Chapter 2

Experimental Techniques

2.1 Introduction

Our understanding of the various processes related to the temporal evolution of the Earth, Moon and other planetary bodies has been greatly enhanced by studies of chemical and isotopic compositions of representative samples from these objects. Various types of mass spectrometers, e.g., gas source mass spectrometers, thermal ionization mass spectrometer, secondary ion mass spectrometers, etc., have proved to be an essential tool in determining isotopic composition of terrestrial, lunar and meteorite samples and also of planetary atmospheres. The secondary ion mass spectrometer (SIMS), that can be used to obtain elemental and isotopic composition of solid samples, has been extensively used during the last couple of decades in the field of geochemistry (Shimizu et al., 1978; Shimizu and Hart, 1982a). A major advantage offered by SIMS compared to thermal ionization mass spectrometer (TIMS) is its high spatial resolution that allows in situ measurements of extremely small (ten to hundred microns) terrestrial and meteoritic samples. Eventhough these advantages are at the cost of a lower precision compared to TIMS, the high mass resolution secondary ion mass spectrometer has proved to be an extremely useful and the only tool at present to
carry out detail *in situ* studies of isotopic compositions in individual refractory phases of Ca-Al-rich inclusions (CAI). In the present work, which is primarily concerned with isotopic studies of K-Ca and Mg-Al systematics in refractory phases of CAIs, and Mg-Al systematics in specially selected igneous, non-refractory phases of chondritic meteorites, I have exclusively used a Cameca ims-4f secondary ion mass spectrometer (ion microprobe) for isotopic measurements. In this chapter, a brief description of this ion microprobe is presented along with the analytical techniques used in the measurements of K, Ca, Mg and Al isotopic compositions in the meteoritic phases.

### 2.2 Secondary Ion Mass Spectrometer (SIMS)

Matter is ejected from a solid surface via the process of sputtering when it is bombarded by energetic ions. The ejected matter consists of atomic and molecular species present in both neutral and ionic state. The ionized particles can be analyzed for their isotopic or elemental composition to get information about the composition of the solid surface. In SIMS, we make use of this principle to determine elemental and isotopic composition of solid sample. An energetic primary ion beam is used to sputter the sample surface. The ions generated from the sputtering process, termed as secondary ions, are accelerated and energy analyzed prior to passing through an electromagnet for mass (m/q) analysis. The transmitted ions of a given m/q are collected using an electron multiplier or Faraday cup to measure their intensities. In addition to its function as a mass spectrometer, the Cameca ims-4f also has imaging capability that makes it a very versatile tool. A brief description of the basic working of the Cameca ims-4f ion microprobe is presented below.
2.2.1 Primary ion column

In the sputtering process, secondary ion intensities of different species liberated from a solid sample depend upon the nature of the primary ion used for sputtering and the chemical composition of the target material. Negative primary ion (e.g., O\textsuperscript{−}) gives better secondary ion yield for electropositive elements like Mg, Al, K, Ca, Ti, Cr, etc., while the use of positive primary ion beam (e.g., Cs\textsuperscript{+}) leads to better secondary ion yield of electronegative elements like H, C, O, halogens, etc. One can also use other primary ion species like Ar, Ga, etc., depending upon the specific nature of the study. In the Cameca’s ims-4f, primary ion beam from gaseous species (O, Ar, etc.) are produced by a cold cathode duoplasmatron, whereas Cs\textsuperscript{+} beam is produced by a specially designed microbeam source that works on the principle of thermal ionization.

Oxygen gas is introduced into the cold cathode duoplasmatron where oxygen plasma is generated by an arc discharge between the cathode and the anode kept at a potential difference of several hundred volts. An intermediate electrode and a magnetic field generated by a coil surrounding the intermediate electrode confines the plasma to a very narrow region near the anode hole. The O\textsuperscript{−} and O\textsuperscript{2+} charges inside the plasma are stratified with O\textsuperscript{2+} ions at the center of the arc and O\textsuperscript{−} ions at its periphery. The ions can be extracted from the anode hole by the relative displacement of the arc and the anode hole. This movement is brought about by mechanically moving the intermediate electrode and cathode with respect to anode. As the ions of required species diffuse out of anode hole, they are accelerated by a potential difference of up to 17.5 kV between the duoplasmatron, which is floated at high potential, and a grounded extraction electrode.

The cesium microbeam source used in the Cameca ims-4f works on the principle
Figure 2.1: Primary column ion optics of the Cameca ion microprobe ims-4f.
that vapours of Cs are ionized as they come in contact with hot tungsten metal. This results from the transfer of electron from neutral adsorbed Cs atom to conduction band of tungsten at a temperature of 1100°C. Cs vapours are generated from a cesium chromate (Cs₂CrO₄) pellet kept in a reservoir at a temperature of 400°C and are passed through a hot porous tungsten metal where ionization takes place. The ions emerging out of the porous tungsten are accelerated to 10 kV by the potential gradient between the microbeam source and the extraction electrode.

