ISOTOPIC STUDIES OF REFRACTORY PHASES IN PRIMITIVE METEORITE BY AN ION MICROPROBE

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CERTIFICATE

I hereby declare that the work presented in this thesis is original and has not formed the basis for the award of any degree or diploma by any University or Institution.

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Dedicated to mummy & papa

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Chapter One

Introduction

Origin and early evolution of the solar system has remained one of the most intriguing question for a long time. Numerous experimental and theoretical approaches have been employed to seek an unequivocal answer to this question. The progress in experimental techniques and computing capabilities in the last few decades has led to significant advances in this area of research. Owing to unique chemistry and nearly pristine nature, meteorites constitute the most important accessible component of solar system material that may be analyzed to unfold the story of the origin and early evolution of the solar system.

The most widely accepted model for the formation of the solar system suggests that the gravitational collapse of a dense molecular cloud fragment about 4.56 Ga ago led to the formation of the proto-sun at its center and a rotating disk of gas and dust, the so called solar-nebula, surrounding the nascent sun. The solar system objects (planets, satellites, comets and asteroids) formed out of this nebula in a gradual manner starting with the formation of grains that coagulated to form larger-sized objects that evolved to planetesimals and finally to planets through gravitational interactions and collisional accretion processes. An attempt has been made in this thesis to address several important issues related to the formation and early evolution of the solar system using an experimental approach. These are:

- (i) Nature of the initial mix of material characterizing the solar nebula,
- (ii) Event(s) leading to the collapse of the proto-solar molecular cloud,
- (iii) Timescales of formation of the Sun and some of the first solar system objects,
- (iv) Environment and the physical and chemical processes governing the formation of the first solar system solids.

Experimental records that provide clues to the above issues are expected to be present in the first solids that formed in the solar system. It is now known that some primitive meteorites indeed contain such objects and the present work deals with the identification of such early formed solar system objects and study of their isotopic and elemental compositions using ion microprobe technique. The results obtained are analyzed to obtain insight into various aspects of origin and early evolution of the solar system.

1.1 Meteorites and Early Solar System Objects

Meteorites are broadly classified into three groups: stony, stony-iron and iron. These groups are further classified into various other sub-groups (Fig. 1.1). The stony meteorites are grouped into two classes, chondrites and achondrites, the latter being fragments of planetesimals (asteroids) that underwent melting, differentiation and re-crystallization. Stony meteorites of martian origin (SNC group) and of lunar origin have also been detected. The three main types of chondritic meteorites are carbonaceous, ordinary and enstatite chondrites. Seven different classes of carbonaceous chondrites have been identified based on their chemical, petrologic and oxygen isotopic characteristics. These are designated as CI, CM, CV, CK, CO, CH and CR meteorites.



Fig. 1.1 Classification of Meteorites.

Most of the carbonaceous meteorites escaped extensive thermal metamorphism on their parent asteroids and are considered to be primitive sample of solar system matter. For example, the chemical composition of the CI meteorites closely resembles that of the solar photosphere indicating their pristine nature. Most of the carbonaceous meteorites contain some rare objects composed primarily of refractory oxides and silicates. These refractory objects are referred as CAIs (Calcium-Aluminum-rich Inclusions). The commonly found refractory phases in CAIs are spinel, melilite, pyroxene and anorthite along with minor amount of hibonite, perovskite, corundum, grossite, diopside and forsterite. Few CAIs have also been identified in ordinary and enstatite chondrites. Thermodynamic and pertrographic considerations (Grossman, 1972, 1980; Yoneda and Grossman, 1995) suggest CAIs to be some of the first objects to form in the solar nebula as the mineral phases present in CAIs match the first condensates expected during cooling of an initially hot solar nebula (Table 1.1).

Mineral	Major Elements	Temperature (°K)
Corundum	Al_2O_3	1770
Hibonite	CaAl ₁₂ O ₁₉	1743
Perovskite	CaTiO ₃	1688
Melilite	(Ca[Al,Mg][Si,Al] ₂ O ₇)	1628
Spinel	MgAl ₂ O ₄	1501
Fassaite	Mg[Fe,Ca]SiO ₃	1449
Forsterite	Mg_2SiO_4	1443
Anorthite	CaAl ₂ Si ₂ O ₈	1416

Table 1.1 Condensation temperature of refractory minerals at 10⁻³ atm in the solar nebula (Yoneda and Grossman, 1995).

1.2 Hibonites

Hibonite (CaAl₁₂O₁₉), one of the early condensates to form in the solar nebula, is a potential recorder of events taking place in the early solar system. Earlier studies of meteoritic hibonites showed that they host large magnitude isotopic anomalies and are also characterized by enrichment of rare earth and refractory trace element abundances (Fahey et al., 1987a, 1987b; Hinton et al., 1988; Ireland, 1988, 1990; Ireland et al., 1988). They are commonly found in CM meteorites (Macdougall and Goswami, 1981;

Armstrong et al., 1982; MacPherson et al., 1983; MacPherson et al., 1984; Ireland, 1988). Occurrence of hibonites in other carbonaceous meteorites like CV (Keil and Fuchs, 1971; Allen et al., 1978; Christophe Michel-Levy et al., 1982; Kornacki and Wood, 1985), CO (Ireland et al., 1991; Simon et al., 1998; Russell et al., 1998), CH and unique carbonaceous chondrites (Grossman et al., 1988; MacPherson et al., 1989), ordinary chondrites (Bischoff and Keil, 1984) and enstatite meteorite (Bischoff et al., 1985) have also been reported. In the present study, a suite of hibonites from two CM meteorites have been analyzed to obtain information relevant to origin and early evolution of the solar system. Hibonites are rare in terrestrial environment and so far it has been found only at three places, alluvial deposit at Elvisa, fort Dauphin region (Madagascar), Gornaya shoriya (Siberia) and Tanzania (Maaskant et al., 1980). The chemical composition of hibonites from these three places are summarized in Table 1.2. Unlike highly refractory meteoritic hibonite, terrestrial hibonites are metamorphosed and contain high amount of iron.

	MgO	Al_2O_3	SiO ₂	CaO	TiO ₂	Fe ₂ O ₃	FeO	Other	Total
Tanzania	0.27	72.8	0.75	6.2	5.6	2.7	7.3	4.1	99.72
1 adagascar	2.8	76.1	0.6	7.5	6.9	1.9	2.5	1.8	99.5
Siberia	1.59	73.67	1.03	8.67	5.3	9.9	0.35	-	100.3

Table 1.2 Chemical composition of terrestrial hibonites (Maaskant et al., 1980).

Hibonite belongs to the hexagonal group (dihexagonal dipyramidal). Its structure is discussed at length by Burns and Burns (1984). Ideal crystal structure of hibonite is shown in Fig. 1.2. The colour of hibonites varies from colourless to orange to blue. Experiments exploring factors affecting colour of hibonite by Ihinger and Stolper (1986) show that hibonite can be used as an index of the partial pressure of oxygen during their formation. Blue colour has been attributed to presence of Ti^{3+} indicating a reducing environment. The possibility of orange hibonite formation in a reducing environment and subsequent oxidization leading to a change of Ti^{3+} to Ti^{4+} has also been suggested (Beckett et al., 1988; Simon et al., 2001). Results obtained by Simon et al. (2001) do not show strong depletion in Ce and V in orange hibonites from Allende CAIs implying oxygen fugacity to be within ~2-3 orders of magnitude of the generally accepted value for the solar nebula, at the time of their formation.



Fig. 1.2 Hibonite Crystal structure (from Burns and Burns, 1984). The contents of onehalf of the hexagonal unit cell between z=1/4 and z=3/4 along the c axis are shown.

Hibonite inclusions in meteorites have been classified into several types based on their morphology/mineralogical assemblages and variation in TiO_2 content (Table 1.3; Ireland et al., 1991). The most abundant type is the spinel-hibonite spherules found commonly in CM meteorites where hibonite laths are embedded within a spinel matrix.

Туре	Mineralogy / Morphology	TiO ₂ (%)
Platelet (PLACs)	Platy hibonite crystals	0.5-2.0
Spinel-hibonite Spherules (SHIBs)	Bladed hibonite crystals in spinel with perovskite inclusions	0.5-9.0
Blue Aggregates (BAGs)	Blue hibonite plates	5.5-6.5
Silicate-bearing	Hibonite occurs as an accessory phase	Variable
HAL-type	Large hibonite crystals	< 0.2
Glass Spherules	Hibonite-glass	1.5-2.3

Table 1.3 Classification of hibonite based on morphology and TiO_2 content (Ireland et al., 1991).

1.3 Aim of the Present Study

The objective of the present work is to obtain experimental data that will provide clues for a better understanding of the origin and early evolution of the solar system. Detail investigation of isotopic and elemental compositions of hibonites from two primitive carbonaceous meteorites have been carried out to achieve this objective.

The meteoritic hibonites are basically Ca-Al-oxide with minor amount of Mg and Ti (CaAl_{12-2x}Mg_xTi_xO₁₉). As mentioned earlier hibonite is one of the first solids to form during the cooling of an initially hot (>1700 °K) nebular gas of solar composition (Table 1.1). The only other refractory phase with condensation temperature higher than hibonite, that is present in trace amount in primitive meteorites, is corundum (Al₂O₃). We have identified hibonites occurring either as individual platy grain (platelet) or as a part of spinel-hibonite aggregates (spherules) from two carbonaceous chondrites, Murchison and Murray, belonging to the CM group. A total of 18 objects (platelets and spherules) were selected for the study of their isotopic and trace element compositions using ion microprobe technique. The specific investigations carried out include:

(i) Identification of fossil records of the now-extinct short-lived nuclides, ²⁶Al ($t_{1/2}$ ~7x10⁵ years) and ⁴¹Ca ($t_{1/2}$ ~10⁵ years), to address questions pertaining to the source of these short-lived nuclides and its implication for the processes leading to the formation of the solar system,

- (ii) Measurement of stable isotopic composition of O, Ca and Ti in the hibonites to look for abundance anomalies in oxygen isotopes and in the neutron-rich isotopes, ⁴⁸Ca, ⁴⁹Ti and ⁵⁰Ti, to identify specific stellar and/or local inputs contributing to the initial mix of material represented by the solar nebula,
- (iii) Studies of rare earth and refractory trace element abundance in the hibonites to infer their probable formation environment in the solar nebula, and,
- (iv) Formulation of a self-consistent scenario that may account for the formation of the early solar system solids (hibonites) as well as their isotopic and elemental compositions.

A schematic representation of the present study, the approach and the expected outcome is shown in Fig. 1.3.

Isotopic composition and trace element abundances in CM hibonites have been studied in detail by Fahey et al. (1987a), Ireland (1990) and Sahijpal et al. (2000). All these studies concentrated on hibonites from the Murchison meteorite. Measurement of ⁴¹Ca was not attempted in the first two studies, while oxygen isotopic analysis was not done in the latter work. No comprehensive study of hibonites from other CM meteorites has been reported yet. The present study reports the results obtained from the first detailed analysis of hibonites from the CM meteorite, Murray, and additional data for hibonites from the Murchison meteorite.

In the following sections, a brief summary of the various aspects relevant to our understanding of the origin and early evolution of the solar system based on the studies of early solar system solids is presented.



Fig. 1.3 Flowchart depicting the studies carried out on refractory grains (hibonites) in CM meteorites and their broad implications

1.3.1 Short-lived Radionuclides in the Early Solar System

Meteorite studies have revealed the presence of a large number of now-extinct shortlived nuclides (e.g. ²⁶Al, ⁴¹Ca, ⁵³Mn, ⁶⁰Fe, ¹⁰⁷Pd, ¹⁸²Hf, ¹²⁹I, ²⁴⁴Pu) with half-lives ranging from 10⁵ to ~10⁸ years in the early solar system. The one time presence of these shortlived radionuclides can be inferred by looking for excess in the abundances of their daughter nuclides in suitable meteorite samples. If this excess correlates with the stable isotope abundance of the parent element, it can be attributed to in-situ decay of the shortlived nuclide within the analyzed sample, thereby confirming the presence of the nuclides at the time of formation of the object.



Fig. 1.4 Al-Mg isotopic systematics in hibonites (literature data). The expected trend line for an initial 26 Al/ 27 Al value of 5 \cdot 10⁻⁵ is also shown. 'd' is the deviation in measured 26 Mg/ 24 Mg ratio from of the reference value (26 Mg/ 24 Mg = 0.13932) at per mil level. The dotted line represents normal 26 Mg/ 24 Mg (d 26 Mg = 0). Data from Fahey et al., 1987a; Ireland, 1988; Ireland, 1990; Ireland et al., 1991; Simon et al., 1998.

As an illustration, if we consider the literature data for Al-Mg isotopic systematics for hibonites (Fig. 1.4), it is clear that excess ²⁶Mg is present in many hibonites and this excess correlate with the Al/Mg ratio in these objects. These data, therefore, suggest insitu decay of ²⁶Al within the hibonites as the cause of the excess and confirm the presence of the short-lived nuclide ²⁶Al in the early solar system at the time of formation of the hibonites. The data for hibonites with excess ²⁶Mg shows a general trend indicating that the initial ²⁶Al/²⁷Al ratio at the time of formation of these hibonite was ~5 × 10⁻⁵, a value also inferred from studies of other refractory early solar system objects (CAIs) from different meteorite groups (e.g. MacPherson et al., 1995). It may also be noted that a good number of hibonites are devoid of ²⁶Al.

Several plausible sources of the short-lived nuclides present in the early solar system have been proposed. These are:

- (i) Freshly synthesized nuclides from a stellar source injected into the collapsing protosolar cloud,
- (ii) Production by interaction of energetic particles with dust and gas in the protosolar cloud,
- (iii) Production by interaction of solar energetic particles with dust and gas in the solar nebula.

It is important to identify the exact source of the short-lived nuclides present in the early solar system. If the short-lived nuclides were injected into the protosolar molecular cloud from a stellar source, their presence in early solar system solids puts a very strong constraint on the time interval between the production of these nuclides in the stellar source and the formation of the early solar system solids and hence on the time scale of protosolar cloud collapse. On the other hand, if the short-lived nuclides are products of solar energetic particle interactions with material in the solar nebula, they cannot be used as time markers of pre-solar processes (e.g. time scale for proto-solar cloud collapse). Their presence provides us specific information about the energetic environment in the early solar system. I have further investigated this issue based on results obtained in this study and those reported earlier for CM hibonites.

Introduction

1.3.2 Stable Isotopic Anomalies in Early Solar System Solids

The discovery of oxygen isotopic anomalies in CAIs (Clayton et al., 1973) demonstrated that the solar nebula was not isotopically homogenized and it is possible to identify the presence of specific stellar nucleosynthetic components contributing to the material constituting the solar nebula. This was confirmed by the presence of abundance anomalies in other stable isotopes such as ⁴⁸Ca, ⁵⁰Ti, ⁵⁴Cr, ⁶⁶Zn as well as several noble gas isotopes in specific samples of primitive meteorites. Isotopic studies of CM hibonites show that they are characterized by anomalous oxygen isotopic composition that follow the general trend seen in other CAIs with enrichment in ¹⁶O (Fig. 1.5). Both enrichment



Fig. 1.5 A plot of d^{17} O vs d^{18} O for hibonites (literature data). The *d* values represent deviations in measured 17 O/ 16 O and 18 O/ 16 O ratios from reference SMOW values (SMOW = standard mean ocean water; 17 O/ 16 O = 0.00038309, 18 O/ 16 O = 0.0020057; *d* = 0) in parts per mil. Data from meteoritic CAIs fall along the Carbonaceous Chondrite Anhydrous Mineral (CCAM) line. Terrestrial samples fall along the Terrestrial Fractionation (TF) line. Data from Fahey et al., 1987b; Ireland, 1988; Ireland et al., 1991.

and depletion in the n-rich isotopes ⁴⁸Ca and ⁵⁰Ti have also been observed in CM hibonites and they are correlated in the sense that δ^{48} Ca and δ^{50} Ti show the same sign. However, unlike the oxygen isotopic anomalies, large magnitude n-rich isotopic anomalies appears to be an exclusive characteristics of the CM hibonites; silicate-rich CAIs from other meteorites show very small anomalies (a few per mil) in n-rich isotopes.

The inventory of the stable isotopes in the protosolar cloud represents contributions from a variety of stellar sources over the entire lifetime of this cloud. In contrast, the shortlived nuclides present in the early solar system were produced just prior to or soon after the collapse of this cloud, either as freshly synthesized stellar products or as a product of energetic particle interactions. Inspite of this difference, certain trends between the presence of radiogenic isotopic anomalies and stable isotopic anomalies in early solar system solids have been reported. The present study extends and explores the possibility of constructing an evolutionary scenario for the CM hibonites that might explain both the radionuclide and stable isotope data in these objects.

1.3.3 Rare Earth and Refractory Trace Elements in CAIs

Studies of rare earth and refractory trace element (REE and RTE) abundances in CAIs help in deciphering the nebular environment and processes that led to the formation of these early solar system objects. The REE abundances in refractory objects that are high temperature nebular condensates depend on their respective volatilities, while for any igneous process (e.g. melting and re-crystallization), their abundances will depend on relevant solid/melt partition coefficients. The REE patterns in CAIs is grouped into several types (Martin and Mason, 1974; MacPherson et. al., 1988), that are illustrated in Fig. 1.6. All of them show enrichment relative to chondritic abundances by a factor of 15-20 or more. These REE patterns mostly reflect volatilities of the elements and can be used as tracers to infer about the environment in which the CAIs formed. CAIs with ultra-refractory pattern suggests formation in a very high temperature environment with enrichment in refractory heavy REE (HREE), and relative depletion in Yb and less refractory light REEs (LREE). The Group III REE pattern shows nearly uniform enrichment of all REE except for less refractory Eu and Yb. The Group II pattern can be considered to be complimentary to the ultra-refractory pattern and suggest that source material of objects showing Group II pattern could be nebular material from which the ultra-refractory component has already been removed (Boynton, 1975; 1984). Group II

REE pattern thus appears to be a slice out of the middle of the REE condensation sequence, deficit in both the most refractory and the most volatile REE.

Earlier studies of hibonites show that the platelet hibonites are generally characterized by the Group-III REE pattern with nearly a hundred-fold or more enrichment of refractory REE over chondritic (CI) abundances and relative depletion in the less refractory REE, Eu and Yb. On the other hand, hibonites in spherules often show Group-II REE pattern with a relative enrichment of light REEs with respect to heavy REEs and a positive Tm and a negative Eu anomaly. In this study we have measured REE and RTE abundances in both types of hibonites from the CM meteorites, Murray and Murchison, to infer their



Fig. 1.6 REE patterns observed in meteoritic CAIs (from MacPherson et al., 1988).

plausible formation environment. An attempt has also been made to develop a selfconsistent scenario that can explain both the trace element and the isotopic data for these objects.

1.4 Scope of the Present Thesis

This thesis presents the results obtained from a study of isotopic and trace element compositions in a suite of hibonites with distinct morphologies from two CM meteorites, Murchison and Murray. All the data reported were obtained using secondary ion mass spectrometry (ion microprobe) technique. The results obtained in this study are interpreted in terms of the time scales of events and processes taking place during the formation and early evolution of the solar system.

A description of the secondary ion mass spectrometer used in this study along with the techniques used for determining isotopic composition of Mg, K, Ca, Ti and O and trace element abundances in CM hibonites is given in Chapter II. Description of the samples analyzed in this study along with their chemical compositions obtained by electron microprobe are given in Chapter III. Chapter IV presents the results obtained in this study. Discussion of these results are presented in Chapter V with emphasis on their implications for our understanding of specific aspects of formation and early evolution of the solar system. The last chapter (chapter VI) provides a summary of the work done along with the main conclusions and outlines the scope for further work in this area of research.

Chapter Two

Experimental Techniques

Many of the individual refractory phases in CAIs, and in particular the hibonites from the CM meteorites are rather small in size ranging from a few tens of microns to about a hundred micron. Study of multiple isotopic systematics in such small objects requires an instrument capable of measuring isotopic abundances with high spatial resolution. Secondary Ion Mass Spectrometer (SIMS) with high mass resolution is ideally suited for this purpose. In the present study, a Cameca ims-4f secondary ion mass spectrometer, often referred to as ion microprobe, was utilized for analyzing the hibonite samples from the two CM meteorites, Murchison and Murray. The basic principle of secondary ion mass spectrometer and its application to problems in earth and planetary sciences have been discussed in detail by Lovering (1975), Shimizu et al. (1978), Shimizu and Hart (1982), Benninghoven et al. (1987), and Ireland (1994). In this chapter, a brief discussion on the working principle of SIMS is presented along with the analytical techniques used to measure isotopic and elemental composition in the CM hibonites.

