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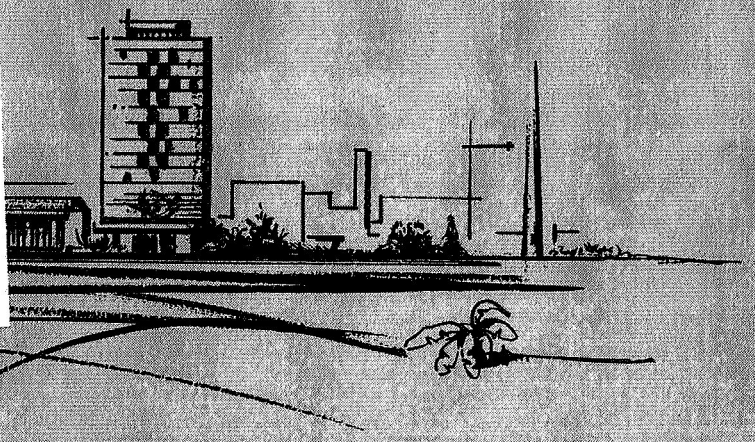

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DEVELOPMENT OF CHEMICAL ANALYSIS TECHNIQUES FOR ADVANCED MATERIALS

FINAL REPORT
covering the period
January 17, 1967, to July 16, 1968

JPL Contract 951578

Prepared for: Jet Propulsion Laboratory
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FOREWORD

It is a pleasure to acknowledge the contributions of many persons to the research described in this report. Of the Battelle staff, the following were active in particular phases of the work: R. B. Iden and R L. Livingston, development of hydroxyl-determination techniques and chlorination experiments; R. E. Heffelfinger and B. Snyder, optical emission spectrographic techniques; D. L Chase, C. T. Litsey, J. Lathouse, and B. L. Moomaw, chemical-analysis techniques; F. E. Huber, Jr., carbon-content experiments; E. H. Hall and C. A. Alexander, thermodynamic calculations; R. W. Pfeil and F. R. Moore, TGA studies; D. C. Walters and T. L. McKendrick, mass spectrographic technique development; and W. M. Henry and H. L. Goering, supervision and technical consultation. Persons not on the Battelle staff whose cooperation, encouragement, and advice are deeply appreciated include M. H. Leipold, The University of Kentucky; J. J. Gangler, NASA Headquarters; J. I. Mueller and A. D. Miller, University of Washington; and F. D. Leipziger, Kennecott Copper.

ABSTRACT

Techniques have been developed to determine all elemental impurities in magnesium oxide and, to a limited extent, impurities in several other compounds. By combining data obtained by use of the mass and optical emission spectrographs, wet chemistry, and combustion and thermal chemistry, every element either has been determined at levels ranging from subparts per million to many percent or found not to be present. One particularly troublesome determination, that of hydroxyl in MgO, has been solved by the use of an oxygen atmosphere and heat.

In appendixes the experimental details of this work are given, as well as tabulations of the data generated during the program.

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DEVELOPMENT OF CHEMICAL ANALYSIS TECHNIQUES FOR ADVANCED MATERIALS

by

E. R. Blosser

INTRODUCTION

This report summarizes the research performed and the results obtained during the 18-month period ending July 16, 1968. Not all the experiments are described in detail because in some instances they led to dead ends or were superseded by better techniques. Rather, the intent of this report is to present in some detail the analytical techniques developed under this contract and currently being used for refractory samples; in addition, the appendix contains tables of analytical data for the materials analyzed during this period and descriptions of the various techniques developed and employed.

Dr. Martin Leipold, the technical monitor during the first third of this contract, suggested that MgO be the material studied most intensively and that certain key impurities, specifically hydroxyl (OH), be investigated sufficiently so as to make their determination reliable. After Dr. Leipold left JPL, this work continued until the end of the project. At the suggestion of Mr. James Gangler at NASA Headquarters, materials originating in the Ceramic Engineering Department of the University of Washington were analyzed; Dr. James Mueller served as coordinator of this phase of the program.

As explained above, this report deals primarily with MgO; other materials such as ZrO_2, TaC, etc., were not studied at all, and a few, including Al_2O_3 and a material nominally Zr_2CO, were examined to a limited extent.

EXPERIMENTAL WORK

Magnesium Oxide

Metallic Impurities

Metallic impurities in research-grade MgO usually are the lower atomic weight elements, primarily Al, Si, Ca, and Fe. In all but a very few samples analyzed during this program, one or more of these elements were present at the hundred-parts-per-million, atomic-basis (ppma) level, and frequently in the thousand ppma range. These concentrations are ideally suited for emission spectrographic and wet-chemical techniques, both of which are capable of good accuracy (1 to 10 percent of the amount present). In fact, the mass spectrographic technique that was employed extensively in this work frequently is unable to determine these high-level impurities with satisfactory accuracy because it is difficult to make and measure the short exposures on which these elements are measured.

Throughout this program many cross-check data were obtained to establish the accuracy of the reported values. For example, in the original batch of Fisher M-300 MgO (BMI 90940) the Ca and Si values reported by others were not confirmed in the first few analyses at Battelle. Therefore this material was analyzed by wet-chemical methods and by several optical emission techniques, all of which gave essentially the same results as the first Battelle analyses. Furthermore, various other M-300 samples (another bottle of powder, a calcined sample, and a pressed sample) also gave similar results for these two elements. Because these three distinctly different techniques based on different chemical and physical properties of an element all gave about the same result, it was concluded that the result is accurate.

In general, the approach to the analysis of powdered MgO was, and is, to make one or more mass spectrographic runs. If any elements appeared quite high, or if "unusual" elements were present, an optical emission determination was made. Elements whose determination was erratic

or inaccurate in the mass spectrographic analysis were detemined chemically if the optical emission methods were not suitable. The mass spectrograph still remains the foundation of MgO analyses because of its excellent detectability, its complete elemental coverage, and its fair accuracy.

Compact MgO, whether hot or cold pressed, presents a different set of problems. First, MgO is of course an excellent insulator and could not be sparked as two MgO electrodes in Battelle's mass spectrograph. It was found necessary to use a conducting counterelectrode (Au) versus one MgO electrode. This technique was only partially satisfactory for several reasons: the Au contribution was erratic and often high, but in any case could be estimated only roughly; the spectra were often nonlinear, and did not appear "normal" in the +1/+2 ratio of ions and in the extent of thermal ionization; and the ion beam was often quite low in intensity.

Second, MgO is quite hard, and attempts to grind it would be expected to lead to contamination from the mortars, even though they had been cleaned. However, one sample, OP 366, showed little if any Si pickup after being ground in an agate mortar. The Si was at the 500-ppmw level; in purer samples, pickup might be observed.

Third, if the unground sample is sparked directly, the danger exists that a nonrepresentative analysis will be obtained because of inhomogeneity or surface contamination.

In spite of these problems, the mass spectrographic analyses of most compact MgO samples checked reasonably well with available cross-check data. Generally this required multiple runs--three or four plates of exposures were made for most samples. Having many spectra to read permits one to reject those that appear abnormal and to average out the fluctuating Au contribution. Even though this practice is expensive, both in time and in plates, it results in better data than would be available from only one run.

Some effort was put into standardization of the mass spectrographic technique, in addition to the use of cross checks. To powdered MgO were added solutions containing elements to be standardized. Care was taken to moisten all the powder but not to have any free solution.

This practice avoids the possibility of fractional crystallization on the sides of the crucible and results in a standard that is quite homogeneous. The mixture was dried and ignited at a low temperature (120 C) to avoid possible volatilization of fluorides or chlorides. After thorough mixing by shaking, the standards were analyzed in the same way as a sample, and the results were compared with the known values. Correction factors were determined which, when applied to the raw data as read from the mass spectra, brought the results into better agreement with cross-check data.

Nonmetallic Impurities

Because nonmetallic impurities (primarily C, Cl, F, and S) are not detected by an optical emission spectrograph without special equipment and techniques, their determination was limited to wet chemistry (or combustion in two instances) and mass spectrography. The latter, as has been mentioned earlier, is capable of complete elemental coverage, and there is no basic reason why these elements can not be determined. In practice, however, F and perhaps C appear to have sensitivity factors appreciably different from 1.0.

Carbon at m/e 12 and 13 is obscured by $^{24}Mg^{+2}$ and $^{26}Mg^{+2}$ but at the m/e 6 and $6\frac{1}{2}$ positions the Mg^{+4} contribution is not very serious and in any case can be estimated from the m/e $6\frac{1}{4}$ line. Interferences aside, C determinations by mass spectrography are difficult at low levels owing to the background. The residual background arises from several sources including mechanical-pump oil during roughing, diffusion-pump oil (CO, CH_4, etc.), and adsorption on the sample surfaces before loading in the source. Considerable improvement is realized by baking the loaded source overnight, but enough residual C remains to give a blank in the thousands of ppm range for the first few exposures and (as determined on metals) in the few ppm range after prolonged sparking.

At least with powders, the C value is related to the extent of exposure to the atmosphere. Even chunks crushed in air showed an appreciable

increase in C upon standing, probably from $MgCO_3$ formation. Thus it seems unlikely that a meaningful C value for the bulk powdered material can be determined unless a means can be devised to remove the surface $MgCO_3$. In any case, a combustion determination of C is preferable to a mass spectrographic determination because the former appears to pose no problems and is fast and inexpensive.

Of the halogens, only F and Cl were noted in most samples. The Cl values by mass spectrography varied with respect to the chemical values, but tended to be on the high side. Nevertheless, the mass spectrographic results were usually less than plus or minus a factor of 2.0 from the chemical values. Fluorine was quite low by mass spectrography in the first few samples analyzed, so a correction factor was introduced. Later data showed fair agreement between corrected mass spectrographic and chemical values.

The only other nonmetals (other than OH) present in the MgO samples examined were N, S, and P. Few cross-check data are available for P. The S results by mass spectrography tended to be high by perhaps a factor of two as compared with chemical values. Nitrogen results by mass spectrography were quite erratic compared with chemical data, but appeared high. In view of the simplicity and accuracy of the Kjeldahl method, it is recommended that N be determined by Kjeldahl unless the N is present at levels too low to be determined, in which case mass spectrography could be used after some standardization. It should be noted that little effort was made to quantify the mass spectrographic determination of N because that element was not judged to be of much significance in MgO.

Hydroxyl

By far the largest amount of time and effort was spent trying to determine accurately the amount of OH in MgO. Under a previous contract (JPL Contract No. 950992), Dr. Leipziger, then of Sperry Rand Research Center, concluded that hot extraction of H_2 from MgO was not satisfactory because the results were higher than those from the mass spectrograph.

During the work covered by this report it became evident that neither technique was satisfactory without extensive development. The work leading to the presently recommended technique is described in some detail in Appendix A. In this section, an overall summary of the experiments and the conclusions is presented.

The picture of OH in MgO suggested by Dr. Leipold (and which formed the basis for the experimental work) is that there exist in MgO three types of OH. First, there is surface H_2O bound by physical and chemical bonds to the surfaces of the particles. Second, there is chemically bound OH within the particles; this type may be thought of as "brucite water"--$Mg(OH)_2$. Third, there is a more tightly bound OH that substitutes for an O atom in the lattice and is present not as $Mg(OH)_2$, but as Mg·OH. If this picture is correct and if the supposition is correct that this last form of OH is very tightly bound, it then follows that treatment more vigorous than heating to a few hundred degrees is needed to remove all of the OH. It was shown early in the program that brucite could be decomposed quantitatively below 400 C, in agreement with handbook data. Therefore considerable effort was expended in subjecting the MgO mixed with C to higher and higher temperatures, in the hope of rupturing all MgO bonds (forming CO and Mg) and thus liberating the OH. Repeated attempts using induction heating to as high as 3300 C failed to give reproducible data. As a sidelight, an actual loss of H_2 was noted at higher temperatures--H_2 present in the reaction vessel diminished upon a second, higher temperature run. This effect was not studied, but it suggested that high temperatures were not producing the desired result.