Depending upon the nature of secondary ions to be analyzed, one of the three primary ion beams: O⁻, O₂⁺ or Cs⁺, is selected and passed through a primary beam mass filter. Primary beam mass filter consists of a magnet that deflects the beam coming either from the duoplasmatron or the Cs microbeam source to the primary column. Singly or doubly charged impurity ions of hydrides and oxides associated with leak in the oxygen supply pipe or duoplasmatron surface contamination can be removed and pure ¹⁶O⁻, or ¹⁶O₂⁺ primary beams can be obtained with the help of the primary beam mass filter. The selected ion beam passes through a set of three electrostatic einzel lenses and deflectors in the primary column prior to bombarding the sample surface (Fig. 2.1). The intensity of the beam is controlled by the lens L₁ and the primary beam aperture. Lens L₂ along with the primary beam mass filter is used to maximize the beam current. The third lens L₃ focuses the primary beam on the sample surface. The diameter of the focussed beam spot could be as small as few microns for primary beam current of ≤ 1 nanoampere. Astigmatism in the primary beam caused by off centering of primary beam from the principal optical axis of various apertures and lenses, can be removed by a pair of stigmators. The primary beam current is monitored by a Faraday cup. Stable primary currents of the order of tens of picoampere to as high as few hundred nanoampere can be obtained. The isotopic analyses performed in this work were carried out with primary current in the nanoampere range.
2.2.2 Production of secondary ions

The collisions of energetic primary beam ions with a solid surface lead to transfer of energy and momentum to the lattice atoms. As a result, the lattice bonds are broken and these atoms are set free from their lattice sites. The liberated atoms in turn undergo collisions with their neighboring atoms and continuation of this process leads to collision cascade. The net result of this collision cascade is ejection of surface atoms that have received sufficient momentum to overcome the surface barrier. The ejected particles mostly contain neutral atoms and molecular species (e.g., oxides, hydrides, dimers, etc.), with a small fraction in ionized form. Intensities of both the neutral and ionic species represent the elemental and isotopic abundances of the sample surface.

The secondary ion yield, which is the number of secondary ions emitted of a particular species per primary ion incident on the sample, depends principally upon the chemical composition of the sample (matrix effect) and the nature of the primary beam. The energy and angle of incidence of the primary beam are also important parameters. Although, the role of various parameters that determine the secondary ion yield has been studied extensively (see e.g., Benninghoven et al., 1987), it is difficult to quantify these results in absolute terms as the exact processes leading to the secondary ion emission are not yet properly understood. Several models have been proposed to explain the production of secondary ions. Among these, the local thermodynamic equilibrium model proposed by Andersen and Hinthorne (1972) has been successful to some extent in quantifying the observed sputtered yields. According to this model, a plasma layer exists at the surface of sample during ion bombardment in which sputtered atoms, ions, molecules and electrons are in local thermodynamical equilibrium. Concentration of various charge species is then estimated on the basis of Saha-Eggert equation.
2.2.3 Secondary ion optics and mass spectrometer

The secondary ions generated by sputtering of a solid surface can have a wide angular as well as a large energy spread. For the typical primary beam energy used in SIMS, the energy spread of sputtered ions is \(\sim 150\,\text{eV}\), whereas, angular dispersion could even be close to \(2\pi\) radians. The role of secondary ion transfer optics is to produce a real, magnified and low-aberration image of the bombarded sample surface which is then transported through a double focussing mass spectrometer for energy and mass filtering. The final image produced by the mass spectrometer has only mass-dispersive property with no energy dispersion.

The real, magnified secondary ion image in the Cameca ims-4f mass spectrometer is produced by the combination of an immersion lens system and a set of three transfer einzel lenses (Fig. 2.2). One of these transfer lenses is energized at a time. The immersion lens part consists of an accelerating gap (field gradient) and an einzel lens. The sample is kept at a potential difference of 4.5 kV with respect to the grounded extraction plate. Secondary ions are accelerated in this potential gradient and emerge out from the extraction plate hole. In Fig. 2.3, trajectories of secondary ions with initial velocity perpendicular to the surface, and ions having the same energy 'E' and angle of emission '\(\alpha\)', are shown. After acceleration in the field gradient, ions appear to come from the virtual image A-B-C. A virtual cross over of this image is produced at \(C_o\), where ions having same energy and initial emission angle are represented by a single point. The virtual image and virtual cross over produced by extraction electrode and sample acts as object for the immersion lens and the transfer lens. A real magnified image of sample surface and its cross over are produced in the planes of field aperture and the contrast aperture, respectively. The transfer lenses allow changes in magnification of both the surface image and its cross over, which determines the size of the image field being analyzed.
Figure 2.2: Secondary column ion optics of the Cameca ion microprobe ims-4f.
Figure 2.3: Trajectories of secondary ions emitted from sample surface.
The real magnified image of the sample and its cross over, produced at field aperture and contrast aperture, respectively, serve as object for the double focussing mass spectrometer which consists of a 90\(^\circ\), spherical electrostatic analyzer and a 90\(^\circ\), homogeneous magnetic sector. The electrostatic sector is used to reduce the momentum dispersion of the incident secondary ions having an initial energy spread of \(\sim 150\) eV. In the electrostatic analyzer, the secondary ion beam undergoes energy dispersion, and with the help of an energy slit, a narrow energy band (usually \(\sim 25\) eV) of this dispersed beam is selected to transmit further through the spectrometer lens into the magnetic sector. As this energy filtered beam passes through the spectrometer lens and the magnetic sector, it further undergoes an energy dispersion which is equal in magnitude and opposite in sign to that of the dispersion produced by the electrostatic analyzer. This state of achromatism is attained by tuning the spectrometer lens appropriately. Besides this energy focussing, the coupled electrostatic analyzer and magnetic sector also produce a directionally focussed sample image. This mass filtered image can be projected on channel multiplier using projector lenses. The capability of transporting image by the Cameca ims-4f ion microprobe allows the system to work as an ion microscope which facilitates mapping of lateral distribution of various elements in a sample with high spatial resolution and magnification. The final cross over of the mass filtered sample surface image is produced at the exit slit. The mass resolving power of the instrument primarily depends upon the width of the entrance and the exit slits and also on the energy band pass allowed by the energy slit.