2.1 Secondary Ion Mass Spectrometer (SIMS)

The basic principle of SIMS involves sputtering of a small localized area of a solid sample by an energetic (10-20 keV) primary ion beam under high vacuum conditions to generate energetic secondary ions from the sample surface that are mass analyzed using a combination of an electrostatic and a magnetic analyzer. Transfer of energy from the primary beam to the atoms/molecules of the surficial layers of solid leads to breaking up of chemical bonds and these atoms/molecules are sputtered from the topmost atomic layers of the sample, either as neutral or charged species (ions). The sputtered secondary ions are accelerated, energy-filtered and then mass analyzed to determine their mass-to-charge ratio. The Cameca ims-4f setup can be divided in two sectors: the *primary column*, from the primary ion source to the sample, and the *secondary column*, from secondary ions extraction to the detection system. These two sectors are briefly described below.

2.1.1 Primary Column

Cameca ims-4f has two primary ion beam sources: (1) *Duoplasmatron*, for generating positive and negative ion beams from gaseous species (e.g. oxygen, argon) and (2) *Cesium microbeam source*, for obtaining Cs^+ beam. The duoplasmatron consists of a hollow (cold) cathode, an anode and an intermediate electrode surrounded by a Cu-coil

and creates a plasma of the primary gas used, usually oxygen, that is efficient in sputtering secondary ions from electropositive elements. The intermediate electrode focuses this plasma into a small region in front of the anode. Choice between O^+/O^- as primary beam can be made by changing position of the intermediate electrode and cathode with respect to the anode. The duoplasmatron is kept at a potential ranging from 5 - 17.5 keV, and O^-/O^+ ions are extracted from the anode hole with the help of a grounded extraction plate. In the present study, the duoplasmatron was kept at a potential of 12.5 keV.



Fig. 2.1 A schematic of the primary beam sources and the primary column of the secondary ion mass spectrometer (Cameca ims-4f).

The cesium microbeam source works on the principle of thermal ionization. A cesium chromate (Cs_2CrO_4) pellet is heated upto 400°C to create Cs vapours. This vapour when passed through heated (1100°C) porous tungsten plate, generates Cs^+ ions by electron transfer to the tungsten atom. The Cs-microbeam source is generally kept at a potential of 10 keV and Cs^+ ions are extracted with a grounded extraction plate. Cs^+ beam is used mostly during isotopic analysis of electronegative elements (e.g. oxygen), in the negative secondary mode.

Several deflectors, apertures and electrostatic lenses are used to focus either of the two primary beams onto the sample surface (Fig. 2.1). *Deflector-2* deflects the primary beam into the *mass filter* that has a mass resolving power of ~100 and eliminates impure species in the primary beam (e.g. hydrides or molecular species or ions generated at inner surface of the duoplasmatron). The clean ion beam emerging from the mass filter passes through a set of three *electrostatic einzel lenses (L1, L2, L3)* and two *apertures (mass selection aperture* and *primary beam aperture)*. These lenses can focus the beam down to a small size (a few micron in diameter) and help in adjusting the primary beam intensity. A pair of stigmators is provided before lens L3 to remove astigmatism, if any, in the primary beam. Primary current can be measured with the help of a *faraday cup*.

Focused primary beam hits the sample kept at 4.5 keV and sputters neutral and charged atoms and molecules from the *sample* surface along with resputtered primary ions, electrons and photons. The polarity of the sample voltage, can be positive or negative depending on selection of positive or negative secondary ions for analysis. The sputtered secondary ions carry energy of the order of few eV to about a hundred eV.

2.1.2 Secondary Column

Secondary ions generated due to sputtering of the sample surface by the primary beam are extracted by a grounded electrostatic lens (*immersion*) (Fig. 2.2) and have nominal energy of ~4.5 keV. The extracted ion beam is focused on a contrast aperture by selecting one out of a set of three-transfer *lens* (25 μ m, 150 μ m, 250 μ m) that provide different image magnifications. The secondary ion beam then passes through an *entrance slit* (coincident on the plane of the contrast aperture) and a *field aperture* before entering



Fig. 2.2 A schematic diagram of the secondary ion column of the secondary ion mass spectrometer (Cameca ims-4f).

the *electrostatic analyzer*. Field apertures of different sizes can be used to select ions from within the sputtered area and avoid non-axial components. Energy sorting of the secondary ions takes place in the electrostatic analyzer, and selection of secondary ions within a narrow energy band for mass analysis can be made by adjusting the energy slit placed after this analyzer. The *spectrometer lens*, placed between the energy slit and the magnetic sector, focuses the ion beam into the *mass analyzer (magnetic sector)*.

The mass analyzer (electromagnet) separates the ions according to their m/q (mass to charge) ratios. The combination of a magnetic and an electrostatic sector makes the ims-4f a double focusing instrument. Separated ions pass through an exit slit (placed at ion beam cross over) and the projector lenses guide the selected ions to a *faraday cup* or an *electron multiplier* for ion counting or to a *channel plate* for ion imaging of the analyzed area.

The Cameca ims-4f is also equipped with a normal-incidence electron gun, so that a cloud of low energy electrons can be focused on the sample surface to neutralize sample

charging that may take place during analysis. Sample charging is a major problem during analysis of insulators in the negative secondary mode.

The instrument is backed-up by a vacuum system consisting of a couple of rotary pumps, three turbo molecular pumps in the primary column, a cryo-pump connected to the sample chamber and two ion pumps in the secondary column. Typical vacuum in the sample chamber is $\sim 10^{-9}$ torr and in the secondary column around 3 x 10^{-8} torr.

2.2 Analytical Techniques and Precautions

The important aspects that needs to be checked before any analysis with the ion microprobe are briefly described here.

(1) Status of the ion counting system:

In most analysis, ion counting is done in the pulse-counting mode using electron multiplier. The background of the total counting system and the counting efficiency of the electron multiplier need to be checked at regular intervals. The background countrate in the PRL ims-4f is usually below 0.01c/s. The efficiency of the electron multiplier (EM) is checked by comparing the electron multiplier count-rate with that measured by the faraday cup. When the EM efficiency falls below 70% due to aging effect, the electron multiplier is replaced. Dead time of the electron multiplier is estimated by repeated measurements of magnesium or titanium isotopic composition in terrestrial standards (Burma spinel, Madagascar hibonite, Ti-metal). In general, deadtime increases with aging of the electron multiplier. The typical values for deadtime ranges between 18 to 25 nanosecond (ns) with deviations within ± 2 ns (2σ) over periods of several weeks.

(2) Mass interferences:

Interferences at any given mass of interest can be either molecular (singly ionized hydrides, oxides, dimmers etc) or isobaric with same m/q of interest. Most of the important interferences can be removed at high mass resolution. For example, magnesium isotopic analysis requires a mass resolution (M/ Δ M, where Δ M is the width of the peak at 10% peak height for mass M) of about 4,500 to resolve hydride (²⁴MgH on ²⁵Mg) and doubly ionized (⁴⁸Ti⁺⁺ on ²⁴Mg) interferences. On the other hand titanium isotopic analysis in hibonite requires a mass resolution of ~10,000 for resolving the isobaric interference of ⁴⁸Ca on ⁴⁸Ti. However, additional precautions are needed to

ensure that possible residual interference due to scattering is absent. Specific instances of this is discussed later (§ 2.2.4, 2.2.5). When the mass resolution required to resolve interference exceeds 10,000, other approaches e.g. 'energy filtering technique' is used as in the case of measurement of rare earth element abundances (§ 2.2.7).

(3) Spatial resolution

High spatial resolution is often needed to analyze small phases within a multi-phase sample so that possible contributions from neighbouring phases are avoided. This is very crucial in the case of CM hibonites, and particularly while analyzing the spinel-hibonite spherules. High spatial resolution is achieved by reducing the primary beam current to obtain small beam spots ($\leq 5 \mu$ m) and at the same time ensuring that the intensity of the secondary ions is not too low. In some cases when sputtering takes place from more than a single phase, as can be inferred from the ion images, a small field aperture is used to collect secondary ions from the particular phase of interest.

(4) Analyses of standards

Isotopic analysis of meteoritic phases is preceded by analysis of a suitable analog standard that closely matches the matrix and elemental composition of the sample. In the present study of CM hibonites, we have primarily used Burma spinel and Madagascar hibonite as standards.

(5) Identification of the phases of interest

Identification of small phases of interest (e.g. hibonite) in a composite matrix needs proper attention. Using a defocused beam, ion images of diagnostic elements (Al, Ca, Ti, Mg) are obtained to distinguish the closely spaced hibonite and other phases (e.g. spinel) present in the samples, particularly in some of the spherules. The beam spot is then focussed on the hibonite, and appropriate field aperture is chosen to ensure that secondary ions from phases other than hibonites are excluded.

(6) Isotopic mass fractionation

The isotopic ratios in a sample measured using an ion microprobe usually deviates from the standard (reference) values due to isotopic mass fractionation effect and/or the presence of additional components (e.g. nucleogenic/ cosmogenic) contributing to one of the isotopes of interest. The isotopic mass fractionation in addition has two components, an "intrinsic" component inherent to the sample and an "instrumental" component induced by the measurement process itself. The intrinsic isotopic mass fractionation results from the processes leading to the formation of the sample, while the instrumental mass fractionation arises from the processes like sputtering, transmission and detection involved in isotopic studies using an ion microprobe. It is possible to infer the intrinsic mass fractionation of a sample and to obtain the magnitude of the instrument mass fractionation effect by analyzing a suitable analog standard. If we consider a two isotope system (i, j) and use "j" as the normalizing isotope, the instrumental mass fractionation, F_{instr} , may be obtained by analyzing a standard and using the following relation:

The intrinsic isotopic mass fractionation F_{μ} in a sample having matrix composition similar to the standard can then be obtained from the relation:

$$F_{\mathbf{m}}(\%_{\mathbf{0}}) = (F_{sample} - F_{instr.}) \tag{2.2}$$

One has to be careful in the selection of M_i and M_j to ensure that they are free of any contribution from cosmogenic or nucleogenic component. If an element has n isotopes (n \geq 3), the magnitude of instrumental mass fractionation effect can be inferred by choosing two isotopes that are free from above contributions. It is then possible to look for contributions from cosmogenic or radiogenic component in the other (n-2) isotopes after taking into account the mass fractionation effect.

If we consider a power law expression for isotopic mass fractionation, the value for fractionation parameter, α , can be obtained from the relation:

$$(R_{kj})_m = (R_{kj})_r (l+a)^{DM}$$
(2.3)

where 'R' stands for abundance ratio of a pair (k, j) of isotopes, 'm' stands for the measured ratio, 'r' for the reference value and $\Delta M = M_k - M_j$.

For small values of ΔM , one can use the linear approximation, to obtain value of α :

If the mass range of the isotopes of interest is rather large (e.g. in case of Ca and Ti isotopic analysis) it has been shown that an exponential mass fractionation relation is more appropriate (Fahey et al, 1987a) and the value of the exponent α can be obtained using the relation:

$$\frac{\left(R_{ij}\right)_m}{\left(R_{ij}\right)_r} = \left(\frac{M_i}{M_j}\right)^{a} \qquad (2.5)$$

Any deviation in the fractionation corrected isotopic ratios for the sample from the standard (reference) values can be attributed to the presence of additional component (cosmogenic, radiogenic) contributing to the abundance of specific isotopes in the analyzed sample.

2.2.1 Sample Preparation and Measurement Procedures

Each of the CM hibonites sampled for the present study, along with two standards (Burma spinel and Madagascar hibonite), were mounted in epoxy within a 2 mm hole of an aluminum disc. The samples were grinded and polished with 3.0 μ m diamond paste to expose the hibonite surface and was given a finer polish with 0.3 μ m alumina powder. The sample mount was ultrasonically cleaned with soap solution, double distilled water and finally with ethanol. Each sample mount were kept in an oven at 60°C for couple of hours and the clean dry polished surface was gold-coated (~1000A⁰) to avoid problems related to sample charging during analysis. For Ca-K analysis, special care was taken to avoid K contamination and the sample was cleaned in warm (60°C) ultra-pure water (filtered through Millipore TMMilli-Q-Plus-System) for a couple of hours and dried before gold coating.

All the samples were documented using a scanning electron microscope (Chapter 3; § 3.1). Al-Mg and Ca-K isotopic analyses were done following the procedure described by Srinivasan et al. (1996) and Sahijpal et al. (2000). Titanium and calcium isotopic compositions were measured following the procedures described by Zinner et al. (1986), Fahey et al. (1987a) and Sahijpal et al. (2000). The measurement sequence followed during the analysis was Al-Mg systematics, Ca-K systematics, Ti isotopic compositions, Ca isotopic composition, O isotopic compositions and rare earth & refractory trace element abundances. Only a few samples with low Ca/K ratios were analyzed to look for the presence of ⁴¹Ca. Samples with small ⁵⁰Ti isotopic anomalies were not analyzed for
stable isotopic anomalies in the neutron-rich isotope, ⁴⁸Ca. Earlier studies (Zinner et al., 1986; Ireland, 1988; Sahijpal et al., 2000) have shown that isotopic anomalies for the neutron-rich isotopes, ⁵⁰Ti and ⁴⁸Ca, are correlated and unambiguous detection of low-magnitude ⁴⁸Ca anomalies in the presence of isobaric interference from ⁴⁸Ti peak is rather difficult even while working at high mass resolution.

In the present study, a 17 keV focused ¹⁶O⁻ primary beam was used for all the analysis. The isotopic measurements were done using the 150 μ m contrast aperture and the 750 μ m field aperture except in some cases (particularly for hibonites in spherules) where smaller field apertures were used to select the secondary ions from the phase of interest (hibonite). For all the analyses, a narrow energy window of 25 eV was selected and possible shift in the energy of the transmitted secondary ions during analysis was checked at the end of each analysis. Mass resolution used for studying different isotopic systematics was optimized for removal of prominent mass interferences. The measurements of rare earth and refractory trace element abundances were carried out at low mass resolution (fully open entrance and exit slit) using the largest contrast and field apertures of 400 μ m and 1800 μ m, respectively, to maximize secondary ion

2.2.2 Al-Mg Isotopic Systematics

Al-Mg isotopic analysis was performed using a low primary current of ~0.5 - 1.0 nA and at a mass resolution (M/ Δ M) of about 4,500 (fig. 2.3), sufficient to resolve ²⁵Mg⁺ (24.98584 amu) from ²⁴MgH⁺ (24.99760 amu), as well as doubly charged interfering species (e.g. ⁴⁸Ti⁺⁺ on ²⁴Mg⁺). The measurements were carried out in the peak jumping mode in which the magnet sequentially scans the masses 24 (²⁴Mg), 25 (²⁵Mg), 26 (²⁶Mg) and 27 (²⁷Al). Counting time at each of the four masses were chosen to obtain a reasonable precision (~per mil level) in the Mg isotopic ratios. The typical counting time were 2, 5, 5 and 1 second for masses 24, 25, 26 and 27, respectively, during each scan (cycle) for ²⁴Mg⁺ count rate of ~10⁴ cps. Data for twenty blocks, each block constituting five cycles through the above mass sequence, were acquired during each analysis.

Magnesium isotopic ratio with ²⁴Mg as the reference isotope along with Al/Mg ratio were determined for each block of data and values for Δ^{25} Mg and Δ^{26} Mg were also estimated using the standard relation:

The reference values used for estimating Δ values are 0.12663 [²⁵Mg/²⁴Mg] and 0.13932 [²⁶Mg/²⁴Mg] (Catanzaro et al., 1966). The Al/Mg ratios were obtained from the measured ²⁷Al^{+/24}Mg⁺ ratio using a sensitivity factor of 1.4 (Sahijpal, 1997).



Fig. 2.3 High resolution (*M/***D***M* ~ 4,500) spectra at mass 25 in terrestrial hibonite showing well resolved peaks of 25 Mg and 24 MgH.

The fractionation corrected residual δ^{26} Mg was estimated for each block of data, using a linear mass fractionation law using the relation:

$$\delta^{26}Mg = \Delta^{26}Mg - 2 \Delta^{25}Mg$$

Data for twenty blocks in each analysis were combined to obtain the value of the mean δ^{26} Mg and associated standard deviation.

2.2.3 Ca-K Isotopic Systematics

Potassium has three isotopes (³⁹K, ⁴⁰K and ⁴¹K). However, the abundance of the longlived isotope, ⁴⁰K, is very low (0.012%), and all the analysis were performed treating K as a two-isotope (³⁹K and ⁴¹K) system. A primary beam of ~2 nA was used for carrying out Ca-K isotopic studies on the same spot where Al-Mg isotopic analysis was performed earlier using low primary beam current. A mass resolution of ~5000 is sufficient to resolve the hydride interference ⁴⁰CaH (40.97041amu) on ⁴¹K (40.96183 amu) (Fig. 2.4) as well as several of the doubly charged interfering species (e.g. $[^{27}Al_2{}^{28}Si]^{++}$, $[^{25}Mg^{16}O]^{++}$ and $[^{50}Ti^{16}O_2]^{++}$). Interference from $[^{26}Mg^{56}Fe]^{++}$ was neglected because of the very low Fe content in the hibonites.



Fig. 2.4 High resolution ($M/DM \sim 5,000$) mass spectra at mass 41 showing well resolved peaks of ⁴¹K and ⁴⁰CaH.

However, it is not possible to resolve the $[{}^{40}Ca{}^{42}Ca]^{++}$ interference on ${}^{41}Ca$ at this mass resolving power. We have corrected for this interference by estimating the magnitude of $[{}^{40}Ca{}^{43}Ca]^{++}$ signal at mass 41.5 and using the relation:

$$[{}^{40}\text{Ca}{}^{42}\text{Ca}]^{++} = [{}^{40}\text{Ca}{}^{43}\text{Ca}]^{++}. ({}^{42}\text{Ca}{}^{+}/{}^{43}\text{Ca}{}^{+})$$

Additional precaution was also taken to ensure that scattering from the high intensity 40 CaH peak does not contribute to the 41 K peak (Fig. 2.4). The magnitude of this contribution is monitored by determining the count rate at (42 Ca- Δ M),

where,
$$\Delta M = (42/41)[M(^{40}CaH)-M(^{41}K)] \sim 0.009 \text{ amu};$$

and normalizing the same to ⁴⁰CaH count-rate.

Thus the contribution from the left hand edge of the 40 CaH peak on the center of 41 K peak can be obtained as:

$$[{}^{40}CaH]_{tail}$$
 (c/s) = $[{}^{42}Ca-0.009 \text{ amu}]$ (c/s) . $[{}^{40}CaH^+/{}^{42}Ca^+]$

Since the ⁴¹K counts are generally very low (typically < 0.5 c/s), the background of the counting system was carefully monitored by including the mass 40.7 in the analysis sequence. In fact the count rate at this mass include both background count as well as the maximum possible contribution due to scattering from the ⁴⁰CaH peak, at ⁴¹K.

In a typical Ca-K analysis, the magnet is cycled through the mass sequence: 39 (39 K), 40.7(background), 41 (41 K), 41.009 (40 CaH), 41.991 (42 Ca- Δ M) and 42 (42 Ca). The typical counting time at these different masses were 30, 10, 60, 2, 10, 1 sec, respectively. Ten to twelve blocks of data, each block consisting of six cycles through the mass sequence, were obtained to determine the 41 K/ 39 K ratio of a sample. The Ca/K values were inferred from the measured 42 Ca⁺/ 39 K⁺ ratio by using the standard 40 Ca/ 42 Ca ratio 151.02 and a sensitivity factor of 3.2 (Srinivasan et al., 1996).

2.2.4 Ti Isotopic Measurement

Titanium has five isotopes with ⁴⁸Ti being the most abundant isotope. In Table 2.1 the abundances of the different isotopes and important interfering species (other than hydride) at each of these masses are indicated along with the mass resolution required to resolve them. While the hydride interferences (e.g. ⁴⁶TiH on ⁴⁷Ti etc) can be resolved at a mass resolution of ~ 5,400, the isobaric interference at mass 48 from ⁴⁸Ca can be nearly resolved only at a mass resolution of ~9,000 (Fig. 2.5). Resolution of the isotopic interferences at ⁴⁶Ti and ⁵⁰Ti are beyond the capability of the ion microprobe at present.

