# Chapter 1

# Introduction

The solar system originated from a cloud of gas and dust, the so called solar nebula, about 4.6 billion years ago. Our present day understanding of the solar system is based mainly on studies of various constituent members of the solar system : the Sun, the planets and their satellites, meteorites and comets. Amongst all the constituent members, samples from our own planet are most easily accessible for scientific studies.

Samples from the three major reservoirs of the Earth, the landmass (continents), the oceans and the atmosphere have been extensively studied to understand their evolution over geological time scales. Geophysical techniques and laboratory based simulation experiments have also helped us to decipher the internal structure of the Earth. However the records of events that took place during the very early epochs of Earth's history are difficult to obtain as the terrestrial samples have undergone extensive geological alteration and weathering that led to obliteration of the records of the earliest era. The oldest dated terrestrial sample has an age of about $\sim$ 4.27Ga (Compston and Pidgeon 1986), much lower than the formation age of the Earth and the solar system. The situation is similar in the case of the lunar rocks which have been studied extensively following the successful Apollo and Luna missions. Most of the returned lunar samples from the Mare regions have ages between 3.3 to 3.9Ga, and only a few of the anorthositic highland rocks are older than 4.2Ga, but none of them closer to 4.6Ga. On the other hand, most of the meteorites have formation ages close to 4.6Ga ( Tilton 1988) and many of these have not been disturbed since their time of formation. The antiquity of meteorites gives them a position of prime importance in the investigation of the early evolutionary history of the solar system.

Meteorites are rock bodies that have mostly originated from the present day asteroid belt although some may be of cometary origin. Gravitational perturbations by Mars and Jupiter can disturb their orbits and this can lead to their capture by Earth or other planets (Wetherill and Chapman, 1988 and references therein). On the basis of their composition, meteorites have been classified broadly into three different types: stones, stony-iron and iron. The stones are like rocks on the surface of the earth made primarily of silicate minerals, irons are pieces of metal (essentially Fe-Ni alloys) and stony irons are a mix of both silicates and metals. Meteorites belonging to each type exhibit great diversity in their physical and chemical properties, and this leads to further classification of each type. On the basis of presence or absence of small ( 0.1 - 1 mm ) rounded objects, known as chondrules, the stones have been classified into two groups: chondrites and achondrites. As a group chondrites display a very important property which sets them apart from other classes of meteorites. Their bulk chemical composition, except for several highly volatile elements and Li, is similar to solar composition and this is particularly true of the carbonaceous chondrites (Sears and Dodd 1988). This bears testimony to the fact that these meteorites have preserved primitive signatures from the time of their formation and makes studies of chondritic meteorites and particularly that of carbonaceous chondrites extremely important for our understanding of the early evolution of the solar system.

A great deal of information about the earliest stages of evolution of the solar system comes from the study of a particular group of objects, the so called Ca-Al-rich refractory inclusions or CAIs, that are found only in carbonaceous chondrites belonging to CV, CO and CM groups. The CAIs are composed of refractory oxides and silicates like hibonite ($CaAl_{12}O_6$), pervoskite ($CaTiO_3$), spinel ($MgAl_2O_4$), melilite ($Ca_2Al_{12}SiO_7$ - $Ca_2MgSi_2O_7$), anorthite ($CaAl_{12}Si_2O_8$), fassaite ($Ca(Mg, Ti, Al), (Al, Si)_2O_6$) and diopside ($CaMgSi_2O_6$), and have high concentrations of refractory major and trace elements like Ca, Al, Mg, Ti, and Sc, V, refractory rare earth elements etc. The CAIs were first observed in the carbonaceous chondrite Allende (Marvin et al. 1970) which fell in 1969 and were subsequently identified in other carbonaceous chondrites. The present thesis exclusively deals with the study of early solar system processes based on isotopic studies of CAIs using the ion microprobe.

## 1.1 Ca-Al-Rich Inclusions (CAIs)

The CAIs are refractory objects with sizes ranging from submillimeter to a couple of centimeters. Their chemical and mineralogical composition are in general accord with those expected for the first solids to form during the cooling of a hot nebular gas with average solar system composition (Grossman 1972). Many workers have reviewed the properties of CAIs found in different types of carbonaceous chondrites (Grossman 1980, McDougall and Goswami 1981, MacPherson et al. 1988), and a brief summary of these are presented here.