2.2.4 Detection system

There are three modes of detecting the mass filtered secondary ions in Cameca ims-4f, ion microprobe. These are: (1) channel multiplier, (2) electron multiplier, (3) Faraday
cup. The channel multiplier is coupled to a fluorescent screen and is used to visualize the magnified mass filtered secondary ion image of the sample and its cross over. In this mode, the instrument works as an ion microscope. This mode of operation is extremely useful in tuning the instrument to high mass resolution.

In the counting mode, the secondary ions are directed toward the electron multiplier and the Faraday cup assembly with the help of an electrostatic prism. For isotopic analysis, ion counting is primarily done by using an electron multiplier. A 17 stages Cu-Be coated dynode, electron multiplier (Balzer SEV217) is used and is operated in pulse counting mode during isotopic analysis. The efficiency, dead time and background of the counting system are checked regularly during the operation of ion microprobe. The operational efficiency of electron multiplier deteriorates with ageing of dynodes as their coating gets corroded. It is generally replaced once the efficiency goes below 70%. The ‘effective’ dead time of the system is monitored as their coating gets corroded. It is generally replaced once the efficiency goes below 70%. The ‘effective’ dead time of the system is monitored. The operational efficiency of an electron multiplier depends on the electron multiplier, pre-amplifier, discriminator and the死 time, which is generally 20 ns (nanoseconds) with a standard deviation of +1 ns for a period of several weeks. It is determined from isotopic analysis of magnesium, silicon or titanium on standard samples. The background of the counting system is usually monitored on a weekly basis and the static background is typically below 0.01 counts per second.

2.3 Isotopic Analysis and Mass Fractionation

The most important factor that has to be considered in isotopic studies by an ion microprobe is the interferences of various species at a given mass of interest. Such interferences can result from the presence of molecular and isobaric species in the secondary ion beam that have the same mass to charge ratio as that of the isotope.
Figure 2.4: Static background of the secondary counting system at mass 40.7.
of interest. The most common among the molecular interference are singly ionized hydrides, oxides, dimers etc. Doubly ionized species with \((m/q)\) similar to the isotope of interest are also important in certain cases. Most of these interferences are resolved by high mass resolution analysis. Typical mass resolution \((M/\Delta M; \Delta M\text{ measured at } 10\%\text{ of the peak height})\) needed for resolving hydride and oxide interferences for \(M < 60\) is \(\sim 4,000\). However, resolution of very specific isobaric interferences e.g., \(^{48}\text{Ca}\) and \(^{48}\text{Ti}\) needs mass resolution of \(\sim 10,000\). We have been able to achieve both high mass resolution and stability (effective \(\Delta M/M \leq 10 \text{ ppm}\)) in our instrument in a routine manner.

The isotopic ratios measured by the ion microprobe can show departure from its true value because of isotopic mass fractionation principally taking place at the time of secondary ion emission through the sputtering process. Isotopic mass fractionation is a process in which the isotopic composition is altered in a systematic manner, whereby, there is either an enrichment of the lighter isotopes compared to heavier one or vice versa. Based on ion microprobe isotopic analyses of \(\text{Li, Mg, Si, K, Ca and Zr in various minerals, Slodzian et al. (1980)}\) observed that the lighter isotopes of all the elements are enriched relative to the heavier ones and the magnitude of the mass fractionation depends upon the difference in their masses, and also on the secondary ion energy. These observations were also supported by work carried out by Shimizu and Hart (1982b).

In general, the isotopic mass fractionation observed in a sample will be due to instrument mass fractionation as well as intrinsic mass fractionation. The later represent effect of processes that affected the samples at the time of their formation and/or subsequent evolution. The intrinsic mass fractionation effect, if present, can be determined by analyzing the sample and an analog standard under identical instrument operating condition and assigning the observed isotopic mass fractionation

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in the standard as due to instrument mass fractionation effect. It is always preferable to use a standard for which intrinsic mass fractionation effects have been shown to be negligible by analysis performed using thermal ionization mass spectrometry.

In the following sections, I describe the sample preparation and analytical techniques used for K-Ca and Mg-Al isotopic analysis of various meteoritic samples and standards.