Mass	% Abundance	Inteferences	Required Mass resolution
⁴⁶ Ti	8.00	⁴⁶ Ca	~ 43,000
⁴⁷ Ti	7.29	-	-
⁴⁸ Ti	73.98	⁴⁸ Ca	~ 10,000
⁴⁹ Ti	5.51	-	-
⁵⁰ Ti	5.34	⁵⁰ V, ⁵⁰ Cr	~ 39,700 / ~ 21,000

Table 2.1 Titanium isotopes and interfering species



Fig. 2.5 High resolution (*M*/**D***M* ~ 9,000) spectra at mass 48 showing partially resolved peaks of ⁴⁸Ti and ⁴⁸Ca. The tail of ⁴⁸Ca peak is ~3 field bits off from the center of ⁴⁸Ti peak at 1‰ level. The stability of the magnetic field between calibration is better than \pm 2 field bits.

We have therefore taken the following approaches to take care of these interfering species:

(i) The residual interference from 48 Ca on 48 Ti, even at a mass resolution of 9,000, (see Fig. 2.5) was obtained by monitoring counts at (40 Ca- Δ M)

where,
$$\Delta M = (40/48) [M (^{48}Ca) - M (^{48}Ti)] \sim 0.004 amu.$$

and using the relation:

$$[{}^{48}Ca]_{tail} (c/s) = [{}^{40}Ca - 0.004 \text{ amu}] (c/s) . [{}^{48}Ca^+/{}^{40}Ca^+]$$

(ii) Contribution from ⁴⁶Ca at ⁴⁶Ti was inferred by monitoring the ⁴⁴Ca peak and using the relation

$$({}^{46}\text{Ti}/{}^{48}\text{Ti})_{\text{measured}} = ({}^{46}\text{Ti}/{}^{48}\text{Ti})_{\text{true}} + {}^{46}\text{Ca}/{}^{48}\text{Ti}$$

where,
$$({}^{46}\text{Ca}/{}^{48}\text{Ti}) = ({}^{46}\text{Ca}/{}^{44}\text{Ca}) \times ({}^{44}\text{Ca}/{}^{48}\text{Ti})_{\text{measured}}$$
$$= 0.001518 \times ({}^{44}\text{Ca}/{}^{48}\text{Ti})_{\text{measured}}$$

(iii) The interferences of 50 V and 50 Cr at mass 50 Ti were corrected indirectly by obtaining count rates at masses 51 V and 52 Cr and using the relation:

$$({}^{50}\text{Ti}/{}^{48}\text{Ti})_{\text{measured}} = ({}^{50}\text{Ti}/{}^{48}\text{Ti})_{\text{true}} + {}^{50}\text{V}/{}^{48}\text{Ti} + {}^{50}\text{Cr}/{}^{48}\text{Ti}$$

where,

$$({}^{50}\text{V}/{}^{48}\text{Ti}) = ({}^{50}\text{V}/{}^{51}\text{V}) \times ({}^{51}\text{V}/{}^{48}\text{Ti})_{\text{measured}}$$

= 0.002503 x (${}^{51}\text{V}/{}^{48}\text{Ti})_{\text{measured}}$

similarly,
$$({}^{52}Cr/{}^{48}Ti) = ({}^{50}Cr/{}^{52}Cr) \times ({}^{52}Cr/{}^{48}Ti)_{measured}$$

= 0.051859 x (${}^{52}Cr/{}^{48}Ti)_{measured}$

The position of the weak ⁵¹V and the ⁵²Cr peaks were identified by looking for the more prominent ²⁴Mg²⁷Al and ²⁵Mg²⁷Al peaks, that are separated by 0.0226 amu and 0.02687amu, respectively, from the ⁵¹V and ⁵²Cr peaks. Each Ti isotopic analysis consisted of twenty blocks of data, each block comprising of eight cycles through the mass sequence, 39.996 (⁴⁰Ca- Δ M), 44 (⁴⁴Ca), 46 (⁴⁶Ti), 47 (⁴⁷Ti), 48 (⁴⁸Ti), 48.004 (⁴⁸Ca), 49 (⁴⁹Ti), 50 (⁵⁰Ti), 51 (⁵¹V), 52 (⁵²Cr) with typical counting times of 1, 1, 3, 3, 2, 2, 5, 5, 1, 1 sec, respectively. A primary current of ~2 nA was used during the analysis.

The Ti isotopic ratios were normalized to ⁴⁸Ti, after making appropriate corrections for the interfering species in each case. The magnitude of instrument mass fractionation was inferred by using ⁴⁶Ti and ⁴⁸Ti as the reference isotopes. The exponent " α " in the power law fractionation expression was obtained using the relation:

$$\left(\frac{46}{48}\right)^{\mathbf{a}} = \frac{\left(\frac{46}{Ti}/\frac{48}{Ti}\right)_{meas}}{\left(\frac{46}{Ti}/\frac{48}{Ti}\right)_{ref}}$$

The fractionation corrected isotopic ratios were then determined using the following expression:

$$\boldsymbol{d}^{i}Ti (\infty) = \left\{ \frac{(m_{i}/48)^{-\boldsymbol{a}} \times (iTi/48Ti)_{measured}}{(iTi/48Ti)_{standard}} - 1 \right\} \times 1000$$

2.2.5 Ca Isotopic Measurement

The abundances of the six stable isotopes of calcium and interfering species (other than hydrides) in each case, are listed in Table 2.2, along with the mass resolving power needed to resolve these interferences.

Mass	% Abundance	Interferences	Required Mass resolution
⁴⁰ Ca	96.97	-	-
⁴² Ca	0.64	-	-
⁴³ Ca	0.146	⁸⁶ Sr ⁺⁺	~ 10,500
⁴⁴ Ca	2.06	⁸⁸ Sr ⁺⁺	~ 18,000
⁴⁶ Ca	3.3	⁴⁶ Ti	~ 43,000
⁴⁸ Ca	0.185	⁴⁸ Ti	~ 10,000

Table 2.2 Calcium isotopes and interfering species.

At the operating mass resolution of ~9,000, it is not possible to resolve ⁴⁶Ca and ⁴⁶Ti and thus ⁴⁶Ca was excluded from the analysis routine. Further, ⁴⁸Ca is only partially resolved (Fig. 2.5) and it is essential to correct for the interference from the high mass tail of the ⁴⁸Ti peak. The magnitude of this interference is estimated by monitoring counts at (⁴⁰Ca+ Δ M)

where,
$$\Delta M = (40/48) [M (^{48}Ca) - M (^{48}Ti)] \sim 0.004 amu,$$

and using the relation

$$[{}^{48}\text{Ti}]_{\text{tail}}$$
 (c/s) = $[{}^{40}\text{Ca} + 0.004 \text{ amu}]$ (c/s) . $[{}^{48}\text{Ti}{}^{+/40}\text{Ca}{}^{+}]$

For Ca isotopic measurement the magnet was cycled through the masses: 40 (⁴⁰Ca), 40.004 (⁴⁰Ca+ Δ M), 42 (⁴²Ca), 43 (⁴³Ca), 44 (⁴⁴Ca), 48 (⁴⁸Ti), 48.004 (⁴⁸Ca) in a peak jumping mode; the typical counting times were 1, 2, 10, 12, 2, 1 and 12 sec, respectively. Twenty blocks of data with each block comprising of five cycles through the above mass sequence were acquired during each analysis. ⁴⁰Ca and ⁴⁴Ca were used as reference isotopes to estimate the magnitude of instrumental mass fractionation and the exponent " α ' in the power-law fractionation expression was obtained using the relation:

$$\left(\frac{44}{40}\right)^{a} = \frac{\left(\frac{44}{Ca} / \frac{40}{Ca}\right)_{meas}}{\left(\frac{44}{Ca} / \frac{40}{Ca}\right)_{ref}}$$

Deviation in isotopic abundances for the other isotopes ⁴²Ca, ⁴³Ca, ⁴⁸Ca from their reference values were estimated using the relation:

$$\boldsymbol{d}^{i}Ca~(\infty) = \left\{ \frac{(m_{i}/44)^{-\boldsymbol{a}} \times (^{i}Ca/^{44}Ca)_{measured}}{(^{i}Ca/^{44}Ca)_{standard}} - 1 \right\} \times 1000$$

2.2.6 Oxygen Isotopic Measurement

Oxygen isotopic analysis was carried out in the negative secondary mode using a Cs⁺ primary ion beam. Sample charging is a major problem during analysis of insulating samples like the refractory hibonites in the negative secondary mode. We have used the electron gun attached to the ims-4f to offset the problem of sample charging and have measured oxygen isotopic composition in terrestrial hibonites. Although we could obtain precise values for ¹⁸O/¹⁶O (\pm 3 ‰; 2 σ_m), it was problematic to achieve similar precision for ¹⁷O/¹⁶O ratio both due to the low abundance of ¹⁷O and possible shift in energy spectra of the selected secondary ions during analysis. Further, results for Δ^{17} O obtained during different analysis sessions often differed for the same sample. Because of these difficulties, the oxygen isotopic compositions reported here were obtained using a large geometry ion microprobe (Cameca 1270) at the University of California, Los Angeles. This work was done in collaboration with Prof. K. D. McKeegan.

The analysis procedure followed was adopted from McKeegan et al. (1998). A 20 keV Cs^+ primary beam of ~0.3 nA was defocused to a spot size of around 10 µm on the sample surface. The sputtered negative secondary ions are accelerated to 10 keV. Ions within a narrow energy band (~30eV) were analyzed at a mass resolution (M/ Δ M) of around 6,500 that is sufficient to resolve ¹⁶OH from ¹⁷O peak. Normal incident electron gun was used to generate a cloud of low energy electrons at the surface of the sample to compensate for sample charging. The interference from the edge of ¹⁶OH peak on ¹⁷O peak center was estimated to be less than 0.5‰.



Fig. 2.6 High resolution ($M/DM \sim 6,000$) mass spectra at mass 17 obtained using the Cameca ims-4f showing nearly resolved ¹⁷O and ¹⁶OH peaks.

Each analysis consists of twenty blocks of data of five cycles each through the mass sequence ¹⁶O, ¹⁶OH, ¹⁷O and ¹⁸O. The typical counting time was 1, 1, 15 and 10 sec, respectively. The intensity of ¹⁶O ions was measured using a faraday cup while ¹⁷O⁻ and ¹⁸O⁻ ions were counted using an electron multiplier. A linear mass fractionation law (eq. 2.5) was used to obtain the true ratios. SMOW values (¹⁸O/¹⁶O = 0.0020052 and ¹⁷O/¹⁶O = 0.0020052 and ¹⁷O/¹⁶O = 0.00038309) were used as reference to calculate the δ -values. Burma spinel and

Madagascar hibonite with known oxygen isotopic composition (relative to SMOW) were used as standards.

2.2.7 Measurement of Rare Earth and Refractory Trace Element (REE & RTE) Abundances

The presence of molecular and isobaric interferences makes measurement of rare earth elements (La to Lu) by ionprobe rather difficult. Molecular interferences include simple elemental mono-oxides or complex molecular species resulting from combination of various major elemental species present in the sample. (eg. interference of ${}^{40}\text{Ca}_2\text{P}{}^{16}\text{O}_3^+$, & ${}^{143}\text{Nd}{}^{16}\text{O}^+$ at ${}^{159}\text{Tb}^+$). It is difficult to resolve some of these interferences even at a high mass resolution. We have used the energy filtering technique (Zinner and Crozaz, 1986; discussed in next section) to eliminate/reduce the molecular interferences. The data thus obtained at each mass represents the sum of (REE)⁺ and unresolved (REE-oxide)⁺ ions. This data set is deconvulated to obtain REE abundances using an analytical approach.

High primary beam current in the range of ~8-20 nA was used to obtain count rates in the REE and RTE mass range (22-58 amu, 85-95 amu, 137-180 amu) in the peak jumping mode. ⁴²Ca counts are used to determine the absolute concentration of REE in terms of known concentration of Ca in the hibonites. Contrast aperture and field apertures were kept at their maximum (400 μ m and 1800 μ m) and analysis was performed at a low mass resolution (M/ Δ M) of 270, (entrance and exit slits wide open) to achieve maximum transmission of secondary ions. A sample voltage offset of 80V was applied and the energy widow was set at 25eV to select secondary ions for mass analysis. Counting time in the mass range 22-58 and 85-95 was 10 secs, whereas, in the mass range 137-180, it was 35 secs. The counting was done in the peak-scanning mode with the magnet scanning a small interval of mass (~0.05 amu) around the peak center.

The deconvolution of the data was done using a program obtained from NIST (*National Institute of Standards and Technology*), USA (courtesy Dr. A. J. Fahey). The general feature of the program involves solving an over-determined set of simultaneous equations by minimizing the χ^2 . Three iterations are performed to solve the unknowns, starting with the least square solution which gives elemental ion intensities for lower mass ≤ 150 REE & RTE. The second iterations invokes measured oxide-to-element [(REE-oxide)⁺/(REE)⁺] ratios (LaO⁺/La⁺, CeO⁺/Ce⁺, PrO⁺/Pr⁺, etc.) and provide REE ion

intensities in the mass range 155 to 169 amu. The third iteration takes input from second iteration to deconvolute ion signals in the mass-range 170-179 amu to infer intensity of REE ions. Apart from oxide factors, the program needs sensitivity factors as input to estimate correct elemental ion intensities for all REEs and RTEs. The REE sensitivity factors and oxide factors were obtained independently (§ 2.2.7.3, 2.2.7.4) by analyzing synthetic NIST silicates standards of known REE concentrations [SRM 610, SRM 612, KW-3160, K-3399 and K-3400].

2.2.7.1 Energy Filtering Technique

The secondary ions generated by sputtering of any sample generally have a very large energy dispersion (~1 to 150eV) with the maxima at the low energies (~ few eV) comparable to the surface binding energies of the elements. The normalized secondary ion energy spectra obtained from major elements Al, Si, Mg, Ca, REE (La, Ce, Eu, Ho) and REE mono-oxide (CeO, HoO, ErO) are shown in Fig. 2.7. NIST standard



Fig. 2.7 Normalized count rates for complex molecules, rare earth and other major elements (such as AI, Ca, Si) as a function of sample voltage offset obtained on Arizona REE standards.

2.8).

(KW-3610) as well as Arizona REE standards (Drake and Weill, 1972) were analyzed under different instrument conditions (different apertures and entrance/exit slit position).

The three major features evident from Fig. 2.7 are:

- 1. The intensity of complex molecular interferences reduces sharply at energy offset greater than ~50 volts compared to elemental and elemental mono-oxide signals.
- Signals from REE mono-oxides drop faster in intensity as compared to REE. For energy offset greater than ~70 volts, the drop in intensity of REE mono-oxide is an order of magnitude greater than that for REE.
- 3. The drop in elemental (including major elements and REE) signals at energy offset greater than 60 volts shows similar trend. Hence the relative sensitivity factors of REE with respect to any major element will be independent of the energy of secondary ions selected for the mass analysis as long as it is above this value. A sample voltage offset of 80 V was used in the present study.

2.2.7.2 Mass-Magnetic Field Calibration

A mass-magnetic field calibration was done by using secondary ion signals of various elemental and molecular combinations of silicon and oxygen from a silicon wafer (Fig.



Fig. 2.8 Mass-Magnetic field calibration based on analysis of a silicon wafer.

The calibration was done with wide-open slits (mass resolution, $M/DM \sim 270$), largest contrast and field apertures, 400 µm and 1800 µm respectively, and zero-volt energy offset, conditions similar to REE analysis except for the energy offset value.

The mass-magnetic field validation for a given mass was done at the center of peaks except for the masses 148, 164, 180 and 200 amu. In these cases, the validation was done at a mass ($M_c+\Delta M$), where, M_c represents the peak center for the Si_xO_y molecule, and ΔM is the mass difference between this molecule and the nearest REE.



Fig. 2.9 Mass spectra (for NIST SRM 610 standard) at low mass resolution. The hatched regions represent the mass interval around the peak center scanned in each case.

The ΔM values for the four masses are, 0.006 (¹⁴⁸Nd; (Si₂O₄)⁺), 0.023 (¹⁶⁴Dy; (Si₃O₅)⁺), 0.046 (¹⁸⁰Hf; (Si₃O₆)⁺) and 0.117 (¹⁶⁸ErO₂; 2(Si₃O)⁺) amu. Mass spectra for REE were obtained with 80 volt energy offset to ensure that all the mass spectra peaks corresponding to REE/REE mono-oxide signals were properly centered (Fig. 2.9). Hatched bars in Fig. 2.9 shows the mass region scanned during REE analysis for a given mass.

2.2.7.3 Oxide Factors

The oxide factors are found to be dependent on sample voltage offset (Fahey, 1998). Fig. 2.10 shows the results obtained in several NIST standards. K-3399 silicate standard was used to determine the ratio of oxide (MO^+) to elemental ratio (M^+) for La, Ce, Nd, Sm and Eu whereas silicate standard K-3400 was used in the case of Gd, Dy and Tb.



Fig. 2.10 MO^+/M^+ ratio as a function of energy offset measured in NIST standards, K3399 and K3400.

2.2.7.4 Sensitivity Factors

It is necessary to determine the sensitivity factor for different REE relative to the reference element (Ca in the present study) to infer the absolute concentration. The NIST synthetic silicate standard SRM 610 with known concentration of REE (~ 500 ppm) was analyzed using calcium as the reference element. Five to six REE analyses were generally carried out on the standard to obtain the sensitivity factor using the relation:

Sensitivity factor (SF)_{silicate} =
$$\frac{[REE]^{+}/[Ca]_{absolute conc}}{[REE]^{+}/[Ca]_{ion probe}}$$

The sensitivity factor was found to be independent of primary beam current as well as energy voltage offset. However, they do vary depending on the matrix composition as well as instrumental operating condition (Fahey, 1998). In the absence of a hibonite REE standard, the sensitivity factor for hibonites for our instrument operating condition was inferred from the sensitivity factor given by Fahey (1998) and normalizing it to the sensitivity factor of the NIST silicate standard obtained by us

2.2.7.5 REE Analysis of Standards

Several sets of standards were analyzed to check the precision and reproducibility in determining REE abundances by our ion microprobe. Repeated analyses of the NIST standard SRM 610 that was used initially to obtain the sensitivity factor for silicates, reproduces the REE abundances with uncertainties of < 5% (Fig. 2.11). Analyses of NIST silicate standards SRM 612 and KW 3610 (50 ppm and 500 ppm) yield uncertainties of \leq 15% (Fig. 2.11). Thus, the absolute REE abundances obtained for the hibonites in this study may have uncertainty at 10-15% level.



Fig. 2.11 Measured REE abundances in NIST standards (SRM 610, SRM 612, KW 3610) using sensitivity factors obtained independent from analysis of SRM 610. The lower panel in each case shows the deviation in the measured abundances from the reference values.

Chapter Three

Sample Description

The Ca-Al-rich refractory inclusions (CAIs) found in CM meteorites have refractory oxides such as spinel, hibonite and perovskite as the dominant phase with melilite and pyroxene as minor constituents. Compositions of the hibonite-bearing inclusions in CM meteorites suggests that they are more refractory than the CAIs found in other carbonaceous and ordinary chondrites (see e.g. MacDougall and Goswami, 1981; Ireland, 1990). In the present work, hibonites from two primitive carbonaceous (CM) chondrites, Murchison¹ and Murray² were studied for their chemical and isotopic characteristics. Hibonite-bearing inclusions in meteorites are classified into several types (Table 1.3). In the present study, the analyzed hibonites belong to the 'platelet' and 'spherule' type that were designated as "PLAC" and "SHIB" by Ireland (1988). Platelets represent platy grains of hibonite, while spherules consist of spinel-hibonite intergrowths often with tiny perovskite inclusions.