Confirmation of this conclusion came in experiments with a laser. Focused beams gave a certain amount of H_2 per unit of sample decomposed; defocused beams gave a higher relative H_2 value. Thus the inescapable fact had to be faced: high temperatures gave low results for H_2 in the MgO-C system.

A different approach clearly was needed. Upon examining the thermodynamics of the MgO-H system, it was noted that the reaction

$$2MgOH + \tfrac{1}{2}O_2 \longrightarrow Mg(OH)_2 + MgO$$

is favored by heat and of course by a large partial pressure of O_2. If

$Mg(OH)_2$ could be formed, it should be possible to break it down in accordance with the reaction

$$Mg(OH)_2 \longrightarrow MgO + H_2O,$$

which had been shown to proceed below 400 C. Several experiments showed that there was, in fact, a distinct amount of H_2O liberated in each of three steps: (1) at 100 C in vacuum, (2) at 500 C in vacuum, and (3) at 500 C in O_2. The results [except for Step (1) which measures only some of the variable surface H_2O] were reasonably reproducible.

The question was raised by Dr. Leipold of whether only surface water was being measured and whether each heating step merely removed the surface H_2O more nearly quantitatively. Three points answer this question. First, repeated heating at 500 C without O_2 released very small amounts of additional H_2O but, when O_2 was added, more H_2O was released. Second, a sieved sample (-100 +120 mesh or 125 to 149-μ particle size) gave essentially the same results as an unsieved sample. Third, and most important, was the behavior of a sieved sample that was exposed to moist air (about 15 torr partial pressure of H_2O) after having been heated in the various steps as described in the appendix. After about 18 hours' exposure the MgO certainly would have picked up a large amount of surface water. In fact, the first heating step (100 C in vacuum) did release about the same amount of H_2O as had been found in the corresponding step earlier. However, the subsequent heating steps released only small fractions of the amounts of H_2O that had been found in the previous corresponding steps.

In weighing the above evidence (see the appendix for complete data and experimental descriptions), it was concluded that the developed procedure is satisfactory for the removal of OH from MgO. Little attempt was made to optimize the exact conditions. There may be better times, temperatures, and pressures for this determination, but the concept has been shown to be valid when the conditions described in the appendix are used.

Summary

The analysis of MgO for all impurities is satisfactory for present-day impurity levels. By combining chemical, optical emission and mass spectrographic, and thermal techniques, reliable values are obtained for all elements, including those that presented difficulties at the beginning of the program. If only one were to be selected it would be the mass spectrographic technique, with the recognition that some elements have sensitivity factors and that others are subject to erratic behavior. Standardization, either via synthetic standards or cross-check data, is essential for any technique, but especially so for the mass spectrographic technique when dealing with a compound system such as MgO. If these limitations are accepted, the mass spectrographic analysis of MgO may be considered the best overall technique.

Other Materials

Zirconium-Carbon-Oxygen Compound

A material produced at the University of Washington, believed to be Zr_2CO, was characterized chemically. After several attempts to liberate the O_2 (as CO) by vacuum fusion, a chlorination method was developed to decompose the material and liberate the CO. Far less than theoretical recovery was attained, suggesting (1) a loss of CO, (2) an incomplete reaction, or (3) an incorrect formula for the material. Analyses were made for individual elements--Zr, C, Hf, Al, Si, and Sn--and for traces of many other elements. The total amount of material found accounted for over 98 percent, so that even if all the remainder is O_2, only about 25 percent of the material could be Zr_2CO. It is probable that the material is a mixture of ZrC_x, ZrN, ZrO_y, and C, plus compounds of the impurities and perhaps some Zr_2CO. The presence of some Zr_2CO could be inferred from the release of CO upon chlorination; on the other hand, the CO could have

been produced from a reaction between ZrO_y and ZrC_x (and C) in the presence of Cl_2. This possibility was not explored.

This study illustrates a means of studying materials by chlorination. By no means new, the technique is useful because many metals and compounds will form metallic chlorides that are more volatile than the sample material and, therefore, can be separated from the phases that do not react. On the other hand, the chlorides are less volatile than some of the liberated species--CO, CO_2, N_2, etc. The technique was used a few years ago to determine N_2 in Be metal with good results and to determine the stoichiometry of ZrO_2. Removal of the excess Cl_2 without removing any sought components remains a problem. Presently it is done by freezing the Cl_2 in a cold finger but there is the possibility of entraining other gaseous reaction products.

Stoichiometry of ZrO_2

Near the end of this program several dozen ZrO_x samples were received from the University of Washington for analysis. Each sample weighed only 5 to 10 mg, not nearly enough for the U_3O_8 stoichiometric determination developed at Battelle. Several trials were made with a standard ZrO_2 whose Zr-O ratio is known accurately, but the final calculated formula was $ZrO_{1.947}$ (rather than $ZrO_{2.000}$). Five mg of the standard was heated for several hours at 750 C in 760 torr O_2. A Cahn microbalance in a Thermal Gravimetric Analysis (TGA) instrument was employed after careful standardization in the 5-mg range. Despite the inability to check the known standard precisely, about 5 mg of an unknown ZrO_x (University of Washington's No. 30) was oxidized in a similar manner. Assuming it also equilibrated at $ZrO_{1.947}$, its starting formula was calculated to be $ZrO_{1.696}$. Both the sample and the standard failed to reach the dead-white color indicative of true $ZrO_{2.000}$, but had a tinge of gray. Usually, this off-white appearance is associated with deficient zirconia, although an impurity conceivably could cause it. No impurity analyses were made of either material. Time and funds were insufficient to establish the conditions

necessary to oxidize completely these very small samples. Thus, the stoichiometry of the remaining samples was not determined.

DISCUSSION

Many other areas of research in the analysis of refractory materials were not explored in this work because the development of techniques to analyze MgO was considered of prime importance at the outset of the program. It was believed preferable to study one compound thoroughly rather than to investigate many compounds superficially. However, the techniques developed for MgO should be applicable to other refractory-oxide systems with little, if any, modification. As a case in point, the mass spectrographic technique developed for MgO was found to be suitable with only minor modifications for another research program concerned with Nb_2O_5. Some adjustment of sensitivity factors for certain elements also was necessary.

Other types of compounds--the carbides, for example--were not studied. It would be expected that different problems would be encountered and that the MgO techniques would not be applicable without considerable development. The determination of O, N, and H in carbides probably would be the major problem. Experiments using thermal and chemical means to extract these elements are clearly needed to develop reliable techniques. Other elements, such as the halogens and metals, should present no unusual difficulties other than solubility problems in wet-chemical methods in some matrices.

Another area of research that was not explored was the spatial distribution of impurities. For dealing with submicron particles, the current state of technology is not adequate to locate impurities. Electron microprobes (EMP), ion probes, and lasers have, at best, resolutions of a few tenths of a micron up to tens of microns. Spatial resolution to a few hundred angstroms ($>0.01\ \mu$) is theoretically possible with

the EMP, but is not likely to be achieved quickly or easily. Thus, examination of impurity distribution within single particles seems impossible unless a new approach is found.

Possibilities are seen in the ion microprobe or ion microscope, fairly recent developments. There seems to be little chance of getting the two dimensions seen by the impinging beam (the plane of the surface) smaller than serveral tenths of a micron. The ion beam itself is in the 1 to 2-micron diameter at best. However, in the ion microscope (as distinguished from the ion microprobe) the spatial resolution is a function not of the beam diameter but of the optics of the system that mass analyzes the sputtered ion beam. Currently this ion microscope is giving resolution in the tenths of a micron range.

It should be noted that the resolution of ion probes and microscopes in the Z-dimension (normal to the sample surface) is very much better, approaching several atomic layers ($<0.01\ \mu$). Therefore, if a particle were oriented in such a way that the impinging ion beam would pass through a known grain boundary after a certain amount of sputtering, it should be possible to check the concentration of one element at a time as a function of depth in the particle. Sensitivity might be a problem because a single particle would be "seen" by only a small fraction of the primary beam.

From the foregoing discussion, it is apparent that, while gross analyses for impurity elements are either developed or at least judged feasible, the techniques for pinpointing their location within a particle have not been developed, nor are there any obvious means in sight for accomplishing this. An extensive development program is called for if spatial distribution of impurities must be determined.

CONCLUSIONS AND RECOMMENDATIONS

For the analysis of impurities in MgO, the techniques discussed above and described in more detail in Appendix A have been shown to give at least semiquantitative data and in many cases, quantitative data. Even

determinations whose reliability was in doubt, such as for the halogens, a few nonmetals, and OH, can be determined by a variety of methods. No single approach is totally satisfactory; every technique suffers from either accuracy, elemental-coverage, or detectability limitations, to say nothing about sample requirements and cost. Combining wet-chemical, combustion, thermal, and optical emission and mass spectrographic procedures is the key to complete and reliable analyses. It is therefore concluded and recommended that each technique be used, where applicable, when a complete analysis of MgO is required.

Application of the methods described in this report to other refractory oxide materials should be straightforward. A certain amount of preliminary checking should be done to insure accuracy. Other types of compounds such as carbides would require considerably more investigation before their analysis would be satisfactory.

It is becoming increasingly obvious that many, if not most, of the materials used in ceramic research should be characterized. To assume that a vendor's analysis is correct and complete is to court trouble when measured properties may depend on unsuspected impurities. Further, even if the starting material is known, to assume that processing this material will not change the impurities or that these impurities will change in a predictable manner is risky indeed. It is recommended that a requirement be established for key research materials to be characterized to an extent sufficient to assure that any measured properties are not being influenced by unknown trace (or major) impurities.

It is further recommended that sufficient time and funds be allocated in materials programs to allow for such characterization, including extensive developmental effort in cases where workable techniques do not exist. In most instances this phase of a program--development and/or application of analytical methods--would be a minor part of that program in cost, but would, hopefully, assure the researcher that his observations were based on known materials.

As a practical means of accomplishing this objective and to reduce the paper work involved in dealing separately with many NASA researchers, it is recommended that a program of development and application of chemical-analysis techniques for research materials be established by NASA Headquarters, with coordination and priority assignments being through that office. A proposed program along this line has been submitted to NASA by Battelle's Columbus Laboratories.

NEW TECHNOLOGY

The determination of hydroxyl in magnesium oxide is believed to have been solved by a simple but unique technique. Adding oxygen to an evacuated furnace containing MgO helps liberate the hydroxyl (as water) and gives reproducible data. A separate report on this item will follow shortly.

APPENDIX A

DETAILS OF EXPERIMENTAL WORK

APPENDIX A - DETAILS OF EXPERIMENTAL WORK

GENERAL STUDIES RELATED TO THE ANALYSIS OF MAGNESIUM OXIDE

Sparking of Insulators

Insulating powders such as MgO present an initial obstacle to a mass spectrographic spark-source analysis. Their extremely high resistivity has forced the analyst to employ various techniques to obtain a spark discharge and thus an ion beam. These techniques have included "piggy back" mounting of a conductor and the solid insulator side by side, briquetting the powder with a conductive binder, using a conductive counter electrode to spark directly to a solid insulator, and sparking two insulators directly by employing high rf voltages. None of these techniques is completely satisfactory. Diluents or conductive binders reduce the amount of sample ionized and recorded per given exposure, and introduce into the spectra impurities present in the diluent. They also may cause interferences from complex and multiply charged ions. "Piggy-back" and counter-electrode techniques have the above disadvantages plus the very real problem of an unknown and varying ratio between the quantity of sample ions and the quantity of conductor ions being produced and recorded at any moment.