2.4 Sample Preparation and Isotopic Measurements by Ion Microprobe

Most of the samples (refractory as well as igneous inclusions) analyzed in this study were cast in standard one inch diameter epoxy mounts and polished using diamond paste and alumina powder. For analyzing individual refractory phases e.g., Murchison hibonites, the samples were mounted in small epoxy beads (< 2 mm) within aluminium discs and polished to expose the grain surface. We found that the later method of sample mounting greatly reduces the hydride signal because of the small amount of epoxy present in the sample-mount as compared to the standard one inch diameter epoxy mount. Reduction in hydride signal was also observed in thin section of Allende inclusion that was mounted on a glass disc. The reduction in hydride signal is extremely useful during K-Ca isotopic studies to fully resolve the $^{41}$K peak from the $^{40}$CaH peak. The polished sample mounts were thoroughly cleaned in an ultrasonic bath using soap solution, distilled water and ethanol in steps to remove any contamination on the sample surface during handling and polishing. The cleaned mounted samples were then coated with a 1000-1500 Å thick gold film to obtain a well defined beam spot and to reduce possible sample charging effects during analysis. In the case of potassium isotopic analysis, the final cleaning prior to gold coating was
done by slowly heating the mounted samples in ultrapure water (filtered through Millipore \textsuperscript{TM} Milli-Q-Plus-System) for a period of one to two hours. This ensures the removal of any extraneous potassium on the sample surface that could have come during the sample preparation procedure. The samples were documented in detail using an optical and a scanning electron microscope.

\textbf{2.4.1 Magnesium isotopic measurement}

The measurement of magnesium isotopic composition in various meteoritic phases and terrestrial standards were carried out at a mass resolution of \( \sim 4,000 \), adequate to resolve hydride (NaH\textsuperscript{+}, MgH\textsuperscript{+}) and other molecular (\(^{+}\text{Ca}^{++}, \text{Ti}^{++}\)) interferences at the masses of interest (Fig. 2.5). A focused \(^{16}\text{O}^{-}\) primary ion beam of energy 17 kV was used and the beam current was typically 1-2 nanoamperes with a beam spot size of \( \leq 10 \mu\text{m} \) on the sample surface. Lower beam currents with smaller beam spot sizes were used while analyzing very small Al-rich (Mg-poor) phases surrounded by Mg-rich phases, particularly in the case of igneous inclusions of chondritic meteorites. This was done to avoid contributions to the ion signal from the surrounding Mg-rich phases. This, however, reduces the secondary ion signals in these cases that resulted in higher statistical uncertainties (lower precision) in the measured isotopic ratios.

Isotopic analyses were carried out in peak jumping mode by cycling the magnet through the mass sequence 24(\(^{24}\text{Mg}\)), 25(\(^{25}\text{Mg}\)), 26(\(^{26}\text{Mg}\)) and 27(\(^{27}\text{Al}\)). When the Al/Mg ratio of any analyzed sample was very high and the count-rate for \(^{27}\text{Al}\) exceeded a few times \( 10^{5} \), \(^{27}\text{Al}\) was excluded from the isotopic analysis and the \(^{27}\text{Al}^{+}/^{24}\text{Mg}^{+}\) ratio was determined independently both before and after individual analysis. A typical analysis consisted of 20-25 blocks, with each block representing 5 cycles of data. The deviations in the measured magnesium isotopic ratios (\(^{26}\text{Mg}/^{24}\text{Mg}\) and \(^{25}\text{Mg}/^{24}\text{Mg}\)) from their reference values were obtained using the relation.
Figure 2.5: Mass spectra of Mg and Al isotopes in Madagascar Hibonite taken at a mass resolution, $M/\Delta M \sim 4,000$. 
\[ \Delta^i Mg = \left( \frac{\left( \frac{1^i Mg}{2^i Mg} \right)_{\text{sample}}}{\left( \frac{1^i Mg}{2^i Mg} \right)_{\text{ref.}}} - 1 \right) \times 1000 \text{ permil,} \quad (i = 25, 26) \quad (2.1) \]

The reference magnesium isotopic ratios used by us are: \((^{25}\text{Mg}/^{24}\text{Mg}) = 0.12663\) and \((^{26}\text{Mg}/^{24}\text{Mg}) = 0.13932\) (Catanzaro et al., 1966). Correction for instrumental and intrinsic (sample) isotopic mass fractionation was done using the linear mass fractionation relation, \(\Delta^{26}\text{Mg} = 2 \Delta^{25}\text{Mg}\), to calculate any excess \(^{26}\text{Mg}\) as:

\[ \delta^{26}\text{Mg} = \Delta^{26}\text{Mg} - 2 \Delta^{25}\text{Mg} \quad (2.2) \]

In the case of terrestrial analog of meteorite phases, \(^{26}\text{Mg}\) should be zero within experimental uncertainties. We have analyzed a set of standards and showed this to be true under our instrument operating conditions (Table 2.1).