On the basis of the sizes of the constituent minerals, CAIs can be classified into two groups: fine-grained (typical grain size 1-20 μm) and coarse-grained (grain size upto 0.5 mm). The coarse grained CAIs, found generally in CV and CO meteorites like Allende, Efremovka, Vigarano, Ornans etc. range in size from < 1mm to ~ 2cm. The coarse-grained CAIs can be further classified on the basis of their petrographic and mineralogical composition (Grossman 1980, Wark and Lovering 1982, and Wark 1987). The generally accepted sub-types and their constituent phases are: type A (melilite + Spinel), type B (melilite + spinel + fassaite + anorthite), and type C (anorthite + melilite + spinel) (Table 1.1). The type B inclusions are further divided into B1 and B2, the former having an outer mantle consisting mostly of melilite while it is absent in the latter. CAIs can also be classified by their bulk chemical composition and REE patterns (Mason and Taylor 1982). An alternative scheme of classification of CAIs was also proposed by Kornacki and Fegley (1984). It has been observed that chemical classification and petrographic classification do not necessarily correlate and there is significant overlapping of different petrographic types with different types based on chemical composition. However the petrographic classification is more commonly used to describe the CAIs and we shall follow this terminology here. In

Table 1.1: **Mineralogical Compositions of CAIs***

| | CV meteorites | | | CM meteorites | |
|---|---|---|---|---|---|
| **Mineral** | **Type A**† | **Type B**† | **Type C**‡ | **Hibonite-Rich**† | Spinel-Rich† |
| Corundum | - | - | - | Trace | - |
| Hibonite | $\sim 5$ | - | - | 5-85 | 0 |
| Perovskite | 1-3 | - | - | 1-10 | 1-20 |
| Spinel | 5-20 | 15-30 | 2-12 | 10-80 | 60-90 |
| Melilite | $> 75$ | 5-20 | 0-25 | - | - |
| Fassaite | - | 35-60 | 18-34 | 0-5 | - |
| Diopside | - | - | - | 2-5 | 2-5 |
| Anorthite | - | 5-25 | 45-60 | - | - |

†Grossman 1980, MacDougall and Goswami 1981
‡Wark 1987 *Abundance is in percentage

addition, it is important to note that there are differences in the mineralogical composition of CAIs from different groups of carbonaceous chondrites; hibonite which is one of the most refractory phase is rarely seen in CAIs from CV or CO meteorites whereas they are more common in CM meteorites.

Petrographic, chemical and isotopic studies, as well as laboratory based simulation experiments, carried out over the last two decades, have revealed that CAIs are a complex and diverse group of objects that are some of the first solids to have formed in the solar system. Some of the CAIs could be direct nebular condensates while others must have undergone complex formation history with one or more episodes of evaporation, melting, and recrystallization. Some of them have also been subjected to late stage secondary alteration. A brief summary of isotopic studies of CAIs and important conclusions obtained from these studies are presented in the following section before describing the scope and the aim of the present work.

## 1.2 Isotopic Studies of CAIs

Isotopic studies of CAIs have been carried out using mass spectrometric techniques for more than a decade. The main emphasis in these studies was to look for possible deviations in the isotopic compositions of constituent elements of bulk CAIs and/or individual refractory phases in them from "solar system" values. Such deviations, if present, allow us to decipher several important aspects related to the early evolution of the solar system that includes: the state of the solar nebula, the processes responsible for the formation of some of the first solar system solids (CAIs), time scales for the formation of CAIs etc. Presence of non-solar isotopic composition in CAIs, commonly termed as isotopic anomaly, can be due to one or more of the following reasons:

(i) mass dependent isotopic fractionation at the time of formation of CAIs resulting from the physical or chemical processes responsible for their formation,

(ii) presence of non-solar nucleosynthetic components from distinct stellar sources in the nebula in the region of CAI formation,

(iii) incorporation of radioactive nuclei into the CAI at the time of its formation and their subsequent *in situ* decay resulting in an anomalous concentration of the daughter nuclei,

(iv) enhancement of particular isotope caused by interaction of energetic particle (cosmic rays) with CAIs in interplanetary space.