Efforts to reduce these problems have been made. Reduction and elimination of the binder (Ag) was attempted first, with poor results. MgO briquettes prepared with no binder failed to spark and were very weak mechanically. Built-up electrodes, with a thin layer of MgO backed up with pure Ag, tended to flake off the MgO layer and also produced an unexpectedly large amount of Ag in the spectra. Direct sparking of two solid samples met with no success, even at open-circuit voltages up to 80 kv. Other laboratories have reported some success with this technique, but it was not possible to duplicate their results in the present research.

Powdered MgO as briquettes mixed 2:1 or 1:1 Ag:MgO spark nicely and the Ag:Mg ion ratio seems fairly reproducible and constant, at least for short exposures, in which it is possible to read the Ag and Mg lines. Visually, the ratio remains about constant for heavier exposures as well.

Solid MgO samples can be sparked using a Au-wire probe as the left-hand (rf side) electrode. The ratio of Au to Mg ions is difficult to determine (Au is monoisotopic), but visually the ratio is about 1:1 and reasonably constant. Sparking occurs without difficulty.

Determination of Relative Amounts of Sample and Conductor in Ion Beam

To improve accuracy appreciably, a system is needed whereby either the conductor is not ionized to a significant extent or the Mg ion beam can be monitored alone, not together with the O, Au, or Ag, as is the case in present instruments. Such a system would require a collector positioned over the Mg lines and connected to an amplifier and readout system. Previously a collector had been mounted between the magnet gap and the photoplate to collect Be (m/e 9) during the extensive analysis of Be. This collector was used to reduce plate fog and was not connected to an amplifier. Some modification of this scheme might be feasible for electrically monitoring Mg. Alternatively, if a known-level impurity were present in the binder or counter electrode, its contribution to the spectra would serve as an index of the Au or Ag contribution. However, the Au and Ag used do not have impurities (in the 1 ppm and above range) that are not also found in MgO.

As noted above, the relative contributions of Au or Ag and Mg to the spectra are of vital importance in accuracy considerations because the value for an impurity element is based on an exposure level obtained by measuring total ion current. The ratio of Ag to Mg was studied on eight plates having sufficiently light exposures to permit microphotometric reading of the $^{109}Ag^+$ and $^{25}Mg^+$ lines. The individual ratios for each spectrum were determined for each plate and corrected for isotopic abundances. For all eight plates the overall average was 0.66 $\frac{Ag}{Mg}$; if one high plate (ratio = 1.77) and one low plate (ratio = 0.22) was excluded, the overall average

for the remaining six plates was 0.54. Individual spectra on a given plate showed more variation, the range being from 0.13 to 2.7. About 75 percent of the individual ratios were within the 0.3 to 0.8 range. If it is assumed that the O ions are equal in number to the Mg ions, then the probability is that the Ag in 2Ag:1MgO briquettes will contribute considerably less than one-half of the total ions recorded. It is concluded that, in about three out of four light exposures, the error introduced by not making a Ag correction would not exceed about 20 percent.

Internal Standard and Synthetic Standards

Another way to improve accuracy by assessing the amount of MgO ionized is to add an internal standard to the powder before briquetting. Ideally, the intensities of impurity-element lines are compared directly with lines of the matrix element or a known-level impurity. In MgO this is not possible because Mg has only two levels of isotopes--one at about 80 percent and two at about 10 percent. The minor oxygen isotopes are assumed to be unreliable because of OH^+ and H_2O^+ contributions and because the Mg^+ to O^+ ion ratio may not remain constant owing to thermal decomposition. Measured volumes of dilute solutions of Yb therefore were added as an internal standard at the 29-ppma and the 350-ppma levels to separate samples of Kanto MgO. The slurries were stirred with Teflon rods, dried under a hot plate, and muffled at 1200 C. The dried powder was mixed with Ag, briquetted, and sparked as usual. The spectra were read on the microphotometer. Copper, m/e 63, and Yb, m/e 170, 172, and 174, were used for this work. After obtaining intensities from the usual plate-calibration curve, the amount of copper was calculated using the known levels of Yb and making the appropriate corrections for isotopic abundances. The values for Cu ranged from 8 to 21 ppma, the average for four plates being 14 ppma. The mass spectrographic value (visual reading) was 2 ppma and the emission spectrographic result, 0.6 ppma. It is likely that the visual mass and emission are in error, that some Yb was lost, that the mixture was not homogeneous, or that there is a considerable difference in sensitivity for Yb and Cu. The ratio that was obtained between

the two levels of Yb is evidence that the Yb is probably not being lost and is homogeneously distributed. The intensities of the Yb lines, corrected for isotopic abundances, were averaged for the first two plates (29 ppma Yb) and the last two (350 ppma Yb). The ratio of these averages was 10.9, whereas the ratio of $\frac{350}{29}$ is 12.1. Because these are raw intensities they would reflect any error in the analysis, including variations of sample-to-Ag consumption, nonuniformity, and Yb loss. On the basis of these limited data, it appears that reproducible and proportionate amounts of the added Yb are sparked and ionized and that the technique would be useful if the sample-to-conductor ratio becomes a limiting factor for accuracy.

Another question that arose was the relative sensitivities of impurity elements in MgO. To determine these factors for some of the more important elements and elements suspected of having factors appreciably different from 1.0, synthetic standards were prepared using as a base Kanto MgO, BMI S-0430, and BMI S-0429. The total amount of each added element present and the amount subsequently found by mass spectrographic analysis are shown in Table 10, Appendix B. In most instances the agreement was good, particularly so for elements that might have been expected to be problems. The two high-weight alkalies, Rb and Cs, appear to have unit sensitivity, i.e., they are not abnormally ionized. But two low-weight alkalies, Na and K, are severely enhanced at the +1 positions, and apparently the +2 positions (m/e 11-1/2 and 19-1/2 for Na and K) require correction factors in the range of 100 to 300 for Na, and 30 to 50 for K. The reported values were obtained from the +2 lines using a correction factor of 10. Lithium, the lowest weight alkali, has a sensitivity of about 3 at the +1 position.*

The halogens behave in a peculiar manner. Br has nearly unit sensitivity. Cl and F have been inconsistent, Cl usually being too high and F too low as determined mass spectrographically. This was true for the standards as well.

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* The observed concentration must be divided by 3 to arrive at the proper result.

The standards were made by adding small volumes of solutions containing water-soluble salts of the cations and anions of interest. Care was taken to moisten essentially all the powdered MgO but not to have left-over solution that could fractionally crystallize. The paste was mulled thoroughly, then muffled at as high a temperature as possible, considering the decomposition temperatures of the various ingredients and the corresponding MgX compounds (where X indicates the added anions). In the present case, this was 120 C. After muffling, the mixture was shaken in plastic vials with plastic balls for 15 to 30 minutes, then mixed with Ag or C as usual. This technique, long used by emission spectroscopists, probably insures a more homogeneous standard than is possible by dry mixing.

The Cl results are so far above the know addition level as to suggest that Cl was added inadvertently. The first set of standards was made with the salts RbCl, CsBr, Na_2SiO_3, KF, Li_2SO_4, and $Sr(NO_3)_2$. The second set was made using NaOH, $MgCl_2$, and MgF_2 in the hope of avoiding chance Cl pickup. However, the one unknown item is the Yb, made by dilution of a stock of Yb in unknown acid. This stock was checked for Cl and was found to contain HCl. The amount was not determined.

Electron Microprobe

Because of the variations in the Ag-to-Mg ion-intensity ratio in the briquettes, a briquette (Fisher M-300 MgO, BMI 90940) was examined using the electron microprobe. Both the Ag and the Mg appeared to be uniformly distributed on tens of micron areas on an unsparked sample surface. In a sparked area the distribution was still fairly uniform but the Ag appeared to be higher (or the Mg lower) than before. These results are quite inconclusive because the sparked electrode surface is very rough. The microprobe is very sensitive to surface topography: only the peaks of the "hills" will emit X-rays that are detected. The apparent depletion of Mg on the surface is in line with the preferential sparking to MgO

rather than Ag, as shown by the Ag-to-Mg ion-intensity ratios. An increase in the Ag contribution with continued sparking has also been observed. In neither the unsparked nor the sparked areas was the Ca visible, although it is believed to be present at the 2000-ppma level.

Brucite Studies

At the suggestion of Dr. Leipold, brucite [natural $Mg(OH)_2$] was used in preliminary experiments to determine whether quantitative recovery of H_2 or H_2O from $Mg(OH)_2$ was feasible using thermal means, which could then be applied to MgO.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was the first technique employed. Small, weighed amounts of fibrous brucite were placed on the pan of the TGA apparatus. TGA thermograms were obtained at a heating rate of 4 C per minute from room temperature to 900 C and at a pressure of about 0.1 torr. Duplicate runs were obtained on the fiber sample. The first sample exhibited a weight loss of 2.0 percent between room temperature and 50 C, undoubtedly due to free or surface water. Dehydration began between 250 C and 300 C and appeared to progress in two steps, with the major dehydration complete by 400 C. Total weight loss at 900 C was 32.5 percent. Correcting for the 2 percent free water, the net loss of 30.5 percent is in excellent agreement with the calculated value of 30.85 percent. The second sample contained 1.3 percent free water, which was removed by heating to 50 C. Again, dehydration began between 250 C and 300 C and progressed in two steps, with the major loss occurring by 400 C. Total weight loss at 900 C was 31.8 percent. Correcting for the 1.3 percent free water, the net loss of 30.5 percent again is in excellent agreement with the calculated value.

Vacuum-Fusion Furnace

The second and third approaches to the OH determination were basically similar, differing primarily in the apparatus used. The vacuum-fusion technique will be described first, then the quartz-tube graphite-crucible furnace technique.

The vacuum-fusion furnace used in this work is a Battelle-fabricated unit similar to the Guldner-Beach design except that the crucible is supported from the bottom of the furnace instead of by platinum wire from the top. The conventional carbon-crucible, graphite-packing, sample-loading system, and degassing method were used.

A fibrous sample was weighed into a tin capsule to facilitate dropping the sample from the loading arm to the crucible. The open end of the tin capsule was crimped to prevent loss of sample. A tin flux frequently is used in normal vacuum-fusion analysis but in this case the sole purpose was to provide a carrier for dropping the sample.

The encased sample was placed in the loading arm and the system was evacuated and degassed at 2000 C for 3 hours. The loading arm remained at room temperature during this furnace-degassing procedure. After a 3-hour degassing period, a blank was obtained on the furnace assembly by collecting the gases released during a 35-minute period, pumping the gases into an evacuated sample bulb, and analyzing them by mass spectrometric analysis.

The temperature of the furnace was lowered below 1000 C and the capsule containing the sample was dropped into the curcible. The temperature was then raised to 2000 C, and as the gas evolved from the furnace it was pumped into an evacuated bulb for mass spectrometric analysis. The time required to extract the evolved gas from the furnace was 1 hour. The quantity of components found in the blank was adjusted for the longer extraction time required for the sample.

A run was made using 9.39 mg of fibrous brucite obtained from The Ohio State University Mineralogy Laboratory. The results, indicating that approximately 95 volume percent of the gas evolved was H_2O and CO, suggest the following decomposition equation:

$$Mg(OH)_2 + C \xrightarrow{2000\ C} H_2O + CO + Mg.$$

Based on this equation, 9.39 mg of brucite should yield 2.9 mg of H_2O and 4.51 mg of CO. The actual recovery of H_2O in this experiment was 157 percent and the recovery of CO was 59 percent.

The 9.39-mg sample was larger than needed for a good analysis, and the large amount of water was difficult to handle because of possible condensation. The second run was made using the same procedure except that the sample weight was reduced to 1.857 mg and the sample and capsule were heated to 100 C in the loading arm during the furnace degassing period to drive off any surface moisture that might have been on the sample.