Since the secondary ion yield of a given element depends on the chemical composition of the target and its lattice structure, determination of elemental abundance ratios from the measured ion intensities require a knowledge of relative ion yields of different elements from a given matrix. This can be determined by analyzing terrestrial standards whose elemental composition is precisely known from measurements made by using other analytical techniques, e.g., electron probe. We have analyzed terrestrial analog standards of the meteoritic phases investigated in this work to determine the relative ion yield factor \((\lambda)\), by using the relation:

\[ \lambda = \frac{\left( \frac{^{27}\text{Al}}{^{24}\text{Mg}} \right)_{\text{e.p.}}}{\left( \frac{^{27}\text{Al}}{^{24}\text{Mg}} \right)_{\text{i.p.}}} \quad (2.3) \]

where e.p. and i.p. stands for electron probe and ion probe data, respectively. The \(\lambda\) values obtained in this work are shown in Table 2.2.
Table 2.1. Magnesium isotopic analyses of terrestrial standards

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of analyses</th>
<th>$^{27}\text{Al}^{24}\text{Mg}$ ±2σm</th>
<th>$\delta^{28}\text{Mg}(%_\circ)$ ±2σm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake County Plagioclase*</td>
<td>3</td>
<td>218.60 ± 1.10</td>
<td>-1.25 ± 1.85</td>
</tr>
<tr>
<td>Burma Spinel*</td>
<td>3</td>
<td>2.53 ± 0.01</td>
<td>0.36 ± 1.44</td>
</tr>
<tr>
<td>Madagascar Hibonite†</td>
<td>3</td>
<td>31.69 ± 0.11</td>
<td>-0.63 ± 1.20</td>
</tr>
<tr>
<td>Melilite†</td>
<td>3</td>
<td>1.03 ± 0.01</td>
<td>1.45 ± 1.59</td>
</tr>
</tbody>
</table>

* National Museum of Natural History, Smithsonian Institution, Washington, D.C.
† Curien et al. (1956)
‡ Vernadsky Institute, Moscow

Table 2.2. Relative yield factor (λ) for Mg-Al isotopic analyses

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{27}\text{Al}^{24}\text{Mg}$</th>
<th>Yield (λ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lake County Plagioclase*</td>
<td>172.09</td>
<td>1.27</td>
</tr>
<tr>
<td>Spinel*</td>
<td>1.98</td>
<td>1.28</td>
</tr>
<tr>
<td>New York Spinel</td>
<td>2.02</td>
<td>1.26</td>
</tr>
<tr>
<td>Burma Spinel</td>
<td>1.98</td>
<td>1.28</td>
</tr>
<tr>
<td>Madagascar Hibonite†</td>
<td>22.64</td>
<td>1.40</td>
</tr>
<tr>
<td>Melilite†</td>
<td>0.98</td>
<td>1.04</td>
</tr>
</tbody>
</table>

* Vernadsky Institute, Moscow

2.4.2 Potassium isotopic measurements

The potassium isotopic measurements were carried out using a focused 17 kV $^{16}\text{O}$ primary beam with current generally of the order of 1.5 to 4 nanoamperes. The spot size was made as small as possible for the given primary current and was typically < 10 μm. Secondary ions from a restricted area of the sample surface (~ 10 μm) were accepted during isotopic analysis by limiting the size of the field aperture. This was done to avoid contributions from neighbouring phases with relatively high K content.
and also possible surface contamination from outside the sputtered beam spot. The energy distribution of the secondary ions were monitored both before and after each run to ensure that there was no significant change in the energy band over which the secondary ions were accepted for mass analysis. The stability of the magnet, the effective deadtime and efficiency of the counting system were checked routinely using standard procedures (see e.g., Goswami and Srinivasan, 1994). Prior to each analysis, a preburn of the sample spot was carried out for a period of about 15-30 minutes to remove any surficial potassium and to achieve a steady Ca/K value. In the case of Murchison hibonites, magnesium analyses were usually carried out prior to potassium analyses on the same spot with relatively low primary current.

K-Ca isotopic studies of terrestrial and meteoritic phases with high Ca. K were carried out at a mass resolution of \( \sim 5000 \) that is sufficient to resolve the major interference of \( ^{40} \text{CaH} \) at mass \( ^{41} \text{K} \) (see Fig. 2,6). Although K has three isotopes \( ^{39}, ^{40}, \text{and} ^{41} \), it is not possible to resolve \( ^{40} \text{K} \) from \( ^{40} \text{Ca} \) when Ca is present. Thus for all practical purposes K can be considered as a two isotope system in the present case. Further, the interference of \( ^{40} \text{Ca}^{42} \text{Ca}^{++} \) cannot be resolved at this mass resolution and was determined indirectly. The magnitude of the other unresolved doubly charged interference \( ^{26} \text{Mg}^{56} \text{Fe}^{++} \) was checked by looking for \( ^{25} \text{Mg}^{56} \text{Fe}^{++} \) signal at mass 40.46 amu under our operating condition for K isotopic studies. High mass resolution spectra obtained around this mass with long integration time did not reveal any signal above our system background. This was also expected because of the very low content of Fe (FeO<1%) in all the analyzed phases, and the much lower secondary ion yield of Fe relative to Ca. Possible interference from \( ^{50} \text{Ti}^{16} \text{O}_2^{++} \), that is separated from the \( ^{41} \text{K} \) mass peak by \( \sim 0.0055 \) amu and is nearly well resolved under our operating conditions, was also checked by analyzing terrestrial perovskite and looking for \( ^{46} \text{Ti}^{16} \text{O}_2^{++} \) signal at mass 39.971 amu (separated from the \( ^{39} \text{K} \) mass peak by \( \sim 0.007 \) amu) using high primary beam current and a \( ^{40} \text{Ca}^{++} \) count rate of \( \sim 7 \times 10^6 \text{ s}^{-1} \).
No detectable signal was found and we can rule out contribution from \([^{50}\text{Ti}^{16}\text{O}_2]^{2+}\) to the signal at mass 41 \(^{41}\text{K}\) under our operating condition (typical \(^{40}\text{Ca}^+\) count rates of \(< 2 \times 10^6\) c/s). Contributions from additional interferences (e.g., \([^{27}\text{Al}_{2}^{28}\text{Si}^+]^{2+}, [^{25}\text{Mg}^{16}\text{O}]^+\)) can be neglected as they are well resolved under our operating conditions. Finally, as the count rate at mass \(^{41}\text{K}\) is generally a few orders of magnitude smaller than \(^{40}\text{Ca}^\text{H}\) in the high Ca/K phases, we have checked for possible scattering from the hydride peak that may contribute to the \(^{41}\text{K}\) counts during K isotopic analysis. Contribution due to scattering from the \(^{40}\text{Ca}\) peak towards the signal at mass 41 can be ruled out under our operating condition as we could not detect any signal above our counting system background in the mass region around 40.7 amu even for \(^{40}\text{Ca}\) count rate of \(~ 2 \times 10^7\) s\(^{-1}\), which is almost an order of magnitude higher than the value normally encountered during K isotopic analysis. The measured ion intensity at the mass 41 peak can therefore be written as:

