

Ion Microprobe Evidence for the Presence of Excess ^{26}Mg in an Allende Anorthite Crystal

J. G. BRADLEY,¹ J. C. HUNEKE, AND G. J. WASSERBURG

*The Lunatic Asylum of the Charles Arms Laboratory, Division of Geological and Planetary Sciences
California Institute of Technology, Pasadena, California 91125*

An ion microprobe has been used to observe $^{26}\text{Mg}/^{24}\text{Mg}$ in excess of normal values in anorthite crystals from Allende refractory inclusions. In one crystal, ^{26}Mg excesses up to 40% above normal, correlated with Al/Mg, were observed. These excesses are many times larger than those observed by other techniques. The correlation with Al/Mg indicated that the excess ^{26}Mg in the Allende anorthite is uniformly distributed in the anorthite crystal. Analytical procedures and conditions were carefully controlled. Nevertheless, small but significant apparent $^{26}\text{Mg}/^{24}\text{Mg}$ anomalies in isotopically normal samples were observed in analyses by one ion microprobe. A repetition of the isotopic analyses using another ion probe produced normal ratios in the normal samples and confirmed large ^{26}Mg excesses in the Allende anorthite.

INTRODUCTION

Lee and Papanastassiou [1974] and *Gray and Compston* [1974] demonstrated the existence of isotopic anomalies in Mg in some Ca-Al rich chondrules of Allende meteorite that could not be attributed to mass fractionation. *Lee et al.* [1976] demonstrated clearly that these anomalies could be ascribed to excess ^{26}Mg ; they observed ^{26}Mg excesses as large as 1.3% in high $^{27}\text{Al}/^{24}\text{Mg}$ phases. Most of the analyses were obtained by thermal ionization mass spectrometry of Mg chemically extracted from minerals. Some data were obtained by thermal ionization of Mg from single grains loaded directly on mass spectrometer filaments [*Lee et al.*, 1976]. These techniques require very careful separation of high-Al/Mg minerals from low-Al/Mg minerals in order to observe the largest possible ^{26}Mg excesses, the reward being high-precision analyses for the Mg isotopic composition. It is desirable to analyze the phases with the highest Al/Mg to define more precisely the correlation between ^{26}Mg excess and $^{27}\text{Al}/^{24}\text{Mg}$. The techniques used are somewhat limited, in the magnitude and precision of the effects that can be observed, by the following: difficulty in identifying rare grains with high Al/Mg, coupled with major manipulative difficulties in separating and transferring very small grains with high Al/Mg from surrounding material with low Al/Mg; inability to obtain an accurate Al/Mg ratio and Mg isotopic composition in high-Al/Mg grains which may have low-Al/Mg inclusions; and often, inability to analyze the same material for Al/Mg and Mg isotopic composition. Spatial information about possible zoning in ^{26}Mg excesses or Al/Mg in a single grain is difficult to obtain. Analysis of high-Al/Mg material with an ion microprobe seemed desirable and feasible because of the special analytical capabilities of the instrument. It was recognized that the analyses would be limited to high-Al/Mg phases because of the relatively lower precision of isotopic analyses by the ion microprobe.

Previous experience [*Meyer et al.*, 1974] indicated that the high sensitivity of an ion microprobe for Mg in an oxidized mineral matrix using an $^{18}\text{O}^-$ primary beam would permit measurement of Mg concentrations and isotopic ratios with useful precision well below 100 ppm of Mg. Isotopic ratios of greater than about 0.1 should be readily measurable in an ion microprobe analysis to an accuracy of about 1% so that ^{26}Mg

anomalies of a few percent could be identified. Finally, the spatial resolution of an analysis on a sample is typically $\sim 10\text{--}20\ \mu\text{m}$. This spatial resolution permits ion microprobe analysis of some grains where low-Al/Mg inclusions prevent analysis by other techniques.

The presence of Na in some Allende inclusions has been known for some years. Concentrations of Na from 271 to 8329 ppm by weight in bulk refractory inclusions have been reported by *Grossman and Ganapathy* [1975], but these measurements probably reflect mainly the Na in nonanorthite phases. It was considered useful to make the Na concentration measurements with the ion microprobe to establish the concentration in the anorthite alone.

A number of possibly significant analytical problems were anticipated on the basis of previous experience, and procedures were developed and used to control and understand these problems. The anticipated problems were (1) the presence of specular and continuum scattered secondary ion background; (2) uncertain correspondence between observed secondary ion elemental intensities and concentration of the corresponding elements in the sample; (3) the presence of mass spectral interferences such as $^{48}\text{Ca}^{2+}$ at the same position as $^{24}\text{Mg}^+$; (4) the presence of unpredicted and uncontrolled mass spectral interferences from sample surface contamination by hydrocarbons, Mg, or Na; (5) mass discrimination in isotopic ratio determinations; and (6) the possible day-to-day variability of any of the above problems.

The Applied Research Laboratory's (ARL) ion microprobe mass analyzer (Imma) [*Liebel*, 1967] was used for all the analyses reported here. The analyses of 1976 were done on the instrument in the Probe Applications Laboratory at ARL in Sunland, California. The analyses of 1977 were done on the Imma in the Geochemistry Branch of the NASA Johnson Space Center in Houston, Texas.

SAMPLE DESCRIPTION

Samples from two Allende inclusions were analyzed in the 1976 experiment series. In order to limit the variability of the analyses, each of the repeat ion probe analyses was done within well-defined $\sim 50\text{-}\mu\text{m}$ -diameter regions of the samples. One sample analyzed was a chip from a chondrule (BG3-13) which contained a large clear anorthite grain ($\sim 100 \times 300\ \mu\text{m}$) which was polished to expose a $\sim 200\text{-}\mu\text{m}$ length. The other Allende samples were a large ($\sim 500\ \mu\text{m}$) and a small anorthite grain from another chondrule (WA of *Chen and Tilton* [1976]).

¹ Now at Atomic International, Canoga Park, California 91304.

The large WA anorthite crystal showed very few visible defects or inclusions, and these were easily avoided during analysis. The crystal showed numerous incipient fractures along certain axes, and not all of these fractures could be avoided in the ion probe analyses. The 1977 experiment series included spinel from the Allende WA chondrule (WAS) and C1 chondrule (C1S). The C1 spinel is known to be heavily mass fractionated in its Mg isotopic composition [Wasserburg *et al.*, 1977]. Lee *et al.* [1976, 1977] and Wasserburg *et al.* [1977] discuss these samples more fully.

Because of the anticipated analytical difficulties a number of control samples with known normal isotopic composition and/or with very low Mg concentrations were included. These were a large red, gem-quality Burma spinel (BS) (MgAl_2O_4); a large clear chip of labradorite (An_{67}) from Lake County, Oregon (LC); a clear 100- μm anorthite crystal (An_{91}) from the Moore County achondrite (MC); a chip from a high-purity synthetic sapphire crystal (Al_2O_3); a length of 99.999% pure Al wire; and crystals of reagent grade NaCl. The BS, LC, and MC samples were used as standards for Mg isotopic ratios and for Al/Mg. The LC and MC samples were used as standards for Na/Al. The Al_2O_3 and Al were assumed to have Mg at a far lower concentration than that in the mineral samples and were used to determine the presence of possible surface contaminant hydrocarbons, Na, and Mg and to establish the shapes of specular and continuum scattered ion artifacts in the mass 23–27 secondary ion spectrum. The NaCl was used to determine the presence and shape of the specular scattered $^{23}\text{Na}^+$ peak; the shape of the uncontaminated low-mass tail of the $^{23}\text{Na}^+$ peak was used to infer the shape of the low-mass tail of the $^{27}\text{Al}^+$ peak.

With the exception of the aluminum wire, sapphire, and NaCl crystals, all the samples were potted in epoxy in brass sleeves, hand-polished on SiC paper to expose the desired regions, and then hand-polished with 1- and 0.3- μm alumina powder in tap water to give a smooth finish under $\times 100$ magnification. The sapphire was sufficiently flat that it was polished only with the alumina powders in water. The NaCl crystals were mounted as described above but were cleaned of surface adhesives and epoxy residues by dry rubbing with clean cellulose tissues. The aluminum wire was swaged into a stainless steel sleeve, sheared to the height of the sleeve, and polished with alumina in water. After polishing, the mounted samples (except NaCl) were cleaned by ultrasonic agitation in distilled water, then a few seconds in methanol, and then in distilled water again and were air-dried. The cleaned samples were then coated with ~ 200 Å of Au in a glow discharge sputter coater to provide a conducting surface to control surface charging and ion probe optical properties.

ANALYTICAL PROCEDURES

Most of the ion probe data presented here were obtained in 1976 on five separate occasions over a period of 3½ months. On four occasions, both chemical and isotopic analyses were done; on November 10, 1976, only chemical analyses were performed. During 1 week of June 1977 a limited set of analyses was performed to help clarify some of the analytical problems experienced in the earlier work. The 1976 data are presented with chronological labels to emphasize the repeatability of results despite physical changes in the Imma and repolishing of samples between analyses.