The extraction time was reduced to 30 minutes for the smaller sample. The end of the extraction time was determined as the point at which no additional gas was being released from the sample. After completion of this extraction the furnace was opened for cleaning and some unreacted sample was found at the base of the furnace compartment. Its weight was subtraced from the original weight, which gave an actual sample weight of 1.658 mg. The most logical explanation for this loss of sample is the "splattering" effect, which frequently happens in vacuum fusion if the tin melts too fast and vaporizes, causing turbulence in the carbon crucible.

It again appeared that the decomposition reaction followed the equation given above. Since some hydrocarbons were present, the H_2 value is probably high. Recovery was 63 percent, based on the amount of H_2O found and 7 percent, based on CO. Some additional unreacted material was found on closer inspection of the furnace interior, but was not weighed. It is not known whether the additional sample found in the bottom of the furnace came from the first or the second run. The vacuum-fusion approach appeared to be giving variable and inaccurate results, and was therefore abandoned.

Quartz-Tube Graphite-Crucible Furnace

The third approach used a series of specially designed quartz-tube graphite-crucible apparatus whose designs evolved as various problems were encountered.

Basically, the quartz-tube graphite-crucible equipment is a means of holding a sample of MgO or $Mg(OH)_2$ in contact with graphite at a high temperature in an rf induction-heated coil. The design for the $Mg(OH)_2$ experiments was quite simple--a quartz tube with a removable base, a stopcock, and a split graphite tube supporting a graphite curcible.

The apparatus was assembled, evacuated, and heated by induction to 2200 C for 1.5 minutes. An evacuation system was not available at the site of the induction heating supply; therefore, this procedure was repeated several times until a constant blank was obtained. The apparatus was opened to the air between each heating and evacuation because opening to the air was necessary to load the sample. A 1.625-mg sample of fibrous brucite was weighed into the crucible and the system was evacuated. The temperature was raised from room temperature to 2200 C in approximately 1 minute and held for 1.5 minutes. The apparatus was transferred to the mass spectrometer, and the evolved gas was measured and analyzed.

Analysis showed that 96.6 volume percent of the gas formed was H_2 and CO. The formation of H_2 in the quartz tube and H_2O in the vacuum fusion is probably explained by the catalytic effect of the mercury diffusion pumps in the vacuum-fusion apparatus and perhaps by the longer reaction time and the presence of tin in the vacuum-fusion system. The difference in final products suggests that H_2, not H_2O, is the original form of hydrogen and that the H_2 subsequently reacts with O or CO in the vacuum-fusion system to form H_2O; alternatively, the H_2O may be dissociated into H_2 and O at the high temperature.

The weight of sample used should have produced 0.0562 mg of H_2. The 0.0563 mg of H_2 found represents a recovery of 100.2 percent. In addition to the H_2 present, it would appear that a small portion of the H_2 reacted to form H_2O, which should be added to the amount of H_2 obtained. The total H_2 recovery based on H_2O and H_2 was 108.6 percent. Calculations based on H_2O and CO show an oxygen recovery of only 88.6 percent; however, the analysis for CO by the mass spectrometric technique is not sufficiently precise in the presence of N_2 to be certain of this apparently low recovery.

The experiment using the quartz-tube graphite-crucible apparatus was repeated using the same procedure except that the quartz tube was cooled by submerging the tube in a beaker of water so that the ground-glass joint was completely covered. This reduced the H_2 blank from 0.0135 mg to 0.0047 mg. Analysis of the reaction products from a sample of fibrous brucite weighing 1.891 mg showed 44.0 volume percent H_2 and 56 volume percent CO. No significant amounts of H_2O, CO_2, or hydrocarbons were detected. The calculated weights of H_2 and CO were 0.0654 and 0.908 mg, whereas the observed weights were 0.0684 and 1.242 mg, representing recoveries of 105 and 137 percent, respectively.

Thermal Decomposition of MgO

Quartz-Tube Graphite-Crucible

Having demonstrated that $Mg(OH)_2$ could be decomposed completely under these conditions, three runs were made in the quartz-tube graphite-crucible technique described above to study MgO (Fisher M-300, B-3, Calcined 700 C Vac., BMI 91938). For these experiments the entire reaction vessel and the induction coil were submerged in deionized water to cool the quart tube. No reduction of the blank was noted, suggesting that the CO and H_2 come from the graphite crucible and its support rather than from the walls of the quartz tube.

A sample weighing 0.2012 g was transferred to the graphite crucible without drying. During evacuation, the pump-down rate was extremely slow; therefore, the gas being pumped off was monitored by the mass spectrometer and found to be water. Not all the water had been pumped off after 30 minutes of pumping.

The temperature was raised gradually, but a very small portion of the sample was ejected from the crucible during the low-heat period. No additional loss of sample was observed at the high temperature. The small amount of water left in the sample may have caused the loss of sample.

Two additional analyses were made on a sample that had been dried at 110 C for 75 minutes. The sample was not redried before the last run was made, but stood in a silica-gel desiccant for 24 hours. These runs were normal in all respects and it was possible to raise the temperature without loss of sample.

The gases collected from the blanks and sample were scanned to mass 100, and no compounds except H_2 and CO were detected in any significant amount. Acetylene at the 0.1 percent level was detected in one run. Based on the H_2 evolved from MgO in the last two runs, the $Mg(OH)_2$ content was 5.9 and 6.7 weight percent, respectively, and for the undried first run, 4.8 percent. The relative reproducibility was about 11 percent.

Degassed Quartz-Tube Graphite-Crucible Experiments

These results were encouraging and suggested that even better results would be possible if the quartz-tube reaction vessel were redesigned to permit degassing and sample loading without opening to the air. This was done, and a vessel using a much smaller graphite crucible, a swinging funnel for dropping the sample into the crucible, and a side arm to store the sample during degassing was fabricated. The next experiments used cold-isostatically pressed Fisher M 300 MgO (BMI S-0460) to minimize the problems of water adsorption associated with powders. This material has a density considerably less than theoretical. The sample had been stored in a polyethylene vial, but was not protected from the air. The pressed material was broken, and a sample consisting of eight random pieces, each of about 1/8-inch cross section, weighed 0.5303 g. After the sample had been loaded into the side arm of the reaction vessel, the system could be evacuated to only 20 microns pressure with the diffusion pump. The gas was 98 volume percent H_2O, 1 percent CO_2, and 1 percent CO.

Pumping had to be continued for several hours with infrared-lamp warming of the sample to 70 C before the pressure could be held constant. The apparatus was attached to the portable pumping system, and the empty crucible was heated to 2200 C for 1.5 minutes while pumping.

The crucible was cooled to room temperature and the reaction vessel isolated from the pumps. The isolated vessel was then heated to a crucible temperature of 2000 C for 1.5 minutes. Analysis of the gas obtained in this blank showed 0.00029 cc-atmosphere* of H_2 [equivalent to 0.26 microgram or 0.5 ppmw of $Mg(OH)_2$], 0.0101 cc-atm of CO, and 0.00003 cc-atm of H_2O.

For the next analysis, the container was pumped out while still on the mass spectrometer, the swinging funnel was placed in the loading position, and the pieces of MgO were pushed from the side arm into the crucible by means of a Pyrex-covered iron bar inside by an external magnet. The funnel was moved out of the heat zone, and the sample was heated to 2000 C for 1.5 minutes.

Analysis of gas evolved from this MgO sample showed a total of 147 cc-atm of gas with the following composition, in volume percent: H_2, 17.9; CO, 33.4; H_2O, 46.5; and CO_2, 2.19. The H_2 amounted to 26.3 cc-atm, which is equivalent to 12.82 weight percent $Mg(OH)_2$ in the MgO [the H_2O was not included in the $Mg(OH)_2$ calculation]. During the heating, a white solid deposited on the side walls of the container in the immediate vicinity of the hot crucible. This material was not identified.

To determine the reproducibility of the method, another sample of the same MgO weighing 0.5136 g was loaded and analyzed as described above, except that no blank was run because the blank for the first was so low as to be insignificant. This analysis showed a total of 152 cc-atm of gas containing 16.7 percent H_2. This is equivalent to 25.4 cc-atm of H_2, or 12.85 weight percent of $Mg(OH)_2$.

The sample used in the second run was unloaded from the apparatus and allowed to stand unprotected from the atmosphere for 64 hours. A portion of this sample was reweighed and again loaded. Only 0.2758 g of the original sample was used because two of the pieces were contaminated with black specks of a foreign substance.

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* Cubic centimeters at standard pressure and room temperature (cc-atm).

The apparatus containing the sample was placed on the mass spectrometer and evacuated for approximately 1 hour. No degassing could be detected on the micromanometer when the pumps were isolated. A mass spectrometer analysis showed only those components normally present in the instrument background.

The same procedure was applied to the analyses described below except that the temperature was raised on some of the runs. The blank run at 2000 C showed only 0.0021 microgram of H_2, which is equivalent to 0.06 microgram of $Mg(OH)_2$. This is 0.22 ppmw based on a 0.27-g sample. The sample was transferred to the crucible and ignited to 2000 C. The total H_2 evolved was 0.08 microgram. After subtracting the blank, this is equivalent to 8 ppmw $Mg(OH)_2$ versus the 12.8 percent originally found, indicating very little additional evolution of H_2. The only other materials detected in this analysis were CO and a trace of CO_2. A dark residue appeared on the side walls of the container in the immediate vicinity of the hot crucible.

The gases were pumped from the container and the sample was heated to 2200 C. The only gas detected in this run was CO, which indicated that no additional hydroxyl compounds were being evolved after raising the temperature 200 C. Optical-pyrometer temperature measurements became more difficult because of an increase of the dark residue noted above.

The final heating was made at 2500 C or higher. Since a blank had not been run at this higher temperature, the blank for 2000 C was used. Only 2 ppm $Mg(OH)_2$ was found. The amount of dark residue on the walls around the hot crucible increased, and temperature reading became even more difficult. As the residue increased, the apparent temperature for a given power setting decreased; thus, the temperature given above actually may have been higher.

These experiments, designed to determine the efficiency of the original extraction of OH at 2000 C, indicated no significant release of components on additional extraction at 2000 C, or when the temperature was raised to at least 2500 C. However, no significant decomposition of MgO occurred.

A sample designated as Fisher M-300, OP 243 (BMI 91940) was analyzed twice by the procedure outlined above. The physical appearance of this sample was quite different from the sample reported above. This MgO had a glazed or translucent surface. Another difference was revealed during pump-down. The sample showed no degassing after approximately 20 minutes of pumping and no infrared-lamp heating was needed during evacuation. The pressed sample was broken into pieces and 0.4986 g was loaded. The blank for this run gave 0.0018 microgram of H_2, which is equivalent to 0.052 microgram or 0.1 ppmw of $Mg(OH)_2$.

The sample was heated to 2000 C and no white residue formed around the side walls, as had been observed with the previous sample. Analysis of the evolved gas showed it to be CO and H_2, the latter equivalent to 2 ppmw $Mg(OH)_2$, net. The duplicate run for this sample had a blank equivalent to 0.17 microgram or 0.4 ppmw of $Mg(OH)_2$ and the sample showed a net of 2.7 ppmw $Mg(OH)_2$. A trace of some compound, possible acetylene, was observed in both gas samples at mass 26. The samples were reweighed after both runs. Each lost 0.4 percent of its original weight. This compares with a 23.9 percent weight loss for BMI S-0460. A dark residue deposited on the side walls of the container for these runs in about the same amount and location as for the previous runs. Water was not detected in these runs, while approximately 45 percent of the gas released from BMI S-0460 was water.

A sample of pressed MgO designated as Kanto MgO, OP 366 (BMI S-0432) was analyzed using the procedure described above. Duplicate analyses gave 133 and 144 ppmw of $Mg(OH)_2$. Little if any actual decomposition occurred under the conditions used for these runs. The reproducibility of this method has been established and the blanks are low and fairly constant, but the accuracy remained in doubt because the MgO had not been dissociated completely to ensure complete liberation of any OH in the sample. Experiments were therefore performed in an effort to convert the MgO to CO and Mg.