\[
[mass(41)]^+ = [^{41}\text{K}]^+ + [^{40}\text{Ca}^{16}\text{Ca}]^{2+} + [^{40}\text{Ca}\text{H}]^+ + \text{dyn.bg., (2.4)}
\]

where dyn. bg. refers to the dynamic background of the counting system. Since it is not possible to directly measure \([^{40}\text{Ca}^{42}\text{Ca}]^{2+}\) count rate, we correct for it following the approach of Hutcheon et al. (1984) by finding the magnitude of \([^{40}\text{Ca}^{43}\text{Ca}]^{2+}\) signal at mass 41.5 and assuming:

\[
\frac{[^{40}\text{Ca}^{43}\text{Ca}]^{2+}}{^{43}\text{Ca}^+} = \frac{[^{40}\text{Ca}^{42}\text{Ca}]^{2+}}{^{42}\text{Ca}^+} \quad (2.5)
\]

The \([^{40}\text{Ca}^{43}\text{Ca}]^{2+}\) signal, which can be monitored at m/q=41.5, was found to be extremely low (<0.5 c/s) in both terrestrial and meteoritic phases under our operating condition. The value of \([^{40}\text{Ca}^{43}\text{Ca}]^{2+}/^{43}\text{Ca}^+\) was therefore obtained independently.
Figure 2.6: Mass spectra at masses 39(K), 41(K), 43(Ca) and 41.5 [(40Ca43Ca)++] taken at a mass resolution, M/ΔM ∼ 5,000.
in meteoritic as well as terrestrial analog phases by using high primary current and long acquisition time at mass 41.5 to achieve reasonable precision. The position of the [\(^{40}\text{Ca}^{43}\text{Ca}\)^{++}] peak could be easily identified in perovskite and can be accurately located in the case of other phases (mellilite, fassaite and hibonite) based on the \([^{40}\text{Ca}^{27}\text{Al}^{16}\text{O}]^{++}\) peak that is separated from the \([^{40}\text{Ca}^{43}\text{Ca}]^{++}\) peak by 0.009 amu (see Fig. 2.6). We have obtained the values for the \([^{40}\text{Ca}^{43}\text{Ca}]^{++}/^{43}\text{Ca}^{+}\) ratio for all the analyzed mineral phases, as one could expect a dependence of this ratio on the matrix composition (Hutcheon et al., 1984). The measured values for this ratio in terrestrial and meteoritic phases are shown in Fig. 2.7. Except for hibonite, the values for the other mineral phases are very close to each other. The results shown in Fig. 2.7 clearly demonstrate our ability to reproduce this ratio in all the analyzed mineral phases and we can use the measured values with confidence for the correction of the \([^{40}\text{Ca}^{42}\text{Ca}]^{++}\) interference.

Possible contribution to the signal at mass 41 due to scattering from the hydride peak was generally monitored by obtaining the count rate at mass \((^{i}\text{Ca} - \Delta M)\) or \((^{i}\text{Ca} - \Delta M)\) where \(\Delta M\) is given by the relation:

\[
\Delta M = \frac{i}{41} \cdot M(\^{40}\text{Ca}H) - M(\^{41}\text{Ca}) \geq 0.009\text{amu} \tag{2.6}
\]

where \(i = 42, 43\).