When chemical and isotopic analyses of a sample were performed together, $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$, $^{27}\text{Al}^+ / ^{23}\text{Na}^+$, $^{26}\text{Mg}^+ / ^{24}\text{Mg}^+$, and $^{26}\text{Mg}^+ / ^{24}\text{Mg}^+$ were normally determined simultaneously

from multichannel scaling (MCS) of repeated sweeps from mass 23 through mass 27. A single such analysis on any sample in 1976 consisted of (1) raster scanning the $^{16}\text{O}^-$ primary beam to sputter away the Au sample coating and surface contaminants in a 50- to 100- μm -square pattern larger than the 10- to 30- μm primary beam size; (2) allowing the stationary primary beam to establish stable analytical conditions at the point of interest; (3) making one to 10 slow (0.1 or 0.5 s/channel) magnetic sweeps of the (usually) mass 22.5–27.5 region and storing detected secondary ion counts in 256 computer locations representing that mass range; and (4) printing and plotting the accumulated data to permit assessment of their quality. A single determination containing any number of sweeps then appeared as a single mass scan. This MCS accumulation procedure was normally followed by hand tuning to selected mass peaks and counting the secondary ion intensities to determine the intensity of possible interferences in the mass 23–27 region (e.g., $^{48}\text{Ca}^{2+}$) and quantitatively to confirm that the point of analysis had the appropriate expected composition (plagioclase, spinel, etc.). The analyses of July 28 were not preceded by the raster cleaning of the analysis areas.

The beam intensities for the chemical analyses of November 10, 1976, were determined by hand tuning to the masses of interest and counting the ion intensities one to five times for 1 s each, the magnetic field being static.

A 1977 analysis was similar to the 1976 analyses except that the dwell time was 0.01 s/channel, 4096 channels were used to cover the mass range of interest, and up to 60 sweeps were accumulated to make one determination.

All 1976 analyses were done with a $^{16}\text{O}^-$ primary beam of 21.5-keV impact energy and with 10- to 20-nA current focused into a 10- to 30- μm -diameter spot on the sample. The 1977 analyses were with 1–2 nA of O^- of 18.5-keV impact energy focused into a 15- μm spot. The alignment of the primary beam with respect to the secondary ion mass spectrometer was kept as constant as possible from day to day, since it was known that detected elemental ratios can vary greatly with primary beam position in the Imma ion microprobe [Bradley *et al.*, 1975]. The cold plate above the sample analysis position was kept well chilled with liquid nitrogen to minimize sample contamination from the vacuum environment.

Each day's analyses in 1976 included (1) the analysis of BS to assess the secondary ion mass spectral peak shapes, to set the mass range for multichannel scaling, to calibrate $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$, and to establish the absence of severe mass discrimination; (2) the analysis of Al or Al_2O_3 to determine the 'background' spectrum and low-mass scattered peak shapes in the mass 23–26 region; (3) the analysis of LC and/or MC to calibrate $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ and $^{27}\text{Al}^+ / ^{23}\text{Na}^+$, to determine the apparent $^{26}\text{Mg}^+ / ^{24}\text{Mg}^+$ and $^{26}\text{Mg}^+ / ^{24}\text{Mg}^+$ in plagioclase where the Mg has normal isotopic composition and low concentration, and to establish the shapes and positions of specular and continuum scattered ion artifacts; and finally (4) the analysis of the Allende samples. The 1977 analyses omitted most of the daily controls, since it was not necessary to create as coherent or consistent a data set as the earlier work.

During a single day's analyses in 1976, primary and secondary ion beam operating conditions were kept as constant as possible, but from day to day, primary beam current and spot sizes varied by more than a factor of 2. Secondary ion mass spectrometer mechanical adjustments were the same each day, but the electrical tuning adjustments were the same only to the extent that they were reproduced by qualitative tuning.

Because the 1977 analyses were done on an Imma with a

multichannel scaling system showing a dead time of ~ 140 ns (as opposed to the 30-ns dead time of the Imma used in 1976), the dynamic range of useful count rates was limited, and it was necessary to use different angle and energy band-pass limiting aperture sizes for Mg isotopic measurements at low concentration (e.g., plagioclase) and high concentration (e.g., spinel). This change could produce systematic differences in the relationship between the observed secondary ion ratios and the elemental concentrations in the sample under the two conditions [Bradley *et al.*, 1975]. There was no reason to believe that observed isotopic ratios would be different under the two conditions; this seems to have been confirmed by the Mg isotopic measurements.

All analyses were interfered with by scattered ions from $^{27}\text{Al}^+$, $^{28}\text{Si}^+$, $^{29}\text{Si}^+$, and $^{23}\text{Na}^+$ through the mass 23–27 region. The scattered ion features of concern here are produced by specular and diffuse reflection of major element ion beams from structures within the secondary ion mass spectrometer near the collector slit. Specular scattering produces peaklike artifacts in the mass spectrum. The reflected ions which pass through the collector slit are confused with ions properly at that position. For the 1976 analyses, efforts were made to eliminate the scattered peaks by mechanical modifications to the Imma, but the improvement was minimal. Researchers using this instrument for quantitative analysis should take great care to identify the shapes, positions, and intensities of the scattered ion peaks on both the high- and the low-mass sides of an intense ion signal.

During the 1976 analyses the relative positions of scattered and true ion peaks were shifted by electrical deflection to eliminate the near-perfect superposition of scattered and true peaks. This deflection was achieved by applying a small dc potential ($\sim 5\%$ of sweep range) to the secondary ion electrical mass scan plates directly in front of the detector slit. The value of deflection potential was qualitatively selected to keep some portion of the $^{27}\text{Al}^+$, $^{28}\text{Si}^+$, and $^{23}\text{Na}^+$ specular scattered peaks visibly separated from the $^{24}\text{Mg}^+$, $^{25}\text{Mg}^+$, and $^{26}\text{Mg}^+$ true peaks, respectively. This deflection was not found necessary for the 1977 analyses because the specular scattered peaks were in well-separated positions relative to the Mg, apparently because of hardware differences between instruments.

DATA REDUCTION

Except for the chemical analyses of November 10, 1976, all of the data on Na, Mg, and Al were obtained by synchronizing the sweeping of the Imma magnetic field and the stepping through the channels of a multichannel scaler system while storing ion counts over the mass range of interest. The raw original data are a computer listing of the counts accumulated in each channel and a computer-generated plot of the counts in each channel versus channel number; the plot was usually logarithmic in counts because of the very large range of observed counts.

The raw secondary ion intensities at a mass number are the hand- or computer-calculated count rates determined by summing the counts in the five to 40 channels representing the flat top of an ion peak and by dividing by the total counting time in these channels (dwell time per channel \times number of channels \times number of sweeps). The total counting time in a mass peak varied from 0.7 to 12.6 s. The count rates determined in this manner are, in theory, independent of irregularities in magnetic field sweep rate and the number of channels chosen as long as all the selected channels are from a constant intensity (flat) portion of a peak top. All the 1976 data were

derived from the same number of adjoining channels (5–8) on each peak top in a 256-channel scan that gave the highest total counts. The number of channels summed in a peak top in the 1977 data often varied by ± 1 in 20 or 30 in a 4096-channel scan because computer data reduction was used to handle the large number of channels involved; the channels for summing were visually chosen from an electronic graphical display as representing a central flat portion of the peak. All reported count rates have been corrected for counting system dead-time losses.

The mass 24 count rates in plagioclase have been corrected for the contribution of $^{46}\text{Ca}^{2+}$ count rates. The $^{46}\text{Ca}^{2+}$ rates were determined on the basis of the $^{40}\text{Ca}^{2+}$ or $^{44}\text{Ca}^{2+}$ count rates observed on the sample on the same day under the same conditions that the MCS data were obtained. The correction was calculated by assuming $^{46}\text{Ca}/^{40}\text{Ca} = 1.86 \times 10^{-3}$ or $^{46}\text{Ca}/^{44}\text{Ca} = 8.2 \times 10^{-2}$ (Chart of the Nuclides). The correction was always less than 5% of the $^{24}\text{Mg}^+$ intensity in any sample (the worst cases were MC and WA). A value of $^{27}\text{Al}^+ / ^{46}\text{Ca}^{2+} = 5 \times 10^{-5}$ was typical, some variation being appropriate to different plagioclase compositions. The total count in the $^{40}\text{Ca}^{2+}$ or $^{44}\text{Ca}^{2+}$ peak used to correct the data was always large enough that the counting statistical error in the $^{46}\text{Ca}^{2+}$ correction to any $^{24}\text{Mg}^+$ intensity was $< 0.1\%$ of the $^{24}\text{Mg}^+$.