Identification of the observed isotopic anomaly in CAIs with any one of the above causes can provide useful information to understand processes operating in the formative stages of the solar system. For example, identification of isotopic mass fractionation effects can help us to understand the processes leading to the formation of CAIs and the nature of their parent material, the second type of anomaly allow us to identify specific astrophysical sites that have contributed matter to the solar nebula and the radiogenic isotopic anomalies allow us to infer about times scales of early solar system processes.

Isotopic analyses of major elements like Ca, Mg, Ti, O and Si in CAIs have been carried out using different types of mass spectrometers like thermal ionization mass spectrometer, gas source mass spectrometer and secondary ion mass spectrometer. The isotopic composition of the noble gases (e.g. neon, krypton and xenon ) in CAIs have also been studied extensively. The progress made in the field of isotopic studies of CAIs has been reviewed in a series of articles (Clayton 1978; Podosek 1978; Lee 1979, 1988; Begemann 1980; Wasserburg et al 1980; Wasserburg and Papanastassiou 1982; Wasserburg 1985; Clayton et al. 1988; Thiemens 1988; Harper 1993). We briefly summarize some of the main results that emerged from studies of isotopic composition of the major elements.

### 1.2.1 Studies of Stable Isotope Anomalies

Oxygen and silicon isotopic studies have been carried out using gas source mass spectrometers primarily at the University of Chicago (Clayton et al. 1973, Clayton et al. 1993). Oxygen which consists of three isotopes $^{16}O$ (99.756%), $^{17}O$ (0.039%) and $^{18}O$ (0.205%) is one of the major elements in the solar system. Studies of oxygen isotopes have revealed enormous variations in oxygen isotopic compositions of individual mineral phases in CAIs that cannot be explained by mass dependent fractionation process (Clayton 1973, Clayton et al. 1993 and references therein). This observation shattered the earlier belief of a well mixed isotopically homogeneous solar nebula. It was soon realized that CAIs are in general derived from an oxygen reservoir (dust) enriched in $^{16}O$ which later reequilibrated with gaseous reservoir depleted in $^{16}O$. Initial data from Allende CAIs suggested an enrichment of $\sim 5\%$ in their $^{16}O/^{18}O$ compared to the reference value of O (498.70337).

The observation of oxygen isotopic anomaly led to the search for isotopic anomalies in other elements. Silicon isotopic studies have shown that the coarse-grained CAIs are enriched in the heavy isotopes of Si (i.e. $^{29}Si$ and $^{30}Si$) compared to $^{28}Si$ (Molini-Velsko 1983, Clayton et al. 1985). This enrichment that ranges upto $\sim 5‰$/amu, relative to the solar value can be explained by normal mass dependent fractionation, and unlike oxygen, the silicon isotopic composition is similar in all the mineral phases. This observation can be explained by postulating that source material of the coarse-grained CAIs are evaporative residues that are preferentially depleted in the lighter isotopes.

Studies of isotopic composition of elements in the iron group, e.g. Ca, Ti and Cr, have shown that their is a general enrichment in the neutron rich isotopes ( e.g. $^{48}$Ca, $^{50}$Ti and $^{54}$Cr). The most prominent signatures (isotopic anomalies of large magnitude) of Ca and Ti isotopic anomalies are mainly seen in hibonite. The CAIs from CV meteorites have hibonite only as a minor phase and in general these CAIs do not show large anomalies in Ti or Ca. In contrast hibonite from CM meteorites show large isotopic anomalies in both Ca and Ti ( Zinner et al. 1986b, Fahey et al. 1987a, Hinton et al. 1987, Ireland 1988, 1990). The studies of Ca and Ti isotopic anomalies in CAIs also brought into fore the advantages of secondary ion mass spectrometer or the ion microprobe over thermal ionization mass spectrometer (TIMS) in analyzing individual microphases within the CAIs. Although the data for CAIs obtained by TIMS suggested the isotopic anomalies in $^{48}$Ca and $^{50}$Ti to be linearly correlated with a few exceptions (Jungck et al. 1984, Niederer and Papanastassiou 1984), the conclusive evidence in this regard came from the ion microprobe study of individual hibonite grains from CM meteorites (Zinner et al. 1986b). The enrichment in the neutron-rich isotopes of Ca, Ti and Cr and their qualitative correlation have led to the theoretical investigation of plausible astrophysical sites whose nucleosynthetic output may give rise to the observed features. At present these observations are best explained by considering contribution from neutron-rich nuclear statistical equilibrium process taking place in the expanding supernova envelope (Hartman et al. 1985). Interstellar grains are considered to be the most likely carriers of these isotopic anomalies to the solar nebula. However, no definite signatures of such grains were obtained during the study of the hibonites (Fahey et al. 1985, 1987a).