The contribution due to scattering from the \(^{40}\text{Ca}H^{+}\) peak towards signal at mass 41 is estimated as:

\[
\left[^{40}\text{CaH}\right]_{\text{tail}} (c/s) = \text{signal at } (^{i}\text{Ca} - \Delta M) (c/s) \cdot \frac{^{40}\text{CaH}^{+}}{^{40}\text{Ca}^{+}} \tag{2.7}
\]

where \(i = 42, 43\).
Figure 2.7: $[^{40}\text{Ca}^{43}\text{Ca}]^{++}/[^{43}\text{Ca}]^{+} \times 10^{-5}$ ratio for different terrestrial (filled symbols) and meteoritic (open symbols) phases.
In the case of Efremovka CAIs this contribution was found to be < 5% of the total signal at mass 41 except in a couple of cases. A major improvement on experimental procedure made during this study is the approach used to analyze single grains of refractory phases using the epoxy bead mounting method. With a smaller volume of epoxy in these beads compared to standard one inch diameter epoxy mounted polished section for the Efremovka CAIs, we found a very significant reduction in the hydride signal, and the \( (^{40}\text{CaH})^+ \) and \( (^{41}\text{K})^+ \) peaks were fully resolved (Fig. 2.8). Because of this, the contribution of the scattering from \( (^{40}\text{CaH}) \) peak to \(^{41}\text{K} \) count rate became negligible in most of the single grain analysis. However, as a matter of precaution, the hydride tail was monitored in all the isotopic analysis. The background of the counting system was checked in both static and dynamic mode of operation. In the static mode the system background was always < 0.005 c/s. The dynamic background of the counting system was monitored by including mass 40.7 (acquisition time 30 s) during analysis of terrestrial phases. It was found to be somewhat higher than the static background and had a value of < 0.01 c/s.

Potassium isotopic analysis was carried out by cycling the magnet through the masses, \(^{39}\text{K}, ^{41}\text{K}, ^{40}\text{CaH}, (^{42}\text{Ca} - \Delta M ; \text{if necessary}), ^{42}\text{Ca}, (^{43}\text{Ca} - \Delta M) \) and \(^{43}\text{Ca} \) in the peak-jumping mode. The peak center for \(^{41}\text{K} \) could be ascertained accurately from the \(^{40}\text{CaH} \) peak. The counting times at masses \(^{39}(^{39}\text{K}) \) and \(^{41}(^{41}\text{K}) \) were typically 30-45 and 60-90 seconds, respectively. The counting time at mass \((^{42}\text{Ca} - \Delta M) \) or \((^{43}\text{Ca} - \Delta M) \), used for monitoring the hydride contribution, was typically 10 s. Each analysis consisted of 10-12 blocks of 5-6 cycles each, which lasted for a duration of 90 to 120 minutes. The data reduction was done on block level basis. The value of \((^{41}\text{K}^+ / ^{39}\text{K}^+)_{\text{true}} \) was evaluated for each block of data in a given analysis and the resultant data set was used to get the mean value and associated uncertainties for the analysis. The \([^{40}\text{Ca}^{42}\text{Ca}]^{++} \) correction at block level was based on the independently determined value for \([^{40}\text{Ca}^{43}\text{Ca}]^{++} / ^{43}\text{Ca}^+ \) in meteoritic and terrestrial analog phases.
(Fig. 2.7) and the measured $^{42}\text{Ca}^+/^{39}\text{K}^+$ values for each block. The contribution due to scattering from the hydride peak was corrected by using the mean value of $[^{42}\text{Ca-}\Delta M]^+/^{42}\text{Ca}^+$ or $[^{40}\text{Ca-}\Delta M]^+/^{43}\text{Ca}^+$ for the whole analysis and the $[^{40}\text{CaH}]^+/^{39}\text{K}^+$ ratio for each block.

Studies of K-Ca isotopic systematics using ion microprobe involve the determination of the relative sensitivity factor (relative ion yield) for K and Ca in suitable terrestrial analogs of the meteoritic phases. We have analyzed specially prepared samples of pyroxenes and anorthositic glass with high Ca/K ratios to obtain this value. The results obtained by us are shown in Table 2.3. The value of the relative sensitivity factor $\lambda$, defined as $[(^{39}\text{K}^+)^{/^{40}\text{Ca}^+}]/(^{38}\text{K}^+/^{40}\text{Ca})$, obtained from analysis of the anorthositic glass is somewhat lower than those from pyroxenes and suggests a possible matrix-dependent effect. As most of the analyzed meteoritic phases are pyroxenes and have Ca/K values higher than the anorthositic glass, we have used the mean value of 3.2 for the sensitivity factor for obtaining Ca/K ratios. We note here that in determining the $^{39}\text{K}^+/^{40}\text{Ca}^+$ ratio for the pyroxene with extremely low K content (CAI-PX-1), we faced the problem of contribution from K external to the sample. The $\lambda$ value for this sample given in Table 2.3 is based on the measured $^{39}\text{K}^+/^{40}\text{Ca}^+$ ratios close to (and including) the lowest value obtained for this pyroxene. In the absence of standard samples of perovskite, hibonite and melilite with known Ca/K ratios, we have used a $\lambda$ value of 3.2 for these phases also.
Figure 2.8: High mass resolution spectra around mass 41 taken for samples in standard one inch epoxy mounts and ~ 2 mm epoxy bead in Aluminium discs for: (a) Perovskite, (b) Hibonite. Strong suppression of the hydride signal in the epoxy bead mount is clearly evident.
Table 2.3. Relative yield factor (λ) for K-Ca isotopic analyses