Most of the previous analyses were made at a temperature of 2000 C for 1.5 minutes; however, it became obvious that either a higher temperature,

a much longer time at the same temperature, or an increase in both temperature and time would be required to complete the above reaction. The apparatus and technique was modified to permit these changes. To obtain a greater cooling capacity around the reaction vessel, deionized water was frozen and added to the cooling water during the reaction. The temperature of the cold bath was reduced to about 0 C before the blanks or samples were heated, and the bath was stirred continuously. A new quartz-tube apparatus was fabricated, including a larger sample-storage arm. This sample-storage arm was large enough to contain both the sample and a supply of graphite to cover the sample after it is dropped in the crucible.

A preliminary feasibility run was made with powdered MgO covered with powdered graphite, Grade 38, produced by the National Carbon Company. The sample was preconditioned by igniting it in a muffle furnace at 900 C for 45 minutes. The MgO sample was Fisher M-300 (OP 243, BMI 91940). The powdered MgO was obtained by grinding the pressed MgO in a hardened-steel mortar. Powdered MgO weighing 0.1193 g was placed in the graphite crucible and 0.2 g of the powdered graphite was distributed over the sample. Blanks could not be determined because the sample and graphite had already been loaded in the crucible. The system was evacuated and heated to 2800 C for 4 minutes. The evolved gas was analyzed with the mass spectrometer. Because the quartz tube was not degassed at 2800 C, the hydrogen results probably were not significant. The amount of CO that should have been produced (had the reaction proceeded to completion) is 0.0830 g, but only 0.0480 g was actually found, indicating a 58 percent decomposition of the MgO. A small amount of graphite was found in the bottom of the apparatus after the reaction. These encouraging results suggested that a careful analysis for OH of the same MgO material be made.

A sample weighing 0.1088 g was loaded into the front part of the sample storage arm and 0.2 g of graphite (the same as used before) was placed in the back portion. The system was evacuated and degassed at 2800 C, and the blanks were obtained for H_2 and CO at 2000 C and 2800 C. The sample was dropped in the crucible, but no graphite was added. The sample was heated to 2000 C for 1.5 minutes as in previous runs; analysis of the gas collected showed 3 ppmw $Mg(OH)_2$.

Approximately one-half the graphite was added, more than the theoretical amount required for complete decomposition of the MgO, and covering the sample completely. The temperature was raised to 2800 C for 3 minutes, the power was turned off, and additional ice was added to the cooling bath until the temperature of the water dropped to about 0 C. The temperature of the bath rose to slightly above room temperature during a 3-mintue run at 2800 C. This cycle of a 3-minute heating followed by cooling was continued until a total reaction time of 12 minutes had been obtained. The temperature was raised very slowly each time in an effort to prevent graphite loss from the crucible, as had been observed during the feasibility run. These efforts were not successful, as graphite was again observed in the bottom of the quartz tube after the reaction. Only a 2.6 percent conversion of the MgO was obtained and 38 ppmw of $Mg(OH)_2$ was found.

The rest of the graphite was added to the sample and the above experiment was repeated; the temperature was raised very slowly to prevent loss of graphite. The same heating and cooling cycle was used, but only an additional 7 percent conversion was obtained (a total of 9.6 percent). During the 7 percent conversion, more graphite was lost from the crucible, together with some sample. One additional heating was made at 3300 C for 2.5 minutes, but practically no additional conversion was obtained. After disassembling the apparatus, it was found that the graphite crucible was empty and that all the remaining mateial was on the bottom of the quartz tube or on the side walls. Less than 10 percent total conversion was obtained.

Briquetted MgO-C in Quartz-Tube Graphite-Crucible

In an attempt to prevent the loss of graphite and sample, the sample and graphite were then briquetted. A different type of graphite was used for these runs because a better pellet could be obtained with this new graphite. National Special Spectroscopic Graphite, Grade SP-1 (briquetting), was prefired at 900 C for 45 minutes. A mixture of 0.040 g of this graphite and 0.081 g of the powdered MgO was pressed into a pellet.

The pellet was loaded into the sample-storage arm and the system was evacuated and degassed at 2800 C. Blanks were obtained at 2000 C and 2800 C. The pellet was transferred to the crucible and heated at this low temperature; the calculated $Mg(OH)_2$ content was 24 ppmw. The next reaction at 2800 C for 6 minutes produced an additional 41.5 percent conversion and an additional 346 ppmw $Mg(OH)_2$.

As the temperature was being raised slowly for the next heating, a violent reaction, accompanied by sparks flying from the crucible, took place at about 800 C. This lasted only a few seconds, after which the temperature was raised to 2800 C for another 6-minute period. An additional 15.9 percent conversion had taken place, but no hydrogen was detected. After removal of the apparatus from the heating system, a portion of the pellet, still intact, was observed in the bottom of the quartz tube along with some powdered material. This material from the bottom of the container weighed 0.0214 g. Based on the original weight of the sample, a total conversion of 68.9 percent was obtained. If we assume that one-half the weight of residue was MgO, the conversion was 80 percent, based on the original weight of MgO minus the residue weight of MgO.

Although a new source of graphite was used for this run (with no blank data having been obtained), there was evidence that more OH is released from the sample when it is partially decomposed. If the OH release is linear with the percent decomposition, the total $Mg(OH)_2$ for these two experiments would be 423 ppmw and 539 ppmw (or 465 ppmw if the assumed MgO loss is considered) respectively.

Intimate contact of the sample and graphite is very important for decomposition and retention of the sample in the crucible. A pellet of MgO and graphite produced much better conversion than did layers of each in powdered form. The major problem was a severe loss of sample and graphite from the graphite crucible. The powdered graphite was ejected from the crucible no matter how slowly the temperature was raised. The turbulence was probably due to the electromagnetic coupling of the induction heater and the graphite.

Numerous difficulties in effecting decomposition of the MgO were encountered, owing to the high temperature and long reaction time believed to be required. The sample flew out of the crucible, the cooling water became hot, and the induction coil overheated. Therefore, several changes were made. Another induction unit was used which could operate for long periods of time at high power settings and without dissipating an excessive amount of heat in the coil. The coolant for the quartz reaction vessel was deionized water circulated through an ice bath. A quartz-tube graphite-crucible apparatus without a swinging funnel was used for these exploratory experiments to determine whether this second induction unit could decompose the MgO more efficiently and completely than could the first.

The material used for these experiments was Fisher M-300, B-3, calcined at 700 C in vacuum (BMI 91938). Previous work using this material had shown about 5.8 weight percent $Mg(OH)_2$. The MgO was briquetted with Ringsdorff RWA graphite, 1:1 by weight, at 150,000 psi. A sample weighing 0.05 g was loaded into the graphite crucible, a tight-fitting graphite cap with an 0.08-inch-diameter hole was placed on the crucible, and the apparatus was pumped overnight.

The assembly was placed in the induction coil and the temperature of the crucible was raised to 2500 C for 50 minutes. Upon analyzing the gases in the tube, only 3.07 cc-atm of CO were found, whereas about 13 cc-atm should have been produced from the 0.025 g of MgO. No H_2 was detected. The remaining gas was pumped out and the crucible was heated at 2500 C for 20 minutes, then at about 2700 C for another 20 minutes. Only 0.72 cc-atm of additional CO was released, and no H_2. Thus, only about 29 percent decomposition occurred, judged by the quantity of CO. No loss of sample from the crucible was observed, and the usual deposit on the cool walls of the quartz tube was present.

After the tube had been cleaned, a sample weighing 0.0488 g was loaded into the crucible and covered with a graphite disk placed directly on the pellet. The apparatus was pumped and the temperature was raised to about 2700 C for 10 minutes. The gas produced measured only 2.75 cc-atm, all of it being CO with no detectable H_2. The disk and some of the sample had been ejected from the crucible during the run, making a percent-conversion calculation meaningless.

A third run was made using a freshly briquetted sample of the same material weighing 0.0546 g, held in the crucible by a tight-fitting cap with a small hole as described above. Heating at 2000 C for 10 minutes produced 5.8 cc-atm of gas, of which 0.01 percent was H_2, this is equivalent to 40 ppma as H_2 [55 ppmw as $Mg(OH)_2$]. This relatively small amount of H_2 may have been a "blank" value, since the apparatus was pumped for only 1 hour with infrared heating after loading the sample. After pumping off this gas, the crucible was heated at about 2000 C for 18 minutes and then at about 2700 C for an additional 12 minutes. No H_2 was detected in the 1.26 cc-atm of CO produced. Thus, a total of about 7 cc-atm of CO was formed, about a 46 percent conversion.

Note that more decomposition occurred at a lower temperature (2000 C) and in a shorter time (10 minutes) than at temperatures of 2500 to 2700 C and times of from 10 to 50 minutes, but that in no case did the reaction go to completion, judged by the quantity of CO evolved. Either the reaction proceeds better at a lower temperature, or part of the products recombine in some way at the higher temperature. The latter seems the more probable explanation, but the nature of the reaction is not known.

The lack of H_2 in the evolved gas was puzzling because a relatively large amount had been found in earlier experiments. A sample of MgO (Fisher M-300, B-3, BMI S-0460) had been found to have 12.8 weight percent $Mg(OH)_2$. This material was briquetted with graphite and a pellet weighing 0.0678 g was placed in the graphite crucible capped with a tight-fitting graphite cap with a small hole. It was heated for 1 hour at 1700 C. Whereas 15.9 cc-atm of CO should have been produced (assuming 87 percent purity for the MgO), only 5.24 cc-atm were found and no H_2 was detected.

The results obtained using the second induction unit do not agree with the data obtained using the first unit. The first unit operates at about 0.375 mHz and the second at about 0.450 mHz. Although this is not a large difference, it is possible that the different frequency accounts for the lack of H_2 when the second unit is used. To check this possibility, a pellet of graphite-MgO (Mgo was Fisher M-300, B-3, calcined at 700 C in vacuum, BMI 91938) weighing 0.0555 g was loaded into the graphite crucible capped as before. The sample was heated with the second unit for 30 minutes

at about 2800 C. Larger diameter copper tubing was used for the coil, allowing better cooling and therefore continuous operation at full power, with some loss in maximum temperature attainable because fewer turns surrounded the crucible. The evolved gas, 6.18 cc-atm, had H_2 equivalent to 0.34 percent $Mg(OH)_2$, and the decomposition was 41 percent of theoretical. The gas was not pumped out, leaving about 5.5 cc-atm in the apparatus. After 2 hours of heating at full power, only 2.99 cc-atm remained--a decrease of about 2.5 cc-atm. Heating the sides of the vessel produced no additional gas, and no compounds other than CO and H_2 could be detected. When the apparatus was opened, a residue weighing 0.266 g remained in the crucible. If one assumes that all this was graphite, the decomposition percentage was 96.2; it seems more likely that part of the residue was MgO, and therefore the decomposition percentage was between 41 and 96. The important point is the disappearance of almost one-half of the H_2 upon prolonged heating, an effect mentioned above. Also, H_2 was found while using the second unit, but not with the first.

Laser-Beam Heating

Because so many problems arose using inductive heating, and because the data were not reproducible or easily interpretated, another mode of decomposing the MgO was explored. A Raytheon Model LG12 argon-ion laser was used as a heat source to decompose MgO. This laser has a maximum output of 1.0 watt, of which approximately 0.75 watt was used in this experiment. A graphite-MgO pellet (Fisher M-300, B-3, calcined at 700 C in vacuum, BMI 91938) was placed inside an evacuated Vycor tube with a graphite support in the bottom. This continuous laser did not produce sufficient energy to decompose the MgO. Mass spectrometric analysis of the vessel contents showed no detectable pressure in the container and the spectra were those of normal instrument background.