### 1.2.2 Mg Isotopic Studies

Magnesium isotopic composition of CAIs has been studied most extensively as most of the initial thermal ionization and ion microprobe studies of CAIs concentrated on magnesium isotopic analysis. These studies were carried out mainly to identify intrinsic isotopic mass fractionation effect and the possible presence of excess $^{26}Mg$ due to the decay of the short-lived radioisotope $^{26}Al$ that could have been incorporated into the CAIs at the time of their formation.

The studies of magnesium isotopic composition in CAIs, particularly identification of intrinsic mass fractionation effect, have helped in elucidating the nature of precursor material and/or the processes leading to the formation of the CAIs. For example, most of the coarse-grained CAIs are characterized by enrichment in the heavy isotopes of magnesium suggesting their source material to be evaporative residues. On the otherhand, the fine-grained CAIs are generally enriched in the lighter isotopes indicating that they are comprised of refractory components that may have condensed from a gas depleted in the heavier isotopes (Esat and Taylor, 1984; Niederer and Papanastassiou, 1984; Clayton et al., 1988 and references therein). Many of the inclusions however show complex petrographic and isotopic features and it is difficult to rule out multistage processes leading to their formation. Petrographic studies of the coarse-grained CAIs indicate that most of them are formed by crystallization from refractory melts of appropriate composition and some constraints on the initial temperature of such melts as well as their cooling rate were derived from mineralogical and laboratory simulation studies (Nagasawa et al., 1977; MacPherson and Grossman, 1981; Stolper, 1982; Wark and Lovering, 1982; MacPherson et al., 1984; Kornacki and Fegley, 1984; Stolper and Paque, 1986). Occurrence of additional processes like evaporation/volatilization that could leave their imprint in both petrographic and magnesium isotopic records found in CAIs have also been proposed (e.g., MacPherson et al., 1988). However, instances for sympathetic behaviour of petrographic and magnesium isotopic data are rare and data for only a couple of very special type of CAIs, the so called FUN inclusions, are suggestive of such a trend (Clayton et al., 1984; Davis et al., 1991).

Studies of Mg-Al isotopic systematics in CAIs from primitive meteorites and the observed excess in $^{26}Mg$ in many CAIs have provided strong evidence for the presence of the now-extinct nuclide $^{26}Al$ (meanlife $\sim$ 1.1Ma) in the solar nebula at the time of CAI formation (Lee et al. 1977, Wasserburg 1985). An extensive data set on magnesium isotopic composition have been obtained by ion microprobe studies of CAIs belonging to different petrographic types (A, B1 and B2) from CV and CO meteorites and hibonite grains from CM meteorites (Hutcheon, 1982; Huneke et al., 1983; Armstrong et al., 1984; Clayton et al., 1984; Hutcheon et al., 1986; Ireland et al., 1986; Fahey et al., 1987a,b; Brigham et al., 1988; Hinton et al., 1988; Ireland, 1990; Davis et al., 1991; Podosek et al., 1991; see also reviews by Clayton et al., 1988; and MacPherson et al., 1988). The studies of the coarse-grained CAIs, in particular, showed some specific trends between magnesium isotopic composition and petrographic type. For example, some type B1 CAIs are characterized by the presence of $^{26}Mg$ excess due to the decay of $^{26}Al$, and yield ($^{26}Al/^{27}Al$) at the time of formation of these inclusions (initial $^{26}Al/^{27}Al$) clustering around the value of $5 \times 10^{-5}$, commonly referred to as the canonical value. The Mg-Al systematics in the type B2 CAIs, on the other hand, are often disturbed and are characterized by lower values for initial ($^{26}Al/^{27}Al$). This is suggestive of either a heterogeneous distribution of $^{26}Al$ in the nebula or late disturbances in the magnesium isotopic systematics in these CAIs due to exchange/reequilibration of magnesium isotopes. Relatively few type A CAIs have been studied and the Mg-Al systematics in these inclusions also show disturbances except for a couple of cases (e.g., Fahey et al., 1987b). In addition, hibonite grains from CM meteorites like Murchison, that have large isotopic anomalies in Ca and Ti, either have very low initial ($^{26}Al/^{27}Al$) compared to the canonical value or are characterized by near absence of $^{26}Al$. Most of these variations were generally considered to represent an extremely heterogeneous distribution of $^{26}Al$ in the nebula. There are however alternative suggestions ( e.g. Podosek et al. 1991) that these differences may be due to secondary processes affecting these objects. Thus the idea of an extremely heterogeneous distribution of $^{26}Al$ in the solar nebula need not necessarily be correct.