<table>
<thead>
<tr>
<th>Sample*</th>
<th>K (ppm)</th>
<th>Ca/K</th>
<th>λ***</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyroxene 1</td>
<td>8</td>
<td>2.1 x 10^4</td>
<td>3.34 ± 0.19</td>
</tr>
<tr>
<td>(Ti-Px-1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyroxene 2</td>
<td>0.06</td>
<td>3.0 x 10^6</td>
<td>3.05 ± 0.20</td>
</tr>
<tr>
<td>(CAI-Px-1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anorthositic Glass</td>
<td>17</td>
<td>8.6 x 10^3</td>
<td>2.47 ± 0.10</td>
</tr>
<tr>
<td>An-Mg-5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Samples prepared at Caltech (Courtesy I.D. Hutcheon).
**Relative yield factor favouring K. Errors are 2σ.

In order to ensure that the procedure adopted by us for K-Ca isotopic studies of meteoritic phases with high Ca/K (>10^6) can provide accurate 41K/39K ratios, we have analyzed a set of terrestrial minerals with Ca/K ratios varying over three orders of magnitude. The analyzed samples include Madagascar hibonite, perovskite, melilite, microcline (USNM # 143966), and pyroxenes (Ti-Px-1 and CAI-Px-1). The results obtained from this study are shown in Table 2.4 and Fig. 2.9. As in the case of determination of the sensitivity factor, the data for the pyroxene with lowest K content is based on a couple of analyses where the inferred 40Ca/39K ratio was close to the expected value of 3 x 10^6. The 41K/39K values in all the cases are close to the reference value of 0.072 (Garner et al., 1975), within the limits of our experimental uncertainties. As 40K is excluded from analysis routine, it is not possible to determine the fractionation corrected residual for 41K (i.e., δ 41K). However normal K isotopic composition was found for terrestrial minerals with Ca/K ratios ranging from 10^-4 to ~ 3 x 10^6 (Fig. 2.9), and suggests that isotopic mass fractionation in the case of potassium must be small (≤ a few per mil/amu). It may be noted that instrumental mass fractionation generally favours the lighter isotopes and as such it will tend to suppress the signal at 41K relative to 39K. On the other hand, since the meteorite samples analyzed by us include some coarse-grained CAIs that are considered to be evaporative residues.
Figure 2.9: K isotopic composition of terrestrial standards with extreme variations in Ca/K ratios. The solid line denotes normal K isotopic composition (\(^{39}\text{K}/^{39}\text{K} = 0.072\)).
(e.g., MacPherson et al., 1988), one may expect an enrichment of the heavy isotope \(^{41}\text{K}\) relative to \(^{39}\text{K}\). However, the magnitude of instrumental mass fractionation in ion microprobe is generally more than that of intrinsic mass fractionation and as the measured isotopic ratios in all the terrestrial phases are close to the reference value, we have neglected any possible effect of isotopic mass fractionation in analyzing the \(\text{K}\) isotopic data. We note here that a value of \(\sim 4\) per mil per amu for instrumental mass fractionation has been reported recently by Humayun and Clayton (1995) who have analyzed \(\text{K}\) isotopic compositions in a variety of terrestrial and meteorite samples using an ion microprobe. The measured normal potassium isotopic compositions in the terrestrial phases (Fig. 2.9) also provide credence and validity to the approach used by us to correct the hydride, the doubly charged calcium interferences as well as the absence of other doubly charged interferences under our instrument operating conditions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of analyses</th>
<th>(^{40}\text{Ca}/^{40}\text{K})</th>
<th>(^{41}\text{K}/^{39}\text{K})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microcline*</td>
<td>1</td>
<td>(1.3 \times 10^{-3})</td>
<td>(0.0723 \pm 0.0008)</td>
</tr>
<tr>
<td>Melilite†</td>
<td>1</td>
<td>(4.3 \times 10^{-3})</td>
<td>(0.072 \pm 0.0005)</td>
</tr>
<tr>
<td>Madagascar Hibonite</td>
<td>2</td>
<td>(6.2 \times 10^{-3})</td>
<td>(0.0723 \pm 0.0007)</td>
</tr>
<tr>
<td>Anorthositic Glass** (An-Mg-5)</td>
<td>2</td>
<td>(8.6 \times 10^{-3})</td>
<td>(0.0726 \pm \ldots)</td>
</tr>
<tr>
<td>Pyroxene 1** (Ti-Px-1)</td>
<td>2</td>
<td>(1.7 \times 10^{3})</td>
<td>(0.0731 \pm 0.0005)</td>
</tr>
<tr>
<td>Pyroxene 2** (CAI-Px-1)</td>
<td>3</td>
<td>(3.0 \times 10^{3})</td>
<td>(0.073 \pm 0.0008)</td>
</tr>
<tr>
<td>Perovskite†</td>
<td>4</td>
<td>(4.5 \times 10^{6})</td>
<td>(0.072 \pm 0.006)</td>
</tr>
</tbody>
</table>

**Samples prepared at Caltech (Courtesy I. D. Hutcheon).
†Sample obtained from Vernadsky Institute, Moscow.