3.1 Separation of Hibonite from Host Meteorite

Two separate procedures were used to identify and pick up hibonite platelets and hibonite-bearing spherules from the two meteorites. In the first approach, carried out at our laboratory, ~5 gm sample of each meteorite was crushed and sieved through a 500 μ m mesh. Fraction < 500 μ m was then subjected to several cycle of high power ultrasonic disaggregation. After each cycle, the sample was divided in two parts, 30-150 μ m and 150-500 μ m and the latter fraction was again subjected to the disaggregation process. Potential objects resembling hibonite platelet and spherule were handpicked from the $< 150 \,\mu\text{m}$ fraction under a binocular microscope at high magnification (100 X). The selection of these objects was based on their morphology, colour (mostly light-blue) and texture. Objects representing individual platelet or spinel-hibonite spherule were identified by energy dispersive X-ray spectrometry (EDX) using a Leo-440i scanning electron microscope (SEM) at the Facilitation Center for Industrial Plasma Technology (FCIPT), Gandhinagar. Major peaks at energies corresponding to characteristic X-ray of Al and Ca, with minor peaks at Mg and Ti (see Fig. 3.1) were used to identify hibonite. Twelve hibonites (two platelets and ten spherules) were selected from this set of objects for the present study. In the second approach, carried out at the University of Chicago (courtesy Dr. A. M. Davis), the starting material was HF-HCl resistant residue of the

¹ Fell in Australia on 29 September 1969, recovered mass: 100kg

² Fell in USA on 20 September 1950, recovered mass: 12.6kg

Murchison meteorite, obtained during separation of interstellar grains from this meteorite (Amari et al., 1994). Potential platelets and spherules were hand-picked from this residue and were checked with SEM (EDX) facility at FCIPT for identification of hibonites. Eight Murchison hibonites (five platelets and three spherules) were selected from this set of sample.



Fig. 3.1 Energy-dispersive X-ray spectrum of a hibonite from CM meteorite, Murray, showing the major peaks at AI, Ca and Ti.

3.2 Sample Description

Murchison Platelets:

Backscattered electron (BSE) images of five Murchison platelet hibonites analyzed in this work are shown in Fig. 3.2, (a) to (e). The size of the hibonite grains ranges from $\sim 60 \ \mu m$ to $\sim 110 \ \mu m$ in their longest dimension.

Sample description

Murchison Spherules:

BSE images of the three spinel hibonite Murchison spherules, CH-D4, CH-D7 and CH-D8, are shown in Fig. 3.3. The size of these spherules ranges from 50 μ m to 100 μ m. Hibonite laths (HIB) are present within the spinel matrix (SP). The hibonite laths are typically 20-30 μ m in length and ~10 - 15 μ m in width.

Murray Platelets:

BSE images of two platelet hibonites (~50 x 35 μ m and ~ 60 x 45 μ m, respectively) from the Murray meteorite are shown in Fig. 3.4. In one case, MY-H17 (Fig. 3.4a), the hibonite grain is surrounded by a crescent shaped silicate phase, while in MY-H19 (Fig. 3.4b) the hibonite grains is surrounded by an iron-rich phase.

Murray Spherules:

BSE images of seven out of ten spinel-hibonite spherules from Murray meteorites are shown in Fig. 3.5. Five spherules (Fig. 3.5) show rectangular laths of hibonites with sharp boundaries within the spinel matrix. In case of MY-H9 and MY-H11-a, partially rounded hibonites in the spinel matrix are observed. The size of the hibonite laths ranges from ~ 15-50 μ m in length and ~ 10-15 μ m in width. Size of the spherules range from ~ 50 μ m to 120 μ m in their longest dimension. Perovskite grains (Per) are present as inclusions within spinel matrix in spherule MY H14 (Fig. 3.5e).

No identifiable inclusions are present in both the Murchison and Murray platelets even though some voids are seen. On the other hand, spherules often appear to be porous with lots of voids within them. However, the sharp boundaries between hibonite laths and the spinel matrix suggest absence of post crystallization alterations.







Fig. 3.2 Backscattered electron images of platelet hibonites from the Murchison meteorite.





Fig. 3.2 (Cont'd) Backscattered electron images of platelet hibonites from the Murchison meteorite







Fig. 3.3 Backscattered electron images of spinel-hibonite spherules from the Murchison meteorite





Fig. 3.4 Backscattered electron images of two platelet hibonites from the Murray meteorite surrounded by silicate and Fe-rich phases







Fig. 3.5 Backscattered electron images of spherules from the Murray meteorite







Fig. 3.5 (cont'd) Backscattered electron images of spherules from the Murray meteorite



Fig. 3.5 (cont'd) Backscattered electron images of spherules from the Murray meteorite

3.3 Hibonite Composition

Quantitative estimate of elemental composition of the hibonites was obtained using Wavelength Dispersive X-ray spectrometric (WDX) technique. The details of the

Element	Standard	Diff. Crystal	Detector
Mg	Augite [Mg(Fe,Ca)Si ₂ O ₆]	ТАР	FPC
Al	Anorthite [CaAl ₂ Si ₂ O ₈]	ТАР	FPC
Si	Augite	PET	FPC
Ca	Augite	PET	FPC+SPC
Ti	Ilmenite [FeTiO ₃]	PET	FPC+SPC
V	pure V	LiF	FPC+SPC
Cr	pure Cr	LiF	FPC+SPC
Mn	Ilmenite	LiF	FPC+SPC
Fe	Ilmenite	LiF	FPC+SPC
0	Augite	LSM80	FPC
Na	Plagioclase[NaAlSi ₃ O ₈ -CaAl ₂ Si ₂ O ₈]	TAP	FPC

Table 3.1 Parameters for WDX measurements

Note: TAP: Thallium acid pathalate (7.3130-23.789A°); LSM80: Ni-C (~22-72 A°); PET: Pentaery thristol (2.4827-8.0765 A°); LiF: Lithium fluoride (1.1436-3.7202 A°) FPC: Flow proportional counter (<3A°, polypropylene window, P₁₀ gas) SPC: Sealed proportional counter (1-3A°, Beryllium window, Xe/CO₂ mixture) standards, the diffracting crystals and the type of detectors used during WDX measurements are given in Table 3.1. The compositions in all the nineteen hibonite samples are given in Table 3.2.

Sample (n)	MgO	AI_2O_3	SiO ₂	CaO	TiO ₂	V_2O_3	Cr_2O_3	MnO	FeO	Total
Murchison Platelets										
CH-C1 (2)	1.01	89.49	0.02	8.485	2.23	0.135	0.01	n.d	0.01	101.38
CH-C2 (2)	0.62	91.42	0.01	8.57	1.66	0.05	0.01	n.d	0.01	102.33
CH-C4 (3)	1.14	88.75	0.01	8.61	2.65	0.08	0.01	0.01	0.01	101.26
CH-C6 (2)	1.07	89.21	0.02	8.41	2.49	0.12	0.01	n.d	0.01	101.32
CH-D5 (2)	0.79	91.38	0.00	8.54	1.82	0.09	n.d	n.d	n.d	102.60
Murchison Sp	oherules									
CH-D4 (2)	2.72	84.61	0.19	8.48	5.11	0.24	0.02	n.d	0.01	101.37
CH-D7 (3)	3.79	81.81	0.37	8.25	5.87	0.39	0.02	0.01	0.01	100.52
CH-D8 (2)	3.37	82.88	0.17	8.13	5.31	0.66	0.05	n.d	0.01	100.56
Murray Plate	lets									
MYH17 (3)	1.08	88.48	0.03	7.50	2.25	0.04	n.d	0.01	n.d	99.37
MYH19 (3)	0.89	89.05	0.03	8.46	2.56	0.03	n.d	n.d	0.06	101.09
Murray Spher	rules									
MYH1 (3)	4.68	79.53	0.32	7.56	7.37	0.20	0.05	0.01	n.d	99.73
MYH3 (4)	4.66	81.68	0.13	8.62	6.77	0.23	0.02	0.00	0.01	102.10
MYH5 (4)	4.48	77.86	0.61	7.80	6.62	0.21	0.03	0.003	0.008	97.61
MYH8 (2)	4.045	83.91	0.09	7.53	5.04	0.23	0.06	n.d	n.d	100.89
MYH9 (2)	3.985	81.54	0.12	8.15	6.68	0.45	0.02	0.02	0.06	101.00
MYH11a (2)	2.8	87.59	0.04	7.055	3.58	0.2	0.05	n.d	0.02	101.34
MYH11b (4)	3.945	79.92	0.16	8.69	7.91	0.25	0.03	0.003	0.01	100.90
MYH12 (2)	3.045	81.55	1.765	10.22	5.64	0.27	n.d	n.d	0.06	102.54

Table 3.2 Composition in hibonites from Murchison and Murray meteorites.

Note : *n* = number of analyses performed, *n.d*: not detected

The composition of the hibonites occurring as platelets or within spherules are nearly similar. However, the data suggest that the Ti and Mg are relatively depleted in the platelets. V and Si appears to be present at detectable levels only in hibonites from spherules. The average composition of the platelets and the spherules are shown in Fig. 3.6.



Fig. 3.6 Pie-chart showing the composition of platelet and spherule hibonites.

Murchison Platelets]	Murchison sp	oherules
	C1	C2	C4	C6	D5	D4	D7	D8
Si	0.00	0.00	0.00	0.00	0.00	0.02	0.04	0.02
AI	11.63	11.74	11.56	11.60	11.71	11.07	10.83	10.95
Mg	0.17	0.10	0.19	0.18	0.13	0.45	0.63	0.56
Fe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	1.00	1.00	1.02	0.99	0.99	1.01	0.99	0.98
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ti	0.18	0.14	0.22	0.21	0.15	0.43	0.50	0.45
V	0.01	0.00	0.01	0.01	0.01	0.02	0.04	0.06
Cr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	12.99	12.99	13.00	12.99	12.99	13.00	13.03	13.02
Ca(Al _{11.65} Mg _{0.15} Ti _{0.18} V _{0.01})O ₁₉						Ca _{0.99} (Al	10.95 Si _{0.03} Mg	0.55Ti _{0.46} V _{0.04})O ₁₉

Fable 3.3 Number of cation	ons in hibonites	per 19	oxygen.
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Murray Platelets						Mur	ray sph	erules			
	H19	H17	H1	H3	H5	H8	H9	H11a	H11b	H12	H26
Si	0.00	0.00	0.04	0.01	0.07	0.01	0.01	0.00	0.02	0.19	0.03
Al	11.61	11.68	10.62	10.68	10.62	11.02	10.76	11.38	10.59	10.61	11.59
Mg	0.15	0.18	0.79	0.77	0.77	0.67	0.67	0.46	0.66	0.50	0.22
Fe	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.01	0.01
Ca	1.00	0.90	0.92	1.02	0.97	0.90	0.98	0.83	1.05	1.21	0.95
Na	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ti	0.21	0.19	0.63	0.56	0.58	0.42	0.56	0.30	0.67	0.47	0.17
V	0.00	0.00	0.02	0.02	0.02	0.02	0.04	0.02	0.02	0.02	0.01
Cr	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	12.98	12.96	13.01	13.07	13.03	13.05	13.02	13.00	13.01	13.02	12.99
Ca _{0.95} (Al _{11.65} Mg _{0.17} Ti _{0.20} Fe _{0.01})O ₁₉					Ca _{0.98}	(Al _{10.87} S	Si _{0.04} Mg ₀	. ₆₁ Ti _{0.48}	V _{0.02})O ₁₉	Э	

All the hibonites sampled, are nearly stoichiometric as can be seen from the composition data shown in Table 3.3. This can also be seen in Fig. 3.7, which is a covariant plot of number of Mg^{2+} , Ti^{4+} , Si^{4+} and Fe^{2+} atom plotted against number of V^{3+} and Al^{3+} atoms per 19 oxygen atoms in the Murchison and Murray hibonites.

The exchange of cations during hibonite formation can be understood by the following ideal coupled equation:

$$(Ti^{4+} + Si^{4+}) + (Mg^{2+} + Fe^{2+}) \iff 2(Al^{3+} + V^{3+})$$

Since Fe, Si and V are negligible in concentration compared to Al, Ti, Ca and Mg the above equation can be approximated as:



$$Ti^{4+} + Mg^{2+} \leftrightarrow 2Al^{3+}$$

Fig. 3.7 Compositional data for the analyzed CM hibonites. The reference (solid) line for stoichiometric hibonite is also shown.

Ion probe studies of elemental and isotopic composition were carried out on hibonite from all the samples. The specific studies conducted are shown in Table 3.4; these include, Al-Mg and Ca-K isotope systematics, stable isotopic compositions of the elements, Ca, Ti and O and abundances of rare earth elements (REE) and refractory trace elements (RTE). Sizes of the analyzed hibonite in the samples are also indicated in the table.

Table 3.4 Analyses performed on hibonites from the CM meteorites, Murchison and Murray.

SAMPLE	MINERAL		Isotopic	compo	sition		Abundance	SIZE
		Al-Mg	Ca-K	Ti	Ca	0	REE/RTE	(µm)
Murchison Pl	atelets							
CH-C1	Hib	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	60 x 52
CH -C2	Hib	\checkmark	\checkmark	\checkmark	\checkmark	×	\checkmark	95 x 30
CH -C4	Hib	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	110 x 105
CH -C6	Hib	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	75 x 50
CH -D5	Hib	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	\checkmark	60 x 50
Murchison Sp	herules							
CH -D4	Sp, Hib	\checkmark	\checkmark	\checkmark	\checkmark	×	\checkmark	25 x 12
CH -D7	Sp, Hib	\checkmark	\checkmark	\checkmark	\checkmark	×	\checkmark	20 x 15
CH -D8	Sp, Hib	\checkmark	\checkmark	\checkmark	\checkmark	×	\checkmark	30 x 15
Murray Plate	lets							
MY-H17b	Hib, silicate	\checkmark	×	\checkmark	×	×	\checkmark	50 x 35
MY-H19b	Hib, Fe-rich	\checkmark	×	\checkmark	×	\checkmark	×	60 x 45
	phase							
Murray Spher	rules							
MyH1	Sp, Hib	\checkmark	×	\checkmark	×	\checkmark	\checkmark	40 x 10
MY-H3b	Sp, Hib	\checkmark	×	\checkmark	×	×	\checkmark	45 x 10
MY-H5a	Sp, Hib	\checkmark	×	\checkmark	×	×	×	30 x 10
MY-H8	Sp, Hib	\checkmark	×	\checkmark	×	\checkmark	\checkmark	20 x 10
MY-H9	Sp, Hib	\checkmark	×	\checkmark	×	×	\checkmark	15 x 15
MY-H11a	Sp, Hib	\checkmark	×	×	×	×	×	15 x 10
MY-H11b	Sp, Hib	\checkmark	×	\checkmark	×	×	\checkmark	50 x 10
MY-H12a	Sp, Hib	\checkmark	×	\checkmark	×	×	\checkmark	30 x 12
MY-H14a	Sp, Hib	\checkmark	×	\checkmark	×	×	\checkmark	35 x 10
MY-H26a	Sp, Hib	\checkmark	×	\checkmark	×	\checkmark	×	10 x 10

Note: hib= Hibonite, sp= spinel, per= perovskite, ×: Analysis not performed

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Results

4.1 Short-lived Radionuclides ²⁶Al and ⁴¹Ca in CM Hibonites

meteorites, Murchison and Murray, are presented in this chapter.

4.1.1 Al-Mg Isotopic Systematics

In the three-isotope Mg system, presence of any fractionation corrected residual in ${}^{26}Mg$ ($\delta^{26}Mg$) may be obtained using the following relation

$$\delta^{26}Mg = \Delta^{26}Mg - 2. \ \Delta^{25}Mg$$
(4.1)

the Δ^{i} Mg values are obtained using relation 2.6, and we assume a normal 25 Mg/ 24 Mg ratio in the hibonites and a linear isotopic mass-fractionation. A positive value of δ^{26} Mg indicates excess 26 Mg that may be attributed to the initial presence of the short-lived nuclide 26 Al (t_{1/2} = 0.73Ma), provided this excess shows correlation with the 27 Al/ 24 Mg ratio in the hibonite.

If ²⁶Al was initially present and the Al-Mg system has remained isotopically closed, one can write,

where,

'm' stands for the measured value corrected for mass fractionation,

'i' is the initial isotopic ratio

and the '*' indicates radiogenic component.

Measurements performed over a range of ${}^{27}\text{Al}/{}^{24}\text{Mg}$ values in a given sample allow one to use the above relation to obtain the initial values of ${}^{26}\text{Al}/{}^{27}\text{Al}$ and ${}^{26}\text{Mg}/{}^{24}\text{Mg}$ characterizing the analyzed sample. In a well behaved Al-Mg system, a plot of ${}^{26}\text{Al}/{}^{24}\text{Mg}$ will follow a line whose slope yields the initial (${}^{26}\text{Al}/{}^{27}\text{Al}$) value and the intercept yields initial ${}^{26}\text{Mg}/{}^{24}\text{Mg}$ value.

The measured $({}^{27}\text{Al}/{}^{24}\text{Mg})$ ratios in the CM hibonites along with their $\delta^{26}\text{Mg}$ values and inferred initial $({}^{26}\text{Al}/{}^{27}\text{Al})$ values are presented in Table 4.1. The ${}^{27}\text{Al}/{}^{24}\text{Mg}$ ratios in the Murchison platelet hibonites are higher than that in hibonites from the spherules. Single

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measurement was conducted in most of the cases due to the small size of the hibonites and the nearly uniform value of Al/Mg ratio in them. The only exceptions are hibonites in two Murray spherules, MY-H5 and MY-H11a (Table 4.1) The initial 26 Al/ 27 Al in each case was determined by force-fitting the data points through normal Mg-isotopic composition at Al/Mg=0, *i.e.*,

$$({}^{26}\text{Al}/{}^{27}\text{Al})_i = (0.00013932 \times \delta^{26}\text{Mg} \{\%\}) / ({}^{27}\text{Al}/{}^{24}\text{Mg}) \qquad \dots \dots \dots (4.4)$$

The (²⁶Al/²⁷Al)_i values for the Murchison and Murray hibonites vary over a wide range, most of the platelet hibonites are devoid of detectable ²⁶Al. Five out of twelve spherules [CH-D7, MY-H11a, MY-H12, MY-H14, MY-H26] show presence of ²⁶Al.

	Sample	²⁷ Al/ ²⁴ Mg	δ ²⁶ Mg	(²⁶ Al/ ²⁷ Al) _i x 10 ⁻⁵
Madagascar hib	MH-1	18.8 ± 0.0001	-0.65 ± 1.1	-
Burma Spinel	BS-1	2.48 ± 0.003	-0.11 ± 0.58	-
Murchison	CH-C1	71.72 ± 0.55	-1.06 ± 2.98	≤ 0.37
platelet	CH-C2	123.98 ± 1.59	-2.83 ± 5.50	≤ 0.30
	CH-C4	67.43 ± 0.11	-4.96 ± 4.12	≤ -0.17
	CH-C6	99.01 ± 0.12	-3.55 ± 3.59	≤ 0.006
	CH-D5	111 ± 0.20	$\textbf{-0.18} \pm \textbf{5.40}$	≤ 0.66
Murchison	CH-D4	22.72 ± 0.94	-1.72 ± 4.66	1.08 ± 2.85
Spherule	CH-D7	$16.73\pm\ 0.75$	$\textbf{6.99} \pm \textbf{4.26}$	5.82 ± 3.56
	CH-D8	19.23 ± 0.04	4.19 ± 5.10	3.03 ± 3.69
Murray Platelet	MY H17	71.9 ± 0.08	0.69 ± 2.36	0.13 ± 0.5
	MY H19	49.1 ± 0.13	-0.73 ± 1.98	≤ 0.36
Murray	MY H1	13.5 ± 0.03	1.45 ± 3.05	1.50 ± 3.2
Spherules	MY H3	7.61 ± 0.03	1.81 ± 4.66	3.31 ± 8.5
	MY H5-1	12.5 ± 0.02	1.72 ± 2.89	1.92 ± 3.2
	MY H5-2	17.2 ± 0.09	-0.10 ± 4.0	≤ 3.16
	MY H8	16.5 ±0.02	-0.71 ± 2.72	1.70 ± 2.30
	MY H9	17.7 ± 0.18	5.65 ± 6.44	4.45 ± 5.1
	MY H11a-1	17.4 ± 0.20	7.33 ± 1.76	5.87 ± 1.4
	MY H11a-2	10.6 ± 0.19	5.06 ± 2.58	6.64 ± 3.4
	MY H11b	5.7 ± 0.03	1.47 ± 3.44	3.59 ± 8.4
	MY H12	25.3 ± 0.04	5.79 ± 2.64	3.20 ± 1.5
	MY H14	16.06 ± 0.06	5.41 ± 4.24	4.69 ± 3.7
	MY H26	15.73 ± 0.13	7.46 ± 1.89	6.61 ± 1.7

Table 4.1 Al-Ma da	ta for hibonites in	CM meteorites	Murchison and	1 Murrav*
			mai or noorr and	indianay .