## 1.3 Extinct Radionuclides as "Chronometers" of Early Solar System Processes

Isotopic studies of Mg, Cr, Ni, Ag and Xe in early solar system objects have established the presence of several short-lived now-extinct radionuclides with meanlife $\geq$ 1Ma in the early solar system (Wasserburg 1985, Cameron 1993). The presence of such short-lived radionuclides manifests itself through an excess in the daughter isotopes (e.g., $^{26}Mg$ in the case of $^{26}Al$). Although a fossil origin for these excesses have also been suggested (Clayton 1977, 1982, 1986), there are good reasons (particularly the correlation of excess in daughter nuclide with the abundance of the parent element in the analyzed phases ) to believe that these extinct nuclides were present in the early solar system and were incorporated 'live' into these early solar system objects.

In general, if the meanlife of a radionuclide is $\leq$ 35Ma then such nuclides will be extinct today. The primary criteria to demonstrate the presence of extinct radionuclides at the time of formation of early solar system objects like CAIs are: (i) to establish the presence of an excess in the daughter nuclide concentration, and (ii) show that this excess is well correlated with abundances of parent element in the object. The second observation suggests *in situ* decay of the now-extinct nuclide within the object.

Evidence for the presence of extinct radionuclides in the early solar system can give us valuable information about the time interval '$\Delta$' between the input of freshly synthesized matter to the solar nebula and the formation of some of the first solar system solids (e.g. CAIs). Obviously, the presence of the radionuclide with shortest mean life will provide the most stringent constraint on $\Delta$. At present, $^{26}Al$ with a meanlife of $\sim$ 1.1Ma is the shortest lived radionuclide whose presence in the early solar system has been conclusively established. Search for extinct nuclides with even shorter meanlife like $^{36}Cl$, $^{41}Ca$ and $^{99}Tc$ have not yielded conclusive results ( Gobel et al. 1982; Yin et al. 1992 ), although the data of Hutcheon et al. (1984) provided a hint for the possible presence of excess $^{41}K$ due to $^{41}Ca$ decay in Allende CAIs. In addition, if one can establish that the initial distribution of any one of the extinct nuclides was homogeneous in the nebula, it can also be used as a relative chronometer for studying the evolution of objects that formed at different times during the early history of the solar system. In the following, we describe the aim and scope of the present work keeping in view the above background information already available in the area of isotopic studies of CAIs directed towards understanding early solar system processes.

## 1.4 Aim and Scope of this work

A majority of the earlier isotopic studies of CAIs were restricted to samples from the Allende carbonaceous chondrite in which the CAIs were first identified. Only a few CAIs from the other carbonaceous chondrites belonging to CV or CO group have been studied in some detail (Clayton et al., 1986; Davis and Hinton, 1986; Hutcheon et al., 1986; Fahey et al., 1986, 1987b; Caillet et al., 1991). It is well known that most of the Allende CAIs show distinct signs of secondary alteration and present difficulties for an unambiguous interpretation of their isotopic records (e.g., Hutcheon, 1982; Podosek et al., 1991). Inclusions from some other meteorites (e.g., Ornans, Vigarano and Leoville) are less altered, but they are also less abundant. The refractory inclusions in the Efremovka CV chondrite are however an exception in this regard; they show very little evidence for secondary alteration, they are generally large (mm to cm in size), and one can easily find all the different inclusion types. In fact, petrographic and trace element studies (Ulyanov et al., 1982, 1988; Nazarov et al., 1982, 1984) suggest that the Efremovka CAIs are more pristine than the Allende inclusions. Thus, the Efremovka CAIs are expected to be better suited for isotopic studies to decipher early solar system processes than the Allende CAIs. However, no systematic isotopic study of Efremovka CAIs have been attempted to date.