The secondary ion spectrum from all samples analyzed was quantitatively checked for ion intensities at mass 12, 12.5, 13, 50, and 52 to rule out other possible sources of interferences at mass 24, 25, and 26, such as $^{60}\text{Ti}^{2+}$, $^{60}\text{Cr}^{2+}$, $^{27}\text{Al}^{23}\text{Na}^{2+}$, $^{52}\text{Cr}^{2+}$, $^{29}\text{Si}^{23}\text{Na}^{2+}$, and $^{12}\text{C}_2^+$. All intensities were determined to contribute $< 0.1\%$ to any mass 24, 25, or 26 intensity.

Where Na and Mg concentrations were low and their concentrations and the Mg isotopic composition were to be determined, careful corrections had to be made for diffuse scattered ion background and counting system noise, major element peak tails, and specular scattered peaks. The shapes of major element peak tails were determined to be smooth on the high- and low-mass sides by examination of the peaks from pure NaCl, Al, and Al_2O_3 . The shapes and approximate positions of specular scattering features from $^{23}\text{Na}^+$, $^{27}\text{Al}^+$, and Si^+ were determined by studies of NaCl, Al, Al_2O_3 , and plagioclase samples. It was determined that the specular features on the low-mass side of each major peak had the same shape. Similarly, all high-mass specular features had the same shape. The maximum intensity of a specular peak was typically 1×10^{-4} of the parent peak intensity. Corrections to a particular peak were made by subtraction of interpolated background where the background was smooth or by subtraction of a reconstructed specular feature where one was observed. The corrections for specular peaks were made only to the extent that they were qualitatively visible in the graph of the MCS data and could be quantitatively reconstructed from the digital print-out.

A worst case correction problem for mineral analysis is illustrated in Figure 1 for Moore County. Note that the ordinate is logarithmic in counts, but the intensity above 4 log units of the $^{23}\text{Na}^+$ signal has been offset by $\times 100$ (2 log units), and the $^{27}\text{Al}^+$ by $\times 1000$ (3 log units) in this computer-generated plot. The specular $^{27}\text{Al}^+$ and $^{23}\text{Na}^+$ are drawn in at their actual magnitude as reconstructed from their visible parts in the plot. There are $^{28}\text{Si}^+$ and $^{29}\text{Si}^+$ scatter peaks under the mass 25 and 26 positions, but they are not drawn or subtracted from the Mg^+ peaks, since they cannot be distinguished from the general diffuse background; other scans of plagioclase samples

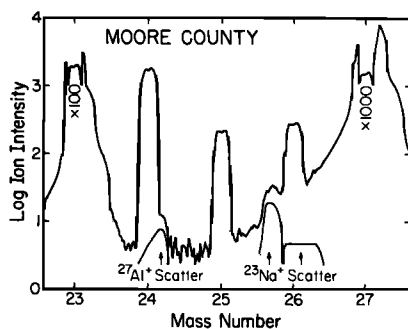


Fig. 1. Moore County mass spectrum from mass 23–27. The positions and approximate intensities of the $^{27}\text{Al}^+$ and $^{23}\text{Na}^+$ scattered ion intensities are shown. There is also a $^{28}\text{Si}^+$ scatter peak about one-third the intensity of the $^{27}\text{Al}^+$ scatter peak located under the mass 25 position but not shown here. Note the logarithmic intensity scale and the offset of the highest intensities of the $^{23}\text{Na}^+$ and $^{27}\text{Al}^+$ peaks by 2 log units and 3 log units, respectively. Corrections applied to these Moore County data are summarized in Table 1.

show the $^{28}\text{Si}^+$ scatter peak to be about one-third the intensity of the $^{27}\text{Al}^+$ scatter peak. The $^{23}\text{Na}^+$ scatter peak was visible above the $^{27}\text{Al}^+$ peak tail and was a significant interference at mass 26 only for LC and MC samples ($^{23}\text{Na}^+ / ^{24}\text{Mg}^+ = 100$).

A summary of the corrections to these MC data is given in Table 1. The errors stated with the corrections are estimated to be $\pm 2\sigma$ (95% confidence limit) on the basis of counting statistics and/or the uncertainty in interpolating or reconstructing the background feature. The largest background correction to any Mg isotope final intensity is the $9 \pm 1\%$ subtraction for the $^{27}\text{Al}^+$ tail and the $2 \pm 1\%$ subtraction for the $^{23}\text{Na}^+$ scatter peak from the $^{26}\text{Mg}^+$ peak. The $\pm 1\%$ associated uncertainties contribute to the final uncertainty in the $^{26}\text{Mg}^+$ intensity, but with only 7794 counts in the $^{26}\text{Mg}^+$ peak the 2σ counting statistical error of $\pm 2.2\%$ dominates. Errors due to counting statistics dominate errors due to background subtractions in all plagioclase analyses for Mg. In the 1977 analyses the scattering features were diffuse, and only smoothly interpolated background subtractions were made. In the case of analyses of Al and Al_2O_3 the background subtractions were as much as 50% of the raw $^{26}\text{Mg}^+$ peak heights.

TABLE 1. Summary of Corrections Applied to Moore County Data of September 27 Illustrated in Figure 1

Correction	Value, %
<i>Mass 24</i>	
Dead time	$< +0.1$
Diffuse background and $^{23}\text{Na}^+$ tail	-0.2 ± 0.1
$^{27}\text{Al}^+$ scatter peak	-0.2 ± 0.1
$^{48}\text{Ca}^{2+}$	-5.4 ± 0.1
<i>Mass 25</i>	
Dead time	$<< +0.1$
Diffuse background	-1.9 ± 0.5
$^{28}\text{Si}^+$ scatter peak	-0.6^*
<i>Mass 26</i>	
Dead time	$<< +0.1$
Diffuse background and $^{27}\text{Al}^+$ tail	-9 ± 1
$^{23}\text{Na}^+$ scatter peak	-2 ± 1

Errors stated with corrections are $\pm 2\sigma$ based on counting statistics and/or uncertainty in reconstructing background features.

*Estimated; correction not made, since peak features are not visible.

The intensities of major sample elements required only dead-time corrections. When Mg isotopic composition was being determined and Mg was a major element, the count rates were kept low enough to keep the dead time $< 10\%$.

ANALYTICAL RESULTS

Chemical Analyses

The work of Lee *et al.* [1976, 1977] established the contribution of ^{26}Al -decay-produced ^{26}Mg to be 50–60 ppm of the Al in certain Ca-Al rich Allende inclusions. This low level demands that phases with the highest possible $^{27}\text{Al}/^{24}\text{Mg}$ be analyzed to obtain the most precise measurement of the excess ^{26}Mg . Plagioclase is a common mineral in the inclusions and a good candidate for high $^{27}\text{Al}/^{24}\text{Mg}$. The results of our 1976 ion probe measurement of $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ and $^{27}\text{Al}^+ / ^{23}\text{Na}^+$ in four anorthite grains from Allende WA, one anorthite grain from Allende BG3-13, and standards LC, MC, and Al_2O_3 are presented in Table 2. The ion probe data are corrected as was described in the preceding section. The $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ and $^{27}\text{Al}^+ / ^{23}\text{Na}^+$ ratios given in Table 2 are calculated directly from corrected count rate data; no theoretical model was used to correct the observed intensities to actual bulk sample concentration ratios. Since there is no reason to believe that the observed $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ or $^{27}\text{Al}^+ / ^{23}\text{Na}^+$ represents the correct atomic concentration ratio in any given mineral or that the ratios should be proportional to concentrations through minerals of widely different compositions (e.g., spinel and anorthite), a comparison between ion probe ratios and those determined by other techniques was made. The results are presented in Table 3. The errors listed for the ion probe are $\pm 2\sigma$ in the mean of multiple determinations. The LC and MC ion probe and electron probe determinations of Al/Mg and Al/Na were made by analysis of the same material in each instrument. The agreement between the ion probe and other determinations of $^{27}\text{Al}/^{24}\text{Mg}$ is good to approximately the errors in the determinations, so we choose to let the measured $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ represent the atomic concentration in the samples. The ion probe $^{27}\text{Al}^+ / ^{23}\text{Na}^+$ is consistently about half of the electron probe $^{27}\text{Al}/^{23}\text{Na}$ ratio (which we assume to be the true value); in further discussions the distinction between the two will be kept clear. Table 4 is a summary of electron probe analyses for major elements in the various samples. In the case of the Allende anorthite, no quantitatively significant analyses for Na, Mg, K, Ti, Fe, or Ba were obtained because of their extremely low concentrations.

