunately, their small sizes prevent thorough bulk chemical studies but for some refractories enrichments of up to $\sim 400$ times the chondritic level can be calculated from mineral analysis [10]. This, as well as the different enrichment level of refractories in white inclusions from different chondrites, also seem easier explained by non-equilibrium processes rather than equilibrium condensation in the solar nebula.

Enrichment factors of 20 [11,12,13-15] to 400 [10] of refractories over the chondritic abundances require fractions of $5 \%$ to less than $1 \%$ being taken out of a bulk of chondritic composition. Probably none of the processes proposed here can produce these enrichments in just one step. Rather, repeated impacts causing partial evaporation and partial recondensation can account for the variety of white inclusions we observe. The early history of the parent - bodies of chondrites as well as other planetesimals and planets is believed to be characterized by high impact rates. This way the observed "primitive" isotopic nature of $\mathrm{Ca}-\mathrm{Al}$-rich inclusions could be brought into accord with all the observations pointing to a secondary origin, like the igneous origin [10,19, 20,22] and the apparent mixed chemistry [12].

The parent material for the white inclusions can either be chondritic material or a material already enriched in real primitive condensates. What we observe now are certainly not "primitive" condensates but rather secondary objects which could have partly originated from such condensates but could also have been formed from a chondritic parent by either partial evaporation and/or condensation of matter in the course of repeated impact events.

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