In this work, isotopic studies of a set of Efremovka CAIs were carried out to determine their magnesium, calcium and potassium isotopic compositions using an ion microprobe. In addition a set of CAIs from the Grosnaja meteorite, which show distinct signatures of secondary alteration, were also studied for their Mg-Al isotopic systematics. The CAIs from Grosnaja were studied to look for possible effects of secondary alteration on isotopic systematics vis-a-vis the Efremovka CAIs that were almost free from secondary alteration. Inclusions from all the major petrographic types (A, B1, B2, hibonite-rich and C) have been included in this study so that we can generalize upon our results.

As already noted there are several advantages of isotopic studies using the ion microprobe technique as compared to thermal ionization mass spectrometric method. Most importantly the ion microprobe offers the distinct advantage of *in situ* analyses of microphases with a spatial resolution of $\sim 10\mu m$. This allows us to carry out isotopic analyses of small mineral grains within the CAIs and also to correlate the isotopic data from different mineral phases within a CAI. Additionally, it is also possible to carry out repeat analyses of the same phase to determine isotopic composition of different elements with relative ease. This helps us to discern possible relationship between isotopic anomalies in different elements.

Application of the ion microprobe technique for high resolution and high precision isotopic studies depends upon the capability of the instrument to resolve interferences at mass(es) of interest and the dynamical stability of the instrument during isotopic analysis. Since the commercially available ion microprobes barely manage to reach the high resolutions and stability needed, it is very important to carry out detailed parametric investigations to establish the capability of individual instrument for precise isotopic studies. We have therefore performed extensive check-tests of our ion microprobe (Cameca Ims-4f) to ensure that conditions necessary for high resolution high precision isotopic studies are adequately met by it. The major goals of the present study and the work approach followed to achieve these are:

(i) to delineate the processes leading to the formation of CAIs and the nebular environment in which they have formed. Studies of magnesium isotopic mass fractionation were carried out on all the Efremovka CAIs towards this end. Special efforts were made to look for possible correlation between Mg isotopic mass fractionation and petrographic features with a view to improve our understanding of CAI forming processes. In addition we also searched for possible presence of isotopic disequlibrium between coexisting mineral phases within individual CAIs that may lead to indentification of "relict" grains. Presence of such grains can provide us with important clues towards understanding the thermal evolutionary history of the CAI and constrain the nebular environment compatible with the inferred thermal history,

(ii) to look for possible presence of excess $^{26}Mg$ due to the in-situ decay of the short-lived now-extinct radionuclide $^{26}Al$ in the CAIs. Studies of Mg-Al isotopic systematics were carried out on all the Efremovka and Grosnaja CAIs to achieve this objective. Possible relationship between disturbance in Mg-Al isotopic systematics and secondary alteration of the CAIs and its effect on the inferred distribution of $^{26}Al$ in the solar nebula was also investigated.

(iii) to look for the possible presence of $^{41}Ca$, that has a much smaller meanlife ( $\sim$ 0.15Ma) than $^{26}Al$, in the early solar system. Studies of potassium and calcium isotopic composition in Efremovka CAIs having $^{26}Mg$ excess were carried out to look for $^{41}K$ excess due to *in situ* decay of $^{41}Ca$. Mineral phases with high Ca/K ratios (pyroxene and perovskite) were chosen for these studies. As already noted the presence of $^{41}Ca$ can be used to provide a stringent constraint on the time interval between the last injection of nucleosynthetic matter to the solar nebula and the formation of the CAIs.

In the next chapter (Chapter 2) we describe the experimental techniques used for isotopic analysis by the ion microprobe. This chapter contains a brief description of the working principles of the Cameca Ims-4f ion microprobe followed by the results obtained from different check tests conducted to test its suitability for high resolution high precision isotopic studies. A brief description of the samples analyzed in this study is given in Chapter 3. The results obtained from magnesium, aluminium, potassium and calcium isotopic studies of Efremovka and Grosnaja CAIs are presented in Chapter 4. The implications of these results in conjunction with other known properties of the analyzed CAIs are discussed in Chapter 5. We summarize the results obtained from this study and discuss the scope for future work in Chapter 6.