The analyses of Al_2O_3 given in Table 2 provide a measure of the contamination background at masses 23 and 24. If it is assumed that the Al_2O_3 has negligible ^{24}Mg and ^{23}Na in the bulk, the observed ratios are a quantitative indication of surface contamination by Mg or Na, of unsuspected scattered ion peaks, or of mass peaks of unknown source (e.g., hydrocarbons). Both Mg^+ and Na^+ signals decreased rapidly during the first minutes of cleaning, indicating that both are present as surface contaminants. The first $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ listed in Table 1 for Al_2O_3 analyses was measured with a much shorter than normal raster cleaning. The normal raster cleaning and burn-in of the primary ion beam yield $^{27}\text{Al}^+ / ^{24}\text{Mg}^+ \sim 10^5$ (mean of the last three measurements in Table 2) and $^{27}\text{Al}^+ / ^{23}\text{Na}^+ \sim 3 \times 10^6$. Thus for the highest $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ (MC) the background blank at mass 24 is only a 1% contribution to the sample $^{24}\text{Mg}^+$, and for the highest $^{27}\text{Al}^+ / ^{23}\text{Na}^+$ (Allende WA area 3) the background blank is only about 15% of the sample $^{23}\text{Na}^+$. Because of their small size, uncertain source, and variability,

TABLE 2. Summary of Chemical Analyses

Sample or Area	Date	Ratio of Count Rates		Count Rate $^{27}\text{Al}^+$, 10^6 c/s	Time, s		
		$^{27}\text{Al}^+ / ^{24}\text{Mg}^+$	$^{27}\text{Al}^+ / ^{23}\text{Na}^+$				
Lake County	mean	244 ± 20	2.8 ± 0.4				
Moore County	mean	980 ± 60	10.5 ± 1.6				
Allende BG3-13	July 28	256	ND	2.36	4.		
		258	ND	2.28	8.		
		266	ND	2.27	8.		
	Sept. 27	299	121	3.88	9.		
Allende WA	Large grain	Spot A	July 28	692	ND	3.11	8.
			Sept. 27	693	220	4.01	9.
	Area 1	Nov. 10	564	309	11.9	*	
		Nov. 12	436	193	13.4	*	
	Area 2	Nov. 10	550	222	5.31	10.5	
		Nov. 12	917	404	12.7	*	
	Area 3	Nov. 10	934	412	6.80	10.5	
		Nov. 12	552	219	14.3	*	
	Area 4	Nov. 10	502	212	12.6	*	
		Nov. 12	434	360	14.3	*	
	Area 5	Nov. 10	398	376	6.90	10.5	
		Nov. 12	594	226	14.2	*	
	Area 8	Nov. 10	912	271	7.08	10.5	
		Nov. 12	707	284	12.8	*	
	Area 9	Nov. 10	324	89	17.9	*	
		Nov. 12	336	134	6.40	10.5	
	Area 10	Nov. 10	315	106	13.7	*	
		Nov. 12	368	134	14.0	*	
	Grain 4, area 11	Sept. 24	12,000	3300	15.0	9	
		Nov. 12	40,000	1800	12.5	12.	
Grain 7, area 12	Sept. 27	130,000	2500	12.6	9.		
	Nov. 12	72,000	4700	12.6	9.		

ND, not determined. Data are corrected for dead time, counting system background, and scattered ions, and $^{24}\text{Mg}^+$ is corrected for $^{46}\text{Ca}^{2+}$. No mass discrimination or blank corrections have been applied.

*Beam intensities determined from one to five counting intervals of 1 s, static field being adjusted to mass of interest.

no blank corrections have been made to $^{24}\text{Mg}^+$ or $^{23}\text{Na}^+$ data. The arguments presented in this paper are not sensitive to small blank corrections.

The range of the WA analyses for $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ given in Table 2 is from 315 to 934, and that for $^{27}\text{Al}^+ / ^{23}\text{Na}^+$ from 89 to 412. An observed $^{27}\text{Al}^+ / ^{24}\text{Mg}^+ = 700$ corresponds to Mg ~ 325 ppm by weight in anorthite, and $^{27}\text{Al}^+ / ^{23}\text{Na}^+ = 250$ corresponds to Na ~ 330 ppm by weight in anorthite.

The observed range of elemental ratios in WA anorthite is not a statistical artifact. The standard deviation of the distribution of all WA $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ and $^{27}\text{Al}^+ / ^{23}\text{Na}^+$ analyses is about 40% of the mean, while for LC, MC, and BS the standard deviation of the distribution in $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ is <10% (a measure of the analytical variability). On any given day for the 1976 series the analytical conditions for all samples were kept

the same as possible. The analytical conditions from day to day varied considerably, yet the variation in elemental ratios was much greater in the WA analyses than in the LC, MC, or BS analyses done on the same days. Thus most of this variation is real and is not an artifact of the analytical technique. There is a tentative statistical correlation between the $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ and $^{27}\text{Al}^+ / ^{23}\text{Na}^+$ for all WA analyses ($r = 0.66$). If area 8 is excluded, the correlation coefficient improves to $r = 0.86$.

Figure 2 is a map of the large Allende WA grain showing the areas of analysis. The November 10 analyses were performed in these marked areas. The November 12 analyses were in areas immediately adjacent to the marked areas. The numerators in the fractions in the figure are $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$, and the denominators $^{27}\text{Al}^+ / ^{23}\text{Na}^+$. No chemical or isotopic analyses

TABLE 3. Comparative Analyses for $^{27}\text{Al} / ^{24}\text{Mg}$ and $^{27}\text{Al} / ^{23}\text{Na}$

Sample or Area	$^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ Ion Probe	$^{27}\text{Al} / ^{24}\text{Mg}$ Other	$^{27}\text{Al}^+ / ^{23}\text{Na}^+$ Ion Probe	$^{27}\text{Al} / ^{23}\text{Na}$ Electron Probe
Burma spinel	2.41 ± 0.16	2.53*		
Lake County	244 ± 20	230 ± 20†	2.8 ± 0.4	5.15
Moore County	980 ± 60	1460, 850‡	10.5 ± 1.6	20.6

*Inferred from assumed stoichiometry.

†Al from electron probe analysis; Mg from isotope dilution [Meyer et al., 1974].

‡Al from electron probe analysis; two Mg values from isotope dilution [Schramm et al., 1970].

TABLE 4. Summary of Electron Probe Analysis

Sample or Area	Na ₂ O	Al ₂ O ₃	SiO ₂	CaO	Sum*
Lake County	3.8	31.1	50.1	13.8	99.5†
Moore County	1.0	34.9	45.3	18.7	100.1
Allende BG3-13		35.8	42.3	20.2	98.6
Allende WA					
Large grain					
Area 2		35.5	43.6	21.0	100.4
Area 3		35.5	42.6	20.7	99.0
Area 8		35.6	43.5	20.9	100.4
Area 9		36.3	42.2	20.6	99.3
High-Mg area		17.9	41.3	25.3	100.1‡
Grain 4, area 11		34.1	41.7	20.1	96.1

*Unless it is otherwise noted, where the sum is not equal to the sum of listed concentrations, the remainder is round-off error and quantitatively insignificant amounts of Na, Mg, K, Ti, Fe, and Ba.

†K₂O ~ 0.1%, FeO ~ 0.5%, and MgO ~ 0.1%.

‡MgO = 10.4%, and TiO₂ = 5.1%.

were made with the ion probe in the high-Mg area outlined in Figure 2. The 2 days' analyses in a given area reproduce within about 20% except in area 9, where apparently, a variation of 50% in ²⁷Al⁺/²⁴Mg⁺ is present on a scale of 10–20 μm; internally consistent data checks indicate that the variation is again not an instrumental artifact. There is some indication of zoning in the large grain toward higher ²⁷Al⁺/²⁴Mg⁺ and ²⁷Al⁺/²³Na⁺ near areas A, 3, and 10. Many more carefully controlled analyses for ²⁷Al⁺/²⁴Mg⁺ and ²⁷Al⁺/²³Na⁺ on more WA anorthite material are necessary to understand the source, spatial relations, and correlation of the variability in both ratios.

It is possible that the range of apparent Mg concentrations in the WA large anorthite crystal might be the result of microscopic high-Mg inclusion such as spinel, but such inclusions are not obvious in this WA crystal under high magnification in reflected or transmitted light. The modestly good reproducibility of very low Mg concentrations at 10- to 20-μm-separated points suggests that the inclusions would have to be very small and rare or very uniformly distributed. A 1-μm-diameter

ALLENDE WA ANORTHITE
LARGE GRAIN

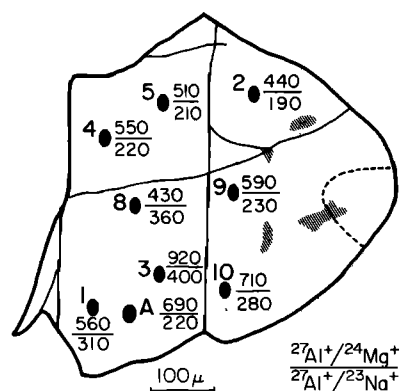


Fig. 2. Map of the large Allende WA anorthite grain showing areas of analysis on November 10, 1976 (July 28 and September 12 for area A). The dark ovals are about 1.5 times the 10-μm beam size used for analysis. The numerator of the fraction near each area is ²⁷Al⁺/²⁴Mg⁺, and the denominator is ²⁷Al⁺/²³Na⁺. The dashed line outlines an area of high Mg (>10%) associated with a nonanorthite mineral (probably fassaite). The shaded areas are 'holes' or rough spots. The grain is ~500 μm overall.

spinel grain imbedded in anorthite containing no Mg and analyzed by a 20-μm-diameter ion beam would give ²⁷Al⁺/²⁴Mg⁺ ~ 400, the lowest ratio observed in the WA large crystal.