A pulsed ruby laser operating at 6943 A and conventional mode was used on the same sample. After approximately 50 shots, the gas content of the sample container was analyzed. The gas produced contained approximately 80 percent CO and 20 percent H_2, with a total gas content of 0.06 cc-atm. Some hydrocarbons were also present, and the amount of H_2 in the

vessel [equal to 35.8 weight percent of $Mg(OH)_2$] exceeded that expected for the sample, which previously had been found to have 5.8 percent $Mg(OH)_2$. The large carbon sample support had not been degassed at an elevated temperature, and therefore probably released the hydrocarbons and some of the H_2.

This encouraging performance indicated that ruby-laser heating might be a solution to the OH determination. A sample container was designed having a quartz optical-flat window, a split-tube graphite pedestal, and a graphite holder and open-end cap to clamp a briquette of MgO-C in place. This briquette, made with the Fisher M-300, B-3 MgO, calcined at 700 C in vacuum, BMI 91938, and briquetting graphite, was about 2.8 cm in diameter and about 0.3 cm thick. A large diameter was chosen to be certain that the laser beam would strike the briquette and not the retaining cap; this precaution proved unnecessary.

The assembly was pumped for 48 hours and then heated for 2 hours with infrared lamps (the Vycor wall temperature was 285 C). The large amount of H_2O and CO_2 evolved indicated considerable degassing of the graphite and/or the briquette. After evacuation, the briquette and its graphite holder and cap were heated inductively for 1 minute at 1000 C. This temperature could not be maintained because the entire support system coupled to the rf coil, exposing the Vycor end cap and the standard-taper joint to excessive heat. A large amount of gas was evolved during this brief heating. The analysis of the 150 cc-atm produced was (in volume percent): H_2O, 52; CO_2, 10; H_2, 22; and CO, 16. At least some of this gas probably came from the massive graphite structures. The gas was pumped out and the apparatus was moved to the ruby-laser site.

Although the preliminary heating was not as thorough as had been planned, the graphite support and the MgO-C briquette probably were outgassed sufficiently, considering that in the subsequent laser work only the immediate area hit by the beam was heated to any appreciable extent.

The laser employed and the operating parameters were: Korad K 1 ruby laser, 6943 A, 0.4-A line width, 1.4-cm beam diameter (focused to about 2.5 mm at the target), about 4 joules output, 0.0005-second pulse width, 100 percent vertical polarization, and 4300-v power setting.

After 10 shots were made in one area, the sample was moved for another 10 shots until a total of about 250 shots had been fired. In one area about 60 shots were fired. Crater depths were of the order of 0.8 mm for 10 shots, and about 3 mm for 60 shots.

The evolved gas measured 1.13 cc-atm and had the following composition (in volume percent): H_2, 7.25; CO, 90.6; CH_4, 0.40; C_2H_2, 1.58; CH_3-C$\equiv$CH (propyne), 0.25; and unidentified hydrocarbon(s), about 0.05. The CO is equivalent to 1.84 mg of MgO, and the H_2 is equivalent to 11.3 weight percent as $Mg(OH)_2$ or 7.9 atomic percent as H_2--about twice the value obtained by induction heating at 2400 C. If the H_2O obtained in the induction heating is included, the total weight percent of $Mg(OH)_2$ is 19.7. However, it is not certain that all the H_2O came from the sample; some may well have come from the massive graphite structure as noted above. Further, the H_2 from the induction heating was not included in the calculations because it was found at a higher level than CO, implying there was more $Mg(OH)_2$ than MgO, a conclusion that certainly would not be in agreement with any other data.

Another run was made using a redesigned sample pedestal of Lavite, a nonconducting material; the distance from the sample to the optical window was also increased to reduce the fogging of the window. Infrared heating produced 0.13 weight percent H_2O, induction heating at 1000 C for 6 minutes produced H_2 equivalent to 20.4 weight percent $Mg(OH)_2$ but no H_2O as such, and 600 laser shots produced H_2 equivalent to only 0.03 percent $Mg(OH)_2$. The total, excluding the "free" water produced by infrared heat, was 20.4 weight percent $Mg(OH)_2$.

Still another run was made using only the laser, 165 shots, with no infrared or induction heating. The H_2 produced was equivalent to 20.2 percent $Mg(OH)_2$ by weight.

To check the laser technique on a coarser sample with less OH, OP 243, BMI 91940, was ground, then mixed 1:1 by weight with graphite and pressed into a briquette. The apparatus in which the MgO C pellet was heated was a quartz tube, with a Lavite pedestal, capped by a platinum disk to which the pellet was attached. One end of the tube was an optical

flat for use with the laser. The assembly was evacuated and heated by infrared until no outgassing could be detected. The sample was heated by induction to 1000 C for 6 minutes and the quantity of gas was measured and analyzed. After subtracting the blank obtained on the graphite, it was determined from the amount of H liberated that the sample contained 0.17 weight percent $Mg(OH)_2$. Since the entire sample is heated by the induction method, calculations are based on the total weight of MgO in the pellet. (Since only a minute quantity of the MgO is heated by the laser, calculations for laser heating are based on the amount of MgO decomposed as calculated from the amount of CO produced.)

Another sample of OP 243 was treated in the same manner except that fine-focus laser heating was used before the induction heating. The amount of CO liberated indicated 4000 μg of the MgO was decomposed, but the amount of $Mg(OH)_2$ was only 85 ppmw. After evacuating the system again, the sample was heated by induction for 6 minutes at 1000 C, and the CO liberated indicated 7240 μg of the MgO was decomposed. Based on the H liberated, the total sample contained 0.16 weight percent $Mg(OH)_2$. The laser result at high energy indicated very low OH content although very good check results were obtained on the low-temperature induction-heating method. These results, together with results obtained earlier on Sample BMI 91938, suggest that increased energy (high-temperature induction heating) produces a loss of H. The focus of the laser beam was changed to reduce the effective energy, and the following experiment was made with the diameter of the beam at the impact point about 1/4 inch.

Another sample of OP 243 was treated the same as before and run by laser, this time with the large-diameter beam and 60 shots. A blank on the graphite was also run under these same conditions. Under these conditions, about one-tenth the amount of MgO decomposed, but the amount of H liberated indicated the sample contains 0.33 weight percent $Mg(OH)_2$.

The same sample was analyzed by 160 laser shots with 10 joules. The fine focus was used, which produced an impact area about 1 mm in diameter. Decomposition of the MgO amounted to 3200 μg, and the $Mg(OH)_2$ was equivalent to 37 ppmw.

The above data verify the evidence from the induction-heating experiments that higher temperatures yield less H from the MgO or that a secondary reaction which consumes H is taking place. The mass spectrometer shows no products other than CO which might account for a secondary reaction. No significant amount of free water was found in any of the above experiments.

Oxygen Reaction

Upon examining the thermodynamics of the MgO system, it was calculated that the reaction $2MgOH + \frac{1}{2}O_2 \longrightarrow MgO + Mg(OH)_2$ was favored by heat, and of course by O_2. Since $Mg(OH)_2$ is known to be unstable above about 400 C, the technique of heating MgO in O_2 is theoretically a means of liberating the H.

Several experiments were made to establish the feasibility of the technique. In the first two runs MgO (Fisher M-300, calcined in vacuum at 700 C, BMI 91938) was used. Briefly, the sample was heated at 100 C and at 500 C in vacuum, and at 500 C with O_2 flowing. Discrete amounts of H_2O were liberated at each step; by far the largest amount came during the 500 C--no O_2 step, but a significant additional amount was obtained when O_2 was added.

A sample of MgO weighing about 10 mg was placed in a Vycor boat inside a Vycor reaction vessel. The latter was designed to pivot about an axis formed by the arms attached to the inlet and outlet gas lines. The main vessel chamber was blanked at the selected temperatures, then was rotated to allow the sample boat to slide into the heating zone. The O_2 supply was tank O_2, purified of H_2O by passing through 13X molecular sieves held at -10 C. The outlet gases passed through a liquid nitrogen trap and into the mass spectrometer inlet or, with O_2 flow, into a trapped mechanical pump.

In the first run the sample was held at 100 C for 20 minutes under vacuum, and the H_2O released was collected and measured. Presumably this is surface or physically bound water. Next, the sample was held at 500 C in vacuum, and again the released H_2O was measured. This is assumed to be water present in the sample as $Mg(OH)_2$. Finally, the sample was maintained at 500 C with about 20 torr O_2 flowing through the vessel. The H_2O released during this step is thought to be that which was held as MgOH in the sample.

The second run was similar, except that at least two heating periods were employed at each step to determine if the increases were real or were merely evidence of insufficient time in the previous step.

The data indicated a definite break in the elution of H_2O between 100 C, 500 C without O_2, and 500 C with O_2 present. Previous runs on this sample using the mass spectrograph, laser beam and induction heat decomposition showed about 20 percent $Mg(OH)_2$; however, the distinction between $Mg(OH)_2$ and MgOH was not made. See Table 15, Appendix B.

For Run 1 the sample was weighed after the reaction and had lost 0.0009 g, about 10 percent. (A small amount blew out of the boat during the run and was not weighed.) The sample from Run 2 was lost during removal from the apparatus.

The $MgO-O_2$ system was further investigated by applying it to Sample OP 366 (BMI S-0432) using the procedure and equipment described above.

The temperatures investigated were 100 C without O_2, 500 C without and with O_2, and 900 C without and with O_2. Blanks were obtained at each condition prior to running the sample by making a complete run without sample in the system.

A 0.0968-gram sample was pumped for 20 minutes prior to starting the heating and collecting period. Starting with the 500 C run without O_2, hydrocarbons appeared in the spectra, voiding the CO_2 values obtained, but the run was continued for the information on the H_2O release. After the runs at 500 C with O_2, the system was heated to 900 C with O_2 by mistake instead of 900 C without O_2. Because hydrocarbons were present, and because the 900 C without O_2 step was omitted, this run was discontinued.

A new sample weighing 0.1116 g was loaded and started at the 500 C without O_2 step. Unfortunately, the cold trap broke just before the analysis of this extracted material; therefore, no check results were obtained against the previous sample. Hydrocarbons were also present in this run and were found to be coming from the standard taper joint at the end of the reaction tube. The previous work on BMI 91938, in which fairly good reproducibility was obtained, did not show any appreciable hydrocarbons. However, because the taper joint had broken twice because the Pyrex top section was fitted inside the quartz bottom section, this joint was reversed, moving the wax seal about 1 inch closer to the heat zone. This evidently was enough to cause a slight pyrolysis of the wax. Two major procedural changes nearly eliminated the problems encountered with hydrocarbon formation from the waxed joint and contamination of the system with some impurities in the O_2 supply. Equipment modifications were made which increased the distance from the heat zone to the joint, and a Dry Ice-acetone bath (approximately -80 C), used on the molecular sieves trap (instead of the saline bath at -10 C), lowered the concentration of the impurities from the O_2 supply in the liquid-nitrogen collection trap.

Another sample of OP 366 was investigated using the same procedure except that at each variation of the reaction the chamber was heated for a 1-hour period instead of multiple half-hour periods. The initial release of moisture at 100 C should be expected to vary, even for the same sample, depending on the humidity during the weighing and loading steps and on any differences in the initial evacuation of the sample. Very good check results for these two runs were obtained at 500 C without O_2, 900 C without O_2, and 900 C with O_2.

A study of the effect of time on the release of H_2O was made. After the first half-hour run at 500 C with O_2, in which 15 ppmw $Mg(OH)_2$ was found, an additional 24 ppm was released on the next day, an additional 12 ppm three days later, no more on two runs later the same day, and finally an additional 15 ppm the following day. It is obvious from this experiment that a slight but measurable diffusion effect takes place in the sample while standing in vacuum at room temperature. Although only a small

additional amount of H_2O was released at 500 C with O_2 over a 6 day period, it had been shown earlier that large quantities of H_2O are released much more rapidly under the same temperature and atmosphere conditions from Fisher M-300 MgO that had been vacuum calcined at 700 C (BMI 91938).