* All errors are $2\sigma_m$

Note : $[({}^{25}Mg/{}^{24}Mg)_{ref} = 0.12663; ({}^{26}Mg/{}^{24}Mg)_{ref} = 0.13932]$

The Al-Mg data for the CM hibonites are plotted in a three isotope diagram (Fig. 4.1). The solid line represents the expected trend for an initial (26 Al/ 27 Al) value of 5×10⁻⁵, the generally considered cannonical value for the early solar system (MacPherson et al., 1995). The dotted line represents normal Mg isotopic composition (26 Mg/ 24 Mg = 0.13932; δ^{26} Mg=0). The data for the terrestrial standards are consistent with normal Mg-isotopic composition.



Fig. 4.1 Measured ²⁶Mg/²⁴Mg ratio plotted as a function of ²⁷Al/²⁴Mg for Murchison and Murray hibonites. The dashed line represents reference ²⁶Mg/²⁴Mg ratio of 0.13932 (**d**=0). The solid line represents evolution of the Al-Mg isotopic system for an initial ²⁶Al/²⁷Al ratio 5 $^{\prime}$ 10⁵. Data for multiple analyses done in two samples, MY-H5 and MY-H11a, are also labeled. 1s error bars are shown for clarity in presentation.

4.1.2 Ca-K Isotopic Systematics

The possible presence of the short-lived nuclide ⁴¹Ca in the CM hibonites may be inferred by looking for excess in its daughter nuclide ⁴¹K and one can write:

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or
$$({}^{41}K/{}^{39}K)_m = ({}^{41}K/{}^{39}K)_i + ({}^{41}Ca/{}^{40}Ca)_i ({}^{40}Ca/{}^{39}K)_m$$
(4.6)

where,

'm' stands for measured ratios,

'i' is the initial isotopic ratio

and the '*' indicates radiogenic component.

Unlike the case for Mg, only two isotopes of K (³⁹K and ⁴¹K) were measured and it is not possible to directly infer the magnitude of isotopic mass fractionation effect in ⁴¹K relative to ³⁹K. However, the measured ⁴¹K/³⁹K ratios for the two terrestrial standards lie very close to the reference value [⁴¹K/³⁹K = 0.072; Fig. 4.2] indicating that the isotopic mass fractionation effect in K isotopes is small. Further, detail study of K isotopic compositions in a suite of terrestrial and extraterrestrial samples indicated isotopic mass fractionation effect to be < 4 per mil (Humayun and Clayton, 1995), and intrinsic mass fractionation, if any, is generally expected to be less than the instrumental mass fractionation. In view of the above and the large uncertainty in the measured ⁴¹K/³⁹K ratio (~10 %), resulting from the very low ³⁹K count rate (typically \leq 0.5 c/s) due to low K content (\leq 80 ppm) in the hibonites, we ignore the effect of possible isotopic mass fractionation effect in the measured ⁴¹K/³⁹K ratio.

It is not possible to resolve excess ⁴¹K in hibonites with low Ca/K ratio ($\leq 10^5$) because of the extremely low value of ~1.4x 10⁻⁸ for the initial ⁴¹Ca/⁴⁰Ca ratio (Srinivasan et al., 1996). We therefore studied Ca-K systematics only in Murchison platelet hibonites with high Ca/K ratio. A few hibonite-bearing Murchison spherules with low Ca/K ratio were also analyzed. The Murray hibonites are characterized by low Ca/K ratio ($\leq 10^4$), and were not analyzed for their Ca-K isotopic systematics. The measured values of ⁴⁰Ca/³⁹K and ⁴¹K/³⁹K for the analyzed samples are presented in Table 4.2. The ⁴¹K/³⁹K ratio are corrected for the unresolved (⁴⁰Ca⁴²Ca)⁺⁺ interference following procedure discussed earlier (chapter 2, § 2.2.3) using the relation:

$$({}^{41}\text{K}/{}^{39}\text{K})_{t} = ({}^{41}\text{K}/{}^{39}\text{K})_{m} - ({}^{40}\text{Ca}{}^{42}\text{Ca})^{++}/{}^{39}\text{K}$$
$$= ({}^{41}\text{K}/{}^{39}\text{K})_{m} - ({}^{40}\text{Ca}{}^{43}\text{Ca})^{++}/{}^{43}\text{Ca}^{+} .({}^{42}\text{Ca}{}^{+}/{}^{39}\text{K})$$
	Sample	⁴⁰ Ca/ ³⁹ K	⁴¹ K/ ³⁹ K
Madagascar hibonite	MH-1	3.0 x 10 ⁶	0.0719± 0.0004
Burma spinel	BS-1	~ 680	0.0720± 0.0060
Murchison platelet	CH-C1 CH-C2 CH-C4 CH-C6 CH-D5	1.5 x10 ⁶ ~ 3 x 10 ⁵ ~ 1 x 10 ³ ~ 3 x 10 ⁵ ~ 3.8 x 10 ⁶	$\begin{array}{c} 0.0698 \pm 0.0076 \\ 0.0700 \pm 0.009 \\ \text{n.m} \\ 0.0684 \pm 0.0076 \\ 0.0738 \pm 0.0092 \end{array}$
Murchison Spherule	CH-D4	~ 530	0.07362 ± 0.0013
	CH-D7	~ 800	0.07276 ± 0.001
	CH-D8	~ 2000	0.07249 ± 0.001
Murray Platelet	MY H17	~ 2 x 10 ⁴	n.m
	MY H19	~ 650	n.m
Murray Spherules	Ten	50 – 8.5 x10 ³ *	n.m

Table 4.2 Ca-K data for Murchison and Murray hibonites.

Note : $({}^{41}K/{}^{\beta9}K)_{ref} = 0.072$; Errors are $2s_m$; n.m = not measured

* Range of Ca/K ratio in the ten spherules from Murray.



Fig. 4.2 Ca-K isotopic systematics in CM hibonites. The dashed line represents reference ⁴¹K/⁸⁹K ratio of 0.072. The solid line represents the expected trend line for an initial 41 Ca/ 40 Ca ratio of 1.4 $\stackrel{<}{}$ 10⁸. An enlarged view of the data for the spherule is shown in the inset. Error bars are 1s.

The data for the seven analyzed hibonites are shown in Fig. 4.2. The expected evolution line corresponding to an initial 41 Ca/ 40 Ca of 1.4×10^{-8} proposed to be representative of early solar system matter (Srinivasan et al., 1996) is also shown. All the analyzed platelet hibonites yielded values close to reference 41 K/ 39 K ratio, within the limits of our experimental uncertainty, and are thus devoid of 41 Ca. The Murchison spherules also indicate 41 K/ 39 K ratio close to normal value.

4.2 Stable Isotopes of Ti, Ca and O

4.2.1 Ti Isotopic Composition

All the hibonite samples except one Murray spherule (MY H11a) were analyzed for their Ti isotopic composition. The results obtained are shown in Table 4.3 in terms of δ^{i} Ti values normalized to 46 Ti/ 48 Ti. The " α " represents the exponent in the power-law mass fractionation expression used for fractionation correction. Isobaric interferences from 46 Ca (at 46 Ti) and 50 V and 50 Cr (at 50 Ti) were inferred in each case from the measured count-rate at 44 Ca, 51 V and 52 Cr, respectively, assuming normal isotopic composition for these elements (Table 4.3). In two samples (CH D5 and MY H17), 46 Ca correction appears to be rather large (7‰ and 10‰), whereas for the other hibonites this interference is much lower. Similarly in the case of 50 Cr, corrections are generally less than 2 ‰ except for three samples. These variations, however, do not affect the inferred δ^{49} Ti and δ^{50} Ti values in any significant manner. δ^{50} Ti anomaly occurs both as depletion and enrichment in 50 Ti and the δ^{50} Ti value for platelet hibonites (-27 ‰ to 92 ‰) has a considerably larger spread than spherules (-14 ‰ to +22‰).

The δ^{50} Ti values for all the analyzed hibonite samples are plotted in Fig. 4.3. Abundance anomalies are also present in ⁴⁹Ti and δ^{49} Ti & δ^{50} Ti have the same sign (Table 4.3). Generally δ^{49} Ti is lower than δ^{50} Ti. However, our data do not allow us to draw specific conclusion about the magnitude of δ^{49} Ti anomalies relative to that of δ^{50} Ti.

Sample	α^{a}	δ^{47} Ti (‰) ^b	δ^{49} Ti (‰) ^b	δ^{50} Ti (‰) ^b	Co	rrection	(‰)
	$\pm 2\sigma_{m}$	$\pm 2\sigma_{m}$	$\pm 2\sigma_{m}$	$\pm 2\sigma_{m}$	⁴⁶ Ca	⁵⁰ Cr	⁵⁰ V
Madgascar Hibonite							
MH1	-0.62 ± 0.12	2.80 ± 4.62	0.75 ± 4.40	1.08 ± 5.40	0.22	0.007	0.02
MH2	-0.58 + 0.06	1.62 ± 2.30	-1.61 ± 2.22	1.87 ± 3.38	0.20	0.006	0.02
MH3	-0.67 ± 0.08	3.61 ± 3.10	-1.30 ± 4.03	-0.001 ± 4.5	0.20	0.006	0.03
Murchisor	n platelet						
CH-C1	-1.10±0.10	6.47±5.86	22.72±6.58	92.90±6.40	5.96	0.17	0.42
CH-C2	-0.53±0.06	1.27±3.02	6.19±3.86	66.95±5.12	6.40	0.21	0.10
CH-C4	-0.79±0.04	0.12±1.82	1.40 ± 2.62	-27.75±2.88	5.57	0.15	0.45
CH-C6	-0.59±0.06	-1.25±3.44	9.55±4.05	73.71±5.22	5.63	0.20	0.28
CH-D5	-0.70±0.10	3.56±7.26	-0.79±5.71	10.31±7.54	7.21	0.41	0.77
Murchisor	Murchison Spherule						
CH-D4	-0.67±0.12	-0.27±3.06	6.04 ± 5.60	14.33±5.66	1.80	0.95	8.40
CH-D7	-0.45±0.06	2.86±3.56	2.38 ± 2.90	5.74±2.22	2.10	1.36	4.75
CH-D8	-0.44±0.13	0.46 ± 6.02	7.90±6.46	3.67±10.84	2.23	6.79	10.76
Murray Pl	atelet						
MY H17	-0.78±0.16	-1.14±7.34	4.73±5.08	16.68±6.46	10.9	1.88	8.31
MY H19	-0.92±0.18	3.69±7.08	-1.03±7.06	25.23±12.7	4.38	0.33	0.32
Murrav Sr	herules						
MY H1	-0.44+0.2	-6.76+8.00	-0.53+9.43	-9.96+12.46	1.16	11.76	53.57
МҮ НЗ	-0.58 ± 0.08	7.00 ± 3.82	5.00 ± 3.36	-3.30 ± 4.26	1.90	10.87	1.87
MY H5	-0.16 ± 0.13	2.25 ± 5.98	-3.26 ± 7.41	-17.72 ± 8.05	1.02	9.07	30.28
MY H8	-1.15±0.09	-1.26±1.82	14.48±3.44	22.08±5.63	1.90	1.59	8.37
MY H9	-0.51±0.08	3.16±2.86	1.61±4.00	-1.36±4.02	1.81	2.67	3.46
MY H11b	-0.11±0.09	6.37±2.44	-2.31±3.42	-14.33±5.66	1.38	2.84	11.03
MY H12	-0.73±0.18	4.73±3.22	8.71±6.06	2.43±9.18	2.11	1.81	5.70
MY H14	-0.75±0.09	-7.78±2.94	-7.10±4.12	-11.77±5.36	1.08	1.32	10.62
MY H26	-0.51±0.12	0.36±3.85	-2.53±5.46	2.53±5.60	2.70	1.18	4.85

Table 4.3 Titanium isotopic composition in CM hibonites

^a α = Exponent defining the instrumental isotope mass fractionation:

$$[{}^{46}\text{Ti}/{}^{48}\text{Ti}]^{\alpha} = [({}^{46}\text{Ti}^{+}/{}^{48}\text{Ti}^{+})_{\text{measured}}]/[({}^{46}\text{Ti}/{}^{48}\text{Ti})_{\text{reference}}]$$

 $^{\text{b}}$ $\delta\text{-value}$ calculated using the relation:

$$\boldsymbol{d}^{i}Ti = 1000 \times \left[\frac{\left(iTi^{+}/^{48}Ti^{+}\right)_{measured} \times (m_{i}/48)^{-\boldsymbol{a}}}{\left(iTi/^{48}Ti\right)_{reference}} - 1\right]$$

[reference Ti isotopic composition: ${}^{46}Ti/{}^{48}Ti = 0.108548$, ${}^{47}Ti/{}^{48}Ti = 0.099315$, ${}^{49}Ti/{}^{48}Ti = 0.074463$, ${}^{50}Ti/{}^{48}Ti = 0.072418$ (from Niederer et al., 1981)]



Fig. 4.3 Abundance anomalies in ⁵⁰Ti in CM hibonites (\mathbf{d}^{50} Ti) expressed in per mil unit using a reference ⁵⁰Ti/⁴⁸Ti ratio of 0.072418. The data for terrestrial standards are consistent with the reference Ti isotopic composition (\mathbf{d}^{50} Ti =0) indicated by the vertical dashed line.

4.2.2 Ca Isotopic Composition

Ca isotopic studies were carried out only in those hibonites that displayed large magnitude Ti isotopic anomalies (δ^{50} Ti >25 ‰). The relatively low Ti isotopic anomalies and small sample size preclude Ca-isotopic analysis of the Murray hibonites.

We have used an exponential mass fractionation expression to obtain δ^{42} Ca, δ^{43} Ca, and δ^{48} Ca values using 40 Ca and 44 Ca as the reference isotopes. Table 4.4 summarizes the results of calcium isotopic data for Murchison hibonites. Possible interference of 48 Ti on

⁴⁸Ca was computed in all the cases following procedure described in Chapter 3. δ^{48} Ca values for the analyzed samples are shown in Fig. 4.4. Both negative (depletion) and positive (enrichment) anomalies for ⁴⁸Ca were recorded in platelets and spherules; and δ^{48} Ca values correlate with δ^{50} Ti, in the sense that both of them have the same sign.

Sample	α ^a	δ^{42} Ca (‰) ^b	δ^{43} Ca(‰) ^b	δ^{48} Ca(‰) ^b	Correction	
	$\pm 2\sigma_{m}$	$\pm 2\sigma_{m}$	$\pm 2\sigma_{m}$	$\pm 2\sigma_{m}$	⁴⁸ Ti (‰)	
Madagascar Hibonite						
MH-1	-0.04 ± 0.01	0.69 ± 3.51	2.1 ± 4.10	1.85 ± 5.10	8.31	
MH-2	-0.03 ± 0.01	0.91 ± 4.02	1.6 ± 3.68	1.15 ± 2.50	7.97	
MH-3	-0.03 ± 0.02	-1.52 ± 4.11	-0.63 ± 3.88	-0.004 ± 3.40	10.39	
Murchison	Murchison platelet					
CH-C1	0.02±0.02	3.72±1.88	10.19±3.62	66.44±10.44	9.85	
CH-C2	0.09 ± 0.04	-3.63±1.48	1.29±3.88	81.19±10.16	4.76	
CH-C4	-0.02 ± 0.08	-2.73±2.82	0.01 ± 5.28	-10.34±9.08	6.16	
CH-C6	0.06±0.03	-8.33±2.24	1.71±5.56	81.07±8.24	6.07	
CH-D5	0.06±0.04	-5.71±3.96	1.12±7.56	-17.75±8.28	8.14	
Murchison Spherule						
CH-D4	0.06±0.06	-4.12±6.01	-0.54±10.24	74.46±20.0	3.28	
CH-D7	0.24±0.04	-5.47±2.42	-3.34±6.80	39.12±9.84	22.64	
CH-D8	0.10±0.06	-5.52±4.72	-1.32±8.06	24.79±9.90	14.95	

Table 4.4 Calcium isotopic composition in Murchison hibonites

^a α = Exponent defining the instrumental isotope mass fractionation:

$$[{}^{40}Ca/{}^{44}Ca]^{\alpha} = [({}^{40}Ca^{+}/{}^{44}Ca^{+})_{\text{measured}}]/[({}^{40}Ca/{}^{44}Ca)_{\text{reference}}]$$

^b δ -value calculated using the relation:

$$d^{i}Ca = 1000 \times \left[\frac{\left(iCa^{+}/44Ca^{+}\right)_{measured} \times (m_{i}/44)^{-a}}{\left(iCa/44Ca\right)_{reference}} - 1\right]$$

[Reference Ca isotopic composition (Niederer and Papanastassiou, 1984): ${}^{40}Ca/{}^{44}Ca=47.153$, ${}^{42}Ca/{}^{44}Ca=0.31221$, ${}^{43}Ca/{}^{44}Ca=0.06486$, ${}^{46}Ca/{}^{44}Ca=0.001518$, ${}^{48}Ca/{}^{44}Ca=0.088727$]



Fig. 4.4 Abundance anomalies in ⁴⁸Ca in CM hibonites (\mathbf{d}^{48} Ca) expressed in per mil unit using a reference ⁴⁸Ca/⁴⁴Ca ratio of 0.088727. The data for terrestrial standards are consistent with reference Ca isotopic composition (\mathbf{d}^{48} Ca =0) indicated by the vertical dashed line.

4.2.3 Oxygen Isotopic Composition

Oxygen isotopic compositions in five platelets (four from Murchison and one from Murray) and in three Murray spherules are presented in Table 4.5. Terrestrial standards (Burma spinel and Madgascar hibonite), with known oxygen isotopic composition, were analyzed to infer instrumental mass fractionation effect. The Δ^{17} O and Δ^{18} O values were calculated with reference to SMOW (standard mean ocean water) values (18 O/ 16 O = 0.0020052 and 17 O/ 16 O = 0.00038309), and range from -57 ‰ to -38 ‰. 16 O excess in the samples were calculated using the relation:

$$^{16}O_{\text{excess}} = [(0.52/(1-0.52))\Delta^{18}O) - ((1/(1-0.52))\Delta^{17}O)]$$

All the samples, platelets as well as spherules, show clear ¹⁶O excess varying from 38 ‰ to 57 ‰. The isotopic data plot along with the carbonaceous chondrite anhydrous mineral (CCAM) line with a slope of unity [Clayton, 1993]. The terrestrial fractionation

line (TF), with a slope of 0.5 is also shown in this figure. Data for the terrestrial standards lie on the TF line.



Fig. 4.5 Oxygen isotopic composition in CM hibonites and terrestrial standards shown in a plot of measured \mathbf{D}^{17} O vs \mathbf{D}^{18} O, the per mil deviations from the standard ratios (17 O/ 16 O= 0.00038309, 18 O/ 16 O=0.0020057). The terrestrial fractionation (TF) line and the Carbonaceous Chondrite Anhydrous Mineral (CCAM) lines are also shown.