Isotopic Analyses

A summary of the 1976 series of ion probe analyses of Allende WA, BG3-13, and standards BS, LC, and MC for apparent Mg isotopic composition and ²⁷Al⁺/²⁴Mg⁺ is given in Table 5. The columns giving isotopic ratios are labeled δ²⁶Mg⁺/²⁴Mg⁺ and δ²⁵Mg⁺/²⁴Mg⁺ and list the percentage by which the observed mass 25 to 24 and 26 to 24 intensity ratios deviate from the normal Mg values of 0.1266 and 0.1398 [Schramm *et al.*, 1970]. It must be recognized that the deviations need not be due to Mg isotopic variation but may be due to instrumental effects or especially to interferences of unknown identity appearing at the mass 24, 25, and 26 positions. These data are illustrated in Figure 3. In this figure and elsewhere we use 'δ²⁵Mg⁺' and 'δ²⁶Mg⁺' to represent δ²⁵Mg⁺/²⁴Mg⁺ and δ²⁶Mg⁺/²⁴Mg⁺, respectively. The error bars plotted are ±2σ in ion counting statistics except for BS, where the error bars are ±2σ in the distribution of measurements. Error bars are not plotted in ²⁷Al⁺/²⁴Mg⁺ because systematic variations greatly exceed counting statistics. The range of LC and MC data serves to indicate the systematic consistency of the elemental or isotopic ratios for all plagioclase analyses. The quantity ²⁷Al⁺/²⁴Mg⁺ is chosen for the units on the abscissa in Figure 3 to be consistent with Lee *et al.* [1976, 1977] and to normalize ion probe sensitivity. It must be realized that since all Allende analyses are on anorthite, there is no variation in Al concentration, and any other major element in anorthite could serve for sensitivity normalization in Figure 3. The normals LC and MC differ in Al content by only about 25%, while the Mg concentrations differ by 300%.

Normals Analyses

The BS, LC, and MC analyses establish a reference for comparison to the Allende data. The 1976 BS mean values of δ²⁶Mg⁺ = -2.3 ± 1.2% and δ²⁵Mg⁺ = -3.9 ± 1.6% (±2σ) indicate a possible mass discrimination in the isotopic measurements, but the presence of some bias due to inaccurate ion counting dead-time correction cannot be ruled out. The mass discrimination observed in this series of Mg measurements may be due to the antiscattering shims added near the secondary ion detector for this project. Because of an uncertainty as to the cause of these isotopic shifts and the limited variability of the shift in the BS sample we choose not to make a mass discrimination correction to any of the data in this paper. The presence of a fixed mass discrimination would represent a fixed shift in δ²⁶Mg⁺ and δ²⁵Mg⁺ independent of ²⁷Al⁺/²⁴Mg⁺ for all isotopic analyses and hence should not hinder our ability to distinguish 'normals' from Allende analyses for large effects.

The isotopic analyses of LC and MC for δ²⁵Mg⁺ and δ²⁶Mg⁺ are consistent with a small mass discrimination-like shift (0% to -2% per mass unit) in the ratios plus components of secondary ion intensity, Δ25_v⁺ and Δ26_v⁺, which are a fixed fraction of the normalizing ²⁷Al⁺ intensity (i.e., Δ25 and Δ26 at a fixed concentration in or on the sample). The Δ26⁺ intensity is conveniently calculated from observed intensities by the relation

$$\Delta 26^+ = [({}^{26}\text{Mg}^+ / {}^{24}\text{Mg}^+) - 0.1398]({}^{24}\text{Mg}^+ / {}^{27}\text{Al}^+)({}^{27}\text{Al}^+)$$

A similar expression holds for calculation of Δ25⁺. A fixed component Δ26⁺ or Δ25⁺ superimposed on a varying concen-

TABLE 5. Summary of Isotopic Results

Date	$^{27}\text{Al}^+ / ^{24}\text{Mg}^+$	$\delta^{26}\text{Mg}^+ / ^{24}\text{Mg}^+$, %	$\delta^{28}\text{Mg}^+ / ^{24}\text{Mg}^+$, %	$^{27}\text{Al}^+$, 10^6 c/s	Time, s	
<i>Burma Spinel (MgAl_2O_4)</i>						
July 28	2.71	-0.5	-1.4	4.17	4.	
	2.65	-0.9	-0.9	4.56	4.	
	2.72	+2.3	+0.5	4.73	0.8	
	2.62	-3.8	-4.1	4.76	4.	
Sept. 24	2.16	-2.2	-5.6	9.93	0.7	
	2.13	-3.6	-6.9	10.1	1.4	
	2.18	-3.7	-5.5	10.5	3.	
Sept. 27	2.29	-3.7	-3.7	6.71	3.	
	2.26	-3.4	-6.7	6.88	3.	
Nov. 12	2.37	-3.2	-4.6	3.32	7.	
Mean	2.41	-2.3	-3.9			
	± 0.16	± 1.2	± 1.6			
<i>Lake County Labradorite (An_{67})</i>						
July 28	264	-2.1	+4.8	2.33	4.	
	264	-1.7	+0.9	2.32	8.	
	263	-2.6	+3.3	2.28	8.	
	216	-3.5	+4.5	2.41	4.	
	243	-0.7	+2.9	2.30	8.	
Sept. 27	216	-1.7	+1.3	4.21	9.	
	244	-2.0	+3.0			
Mean	± 20	± 0.8	± 1.4			
<i>Moore County Anorthite (An_{91})</i>						
Sept. 24	960	-2.4	+6.2	5.00	3.	
	960	+0.9	+7.7	4.94	9.	
Sept. 27	940	+0.8	+11.7	5.22	9.	
Nov. 12	1050	+5.2	+18.3	15.1	10.5	
	980	+1.1	+11.0			
Mean	± 60	± 3.2	± 5.4			
<i>Allende BG3-13 Anorthite (An_{99+})</i>						
July 28	256	+1.5	+12.8	2.36	4.	
	258	-1.5	+13.6	2.28	8.	
	266	-0.7	+13.2	2.27	8.	
Sept. 27	299	+0.1	+12.7	3.88	9.	
	270	-0.2	+13.1			
Mean	± 20	± 1.4	± 0.4			
<i>Allende WA Anorthite (An_{99+})</i>						
Large grain Spot A	July 28	692	-3.3	+37.5	3.11	8.
	Sept. 27	693	+2.1	+39.8	4.01	9.
Area 2	Nov. 12	550	+2.7	+32.1	5.31	10.5
Area 3		934	+6.4	+51.2	6.80	10.5
Area 8		398	-0.3	+23	6.90	10.5
Area 9		912	+5.4	+44	7.08	10.5
Grain 4, area 11	Nov. 12	336	-1.7	+16.1	6.40	10.5

Data are corrected for dead time, scattered ions, and counting system background, and $^{24}\text{Mg}^+$ is corrected for $^{48}\text{Ca}^{2+}$. No mass discrimination or blank corrections have been applied. Individual measurements of $^{26}\text{Mg}^+$ and $^{28}\text{Mg}^+$ have a $\pm 2\sigma$ counting statistical uncertainty of less than $\pm 3\%$. Measurements of $^{24}\text{Mg}^+$ and $^{27}\text{Al}^+$ have proportionally less uncertainty. The errors attached to mean values are $\pm 2\sigma$ uncertainty in the mean.

tration of isotopically normal Mg will cause $\delta^{26}\text{Mg}^+$ or $\delta^{28}\text{Mg}^+$ to increase linearly with $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$.

The LC and MC $\delta^{26}\text{Mg}^+$ data groups define a 'two-point' linear array with an ordinate intercept of $\delta^{26}\text{Mg}^+ \sim -3.0\%$ and slope 0.5×10^{-6} ($^{26}\text{Mg}^+ / ^{24}\text{Mg}^+$ versus $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$). The intercept of -3.0% is consistent with the BS shift of -2.3% . The slope represents an average component $\Delta 25_N^+ \sim 0.5$ ppm of the $^{27}\text{Al}^+$ intensity which appears superimposed on $^{26}\text{Mg}^+$. The scatter in the data is sufficiently large that neither the slope nor the intercept is considered quantitatively significant.

The LC and MC $\delta^{28}\text{Mg}^+$ data define a two-point linear array with an ordinate intercept of $\delta^{28}\text{Mg}^+ \sim 0\%$ and slope 16×10^{-6} . The intercept is not consistent with the BS shift of

-3.9% . We interpret the inconsistency as an extreme of statistical variation in analyses of the samples. The slope represents an average component $\Delta 26_N^+ \sim 16$ ppm of the $^{27}\text{Al}^+$ intensity.