The difference in particle size probably accounts for the apparent tailing of the OH release from OP 366 at 500 C, as compared with the rather sharp cutoff with the M-300 sample. The latter is very fine (submicron) while the former is probably in the 10-100 micron range as it was handground in a mortar. To check this possibility OP 366 (BMI S-0432) was screened using 100 and 120 mesh sieves. The material that passed the 100-mesh sieve and remained on the 120-mesh sieve was used to determine OH content. The material which did not pass the 100-mesh sieve represented approximately three-fourths of the total sample used in previous experiments. Only about one-tenth of the material passed the 120-mesh sieve. The sample taken from the 120-mesh sieve should therefore represent a material of considerably greater surface area for a given weight of sample. If the OH release detected by this method is essentially absorbed moisture which is slow to be released, then the sieved material should show greater and faster release, especially at the 500 C without O_2 step. The release of moisture at 100 C was significantly higher than obtained on the unsieved material. At 500 C without O_2 the results were 8.8 percent higher than found in the unsieved material. The reproducibility is probably about 10 percent relative. Results at 900 C without O_2 were lower than those previously obtained and higher at 900 C with O_2. Subtracting the values obtained at 100 C the sieved material showed a total of 3604 ppmw calculated as $Mg(OH)_2$ and the unsieved material 3383 ppmw. This is an increase of only 6.5 percent relative

As a further check on the surface adsorption possiblity, the sieved sample was removed from the apparatus and exposed to the atmosphere at approximately 52 percent relative humidity for 18 hours. The sample was reloaded and analyzed as before. The surface moisture was 152 ppmw as $Mg(OH)_2$ versus 48 for the unsieved material and 227 for this sample originally. At 500 C without O_2 the $Mg(OH)_2$ was only 3.7 percent of the

original sieved run and at 500 C with O_2 step, 12 percent of the corresponding amount found in the original run of this sieved sample. The amount of $Mg(OH)_2$ obtained at 900 C with and without O_2 was <1 ppmw. The analysis after exposure to atmospheric moisture indicates a pick-up of moisture on the surface but no deep penetration of moisture, and also that the original analysis released approximately 96.3 percent of the moisture, excluding the surface moisture represented by the 100 C step.

During each analysis of MgO by this MgO-O_2 system the samples turned light brown when exposed to heat at 500 C but returned to the original white color at 500 C with O_2. At 900 C without O_2 only a very slight color change can be noted. During the repeat run after an 18-hour exposure to 52 percent relative humidity, the sample showed only a trace of discoloring at 500 C without O_2. This suggests that the material causing the discoloration was either driven off during the first run, or was chemically changed.

Summary

To summarize the OH in MgO work, the release of OH using the MgO-O_2 system is satisfactory and appears to offer the possibility of detecting three types of OH by using different conditions. It has been demonstrated quite clearly that true bulk OH is being determined, not surface adsorbed OH or H_2O alone.

Data relating to the above experiments are summarized in Appendix B.

Mass Spectrographic Determination of OH

Mass Spectrograph

Because the spark employed in the mass spectrograph breaks up any compound (the temperature in the spark gap has been estimated to be as high at 50,000 C), the OH, no matter how it is bound in the crystal lattice, should be seen as H, H_2, or OH. The possible lines are $^1H^+$,

$^{1}H_2^+$, and $^{16}O^{1}H^{+1}$ at m/e 1, 2, and 17, respectively. MgOH or $Mg(OH)_2$ would not be expected in significant and reproducible amounts. In spectra of briquetted MgO powder and Ag (1 MgO:2 Ag) the $\frac{OH^+}{H^+}$ and $\frac{H_2^+}{H^+}$ ratios were determined to be about 0.15 and 0.22, respectively, while the same ratios using Pt wire were 0.0009 and 0.098. This implied that the OH^+ was a function of the OH content of the MgO. At the levels of OH apparently present in the powder MgO (thousands of ppm), there is no significant $^{17}O^+$ contribution. But in some compacts the m/e 17 line gives results approaching or below the expected $^{17}O^+$ contribution. Based on MgO (ignoring the Ag), O would be expected to contribute approximately 50 percent of the ions; of the O ions, ^{17}O would be 0.037 percent, or about 190 ppma of the total Mg + O ions. Any determination of OH at m/e 17 below several hundred ppma is therefore out of the question unless one can correct for the ^{17}O contribution or can resolve $^{17}O^+$ from $^{16}O^{1}H^{+1}$ (resolution necessary = 4700). Very few spark-source instruments can achieve this resolution routinely, which is beyond the resolution of Battelle's instrument. Note that Dr. Leipziger, in his Final Report (March 1966, Contract 950992, page 20), reports H values (presumably read from m/e 1) as low as 15 ppmw (= 600 ppma) in compacts. If his $\frac{OH^+}{H^+}$ ratio were the same as Battelle's, 0.15, his observed ppma at m/e 17 would have been about 90--well below the above-mentioned $^{17}O^+$ level expected.

Dr. Leipziger, in his work at Sperry Rand, tentatively concluded that is was possible to relate the intensities of the lines at m/e 1, 2, and 17 to the true OH content of the sample. Certainly his work on refractory metals proved that H, as determined at m/e 1, could be determined by this technique with reasonable accuracy. His values for H in two solid samples of MgO were 600 and 1400 ppma in OP 14 and OP 111, respectively; Battelle mass results for these same samples were 2000 and 600 ppma H, respectively. The agreement is within a factor of about three, but the reversal in values obtained is disturbing.

Because the $MgO-O_2$ method for OH appears to be quite reliable and accurate, it should be used in preference to the mass spectrographic approach. The mass spectrograph does appear to give order-of-magnitude OH data particularly if the source and samples are baked. At the levels of OH usually found in MgO the background is not a serious problem; other than a lack of reproducibility the main difficulty lies in making and measuring the very short exposures in which tenths of a percent of H are read.

ANALYSIS OF UNIVERSITY OF WASHINGTON MATERIALS

Zr_2CO

Three samples of a material produced by reacting ZrO_2 and C were studied, one in detail, to determine if they were indeed Zr_2CO.

Thermal Decomposition

Two runs were made in the vacuum fusion furnace using degassed graphite crucibles. In Run 1, 8.5 mg of Zr_2CO (Sample 28) was heated for 40 minutes at 1900 C using a bath of Pt at a ratio of 100 Pt:1 sample. Only 20.1 percent O recovery was obtained (based on the composition of Zr_2CO) even when all forms of O were considered (CO, CO_2, H_2O, and O_2). A second run, using 87.6 mg Zr_2CO, an extraction time of 45 minutes, a temperature of 2400 C, and a Pt bath in the ratio of 12 Pt:1 sample gave a recovery of 23.3 percent, only slightly higher. Most of the gas produced is CO, with lesser amounts of other gases. The theoretical weight percent of O in Zr_2CO is 7.60.

Chlorination

Another portion of the Zr_2CO used for the experiments reported above was reacted with Cl_2. The experiment was fairly crude, being made only to see if the reaction would proceed. About 10 mg of Sample 28 was placed in a reaction tube. Tank Cl_2 was bled in and frozen in one end. Air impurities were pumped off (over several percent of air were present in the Cl_2, either from inadvertent contamination or as an impurity from manufacturing). The Cl_2 was allowed to warm and the sample was heated slowly with a torch. Only a very slight reaction took place until the sample reached a certain temperature, not measured but probably in the 400 to 600 C range. Suddenly the Zr_2CO glowed, producing dense white fumes, probably $ZrCl_4$. A trace of black residue remained in the boat (C?). The Cl_2 in the reaction tube was frozen, and the noncondensable gas qualitatively analyzed.

The experiment was repeated carefully to establish the quantities of the gases evolved.

A sample weighing 0.0108 g was placed in a Vycor reaction chamber with an inlet line from a research-grade Cl_2 supply and an exit line to the mass-spectrometer sample-inlet system. The reaction vessel contained a built-in cold finger to freeze out the Cl_2 entering the chamber and also to prevent dilution of the released gases, to freeze it out of the system again after the reaction. The sample, the chamber, and the equipment lines were degassed at 100 C for 24 hours, and a background analysis showed only normal instrument background.

Approximately 0.5 gram of Cl_2 was introduced into the system and frozen with liquid nitrogen; the system than was opened to the micromanometer. The lack of detectable pressure increase indicated that the Cl_2 had few, if any, noncondensable impurities. After the system was pumped a few minutes and then isolated, the reaction vessel was heated at an approximate rate of 20 degrees per minute. A sudden reaction took place at 385 C; heating was continued to 400 C and held at that temperature for 10 minutes. The system was cooled, the Cl_2 frozen out, and the evolved gases measured and analyzed.

The recovery of N_2, CO, and O_2 indicates that only 3.5 percent of the sample could be Zr_2CO and 1.0 percent, ZrN. There is no ready explanation for the difference between the results of this experiment and the vacuum-fusion decomposition experiments. No apparent causes of these very low recoveries were noted in either the chlorination or the vacuum-fusion experiments. In the chlorination runs large amounts of a white film ($ZrCl_4$?) were deposited on the cooler walls of the reaction chamber--more than would be expected from 4.5 percent of the 11-mg sample taken. Further, only a tiny black residue remained in the boat, much less than about 95 percent of the original 11 mg of Zr_2CO.

Elemental Analysis

The black residue in the boat was found to weigh 0.886 mg and to be 43 weight percent C. The remainder was not determined but may have been some compound of Zr. The deposit inside of the reaction vessel was washed into a beaker, and the total recovered Zr was 9 mg. Elemental analyses of the as-received material by optical emission, X ray fluorescence, chemical, and mass spectrographic means accounted for over 98 percent of the material. These data for Sample 28, given in tabular form in Appendix B, quite clearly show that Zr_2CO is not the correct molecular formula for at least Sample 28.

MgO

Two MgO samples from the University of Washington were analyzed by emission and mass spectrography. The results are given in Appendix B. The cube was reported to be "4-9's" pure. The samples were sparked directly versus Ag and Ta counter electrodes, but the ion beam consisted of many more counter-electrode ions than Mg and O ions. The samples were therefore ground in a boron carbide mortar (the reported B values are from the direct sparking runs), briquetted, and analyzed as usual.

Three other samples of MgO were analyzed mass spectrographically for OH only, baking the source and the sample before each analysis. The results, expressed as percent of $Mg(OH)_2$ by weight, were: 0.38, 1.3, and 3.2 for samples A, B, and C, respectively.

Al_2O_3

One of the materials specified for research in this program is Al_2O_3. In an effort to make the research efforts as useful as possible to those working in the refractory ceramics field, other materials of interest were studied near the end of the program. An analysis of a single crystal of Al_2O_3 from the University of Washington is reported in Appendix B. The analysis of this starting material, Linde polishing powder, is the "Given" analysis in the table, and may not represent what would be expected in a finished crystal. It appears that some of the more volatile impurities (Sn, Ag, Mn, B) were removed during the flame fusion growing, and that others (Mg, Ca) were picked up. Most of the other impurities showed good agreement between the vendor's emission spectrographic analysis of the powder Al_2O_3, Battelle's emission spectrographic analysis of the single crystal, and Battelle's mass spectrographic analysis of the single crystal. On the basis of this one sample, it appears that the analysis of Al_2O_3 does not present any unusual difficulty.

It was found, however, that mortar contamination was a serious problem because the Al_2O_3 is so hard. High and unpredictable impurities were picked up from mortars made of sapphire and tungsten carbide, probably reflecting materials previously ground in these mortars and not removed despite careful cleaning. If many samples of hard materials were to be analyzed, it would pay to reserve a new mortar for that material alone to reduce chance contamination.