	Sample	Δ^{17} O ± 2 σ_m (‰)	Δ^{18} O ± 2 σ_m (‰)	¹⁶ O _{excess} (‰)
Madagascar hibonite	MH-1	692 + 14	10 32 + 1 97	-
	MH-2	2.76 ± 1.42	4.53 ± 1.74	-
	MH-3	1.09 ±1.53	2.35 ± 1.83	-
	MH-4	2.97 ± 1.37	3.22 ± 1.70	-
Burma Spinel	BS-1	11.64 ± 1.40	21 68 + 1 71	_
Durina Spinor	BS-2	10.35 ± 1.39	20.89 ± 1.70	-
Murchison platelet	CH-C1	-57 64 + 5 48	-57 68 + 6 60	57 60+13 47
I IIIII	CH-C4	-49.15 ± 2.76	-41.14 ± 3.88	57.83±7.12
	CH-C6	-38.53 ± 2.76	-38.85 ± 3.68	38.18±7.00
	CH-D5	-54.34 ± 3.76	-53.50 ± 4.80	55.25±9.40
Murray Platelet	MY H19	-40.79 ± 3.14	-40.37 ± 3.54	41.25±7.58
Murray	MY H1	-49.43 ± 2.90	-49.36 ± 4.00	49.51±7.44
Spherules	MY H8	-48.88 ± 3.26	-48.19 ± 4.14	49.63±8.14
	MY H26	-53.78 ± 5.18	-51.42 ± 5.38	56.34±12.26

Table 4.5 O-isotopic data for Murchison and Murray hibonites

4.3 Rare Earth and Refractory Trace Element (REE & RTE) Abundances

Five platelets and three spherules from Murchison and one platelet and eight spherules from Murray were analyzed for their REE and RTE abundances. The results obtained are presented in Table 4.6.

	Murchison Platelet					Murray
						Platelets
Element	CH C1	CH C2	CH C4	CH C6	CH D5	MY H17
Sr	75.1 ± 0.5	77.3 ± 0.7	76.5 ± 0.5	88.4 ± 0.7	75.8 ± 0.7	55.9 ± 1.2
Ba	6.0 ± 0.2	4.9 ± 0.2	6.0 ± 0.2	7.0 ± 0.2	5.2 ± 0.2	3.7 ± 0.2
Sc	359.5 ± 0.7	306.7 ± 0.8	412.6 ± 0.7	351.0 ± 0.7	548.7 ± 1.0	140.3 ± 1.1
Y	106.3 ± 0.7	48.2 ± 0.6	128.0 ± 0.7	148.8 ± 0.9	573.7 ± 2.0	62.5 ± 1.3
Zr	483.2 ± 2.9	198.5 ± 2.5	447.7 ± 2.7	551.5 ± 3.5	1568.2 ± 6.4	277.6 ± 5.5
Nb	0.2 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	0.2 ± 0.1	1.0 ± 0.1	0.6 ± 0.2
Hf	9.0 ± 1.1	4.0 ± 0.9	7.4 ± 1.3	6.6 ± 1.2	20.5 ± 2.4	4.2 ± 1.4
V	85.0 ± 0.5	144.9 ± 0.8	51.3 ± 0.4	90.6 ± 0.6	94.3 ± 0.6	197.4 ± 1.8
La	24.2 ± 0.4	8.1 ± 0.3	25.0 ± 0.4	24.5 ± 0.5	52.0 ± 0.8	26.7 ± 0.7
Ce	57.9 ± 0.7	21.3 ± 0.6	67.7 ± 0.8	67.2 ± 0.9	125.3 ± 1.4	67.6 ± 1.3
Pr	8.0 ± 0.2	3.0 ± 0.2	8.8 ± 0.2	8.5 ± 0.3	18.3 ± 0.4	8.7 ± 0.4
Nd	39.7 ± 0.6	12.9 ± 0.4	46.4 ± 0.6	40.1 ± 0.6	90.6 ± 1.0	43.7 ± 1.0
Sm	11.1 ± 0.4	4.3 ± 0.3	16.1 ± 0.5	10.8 ± 0.4	26.7 ± 0.8	16.1 ± 0.9
Eu	0.9 ± 0.1	0.4 ± 0.1	1.1 ± 0.1	1.0 ± 0.1	0.8 ± 0.1	0.9 ± 0.1
Gd	13.4 ± 0.5	3.5 ± 0.4	18.0 ± 0.6	13.7 ± 0.6	37.7 ± 1.1	8.9 ± 0.8
Tb	3.5 ± 0.2	0.9 ± 0.1	4.6 ± 0.2	3.1 ± 0.2	8.3 ± 0.4	2.6 ± 0.3
Dy	17.4 ± 0.4	6.0 ± 0.3	26.7 ± 0.5	22.0 ± 0.5	51.4 ± 0.8	12.5 ± 0.6
Но	3.5 ± 0.2	1.5 ± 0.2	6.5 ± 0.2	4.7 ± 0.2	10.4 ± 0.4	2.7 ± 0.3
Er	6.4 ± 0.3	1.5 ± 0.2	13.2 ± 0.4	10.3 ± 0.4	22.5 ± 0.6	4.4 ± 0.4
Tm	0.5 ± 0.1	0.2 ± 0.1	1.4 ± 0.1	1.1 ± 0.1	1.6 ± 0.2	0.5 ± 0.1
Yb	0.1 ± 0.1	0.4 ± 0.1	0.2 ± 0.2	0.06 ± 0.2	0.8 ± 0.3	0.7 ± 0.3
Lu	0.3 ± 0.1	0.03 ± 0.1	1.2 ± 0.1	1.0 ± 0.1	2.8 ± 0.3	0.0 ± 0.1

Table 4.6 REE and RTE concentration (ppm wt) in hibonites from CM meteorites*.

* All errors are 1s

	Murchison Spherules			1	Murray Spheru	les
	CH D4	CH D7	CH D8	MY H1	MY H3	MY H8
Sr	87.4 ± 1.0	34.2 ± 0.8	50.3 ± 1.4	98.8 ± 3.0	1980.1 ± 24.7	705.4 ± 3.1
Ba	38.5 ± 0.8	111.4 ± 1.6	39.8 ± 1.4	27.2 ± 1.0	449.6 ± 7.7	19.8 ± 0.6
Sc	115.6 ± 0.7	193.3 ± 1.1	115.5 ± 1.2	591.3 ± 4.1	1992.9 ± 14.0	705.4 ± 3.1
Y	24.5 ± 0.6	14.1 ± 0.5	13.5 ± 0.8	76.2 ± 2.8	68.6 ± 4.9	37.9 ± 1.3
Zr	689.4 ± 6.1	139.4 ± 3.3	216.2 ± 6.2	664.6 ±16.1	2448.4 ± 57.6	775.4 ± 11.9
Nb	9.6 ± 0.5	9.0 ± 0.6	1.7 ± 0.4	15.7 ± 1.8	17.7 ± 3.6	11.1 ± 1.0
Hf	11.8 ± 2.5	9.0 ± 1.8	8.6 ± 3.2	3.0 ± 2.8	1.8 ± 9.6	16.3 ± 3.2
V	1229.4 ± 3.2	1206.6 ± 3.8	3364.6 ± 9.5	3000 ± 13.3	3815.1 ± 28.0	2031.0 ± 7.5
La	36.0 ± 0.9	26.6 ± 1.0	8.6 ± 0.8	50.8 ± 1.9	125.9 ± 5.7	29.4 ± 1.0
Ce	85.8 ± 1.4	52.9 ± 1.7	18.1 ± 1.3	86.1 ± 2.8	150.7 ± 6.9	41.6 ± 1.3
Pr	10.1 ± 0.4	9.1 ± 0.5	2.4 ± 0.4	13.0 ± 0.9	27.2 ± 2.4	8.6 ± 0.5
Nd	46.2 ± 1.0	6.4 ± 0.8	9.0 ± 0.9	69.5 ± 2.3	107.2 ± 5.3	44.3 ± 1.2
Sm	8.8 ± 0.6	10.8 ± 0.8	3.7 ± 0.8	21.1 ± 1.7	23.5 ± 3.6	10.3 ± 0.8
Eu	0.8 ± 0.1	2.6 ± 0.3	1.5 ± 0.3	1.6 ± 0.3	2.7 ± 0.9	0.8 ± 0.2
Gd	9.0 ± 0.8	8.8 ± 0.8	2.2 ± 0.7	17.1 ± 2.0	24.3 ± 3.9	13.7 ± 1.3
Tb	1.7 ± 0.2	1.1 ± 0.2	0.7 ± 0.3	4.7 ± 0.7	4.3 ± 1.2	4.4 ± 0.5
Dy	5.9 ± 0.4	6.2 ± 0.5	2.6 ± 0.5	32.0 ± 1.7	29.1 ± 3.1	26.5 ± 1.1
Но	1.6 ± 0.2	1.2 ± 0.2	0.4 ± 0.2	3.4 ± 0.6	3.5 ± 1.1	4.4 ± 0.4
Er	1.8 ± 0.3	2.0 ± 0.3	2.5 ± 0.5	8.5 ± 1.0	14.6 ± 2.3	7.73 ± 0.6
Tm	0.1 ± 0.1	0.3 ± 0.1	0.3 ± 0.2	3.3 ± 0.6	3.4 ± 1.0	2.7 ± 0.4
Yb	0.2 ± 0.2	0.9 ± 0.3	0.5 ± 0.3	2.0 ± 0.7	1.5 ± 1.4	4.5 ± 0.6
Lu	0.03 ± 0.1	0.04 ± 0.1	1.0 ± 0.4	1.8 ± 0.6	1.2 ± 0.8	1.5 ± 0.4

Table 4.6 (cont'd) REE and RTE concentration (ppm wt) in hibonites from CM meteorites

	Murray Spherules				
	MY H9	MYH11a	MYH11b	MY H12	MY H14
Sr	87.8 ± 1.5	54.6 ± 1.7	57.0 ± 2.7	43.1 ± 5.5	83.6 ± 1.6
Ba	20.2 ± 0.5	8.0 ± 0.4	12.5 ± 0.9	28.9 ± 2.9	20.4 ± 0.5
Sc	253.9 ± 1.4	576.6 ± 3.1	818.4 ± 5.8	2417.4 ± 23.1	153.4 ± 1.2
Y	30.8 ± 0.9	68.1 ± 2.0	126.4 ± 4.3	61.5 ± 7.0	9.7 ± 0.6
Zr	335.3 ± 6.1	1763.7 ± 20.4	1821.7 ± 32.4	340.8 ± 32.2	90.2 ± 3.4
Nb	1.2 ± 0.3	16.2 ± 1.4	21.2 ± 2.6	3.6 ± 2.5	39.2 ± 1.6
Hf	5.5 ± 1.5	56.2 ± 4.0	9.0 ± 4.4	-47.8 ± 30.4	-4.9 ± 2.2
V	2005.7 ± 5.8	4941.2 ± 13.3	6170.2 ± 23.3	6420.7 ± 54.7	1726.4 ± 5.8
La	24.2 ± 0.7	75.8 ± 1.8	103.0 ± 3.3	28.1 ± 4.0	34.8 ± 0.9
Ce	39.2 ± 1.0	97.8 ± 2.3	118.5 ± 4.0	65.0 ± 6.7	92.0 ± 1.6
Pr	5.4 ± 0.3	15.9 ± 0.8	23.7 ± 1.5	11.9 ± 2.5	10.4 ± 0.5
Nd	23.7 ± 0.7	81.7 ± 1.9	132.0 ± 3.7	41.0 ± 4.9	51.6 ± 1.1
Sm	5.1 ± 0.5	15.5 ± 1.2	24.2 ± 2.3	13.3 ± 3.9	12.6 ± 0.8
Eu	1.1 ± 0.2	1.4 ± 0.2	1.6 ± 0.4	1.5 ± 1.2	2.8 ± 0.3
Gd	4.6 ± 0.7	14.7 ± 1.4	19.0 ± 3.1	1.1 ± 4.3	7.8 ± 0.9
Tb	1.3 ± 0.2	345.1 ± 4.2	6.6 ± 1.0	6.0 ± 2.3	2.3 ± 0.3
Dy	10.0 ± 0.5	35.9 ± 1.4	37.9 ± 2.4	17.6 ± 3.8	10.5 ± 0.6
Но	1.7 ± 0.2	316.1 ± 4.2	7.2 ± 1.0	1.5 ± 1.3	0.5 ± 0.1
Er	2.4 ± 0.3	8.9 ± 0.7	6.7 ± 1.2	7.1 ± 3.2	1.1 ± 0.3
Tm	0.6 ± 0.1	1.1 ± 0.3	3.6 ± 0.7	7.9 ± 2.6	1.0 ± 0.2
Yb	0.9 ± 0.3	-0.2 ± 0.3	4.6 ± 1.3	21.7 ± 6.4	17.2 ± 0.9
Lu	0.1 ± 0.1	330.5 ± 5.4	-0.6 ± 0.3	-0.8 ± 1.1	0.4 ± 0.2

Note: the values are in ppm, All errors are 1s.

CI normalized REE data for the CM hibonites are grouped into standard REE patterns and these are summarized in Table 4.7. Most of the hibonites belong to Group III or Group II patterns while others show moderate to highly fractionated REE patterns.

Meteorite	Sample	Group	χ^2
Murchison Platelet	CH C1	III	3.251
	CH C2	III + fractionated	1.920
	CH C4	III	2.112
	CH C6	III	6.217
	CH D5	III	9.45
Murchison Spherule	CH D4	Fractionated	2.22
-	CH D7	Fractionated	58.416
	CH D8	Highly fractionated	2.517
Murray Platelet	MY H17	III+fractionated	5.162
Murray Spherules	MY H1	II	1.046
	MY H3	II	1.074
	MY H8	II	1.883
	MY H9	Π	2.491
	MY H11b	II	2.841
	MY H12	Π	1.609
	MY H14	Π	35.3

Table 4.7 REE patterns for the CM hibonites

Representative REE and RTE patterns are shown in Figs. 4.6(a) and (b). Almost all the platelet hibonites show nearly hundred-fold or more excess in the abundance of refractory REE relative to CI meteorites along with minor variations in HREE abundances. They also show relative depletion in the less refractory REE, Eu and Yb, characteristic of the Group III pattern. The refractory trace elements follow a similar trend with enhancement in the more refractory elements (Sc, Zr and Hf) and relative depletion in Ba, Nb and V. A smooth roll-over in the abundances of HREE is also seen in some of them. Eu depletion is lower compared to Yb, and the depletion range of Eu $(Eu/Eu^* = 0.1-0.3)^3$ is smaller than that for Yb $(Yb/Yb^* = 0.008-0.05)^2$ in the platelet hibonite showing Group III REE pattern. Hibonite CH-C6 has lower LREE abundances (~40 times CI) and shows fractionation in HREE from Er to Lu by almost a factor of 10. A similar fractionation pattern is also seen for Murray Hibonite MY-H17. Both samples do not show any Yb depletion.

^{3, 2} Eu/Eu*, Yb/Yb* : * indicates geometerically interpolated abundance

Chapter four



Fig 4.6a Rare earth and refractory trace element abundance patterns in Murchison hibonites normalized to CI abundances.



Fig 4.6b Rare earth and refractory trace element abundance patterns in Murray hibonites normalized to CI abundances.

The hibonites in refractory spherules show significant variations in their REE patterns, even though a majority of them appear to follow a modified Group II pattern with depletion in Eu and enrichment in Tm. Some of them (eg. MY-H1, MY-H8, MY-H11b) are enriched in the relatively less refractory rare earth (La, Ce, Pr, Nd) and trace elements (Ba, Nb and V).

The " χ^2 " value that defines the goodness of fit for the REE data (Fahey, 1988) are also shown in Table 4.7 in each case. The data for two spherules CH-D7 (Murchison) and MY-H14 (Murray) are characterized by high value of χ^2 indicating possible presence of small scale heterogeneity or possible data artifact due to experimental problems (e.g. sample charging) during data acquisition.

Chapter Five

Discussion

The results obtained from elemental and isotopic studies of from the CM chondrites, Murchison and Murray are discussed in this chapter to address the following questions pertaining to the origin and early evolution of the solar system:

- (i) Source(s) of the now extinct short-lived nuclides present in the early solar system,
- (ii) Collapse of the proto-solar cloud: unassisted or triggered,
- (iii) Stable isotopic anomalies in the early solar system solids and their relation to presolar chemical evolution of nebular material,
- (iv) The source of the anomalous oxygen isotopic component, and,
- (v) A formation scenario for the CM hibonites that is compatible with their trace element abundances and isotopic records.

The main results obtained in the present study are:

- (i) The platelet hibonites are devoid of the short-lived radionuclides (²⁶Al and ⁴¹Ca); they show high (> 10‰ and upto ~100 ‰) abundance anomalies in the neutron-rich isotopes ⁴⁸Ca and ⁵⁰Ti, and are characterized by Group-III REE pattern along with higher enrichment in refractory trace elements Sc, Zr, Hf.
- (ii) In contrast, hibonites in the spinel-hibonite spherules display varying trends both in isotopic as well as trace element characteristics. Many of them show presence of ²⁶Al at the time of their formation with initial ²⁶Al/²⁷Al close to the canonical value of $5x10^{-5}$, but have lower magnitude (typically <10 ‰) abundance anomalies in ⁴⁸Ca and ⁵⁰Ti compared to the platelet hibonites and are characterized by modified Group-II and fractionated REE patterns.
- (iii) Hibonites in a smaller number of spinel-hibonite spherules show affinity towards platelet hibonites either in their isotopic signatures (devoid of ²⁶Al and ⁴¹Ca) and/or in REE and refractory trace element (RTE) composition with higher enrichment of the more refractory elements.
- (iv) No platelet hibonites with Group-II REE pattern, common for hibonites in most of the spherules, was found.
- (v) The oxygen isotopic compositions in both platelet hibonites and hibonites in spherules show ¹⁶O excess ranging from 38 ‰ to 57 ‰. No distinctive trend in

oxygen isotopic systematic *vis-à-vis* other isotopic/elemental systematics or hibonite morphology could be discerned in the data.

5.1 Source(s) of Short-lived Nuclides in the Early Solar System:

Several models have been proposed to explain the presence of radiogenic isotopic anomalies resulting from the decay of short-lived nuclides in primitive meteorites. These may be grouped into two classes: 'fossil' origin and 'live' origin.

5.1.1 'Fossil origin' of Short-lived Nuclides

This model advocated by Clayton (1975, 1982, 1986) suggests that short-lived nuclides produced during stellar nucleosynthesis are incorporated into refractory grains condensing in the circumstellar envelope (e.g. grains formed in expanding supernova shells) and are the carrier of isotopic anomalies. If such grains gets mixed with protosolar cloud material having normal isotopic composition, the 'fossil' anomalies present in the grain will show up in the newly processed solar system matter. In the most ideal situation, the system will behave like a mix of two components with the end member composition characterized by the carrier dust grains and the protosolar cloud material, respectively.

Even though circumstellar grains with fossil ²⁶Mg and ⁴¹K excess have been found in meteorites (Hoppe et al., 1994, Amari et al., 1996), the 'fossil' origin hypothesis has several lacuna and does not appear to explain several key observations related to radiogenic isotopic anomalies in early solar system objects. For example, the isotopic composition of presolar carrier grains need to be arbitrarily adjusted to match the meteorite data. Further, distinct correlation of excess in daughter nuclides (e.g. ²⁶Mg, ⁴¹K) with abundance of the parent elements (²⁷Al, ⁴⁰Ca) is seen in CAIs that are clear products of crystallization from a refractory melt. In the 'fossil' scenario, such a formation mechanism would lead to complete homogenization of the source material leading to an uniform composition of ²⁶Mg and ⁴¹K, irrespective of the abundance of their parent elements. The "fossil" origin does not appear to be a viable proposition to explain the presence of short-lived nuclides in the early solar system.

5.1.2 'Live origin' of Short-lived Nuclides

The 'live' scenario postulates that freshly synthesized short-lived nuclides get incorporated into the protosolar cloud prior to or during its collapse that led to the formation of the Sun and the solar system. Two different sources for the presence of freshly synthesized short-lived nuclides have been proposed:

- Production by interactions of energetic particles with gas and dust either in the solar nebula (*local production*) or in the protosolar molecular cloud (Heymann and Dziczkaniec, 1976; Heymann et al., 1978; Lee, 1978; Clayton et al., 1977; Clayton, 1994; Ramaty et al., 1996).
- (ii) Injection of 'freshly synthesized' short-lived nuclides from a stellar source into the proto-solar cloud ('*stellar production*') (Wasserburg, 1985; Cameron, 1993; Goswami and Vanhala, 2000).