The $\Delta 25_N^+$ and $\Delta 26_N^+$ components are of concern if isotopic data from unknowns are to be compared with data of Lee *et al.* [1976, 1977]. The secondary ion mass spectrum was examined during each analysis for sources of matrix ions that might produce interferences at masses 25 and 26 (e.g., $^{50}\text{Ti}^{2+}$, $^{50}\text{Cr}^{2+}$, $^{27}\text{Al}^{23}\text{Na}^{2+}$, $^{52}\text{Cr}^{2+}$, $^{28}\text{Si}^{28}\text{Na}^{2+}$, and NaH_3^+), and none were identified with sufficient intensity to explain $\Delta 25_N^+$ or $\Delta 26_N^+$. We feel that the most likely explanation for the $\Delta 25_N^+$ and $\Delta 26_N^+$ components is hydrocarbon (HC) interferences (e.g., C_2H^+ and C_2H_2^+). The HC interpretation is consistent

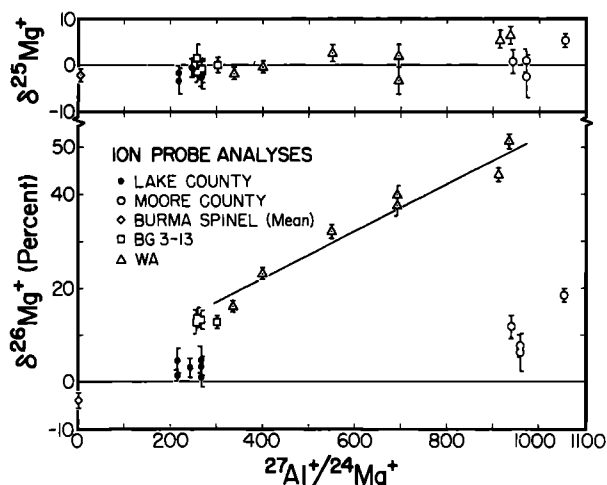


Fig. 3. Plot of 1976 Mg isotopic data showing correlation of excess mass 26 with $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ but no significant correlation between excess mass 25 and $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$. The Lake County and Moore County samples are known to have a normal Mg isotopic composition, so the excess mass 26 cannot be $^{26}\text{Mg}^+$ for these samples. The major portion of the excesses at mass 26 in the Allende samples can be attributed to $^{26}\text{Mg}^+$. The mean $\delta^{25}\text{Mg}^+$ and $\delta^{26}\text{Mg}^+$ observed for many Burma spinel determinations are plotted with $\pm 2\sigma$ in the distribution. The other error bars are $\pm 2\sigma$ in counting statistics. Error bars are not plotted for $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ because sources of systematic variation are not understood; the variability of the Lake County and Moore County data is a reasonable measure of precision in other data.

with the fact that it is common for HC spectra at low mass to show higher intensities at alternate mass position; thus a 'high' intensity at mass 26 is reasonably accompanied by a 'low' intensity at mass 25. The analyses of pure Al and Al_2O_3 summarized in Table 6 show nearly 10 times as much mass 26 excess as mass 25 excess (when it is assumed that mass 24 is only $^{24}\text{Mg}^+$), in rough agreement with the LC and MC data. The presence of a small interference (HC or other) at mass 24 would have the effect of reducing the apparent size of $\Delta 25_N^+$ and $\Delta 26_N^+$. The greater intensity of $^{24}\text{Mg}^+$ relative to $^{25}\text{Mg}^+$ and $^{26}\text{Mg}^+$ would make a mass 24 interference less apparent. For convenience we assume negligible interference at mass 24.

The analyses of June 1977 were made with the intent of clarifying the source of the isotopically anomalous results observed in the earlier analyses of BS, LC, and MC. It was hoped that the use of a different Imma would reveal which anomalies were sample related and which were instrument

related. The results of these analyses are summarized in Table 7 and Figure 4.

The isotopic composition of BS Mg was found to be within 1% of the normal, but there were possible small systematic errors causing the mean values to fall outside 2σ in the mean of five determinations. The counting statistics in the mass 25 and 26 peaks were $2\sigma = 0.5\text{--}0.6\%$. The dead-time corrections to the $^{24}\text{Mg}^+$ intensities were less than 5%.

The isotopic composition of LC Mg was within 2.5% of normal, although at the extremes of 2σ in the mean of three determinations. Counting statistics in the mass 25 and 26 peaks were $2\sigma = 1.7\text{--}3.2\%$. Dead-time corrections to the $^{27}\text{Al}^+$ intensities were up to 60%, so the mean $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ may be in error by $\pm 10\%$.

The isotopic composition of MC Mg was within 1% of normal and well within 2σ of the mean of seven determinations. Counting statistics in the mass 25 and 26 peaks were $2\sigma = 1.6\text{--}2.4\%$. The dead-time corrections to the $^{27}\text{Al}^+$ intensities were up to 150%, so only the range of $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ is reported.

Attempts were made to observe mass 24, 25, and 26 contaminants on the Al_2O_3 sample, but no peaks could be distinguished above background after a normal raster cleaning.

The normality of the isotopic compositions of BS, LC, and MC and a total lack of trends in apparent compositions with $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ indicate that the apparent isotopic anomalies observed earlier in these samples, and Al and Al_2O_3 , were probably a peculiarity of the analytical conditions associated with the analyses on the Imma at the ARL Probe Applications Laboratory. The interfering ions are not inherent within the samples, and this lends substance to the possibility of hydrocarbon contamination.

Allende Analyses

The 1976 analyses of Allende WA and BG3-13 anorthite for $\delta^{25}\text{Mg}^+ / ^{24}\text{Mg}^+$, as shown in Figure 3, are consistent with the normals analysis. The ordinate intercept of the normals plus Allende linear array is at $\delta^{25}\text{Mg}^+ \sim -3\%$, and the slope is 0.7×10^{-6} . Again, because of the scatter in the data, neither parameter is considered quantitatively significant.

The Allende WA analyses for $\delta^{26}\text{Mg}^+ / ^{24}\text{Mg}^+$, as shown in Figure 3, form a linear array, distinct from the normals, indicating a strong correlation between $\delta^{26}\text{Mg}^+$ and $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$. Enrichments of ^{26}Mg up to 50% above normal are apparent, of which a small fraction is due to an interference observed in normals. Six of the WA analyses are from five points on the single large crystal; the seventh point is from

TABLE 6. Summary of Analyses for Background

Sample	Date	$^{27}\text{Al}^+ / ^{24}\text{X}^*$	$^{25}\text{X}^* / ^{24}\text{X}^*$	$^{26}\text{X}^* / ^{24}\text{X}^*$	$^{27}\text{Al}^+$, 10^6 c/s	Time, s
Aluminum	July 28	1,500	0.1270	0.1517	6.72	4.
		6,000	0.1257	0.2311	6.78	4.
		8,700	0.1314	0.2477	6.89	4.
Sapphire (Al_2O_3)	Sept. 24	12,000	0.1425	0.2497	15.0	9.
		40,000	0.1561	0.5317	12.5	12.
	Sept. 27	130,000	0.2207	1.0662	12.6	9.
	Nov. 12	72,000	0.1871	1.3032	15.6	10.5
Allende WA, spot A† Mg‡	Sept. 27	693	0.1293	0.1937	4.01	9.
			0.1266	0.1398		

* ^{24}X , ^{25}X , and ^{26}X refer to observed ion intensities at masses 24, 25, and 26 without implying identification of their source.

†For comparison; background is $\sim 20\%$ of excess at mass 26.

‡Normal Mg ratios taken from Schramm *et al.* [1970].

TABLE 7. Summary of Analyses of June 1977

Sample	Date	$^{27}\text{Al}^+ / ^{24}\text{Mg}^+$	$\delta^{26}\text{Mg}^+ / ^{24}\text{Mg}^+$	$\delta^{26}\text{Mg}^+ / ^{24}\text{Mg}^+$	$^{27}\text{Al}^+$, 10 ⁶ c/s	Time, s
Burma spinel (MgAl_2O_4)	June 9	2.08	0.8	-0.2	0.436	5.5
		1.96	1.1	-0.1	0.454	6.5
	June 11-12	2.01	1.4	-0.5	0.481	3.3
		2.04	0.5	-1.1	0.501	3.3
	Mean	2.02	0.7	-1.3	0.501	3.3
		± 0.04	± 0.4	± 0.5		
Lake County labradorite (An_{87})	June 11-12	212	2.1	0.4	2.84	2.1
		196	4.5	-3.0	2.62	2.1
		194	0.9	-2.9	2.57	2.1
	Mean	200	2.5	-1.8		
		$\pm 20^*$	± 2.1	± 2.2		
Moore County anorthite (An_{91})	June 10	550-820‡	2.9	0.0	4.16	7.5
			5.2	-0.3	4.72	7.8
			-3.2	1.4	5.19	6.0
			2.9	2.2	5.99	11.2
	June 11-12		2.8	-3.3	7.32	12.6
			-5.5	1.0	6.55	6.3
			-0.9	-1.2	5.62	6.3
	Mean		0.6	0.0		
		± 3.0	± 1.4			
Allende WA anorthite (An_{99+}), large grain	June 11-12	500-1000§	2.1	28	3.73	6.2
			1.9	29	3.66	12.6
			2.4	34	1.67	6.3
			0.4	26	1.59	6.0
	Mean		1.7	30		
		± 0.9	± 4			
Allende WA spinel	June 9	1.98	2.1	1.7	0.488	7.2
		1.87	1.5	0.8	0.514	7.1
	June 11-12	1.85	1.5	1.4	0.611	3.1
		1.83	1.5	0.8	0.639	3.0
	Mean	1.88	1.7	1.2		
	± 0.07	± 0.3	± 0.5			
Allende Cl spinel	June 11-12	2.36	3.6	6.9	0.568	3.3
		2.23	5.1	8.2	0.618	3.0
		2.24	5.5	6.6	0.540	3.3
		4.59†	3.9	11.7	0.332	3.4
		3.43†	1.9	3.3	0.332	2.7
		2.97†	4.1	6.1	0.390	2.7
	Mean		4.0	7.0		
			± 1.0	± 2.2		

Data are corrected for dead time, scattered ions, and counting system background, and $^{24}\text{Mg}^+$ is corrected for $^{46}\text{Ca}^{2+}$. No mass discrimination or blank corrections have been made. Differences between the Imma tuning in 1976 and 1977 are largely responsible for differences observed in $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ for the same samples in this experimental series compared to the 1976 series.

*Error is estimated as $\pm 2\sigma$ in the mean based on estimated dead-time correction errors.

†These three analyses are from a spinel imbedded in anorthite; thus the $^{27}\text{Al}^+$ intensity is enhanced.

‡This is a different crystal from that used in 1976, and it may have a different Mg concentration.

§Surface charging leaves these ratios very uncertain.

analysis of a separate crystal of WA anorthite. The $\delta^{26}\text{Mg}^+$ versus $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ correlation is clear within the $\times 2$ range of $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ of the large crystal. The analyses of BG3-13 are essentially consistent with the WA results. The WA data lie about a linear regression line with an ordinate intercept of $\delta^{26}\text{Mg}^+ \sim +2\%$ and slope 7.1×10^{-5} . They span a range of $\times 3$ in $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$, and the $\delta^{26}\text{Mg}^+$ intercept is consistent with that of normals, but neither is consistent with the BS shift of -3.9% ; we do not attribute the differences to any essential differences between samples. The slope of the WA array represents a component $\Delta 26_A$ at a uniform concentration everywhere in (or on) the WA anorthite. The $\Delta 26_A^+$ ion count rate is $\sim 7.1 \times 10^{-5}$ of the $^{27}\text{Al}^+$ signal superimposed on the normal abundance of $^{26}\text{Mg}^+$. It is assumed that the $\Delta 26_A^+$ signal contains a component of ion intensity with the same source as $\Delta 26_N^+$.

Because the source of the component $\Delta 26_N^+$ found in the 1976 series is not well understood, we consider whether circumstantial changes in sensitivity for matrix ions (e.g., Mg^+ , Al^+) or HC ions may have created the apparent distinction between normal and Allende mass 26 excesses. For this purpose we have calculated the absolute count rate excesses at mass 26 ($\Delta 26^+$) (on the assumption that mass 24 is only $^{24}\text{Mg}^+$) for all samples except BS, correcting only for day-to-day (not point to point) sensitivity changes indicated by the $^{27}\text{Al}^+$ count rate from Al or Al_2O_3 . The data are plotted in Figure 4. The error bars are $\pm 2\sigma$ in counting statistics scaled by the sensitivity normalization. A major source of the scatter in $\Delta 26^+$ within the Allende and 'normal' data groups is the small point to point sensitivity changes that occur within a day's operations.

There are two groups of data that are distinguishable by the

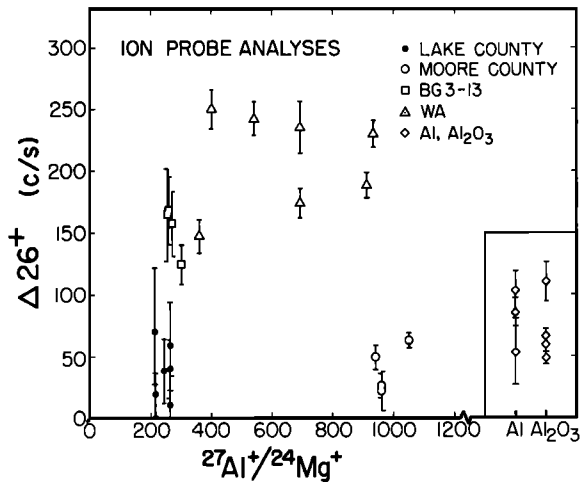


Fig. 4. Plot of absolute count rate excesses observed at mass 26 in plagioclase, Al, and Al_2O_3 analyses, showing lack of correlation with $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ and distinguishing Allende excesses from normal excesses. The data are normalized to a constant $^{27}\text{Al}^+$ sensitivity from Al or Al_2O_3 for each day. The Al and Al_2O_3 excesses in the inset cover a $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ range of 1.5×10^8 and 1.3×10^9 . The error bars in count rate are $\pm 2\sigma$ in counting statistics scaled by the sensitivity normalization; the variability in $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ for Lake County and Moore County gives an estimate of variability for other sample measurements.

$\Delta 26$ dimension in Figure 4: the Allende group and the group containing LC, MC, Al, and Al_2O_3 . The $\Delta 26_N^+$ for LC, MC, Al, and Al_2O_3 range from 10 c/s to 110 c/s, $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ ranging from 240 to 1.3×10^5 . The aluminum atomic concentration varies from 13% in LC to 100% in Al. For clarity in Figure 4 the Al and Al_2O_3 are plotted without a $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ dimension; refer to Table 6 for these data. The $\Delta 26_A^+$ for all Allende samples varies from 124 c/s to 250 c/s as $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ ranges from 256 to 934. The Allende data are quantitatively different from the normals; there is no overlap in $\Delta 26^+$ despite a wide range of 'normals' composition, sensitivity changes from day to day (month to month), and repolishing and gold-coating of the samples between the analyses of July, September, and November. We are confident that there is indeed an additional or different source of mass 26 excess ($\Delta 26_A^* = \Delta 26_A - \Delta 26_N$) in the Allende samples which can be assigned to the Al-correlated excess in ^{26}Mg established by Lee *et al.* [1976].

The June 1977 analyses of Allende materials for Mg isotopic composition are summarized in Table 7 and Figure 5. The mean $^{25}\text{Mg}^+ / ^{24}\text{Mg}^+$ and $^{26}\text{Mg}^+ / ^{24}\text{Mg}^+$ of the Allende WA spinel are within 2% of normal but outside 2σ in the mean of four determinations; there is no obvious explanation for the small deviation from normal, since dead time was $< 5\%$, counting statistics were $2\sigma < 0.6\%$, and background corrections were $< 0.1\%$.

An isotopic analysis was made of the Mg in spinel from Allende CI chondrule, which is known to be mass fractionated at about +3% per mass unit [Wasserburg *et al.*, 1977]. The data are strongly suggestive of such a mass fractionation, although the 2σ errors in the mean of $\delta^{25}\text{Mg}^+ / ^{24}\text{Mg}^+$ and $\delta^{26}\text{Mg}^+ / ^{24}\text{Mg}^+$ are too large to establish the linearity of the fractionation. Dead-time corrections were $< 2\%$, counting statistics were $2\sigma < 1.2\%$, and background was $< 0.1\%$.

The isotopic analyses of the Allende WA large anorthite crystal clearly show a very large ^{26}Mg excess. The $\delta^{25}\text{Mg}^+ / ^{24}\text{Mg}^+$ is within 2% of normal and outside 2σ in the mean of four determinations but consistent with counting

statistics for $2\sigma = 2.2$ –5.6%. The mean $\delta^{26}\text{Mg}^+ / ^{24}\text{Mg}^+$ is +30% with a range of $\pm 5\%$. We tried to establish $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ at the two points of analysis, but this was prevented because the Au sample surface coating had been accidentally scraped off large areas in handling. The sample surface was quite obviously electrostatically charging under the primary beam, and the elemental ratios were not reproducible. The range of $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ was 500–1000. There is no correlation between $\delta^{26}\text{Mg}^+ / ^{24}\text{Mg}^+$ and $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ in these data. The dead-time corrections on $^{27}\text{Al}^+$ were 20–60% even at the low intensities, producing additional large uncertainties in the elemental ratios.