The local production scenario for ²⁶Al, involving interactions of enhanced flux of energetic particles from an active early Sun going through the T-Tauri phase with the nebular gas and dust, was proposed soon after the discovery of the presence of ²⁶Al in CAIs (Heymann and Dziczkaniec, 1976). Interaction of anomalous cosmic rays streaming into the solar system was also proposed (Clayton and Jin, 1995). Recently, Shu et al. (1996, 1997, 2001) proposed the X-wind model in which the production of the short-lived nuclides takes place very close to the Sun and within a very short duration of a few tens of years. Before discussing these models we consider the proposal for production of the short-lived nuclide in the protosolar molecular cloud itself. This suggestion was put forward following the reported observation of enhanced flux of gamma rays (4.44MeV and 6.13MeV) from a star forming region in the Orion molecular cloud indicating the presence of an enhanced flux of low energy heavy ions (¹²C and ¹⁶O) in such molecular cloud complex (Bloeman et al., 1994). Since the protosolar cloud itself was probably a part of a molecular cloud complex, there is a fair chance of production of short-lived nuclides by such energetic particles interacting with gas and dust in this cloud (Clayton, 1994). A detail study of production of short-lived nuclides in such an environment was carried out by Ramaty et al. (1996). Even though production of several short-lived nuclides (e.g. ²⁶Al, ⁴¹Ca, ⁵³Mn) as well as isotopes of some of the light elements (e.g. Li, Be, B) is feasible, it was not possible to match the observed abundances of these short-lived nuclides in the early solar system objects in a selfconsistent manner. Further, a recent reanalysis of the observational data on γ -ray fluxes has led Bloeman et al. (1999) to retract their earlier claim of an enhanced flux of low energy particles. Thus energetic particle interactions within the protosolar cloud does not appear to be the source of the short-lived nuclides in the early solar system.

Although interactions of solar energetic particles (SEP) with nebular material at the asteroidal zone (2-4 A.U) or very close to the Sun can produce the short-lived nuclides 41 Ca, 26 Al and 53 Mn, the problem of a self-consistent explanation of the observed initial abundances of these nuclides in the early solar system remains. Production of 26 Al in the required amount leads to overproduction of other isotopes (Goswami and Vanhala, 2000; Goswami et al., 2001). Further production of 60 Fe, whose presence in the early solar system has been inferred from meteorite studies (Shokolyukov and Lugmair, 1993a, 1993b) is not possible by SEP interaction due to lack of suitable targets. However, the recent evidence for the presence of 10 Be in the early solar system with initial 10 Be/ 9 Be ratio of $\sim 9 \times 10^{-4}$ (McKeegan et al., 2000), suggests that there could be some contribution to the inventory of short-lived nuclides from energetic particle production, since 10 Be is not a product of stellar nucleosynthesis,

Following the approach used in Goswami et al. (2001) for the calculation of SEP production of short lived nuclides such as ²⁶Al, ⁴¹Ca, ³⁶Cl and ⁵³Mn, SEP production of ¹⁰Be for both short and long duration irradiation that mimic X-wind and conventional solar flare irradiation of nebular material, respectively, has been estimated. Calculations were carried out by expressing SEP flux both in terms of kinetic energy E, [dN/dE = K.E^{- γ}] and rigidity R, [dN/dE = C exp (-R/R₀)], where γ and R₀ defines the spectral shape. A flux normalization of N_{E>10 MeV} = 100 cm⁻² sec⁻¹ was used in these calculations. We have assumed targets of solar (=CI) composition that follow grain size distributions of the type dn/dr α r^{- β}. Reaction cross section for O(p,x)¹⁰Be was taken from Sisterson et al. (1997). Self-shielding of SEP by nebular gas and dust was ignored to maximize production. The calculations were carried out for different sets of SEP spectral parameters, β values and irradiation time. In Fig. 5.1, results obtained for one set of these parameters are shown by plotting the SEP flux enhancement factor, relative to the long-term averaged value of N_{>10} = 100 cm⁻² sec⁻¹ (Reedy, 1998), as a function of SEP irradiation time that will match the meteorite data [²⁶Al/²⁷Al = 5×10⁻⁵, ⁴¹Ca/⁴⁰Ca = 1.5 ×

 10^{-8} , ${}^{10}\text{Be}/{}^9\text{Be}= 9 \times 10^{-4}$, ${}^{36}\text{Cl}/{}^{35}\text{Cl} = 1.4 \times 10^{-6}$ (Murty et al., 1997), ${}^{53}\text{Mn}/{}^{55}\text{Mn}$ (H) = 4.4 × 10^{-5} (Brick and Allegre, 1985), ${}^{53}\text{Mn}/{}^{55}\text{Mn}$ (L) = 9 × 10^{-6} (Lugmair and Shukolyukov, 1998)]. In this particular case, co-production of ${}^{10}\text{Be}$ and ${}^{53}\text{Mn}$ (lower initial abundance) appears feasible for irradiation time $\leq 1\text{Ma}$ for a range of SEP enhancement factors, but ${}^{26}\text{Al}$ will be underproduced whereas ${}^{41}\text{Ca}$ will be overproduced. In addition, higher threshold of the O(p,x)^{10}\text{Be} reaction, compared to the low threshold of (p,x) reactions that yield the other nuclides, makes relative production of these nuclides very sensitive to the spectral shape of the interacting SEP.



Fig. 5.1 SEP flux enhancement factor (relative to contemporary long-term averaged value of $N(E>10) = 100 \text{ cm}^{-2} \text{ sec}^{-1}$) required for production of short-lived nuclides present in meteorites in their observed abundances as a function of irradiation time for a power law SEP energy spectrum, $dN=K.E^{-3}.dE$, and targets of solar (CI) composition following a size distribution, dn a dr^{-4} . Results for ⁵³Mn are shown for two values of initial ⁵³Mn/⁵⁵Mn ratio.

For example, a harder spectra (low γ ; high R₀) will lead to enhanced ¹⁰Be production relative to the other nuclides and the reverse will be the case for softer SEP spectra. This can be visualized from Fig. 5.2 (a) and Fig. 5.2 (b), where normalized production of the



Fig. 5.2 Production of short-lived nuclides relative to 10 Be and their initial abundances in the solar system for different SEP spectral parameters (g and R_0) and a specific target size distribution.

short-lived nuclides are shown with ¹⁰Be as the reference isotope for short duration irradiation as in the X-wind irradiation scenario. Thus, even though the observation of ¹⁰Be strengthens the case for production of nuclides by energetic particles in the early solar system, it is not clear whether it is a major contributor to the total inventory of all the short-lived nuclides present in the early solar system.

The main stellar sources that can synthesize and inject the observed short-lived nuclides into the protosolar cloud are: Supernova (SN), non-exploding Wolf-Rayet (W-R) star and thermally pulsating asymptotic gaint branch (TP-AGB) star (Cameron et al., 1995; Arnould et al., 1997 and Wasserburg et al., 1994, 1995). A TP-AGB star appears to be a plausible source for ⁴¹Ca, ²⁶Al, ³⁶Cl, ⁶⁰Fe and ¹⁰⁷Pd; however, it cannot produce ⁵³Mn. On the other hand, a supernova could be a plausible source for ⁴¹Ca, ²⁶Al, ³⁶Cl, ⁵³Mn and ⁶⁰Fe but not for ¹⁰⁷Pd. Although the question of the source of the short-lived nuclides in the early solar system is yet to be fully resolved, major contribution to the inventory of the short-lived nuclides appears to come from a stellar source. However, SEP production of ¹⁰Be and of ⁵³Mn, contributing to this inventory, cannot be ruled out.

The meteorites during their space odyssey are also exposed to high-energy galactic cosmic rays that can produce secondary neutrons by interacting with various target nuclides inside the meteorite. The secondary neutrons can produce some of the short-lived nuclides like ³⁶Cl and ⁴¹Ca via (n, γ) reactions on suitable targets. However, the secondary neutron fluence experienced by the primitive meteorites, Allende, Efremovka, Murchison and Murray, where records of these short-lived nuclides have been detected, are orders of magnitude lower than that required to produce either of these nuclides in their observed abundances (Srinivasan et al., 1996; Murty et al., 1997).

5.2 Extinct Nuclides and Origin of the Solar System

The presence of short-lived now-extinct nuclides in early solar system objects can be used as tracers to infer the nature of processes during the early evolution of the solar system. If these nuclides are locally produced by interactions of SEP from an early active Sun with nebular material, their presence provides clues to the activity of the early Sun. On the other hand, if they are products of stellar nucleosynthesis and are injected into the protosolar cloud at the time of its collapse, they put stringent constraints on the time scales of protosolar cloud collapse and of formation of the early solar system solids. If the distribution of the externally seeded nuclides is considered to be homogeneous in the nebula, these nuclides may also be used to build up a relative chronology of the early solar system events.

The discussion in the earlier section indicates a stellar source to be the most plausible source for the short-lived nuclides present in the early solar system. A strong case for a stellar origin of these nuclides was made by Sahijpal et al. (1998) who demonstrated a correlation in the presence of ⁴¹Ca and ²⁶Al in early solar system solids with well defined initial abundances indicating them to be co-genetic. As already discussed, the energetic particles cannot produce ²⁶Al and ⁴¹Ca in appropriate amount to match their initial abundances in the early solar system solids, and such a correlation is difficult to explain in terms of energetic particle production, but follows directly in stellar origin models. They also showed that objects devoid of ²⁶Al are also devoid of ⁴¹Ca and a model within the framework of stellar injection of radioactivities was proposed to explain this observation (Sahijpal and Goswami, 1998). The data obtained in the present study expanded this database (Fig. 5.3) and reinforce the earlier conclusions. Both platelet hibonites and hibonites in spherules that are devoid of ²⁶Al are also devoid of ⁴¹Ca. The low Ca/K ratio in the hibonites in spherules hosting ²⁶Al did not allow unambiguous identification of ⁴¹K excess in these cases. Nonetheless, the general trend in the ²⁶Al data for spherules match the earlier results with all of them having close to canonical initial 26 Al/ 27 Al ratio.

If the observed correlation in the presence/absence of 26 Al and 41 Ca in CM hibonites is considered as a pointer towards a stellar source for these nuclides, their presence constrains the time scale for protosolar cloud collapse to form the Sun and some of the early solar system solids to less than a million year. Since this time-scale is much shorter than the value of ~5-10 Ma for unassisted collapse of a molecular cloud fragment leading to formation of a Sun like star (Shu, 1995), it argues for an assisted or triggered origin of the Sun and the solar system.

Several studies carried out in recent years (Boss, 1995; Foster and Boss, 1997; Boss and Foster, 1998; Vanhala and Cameron, 1998) addressed the question of the viability of a triggered collapse of the protosolar cloud within the time constraint placed by the presence of short lived nuclides in the early solar system. The basic results obtained from



Fig. 5.3 Plot of measured Mg and K isotopic ratios as a function of ${}^{27}Al/{}^{24}Mg$ and ${}^{40}Ca/{}^{89}K$ ratios, repectively, in CM hibonites. The expected trend lines for initial ${}^{26}Al/{}^{27}Al = 5 \cdot 10^{-5}$ and initial ${}^{41}Ca/{}^{40}Ca = 1.4 \cdot 10^{-8}$ are also shown. The dashed lines indicate normal (reference) isotopic ratio in each case. Error bars are 1*s*.

these studies, summarized by Goswami and Vanhala (2000), indicate that an interstellar shock front with velocities of a few tens of km/sec and appropriate density and temperature can indeed induce collapse of the protosolar cloud leading to the formation of the proto-Sun within the time constraint placed by the short-lived nuclide data. If the shock front material also contains freshly synthesized short-lived nuclides from a stellar source, they will be injected into the collapsing protosolar core via Rayleigh-Taylor instabilities. However, the injection is not instantaneous and may start after a few 10⁵ years following the impact of the shock front on the protosolar cloud.

5.3 Trends in Isotopic and Trace Element Abundance in CM Hibonites

5.3.1 Al-Mg Systematics

The results from this study have further enhanced the database for Al-Mg isotopic systematics in early solar system solids. Our results and earlier data suggest that the initial 26 Al/ 27 Al values for a large number of CAIs from several groups of carbonaceous meteorites (CM, CV, CO, CR) as well as unequilibrated ordinary and enstatite chondrites cluster around the value of ~ 5 × 10⁻⁵ (MacPherson et al., 1995; Russell et al., 1998; Russell et al., 2000; Guan et al., 2000; Sahijpal et al., 2000). Thus, the CAIs may have formed in a restricted region/reservoir in the solar nebula characterized by a 26 Al/ 27 Al ratio of ~5 × 10⁻⁵ and were later dispersed into different regions of the nebula where they got incorporated into different chondritic groups.

Although some CAIs in several CV and CO chondrites have lower than canonical ²⁶Al/²⁷Al ratio, this is generally attributed to secondary disturbances affecting these objects that can often be inferred from their petrographical characteristics (Podosek et al., 1991; MacPherson and Davis, 1993; Caillet et al., 1993; MacPherson et al., 1995). A striking feature of the Al-Mg systematics in CM hibonites is the absence of ²⁶Al in both platelet and spherule hibonites whose chemical composition and trace element abundance do not suggest any late secondary disturbances that could have affected the Al-Mg systematics. This feature was also noticed in earlier studies of CM hibonites (Fahey et al., 1987a; Ireland, 1988; Ireland, 1990; Simon et al., 1998; Sahijpal et al., 2000) and is further strengthened by the present work. In general, the platelet hibonites are devoid of ²⁶Al, while hibonite in spherules often contain ²⁶Al. Ireland (1988) proposed that these two groups of hibonites formed at different regions of solar nebula

with distinctly different ²⁶Al abundances. However, the results obtained in this study do not support a sharp distinction between platelet hibonites and hibonite in spherules. Some hibonites in spherules are devoid of ²⁶Al and show affinity towards platelet hibonite in their trace element abundances. In fact, earlier studies (Ireland, 1988; Fahey et al., 1987a) have also shown the presence of a few platelet type hibonites with ²⁶Al, as well as a few spherules devoid of ²⁶Al (Ireland, 1990). CM hibonites devoid of ²⁶Al may be considered as a distinct group of objects, irrespective of their morphology, and their origin may be related to other CAIs from CV and CO meteorites that are also devoid of ²⁶Al. A plausible scenario for the formation of these objects within the framework of a triggered collapse of the proto-solar cloud was proposed by Sahijpal and Goswami (1998). This will be discussed in a later section while addressing the question of the formation of the CM hibonites.

5.3.2 Ca-Ti Isotopic Anomalies

The observed anomalies in n-rich Ca and Ti isotopes (48 Ca, ${}^{49, 50}$ Ti) in the CM hibonites reflect preservation of distinct nucleosynthetic components in the solar nebula at the time of hibonite formation. Our data (Fig. 4.3 and Fig. 4.4) suggest both enrichment and depletion in 50 Ti and 48 Ca ranging from -28 to +93 ‰ and -18 to +81 ‰ respectively. These results are similar to those reported earlier for CM hibonites that indicate wide variations in isotopic anomalies in 50 Ti (-47 to +273 ‰) and 48 Ca (-56 to +104 ‰) (Zinner et al., 1986; Fahey et al., 1987a; Hinton et al., 1987; Ireland et al., 1988; Sahijpal et al., 2000). Several nucleosynthetic processes have been proposed to explain the anomalous Ti and Ca isotopic composition in hibonites (Zinner et al., 1986; Hinton et al., 1988).

A plot of δ^{48} Ca vs δ^{50} Ti for CM hibonites obtained from this work is shown in Fig. 5.4 (a). We have also included recent data obtained in our laboratory and reported by Sahijpal et al. (2000). A similar plot for all the earlier data is shown in Fig. 5.4 (b). Hibonites classified as platelets, spherules, BAGs, hibonite-glass and hibonite-pyroxene spherules by Ireland et al. (1991) are also labeled in this plot. It is apparent from these plots that the δ -values for the spherules cluster around $\pm 10\%$, whereas, the platelet data display a much larger spread. A simple correlation between the anomalies in the two



Fig. 5.4. d^{48} Ca vs d^{50} Ti plot for [Murchison hibonites [Sahijpal, 2000 and present study; fig. (a)] and for meteoritic hibobnites [literature data; fig. (b)].

neutron-rich isotopes, ⁴⁸Ca and ⁵⁰Ti, exist in the sense that signs in their δ -values are the same baring a single exception. The variations in δ^{48} Ca/ δ^{50} Ti ratio for samples with positive δ values may represent different neutron-excesses characterizing the stellar nucleosynthesis site of these isotopes (Hartmann et al., 1985; Zinner et al., 1986).

Ireland (1990) suggested that atleast four exotic Ti components and three exotic Ca components are required to explain the variations in Ca and Ti isotopic data for the hibonites. A chemical memory model, in which the hibonite precursor material is a mix of interstellar dust grains with varying magnitude of exotic n-rich Ti and Ca components and nebular gas and dust of normal Ti and Ca isotopic composition, appears to best explain the hibonite data. Direct addition of n-rich material from a supernova has also been proposed (Hinton et al., 1987). This model assumed the solar nebula to be depleted in ^{49,50}Ti and ⁴⁸Ca and predicted a normal oxygen isotopic composition for certain specific sample considered to be representative of the solar nebula. However, this pediction turned out to be incorrect (Fahey et al., 1987b). It is also important to note that there is no satisfactory explanation for the depletion in ⁵⁰Ti and ⁴⁸Ca seen in some of the CM hibonites. Large magnitude Ti and Ca isotopic anomalies are mostly associated with hibonite; refractory silicate-rich CAIs from other primitive carbonaceous chondrites have very small anomalies at the level of a few per mil. Neutron-rich isotopic anomalies, however, appear to be widespread and extremely small Ti-isotopic anomalies have been detected in bulk samples of carbonaceous chondrites (Niemeyer and Lugmair, 1984).

5.3.3 Oxygen Isotopic Systematics

Most of the refractory early solar system objects (CAIs) are enriched in their ¹⁶O abundance relative to ¹⁷O and ¹⁸O. This has been attributed to the addition of a nearly pure ¹⁶O component to a nebular reservoir of normal oxygen isotopic composition (Clayton, 1993). It has been proposed that ¹⁶O enriched interstellar/circumstellar grains present in the protosolar cloud are the carriers of this exotic component. The source of the enriched ¹⁶O may be traced to nucleosynthesis processes taking place in massive low-metallicity stars that end up as supernova. An alternative explanation for the observed trend in the oxygen isotopic abundance anomalies that define a slope of unity in the Δ^{17} O vs Δ^{18} O plot, is non-mass dependent fractionation taking place in the solar nebula under non-equilibrium conditions (Theimens and Heidenreich, 1983; Thiemens, 1996). This

proposal is based on laboratory observations of mass independent fractionation of oxygen isotopes during reaction kinectics in a gas phase that results in a slope one line in a oxygen three-isotope plot as seen for the CAIs (Wen and Thiemens 1993).

The oxygen isotopic data for CM hibonites, both platelet and spherule type, follow the general trend seen in CAIs (Fig. 4.5), and no distinctive features can be discerned for the two groups unlike the case for abundance anomalies in the n-rich stable isotopes, with platelet hibonite hosting higher magnitude anomalies compared to hibonites in spherules. This would indicate that the reservoir of ¹⁶O-enriched component did not get depleted during the entire duration of formation of hibonites belonging to these two morphological groups and argue for a larger ¹⁶O-rich reservoir compared to the n-rich component in the region of CAI formation. This is also substantiated by the observation of significant enrichment of ¹⁶O in relatively less-refractory silicate phases like fosterite (McKeegan et al., 1998; Hiyagon and Hashimoto 1999; Leshin et al., 2000; Jones et al., 2000) in which no other isotopic anomalies could be detected. Since oxygen constitute almost one third of all the condensed species in the early solar system, the widespread and large magnitude oxygen isotopic anomalies in the CAIs make the requirement of a large reservoir of nearly pure ¹⁶O a distinct possibility. If this is indeed the case, a local source that can maintain such a reservoir over a relatively long duration cannot be ruled out. Unfortunately, it is not clear how the proposed mechanism for local production of oxygen isotopic anomaly via non-mass dependent fractionation will operate in the nebular condition and how the effect produced in the gas phase will finally get incorporated into oxide and silicate phases. On the other hand, if we consider a stellar source, the absence of any correlation between ¹⁶O and ⁵⁰Ti anomalies suggest that the carrier for both these anomalies cannot be the same. Although, the exact nature of the carrier of the exotic n-rich component is yet to be identified with certainty, no ¹⁶O-rich component has been identified in the major circumstellar (pre-solar) grains, viz., diamond, silicon carbide, graphite and corundum identified in meteorites. Interstellar silicate grains remain a distinct possibility as a potential carrier of the ¹⁶O-rich component. However, this has to wait identification and analyses of interstellar silicate grains in meteorites.

5.3.4 Rare Earth Element Abundances in CM hibonites

The abundance of the rare earth and refractory trace elements (REE and RTE) in CM hibonites analyzed in the present study vary significantly from one sample to other. A distinct feature of the REE abundances in most of the CM hibonites analyzed in this work and reported in literature is their correlation with volatility. This suggests high temperature condensation as the most probable mechanism for the formation of the hibonites or their pre-cursor material. The smooth fractionation pattern seen in the heavy REE abundances in some of the hibonites also indicate partial melting and recrystallization in these cases.

The distinctive group III REE pattern displayed by almost all the platelet hibonites suggest their formation via condensation of gas of solar composition at very high temperature leading to incorporation of refractory REEs and depletion in relative volatile elements like, Eu and Yb. Although the depletion for both these elements is expected to be similar (Boynton, 1975; Konarcki and Fegley, 1986; Davis et al., 1982), the data shown in Fig 4.7(a) suggests that most of the platelets (CH-C1, CH-C4, CH-C6, CH-D5) show larger Yb depletion. This was also observed in the earlier studies (Ekambaram et al., 1984; Ireland et al., 1988; Fahey et al., 1987a). The relatively high Yb depletion in these refractory grains have been attributed to late reequilibration in a reducing environment that led to addition of Eu as Eu^{2+} , substituting for Ca^{2+} (Ekambaram et al., 1984). Ireland et al. (1988) argued against this proposal because of the absence of a similar signature expected for Ce (which behave like Eu in a reducing condition). They proposed this as a primary signature, based on observation of complementary REE pattern in CM hibonites with Eu enrichment. The results obtained in the present study, however, do not reveal such a complimentary pattern in any of the analyzed sample. Thus, whether the higher depletion of Yb relative to Eu is a primary signature or is related to secondary processing remains uncertain.

The REE abundance patterns for the platelets often show a smooth roll-over in the heavy REE abundances. The most probable cause of this is fractionation caused by solid-melt partitioning during crystallization. This effect can also be seen in the data for Y and Ho, similarly affected due to their similar ionic size and valency. Thus, although the platelet hibonite may be primarily considered as condensation products, some of them may have experienced some degree of partial melting and recrystallization.

Hibonites in spherules often show a modified group-II REE pattern. The ideal group-II pattern may be considered as complimentary to the ultra-refractory REE pattern characterized by extreme enhancement in heavy REE (Gd, Tb, Dy, Ho, Er) that is seen in several refractory objects from CM and CO meteorite (Boynton, 1984; Davis and Grossman, 1979, Sahijpal et al., 2000). REE data for hibonite in spherules obtained in the present study (Fig. 4.7) show a range of abundance patterns spanning from nearly ideal group II to highly fractionated. It appears that most of the spherule hibonite have undergone a multi-stage evolutionary process possibly involving one or more episodes of melting and recrystallization. Since the starting material for the spherule was depleted in the ultra-refractory REE, these objects appear to have formed later than the objects characterized by ultra-refractory REE pattern.

Even though earlier studies (Fahey et al., 1987a; Ireland et al., 1988) did reveal a variety of REE patterns for hibonites in spherule, the formation of platelet and spherules were considered to have taken place in different environment. The present study as well as the recent results reported by Sahijpal et al. (2000) show that the REE patterns for hibonites in spherules encompass the whole range from ultra-refractory, affinity towards platelet (group III) pattern, ideal group II pattern and modified group II pattern. Thus a clear-cut distinction between formation of the platelets and spherules cannot be made based on their REE characteristics. The present study indicates that the CM hibonites particularly the hibonite-bearing spherules, represent a continuum that formed under different nebular settings. In the next section, both the isotopic and trace element data for the samples are considered in an attempt to construct a self-consistent scenario for the formation of the CM hibonites in the solar nebula.

5.4 Formation of CM Hibonites

The characteristic features of the isotopic and elemental compositions in the platelet hibonites and hibonite in spherules are summarized in Table 5.1. The platelet hibonites show enrichment in refractory REE and trace elements, host large ⁴⁸Ca and ⁵⁰Ti anomalies and are devoid of the short-lived nuclides, ²⁶Al and ⁴¹Ca. Hibonites in spherules display a range of REE patterns, from ultra-refractory to ideal group II to fractionated group II pattern, host lower magnitude ⁴⁸Ca, ⁵⁰Ti anomalies and a majority

of them have records of ²⁶Al and ⁴¹Ca. In contrast to these specific attributes, no distinct trend can be discerned in the data for oxygen isotopic anomalies for these two groups of hibonites.

In the following, a scenario for temporal evolution of these objects in the early solar system is proposed taking into account the above features. A stellar origin for the short-lived nuclides is assumed and proposals put forward by Sahijpal and Goswami (1998) and Sahijpal et al. (2000) are used in formulating this scenario. We also assume a homogeneous isotopic composition in the formation region of the CM hibonites in the nebula.

In the proposed scenario, spherules with hibonites showing ultra-refractory pattern and affinity towards platelet hibonites as well as the platelet hibonites with Group III REE pattern were some of the first solids to condense in the solar nebula. Following the model of Sahijpal and Goswami (1998), the absence of short-lived nuclides in these objects may be attributed to their early formation prior to arrival of the freshly synthesized stellar material injected from an external source that triggered the collapse of the protosolar cloud. These early forming objects preferentially incorporated the exotic n-rich component present in the collapsing protosolar cloud leading to large abundance anomalies in ⁴⁸Ca and ⁵⁰Ti. If this scenario is correct, the very first solar system solids should display such characteristics. A corundum-hibonite spherule analyzed recently by Simon et al. (2000), has REE and RTE features similar to ultra-refractory pattern and the object is also devoid of ²⁶Al. These authors termed this object as the 'first rock from the Sun' and suggested it to be a direct nebular condensate. Identification and analysis of more such objects will be very important to further consolidate the above scenario.

The formation of hibonite bearing spherules with modified Group II or fractionated REE pattern and showing presence of radiogenic ²⁶Mg and ⁴¹K is considered to have taken place after the formation of the platelet hibonites and following the injection of stellar radioactivities into the formation locale of these early solar system objects. The Group II REE pattern, that compliments the ultra-refractory component, suggests that these spherules or their pre-cursors formed following the removal of the ultra-refractory rare earth and trace elements from the nebula by the early forming objects such as spherules showing ultra-refractory REE pattern. The lower ⁴⁸Ca and ⁵⁰Ti anomalies in these objects may be attributed to the dilution of these exotic n-rich component in the nebula due to

removal by early forming solids as well as mixing induced by the injection of stellar radioactivities.

Table 5.1 Comparison of isotopic and trace elemental compositions in platelets and spherules.

	Platelet	Spherule
²⁶ AI	Absent	Present + absent
⁴¹ Ca	Absent	Present + absent
δ ⁴⁸ Ca	High (> 10 ‰ & < -10 ‰)	Lower than platelets
δ^{50} Ti	High (> 10 ‰ & < -10 ‰)	Lower than platelets
REE Abundance	Group III pattern (condensation)	Ultra-refractory, Group II, Fractionated pattern (Condensation, melting/ recrystallization)
RTE Abundance	Enriched in Sc, Zr, Hf	Refractory elements depleted with few exceptions





Time (*in arbitrary unit*)

Fig. 5.5 A schematic showing a plausible formation sequence of platelet hibonites and hibonite-bearing spherules in CM meteorites.

Chapter five

Discussion

A schematic diagram depicting a possible formation sequence of the CM hibonites is shown in Fig 5.5. The pronounced absence of short-lived nuclide as well as REE abundances other than Group III characteristics in Murchison platelet hibonites led to an earlier suggestions that the platelet hibonites and hibonite-bearing spherules formed in two distinctly different nebular settings (Ireland et al., 1988). The results obtained in the present study show that these two groups of objects, and particularly the spherules, span a wide range of characteristics and both platelets and spherules most probably represent a continuum of objects formed in a nebular setting as suggested in Fig. 5.5. The near absence of platelet hibonites with Group II REE pattern and/or presence of ²⁶Al [only three such objects have been found so far (Fahey et al., 1987a; Ireland et al., 1988 and Sahijpal et al., 2000) and in all the cases the possibility of these platelets being a part of hibonite bearing spherule cannot be ruled out] indicate that the environment conducive for formation of platelet hibonite either did not last long enough or melting and recrystallization rather than direct condensation was the principle mode of formation of the later generation refractory objects. It is difficult to ascertain the exact nebular setting in which this could happen.

Summary and Conclusions

Calcium-Aluminum-rich-Inclusions (CAIs) in primitive meteorites, comprising mostly of refractory oxides and silicates, represent some of the first solar system solids and contain records of the earliest stages of solar system history. Chemical and isotopic composition as well petrographic studies of these objects provide insight into the events and processes leading to their formation in the solar nebula. In the present work, elemental and isotopic compositions of a refractory oxide phase (hibonite) from two carbonaceous (CM) meteorites, Murchison and Murray, have been studied using ion microprobe technique to gain further understanding of several specific aspects pertaining to the origin and early evolution of the solar system.

Fossil records of the presence of the short-lived nuclides ²⁶Al and ⁴¹Ca at the time of formation of the hibonites were looked for to obtain information on the formation time scale of the hibonites as well as the source of these short-lived nuclides and the constraint they place on the plausible mode of formation of the solar system. Stable isotopic composition of Ca, Ti and O in the hibonites were determined to infer the contribution of material from distinct nucleosynthetic sources to the initial mix of material in the solar nebula. Abundances of rare earth and refractory trace elements (REE & RTE) were determined to infer the plausible mode of formation (e.g. condensation, melting, recrystallization) of the hibonites. Finally, an attempt has been made to construct a self-consistent scenario for the formation of the hibonites that is in accord with their elemental and isotopic records. The main results obtained and their implications are briefly summarized here.

1. The results obtained in the present study further substantiate the correlated presence/absence of the two short-lived nuclides, ²⁶Al and ⁴¹Ca, in early solar system solids. The correlated presence of these nuclides suggest a common source for them and a stellar source such as a supernova or a thermally-pulsing asymptotic giant branch (TP-AGB) star appear to be plausible sources. However, the recent evidence for the presence of the short-lived nuclide ¹⁰Be (McKeegan et al., 2000), which is not a product of stellar nucleosynthesis, suggests that there could be some contributions toward the inventory of the short-lived nuclides in early solar system solids from energetic particle production. Even though production of ¹⁰Be and other short-lived radionuclides (²⁶Al, ⁴¹Ca, ³⁶Cl, ⁵³Mn) by solar energetic particles is possible it does not

provide a self-consistent explanation of the meteorite data. Thus, a stellar source appears to be the most dominant contributor to the inventory of the short-lived nuclides in the early solar system with some contribution from energetic particle production, particularly in the case of ¹⁰Be and perhaps for ⁵³Mn.

- 2. A stellar source for the short-lived nuclides present in the early solar system also put a very strong constraint on the formation time-scale of the first forming solids containing fossil records of these short-lived nuclides. The presence of ⁴¹Ca suggest a time scale of less than a million years between production of these nuclides in the stellar source and the formation of these solids implying a collapse time scale of the protosolar cloud less than this duration. This would argue for a triggered collapse of the protosolar cloud as the time scale of unassisted cloud collapse leading to formation of a Sun-like star is ~5-10 Ma (Shu, 1995). Recent computer simulation studies have shown that a triggered collapse of the protosolar cloud within the time constraint placed by the short-lived nuclide data appears to be feasible.
- 3. Studies of stable isotopic abundances of Ca and Ti in hibonites belonging to two distinct morphologies (platelet and spherule) show abundance anomalies of n-rich isotopes of calcium and titanium (⁴⁸Ca and ⁵⁰Ti). Higher anomalies are found in platelets than in hibonites within the spherules. These results are similar to those reported earlier for Murchison hibonites. Several exotic Ti and Ca components are needed to explain the data. The observed variations reflect inherent isotopic heterogeneity in the protosolar cloud resulting from inputs of material from different stellar sources during its entire lifetime. While the enrichment in ⁴⁸Ca and ⁵⁰Ti may be attributed to nucleosynthesis processes operating in n-rich zones in supernova events, a satisfactory explanation for the observed depletion in their abundance in some of the hibonites is still lacking.
- 4. CM hibonites belonging to both morphological groups show enrichment in ¹⁶O varying from 38 ‰ to 57 ‰. No correlation is present between oxygen isotopic anomalies and the radiogenic isotopic anomalies in ²⁶Mg and ⁴¹K or the stable isotopic anomalies in ⁴⁸Ca and ⁵⁰Ti. The lack of correlation between ¹⁶O and n-rich isotopic anomalies suggest that they may not have the same origin/carrier. Our data cannot distinguish between the two suggested sources for the exotic ¹⁶O-rich component *viz.* a stellar
source and mass independent fractionation of oxygen isotopes during reaction kinectics in a gas phase in the nebula. However, if we consider a stellar source for these anomalies, the carrier of n-rich isotopic anomalies cannot be the carrier of ¹⁶O-rich component. The data for the hibonites also suggest a large reservoir of exotic ¹⁶O in the nebula that did not get significantly depleted during the formation of different types of the hibonites unlike the case for the exotic n-rich component.

- 5. The REE abundance patterns for the hibonites are distinctly different for the two morphological groups. The patterns seen for platelet hibonites suggest that they are direct nebular condensates even though partial melting of some of these objects or their precursors cannot be ruled out. On the other hand, the REE patterns for hibonites in the spherules show a wide range, spanning from ultra-refractory to ideal group II to fractionated group II pattern, indicating distinctly different modes of formation with imprints of multiple events in some cases. Some of the hibonites in spherules show distinct affinities towards REE and RTE pattern seen in platelet hibonites and a clear cut distinction between these two groups of objects cannot be inferred from the observed REE patterns; they appear to represent a continuum formed under various nebular settings.
- 6. A plausible scenario for the formation of the CM hibonites that can explain both the radionuclide and stable isotope data as well as their REE and RTE abundances is proposed. In this scenario, the platelet hibonites with Group III REE patterns and hibonite showing ultra-refractory patterns are some of the first solids to form in the solar system followed by the hibonite bearing spherules with modified Group II and fractionated REE patterns The platelets sampled a nebula enriched in exotic n-rich isotopic components that got depleted by removal/mixing by the time of formation of the hibonite-bearing spherules. The absence of ⁴¹Ca and ²⁶Al in platelets may be explained as due to their early formation prior to arrival of the short-lived nuclides injected from an external source. The lack of any trend in oxygen isotopic anomalies can be best explained by postulating a large reservoir of exotic ¹⁶O, although its exact source remains uncertain.

6.1 Future Scope

Isotopic and elemental analyses of refractory CAIs found in primitive meteorites have provided extremely valuable inputs for our understanding of the origin and early evolution of the solar system. Data obtained from these studies also allowed us to test various models proposed for the formation of the solar system as well as some of the first solar system solids. The presence of exotic components of stable isotopes in early solar system solids led to new ideas about the initial state of the solar nebula. The discovery of fossil records of various short-lived nuclides in these objects led to revision of time-scales of processes governing the formation and early evolution of the solar system.

The present study addressed some of these pertinent issues based on a study of a particular group of refractory early solar system objects. Even though several conclusions are reached in this study, there is much scope for further work to strengthen some of the observations and also to gather new inputs that will lead to a better understanding of some of the unresolved issues. These are briefly described in the following.

- (1) The correlated presence of ²⁶Al and ⁴¹Ca in early solar system solid is the strongest argument in favour of a stellar source for these short-lived nuclides (Sahijpal et al., 1998). However, experimental uncertainties make it difficult to detect presence of ⁴¹Ca in samples with Ca/K ratio less than a few times 10⁵ at present. Further, analysis of small (<10µm) sample, even with high Ca/K ratio, is an extremely difficult proposition using a small geometry ion microprobe like the Cameca ims-4f. It will be important to attempt such studies with new generation ion probes that will hopefully help us expand the present database and establish this correlation on a firm footing.</p>
- (2) Presence of other short-lived nuclides such as 36 Cl ($\tau \sim 0.43$ Ma) and 99 Tc ($\tau \sim 0.29$ Ma) has been indicated by the presence of 36 Ar and 99 Ru (daughter nuclides) in the carbonaceous chondrites, Efremovka (Murty et al., 1997) and in Maralinga (Yin et al., 1992), respectively. Further experiments are needed to confirm the presence of both. Detection of 99 Tc, a product of s-process nucleosynthesis will not only strengthen the possibility of a stellar origin of the short-lived nuclides, but

will also establish a thermally pulsing asymptotic giant branch (TP-AGB) star as a major source of the short-lived nuclides in the early solar system.

- (3) Studies of stable isotopic anomalies are mostly restricted to oxygen and the n-rich isotopes, ⁴⁸Ca and ⁵⁰Ti. It will be useful to carry out additional study n-rich isotopic anomalies in ⁵⁴Cr and ⁶⁶Zn to delineate the sources and processes contributing to the n-rich components in the protosolar cloud. It is also important to have a viable explanation for the observed depletion in the n-rich isotopes in some of the early solar system solids.
- (4) Most of the isotopic and elemental data for hibonites are from CM meteorites. Additional data for hibonites from other meteorite groups are needed to better understand their formation and evolution, and to confirm or otherwise some of the general conclusions drawn based on studies of CM hibonites.
- (5) Presence of the short-lived nuclide ¹⁰Be in early solar system solids has a major bearing on the source of the short-lived nuclides in the early solar system. ¹⁰Be, produced in the stellar interiors, gets destroyed in the hot stellar environments (Reeves, 1994) and is considered to be a product of energetic particle interactions. Two possible sources of ¹⁰Be in the early solar system are production by solar energetic particles within the solar nebula and energetic particle interactions within the protosolar cloud prior to its collapse. Our calculations (Goswami et al., 2001) show that although solar energetic particles can produce several short-lived nuclides including ¹⁰Be, it fails to match the meteorite data in a self-consistent manner. Studying of ¹⁰Be records in samples devoid of the short-lived nuclides ⁴¹Ca and ²⁶Al may provide clues to ascertain the possibility of multiple sources contributing to the inventory of the short-lived nuclides found in the early solar system. Additional studies of ⁵³Mn in meteorites will also be useful in this regard.
- (6) The ¹⁶O enrichment found in CM hibonites suggests the presence of large ¹⁶O-rich reservoir in the solar nebula. In fact, studies of forsteritic olivines in CAIs also revealed ¹⁶O enrichment, suggesting sustainence of the ¹⁶O-rich reservoir for an extended duration. Oxygen isotopic studies of late forming objects, e.g. chondrules may provide additional clues in this regard, if the time gap of around 0.5-3 Ma

between the formation of CAIs and chondrules, as implied by ²⁶Al data, is considered to be correct. A large ¹⁶O-rich reservoir also argue for a local production. A study of viable pathways to transfer plausible exotic ¹⁶O-rich component generated during mass independent fractionation in the gas phase in the nebula into the oxide/silicate phases formed in it will be a worthwhile proposition.

(7) The near absence of platelet hibonites with Group II/fractionated pattern and with ²⁶Al needs further investigation. It will be useful to identify isolated platelet hibonites in sections of CM meteorites and check if the broad continuum in isotopic and elemental characteristics seen in the case of hibonites in spherules also holds for platelet hibonites.



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- 1. **Marhas K.K.** and Goswami J.N. (2000) Boron Isotopic composition in the early solar system solids. *Current Science* **78**, 78-91.
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- 4. Sahijpal S., **Marhas K. K**. and Goswami J. N. (1997) ²⁶Al and ⁴¹Ca in the early solar system: constraint on possible sources. *International conference on isotopes in the solar system*, 32.
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- 12. **Marhas K. K.**, Krot A. N. and Goswami J. N. (2001) Al-Mg isotopic systematics in CAIs from CR chondrites. 64th *Annual Meteoritical Society Meeting*.

Papers under Preparation

- 1. **Marhas K. K.** and Goswami J. N. Radiogenic and stable isotopic anomalies in hibonites from CM meteorite.
- 2. Sahijpal S., **Marhas K. K.** and Goswami J. N. Rare Earth Elemental Analysis of CM Hibonites.
- Goswami J. N., McKeegan K. D., Sahijpal S., Marhas K. K., Sinha N. and Davis A. M. Oxygen isotopic composition in CM hibonites: Implications for the exotic oxygen isotopic reservoir in the early solar system.