CONCLUSIONS

Using ion microprobe analytical techniques, we have observed $\delta^{26}\text{Mg} / ^{24}\text{Mg}$ excesses up to 40% above the normal terrestrial $^{26}\text{Mg} / ^{24}\text{Mg}$ in an anorthite crystal from the Allende WA inclusions. The $\delta^{26}\text{Mg} / ^{24}\text{Mg}$ excesses correlated with $^{27}\text{Al} / ^{24}\text{Mg}$ when analytical conditions were well controlled. In the same series of analyses, much smaller but significant $\delta^{26}\text{Mg} / ^{24}\text{Mg}$ excesses were observed in plagioclase samples known to be isotopically normal. The systematic difference between the magnitude of the excesses in Allende and that in normal samples suggests that most of the observed Allende excess is real and due to ^{26}Mg produced by the decay of ^{26}Al originally associated with the ^{27}Al in the crystal. The concentration of Mg in the WA anorthite varies by a factor of 3 in the material examined and by a factor of 2 in a single crystal on a scale of tens of microns. The observed concentration of Mg in the crystal varied from about 240 to 570 ppm by weight. A reanalysis of the Mg isotopic composition in the isotopically normal and Allende WA anorthite samples using another ion probe yielded no significant isotopic anomalies in the normal samples, while $\delta^{26}\text{Mg} / ^{24}\text{Mg}$ excesses of 25–35% were again observed in the WA anorthite crystal, confirming our conclusions from the earlier analyses. Instrumental and sample charging problems prevented establishing $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ to permit correlation with the ^{26}Mg excesses.

Lee *et al.* [1977] found a $\delta^{26}\text{Mg} / ^{24}\text{Mg}$ excess of $\sim 9\%$ in a WA anorthite crystal with a macroscopic average Mg concentration of 900 ppm. Much larger effects were seen in these ion probe analyses because the ion microprobe permitted exploring single crystals on the scale of 20 μm for zones of very low Mg concentration. The observed systematics of $\delta^{26}\text{Mg} / ^{24}\text{Mg}$ versus $^{27}\text{Al} / ^{24}\text{Mg}$ are compatible with the isochron established

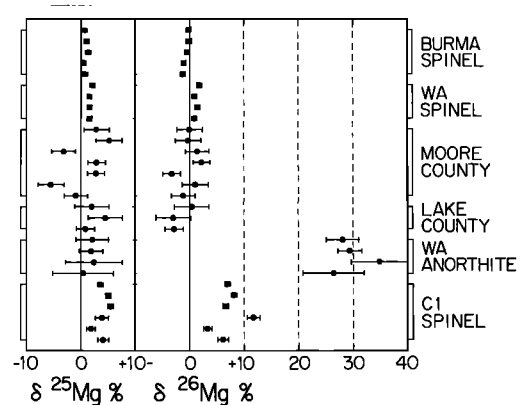


Fig. 5. Results of 1977 Mg isotopic analyses of terrestrial and Allende samples on a second ion microprobe. The error bars are $\pm 2\sigma$ in counting statistics.

by Lee *et al.* [1976, 1977]. The microscopic spatial resolution of the ion microprobe also enables us to draw some conclusions about the distribution of the ^{26}Mg excesses throughout the anorthite crystal. The $\Delta 26_A^*$ component correlates with $^{27}\text{Al}^+ / ^{24}\text{Mg}^+$ as represented in Figure 3 and hence is a constant contribution at mass 26, uniformly distributed in all the WA anorthite examined, independent of ^{24}Mg concentration. The change in $\delta^{26}\text{Mg}^+ / ^{24}\text{Mg}^+$ is due to the change in ^{24}Mg concentration, which is rather variable within the grain on a scale of tens of microns. These analyses do not demonstrate that the $\Delta 26_A^*$ component is correlated particularly with Al. Because the $\Delta 26_A^*$ is at a constant concentration in the anorthite, it is consistent with an interpretation of ^{26}Mg produced by the decay of ^{26}Al , and we infer that $^{26}\text{Al} / ^{27}\text{Al}$ was uniform throughout the anorthite at the time of crystallization and there has been no subsequent alteration. Correcting for the constant background contamination at mass 26 of $\Delta 26_{N^+} / ^{27}\text{Al}^+ = 1.6 \times 10^{-6}$ inferred from normals analyses, we calculate a ratio of ^{26}Mg excesses to ^{27}Al of $\Delta^{26}\text{Mg} / ^{27}\text{Al} = 5.5 \times 10^{-5}$, which is compatible with the results of Lee *et al.* [1976, 1977].

The limited information about the spatial variation of Mg and Na concentrations in the WA large grain does not permit distinguishing between large-scale continuous zoning and a patchy distribution of these elements. The data indicate discontinuities in the Mg (and perhaps Na) concentration, but they also suggest possible large-scale Mg and Na concentration variation that may be continuous. The distinction between the concentration patterns may be extremely important, since a patchy pattern in a single grain could indicate the presence of trapped residual dust grains.

The single large WA anorthite crystal was observed to contain Na from about 200 to 430 ppm by weight in regions $\sim 20 \mu\text{m}$ in diameter. These concentrations are comparable to the lowest found by Grossman and Ganapathy [1975] in the analysis of bulk refractory Allende inclusions; they report a mean concentration of 2100 ppm for 10 inclusions. Grossman and Ganapathy [1975] comment that the high bulk Na concentrations observed are possibly the result of the addition of volatiles to the inclusions after initial condensation. We do not know whether the Na that we observed is in solid solution in the anorthite as a part of its initial condensation composition or is in micron-scale late alteration products imbedded in the anorthite or has been otherwise introduced after initial condensation. Blander and Fuchs [1975] propose that the chondrules were formed by the condensation of a liquid representing metastable equilibrium with the solar nebula over a relatively wide effective temperature range, followed by crys-

tallization of various phases from the melt; this model would allow the Na to be in solid solution with the anorthite from the time of crystallization.

Acknowledgments. We thank A. L. Burlingame, J. H. Chen, and G. R. Tilton for providing the Allende samples to our laboratories. We thank T. Lee for selection of the actual sample grains for analysis, his encouragement, and many useful comments. All the 1976 sample analyses were done as paid service work at Applied Research Laboratories, Sunland, California. We appreciate the thoughtful and energetic work of D. Comaford as actual instrument operator during the analyses and the consideration and efforts of T. Whatley and other ARL personnel in scheduling the work and overcoming instrument problems. We appreciate the cooperation of D. Anderson, C. Meyer, and D. Phinney at the NASA Johnson Space Center in making our visit possible and productive. This work was supported by NASA grants NGL 05-002-188 and NSG 7084. Division of Geological and Planetary Sciences contribution 2866.

REFERENCES

- Blander, M., and L. H. Fuchs, Calcium-aluminum-rich inclusions in the Allende meteorite: Evidence for a liquid origin, *Geochim. Cosmochim. Acta*, **39**, 1605-1619, 1975.
- Bradley, J. G., D. Y. Jerome, and C. A. Evans, A comparison of mass spectra from three ion probes, in *Secondary Ion Mass Spectrometry, Spec. Publ. 427*, pp. 69-77, National Bureau of Standards, Washington, D. C., 1975.
- Chen, J. H., and G. R. Tilton, Isotopic lead investigations on the Allende carbonaceous chondrite, *Geochim. Cosmochim. Acta*, **40**, 635, 1976.
- Gray, C. M., and W. Compston, Excess ^{26}Mg in the Allende meteorite, *Nature*, **251**, 495-497, 1974.
- Grossman, L., and R. Ganapathy, Volatile elements in Allende inclusions, *Geochim. Cosmochim. Acta*, **2**, suppl. 6, 1729-1736, 1975.
- Lee, T., and D. A. Papanastassiou, Mg isotopic anomalies in the Allende meteorite and correlation with O and Sr effects, *Geophys. Res. Lett.*, **1**, 225-228, 1974.
- Lee, T., D. A. Papanastassiou, and G. J. Wasserburg, Demonstration of ^{26}Mg excess in Allende and evidence for ^{26}Al , *Geophys. Res. Lett.*, **3**, 109-112, 1976.
- Lee, T., D. A. Papanastassiou, and G. J. Wasserburg, ^{26}Al in the early solar system: Fossil or fuel?, *Astrophys. J.*, **211**, L107-L110, 1977.
- Liebel, H., Ion microprobe mass analyzer, *J. Appl. Phys.*, **38**, 5277-5283, 1967.
- Meyer, C., Jr., D. H. Anderson, and J. G. Bradley, Ion microprobe mass analysis of plagioclase from 'non-mare' lunar samples, *Geochim. Cosmochim. Acta*, **1**, suppl. 5, 685-706, 1974.
- Schramm, D. N., F. Tera, and G. J. Wasserburg, The isotopic abundance of ^{26}Mg and limits on ^{26}Al in the early solar system, *Earth Planet. Sci. Lett.*, **10**, 44-59, 1970.
- Wasserburg, G. J., T. Lee, and D. A. Papanastassiou, Correlated O and Mg isotopic anomalies in Allende inclusions, II, Magnesium, *Geophys. Res. Lett.*, **4**, 299-302, 1977.

(Received January 31, 1977;
revised August 15, 1977;
accepted August 26, 1977.)