APPENDIX B

ANALYTICAL DATA GENERATED IN THE COURSE OF THIS RESEARCH PROGRAM

APPENDIX B

ANALYTICAL DATA GENERATED IN THE COURSE OF THIS RESEARCH PROGRAM

The tables of data which follow have appeared in previous reports and are presented here for completeness. Except where noted, the samples were sent to Battelle from JPL by Dr. Leipold while he was technical monitor of the program. The data are grouped by type or supplier to facilitate finding a specific item. Where available, cross check data are included. Most of the early thermal data on H (or OH) have been deleted because later experiments showed that these data probably were invalid.

Table 1 provides cross check data for many elements and also shows the levels of impurities in reasonably pure MgO and $Mg(OH)_2$.

Table 2 compares results from different laboratories and techniques for typical impurities in MgO.

Table 3 is an expansion of Table 2, and includes all elements reported.

Tables 4, 5, and 6 give the analytical results for a number of MgO samples received from JPL. Table 6 has some cross check data.

Table 7 compares available values on a single-crystal MgO sample.

Tables 8 and 9 give the analyses of MgO samples with some cross check data.

Tables 10 and 11 report the results obtained using synthetic standards and an internal standard. The data in Table 10 form the basis for currently-used sensitivity factors.

Table 12 shows the cross check data for an Al_2O_3 sample.

Table 13 points out the rapid pickup of CO_2 from the air.

Table 14 is a condensed summary of the many experiments performed to develop a method for the determination of OH in MgO.

Table 15 presents the data that establish the MgO-O_2 method as valid.

Tables 16 and 17 present the results obtained using several techniques to evaluate a sample nominally Zr_2CO.

TABLE 1. ANALYSIS OF KANTO SAMPLES

(ppma)

Element	$Mg(OH)_2$[a] Mass	$Mg(OH)_2$[a] Given[d]	$Mg(OH)_2$[a] Chem	MgO[b] Mass Run 1	MgO[b] Mass Run 2	MgO[b] Given[d]	MgO[b] Chem	Calcined MgO[c] Mass Run 1	Calcined MgO[c] Mass Run 2	Calcined MgO[c] Chem
Li	<2.	--	--	<2.	--	--	--	<0.2	--	--
B	100.	--	--	20.	--	--	--	10.	--	--
C	60.	--	2,200.	2,000.	300.	--	570.	60.	--	7,400.
N	60.	2,500.	7,500.	600.	300.	195.	86.	20.	10.	500.
F	50.	--	<30.	200.	250.	--	310.	6.	25.	110.
Na	20.	--	--	40.	--	--	--	<2.	--	--
Al	10.	22.	--	10.	--	60.	--	20.	--	--
Si	200.	55.	83.	200.	100.	29.	71.	100.	200.	130.
P	20.	10.	--	20.	--	8.5	--	6.	--	--
S	200.	17.	42.	1,000.	200.	--	250.	30.	50.	51.
Cl	600.	17.	26.	600.	25.	45.	52.	20.	50.	19.
K	20.	--	--	20.	--	--	--	<2.	12.	--
Ca	20.	15.	12.	50.	60.	30.	30.	20.	100.	18.
Ti	20.	--	--	20.	--	--	--	20.	--	--
V	<1.	--	--	<1.	--	--	--	0.6	--	--
Cr	≤2.	--	--	≤2.	--	--	--	1.	--	--
Mn	2.	1.1	--	2.	--	3.	--	1.	--	--
Fe	20.	3.5	--	20.	--	11.	--	20.	--	--
Co	<2.	--	--	<2.	--	--	--	0.6	--	--
Ni	3.	--	--	3.	--	--	--	1.	--	--
Cu	3.	--	--	3.	--	--	--	0.3	--	--
Zn	10.	--	--	10.	--	12.	--	1.	--	--
As	2.	0.4	--	2.	--	0.2	--	<0.2	--	--
Br	<1.	--	--	<1.	--	--	--	<0.4	--	--
Zr	<0.5	--	--	<0.5	--	<0.25	--	<0.5	--	--
Mo	<0.4	--	--	<0.4	--	--	--	<0.4	--	--
Ba	<0.6	--	--	<0.6	--	6.	--	<0.6	--	--
Pb	<1.	1.5	--	<1.	--	2.	--	<1.	--	--

(a) BMI S-0431.
(b) BMI S-0430.
(c) BMI S 0429.
(d) Analysis supplied with sample; other values are BMI.

TABLE 2. COMPARISON OF TECHNIQUES FOR CERTAIN ELEMENTS IN FOUR SAMPLES OF MgO (FISHER M-300)

(ppma)

	F	Na	Si	S	Cl	K	Ca
Original Lot (BMI 90940)							
Bell & Howell (M)	4700.	61.	1800.	420.	80.	64.	310.
Sperry Rand (M)	110.	100.	2400.	510.	285.	<1.	150.
Sperry Rand (E)	--	500.	>1000.	--	--	<1.	350.
Battelle (M)	100.	30.	350.	300.	400.	30.	2000.
Battelle (E)	--	200.	450.	--	--	<30.	2400.
Battelle (C)	1330.	--	--	100.	200.	10.	-
B-3 Calcined (BMI 91938)							
Battelle (C)	1310.	340.	350.	121.	435.	12.	2750.
Battelle (M)	1300.	50.	800.	100.	300.	10.	2500.
B-3 As Received (BMI 91939)							
Battelle (C)	1700.	23.	350.	89.	285.	10.	1450.
Battelle (M)	2000.	12.	4000.	150.	200.	3.	2500.
OP 243 (BMI 91940)							
Battelle (C)	1330.	290.	640.	85.	595.	8.	2680.
Battelle (M)	2000.	300.	300.	300.	300.	300.	5000.

(M) Mass spectrographic.

(E) Emission spectrographic.

(C) Chemical.

TABLE 3. COMPARISON OF ANALYTICAL RESULTS FOR FISHER M-300, BMI 90940

(ppma)

Element	Bell and Howell (Mass)	Sperry Rand (Mass)	Sperry Rand (Emission)	Battelle (Emission)[a]	Battelle (Emission)[b]	Battelle (Emission)[c]	Battelle (Emission)[d]	Battelle (Chem.)	Battelle (Mass)
Li	1.2	--	--	--	--	--	--	--	<0.1
B	300.	3.	<10.	80.	--	--	40.	--	100.
C	--	--	-	--	--	--	--	27,000.	300.
N	100.	100.	-	--	--	--	--	--	50.
F	4700.	110.	--	--	--	--	--	1,330.	100.
Na	61.	100.	500.	200.	--	--	--	--	30.
Al	100.	75.	50.	75.	--	--	--	--	10.
Si	1800.	2400.	>1000.	450.	500.	--	430.	--	350.
P	120.	130.	--	--	--	--	--	--	10.
S	420.	510.	--	--	--	--	--	97, 100.	300.
Cl	80.	285.	--	--	--	--	--	200.	400.
K	64.	<1.	<1.	--	--	--	--	300.	30.
Ca	310.	150.	350.	>500.	2300.	2500.	>500.	--	2000.
Ti	66.	10.	<10.	100.	85.	58.	16.	--	15.
V	<1.	--	--	--	--	--	--	--	0.3
Cr	16.	5.	<5.	2.5	--	--	<8.	--	10.
Mn	22.	2.	<5.	30.	35.	15.	30.	--	10.
Fe	510.	85.	65.	110.	80.	90.	220.	--	120.
Co	<1.	10.	5.	2.	--	--	--	--	2.
Ni	10.	10.	<5.	3.5	--	--	<7.	--	4.
Cu	12.	5.?	<5.	<3.(T)	--	--	3.	--	2.
Zn	97.	11.?	5.	<6.	--	--	--	--	4.
As	<1.	--	--	--	--	--	--	--	1.
Br	<1.	--	--	--	--	--	--	--	1.5
Sr	<1.	--	--	2.5	--	--	--	--	--
Zr	<1.	--	--	7.	--	--	--	--	--
Ag	<1.	--	--	1.	--	--	1.	--	--
Cd	15.	--	--	--	--	--	--	--	--
Pb	<1.	--	--	--	--	--	--	--	0.4

(T) Trace.
a 1:1 graphite, enclosed Stallwood jet, 70% Ar, 30% O_2.
b Germanium matrix (MgO:Ge:C = 1:9:10).
c Solution spark.
d Sperry Rand method.
-- No data reported, element not sought, or element not detected.

TABLE 4. MASS SPECTROGRAPHIC ANALYSIS OF BMI-3-PRESSED MgO

(ppma)

Element	Sample Number 1[a]	2[b]	3[c] Run 1	3[c] Run 2
H	30,000.	5,000.	1,000.	--
OH[d]	3,000.	300.	100.	[1,000.]
Li	0.3	0.3	≤1.	2.
B	10.	25.	≤1.	2.
C	2,000.	1,000.	1,000.	[10,000.]
N	300.	100.	50.	[1,000.]
F	10.	20.	1.	5.
Na	10.	≤1.	<1.	10.
Al	10.	3.	30.	10.
Si	100.	100.	400.	500.
P	5.	3.	2.	5.
S	100.	100.	100.	500.
Cl	100.	12.	40.	130.
K	30.	≤1.	10.	30.
Ca	20.	10.	50.	100.
Ti	<4.	<1.	40.	40.
Cr	1.	4.	10.	15.
Mn	≤0.3	1.	10.	3.
Fe	10.	10.	400.	50.
Co	1.	<0.1	1.	≤1.
Ni	1.	1.	15.	15.
Cu	15.	15.	15.	5.
Zn	10.	10.	70.	15.
Pb	1.	3.	1.	<0.4

(a) As pressed.
(b) 1010 C.
(c) 1750 C.
(d) Read at m/e 17.
[ ] Sample not baked.

TABLE 5. MASS SPECTROGRAPHIC ANALYSIS OF POWDER MgO SAMPLES

(ppma)

Element	Sample Number			
	B-62	B-63	B-64	B-65
H	[100,000.]	[50,000.]	[100,000.]	[100,000.]
OH(a)	[10,000.]	[50,000.]	[100,000.]	[10,000.]
Li	0.3	0.3	0.3	0.3
B	2.	<0.1	3.	1.
C	[300.]	[3,000.]	[3,000.]	[2,000.]
N	[20.]	[200.]	[30.]	[10.]
F	3.	<1.	20.	2.
Na	1.	<1.	3.	<1.
Al	10.	50.	20.	10.
Si	15.	<4.	300.	10.
P	3.	0.3	10.	3.
S	15.	10.	300.	30.
Cl	300.	100.	1,000.	150.
K	2.	5.	30.	3.
Ca	≤100.	30.	30.	10.
Ti	40.	40.	40.	10.
Cr	1.	0.3	1.	1.
Mn	1.	0.2	3.	1.
Fe	30.	3.	10.	10.
Co	0.3	0.2	1.	0.1
Ni	5.	≤0.1	20.	1.
Cu	1.	0.5	2.	1.
Zn	15.	0.5	20.	2.

(a) Read at m/e 17.
[ ] Sample not baked.

TABLE 6. ANALYSIS OF JPL MgO 49, 56, AND 63

(ppma)

Element	JPL 49 Battelle Mass	JPL 49 Battelle Emission	JPL 49 Sperry Rand Mass	JPL 56	JPL 63
Li	0.3	--	--	1.	0.5
B	3.	<4.	<1.	1.	≤0.1
C	[200,000.]	--	--	250.	[5,000.]
N	[300.]	--	65.	3.	[300.]
F	30.	--	8.	1.5	<1.
Na	10.	<50.	<1.	0.3	<1.
Al	20.	30.	11.	3.	30.
Si	100.	14.	40.	35.	<3.
P	10.	--	--	3.	0.3
S	200.	--	--	50.	10.
Cl	400.	--	45.	200.	40.
K	30.	--	<0.1	1.	10.
Ca	30.	10.	13.	20.	30.
Sc	--	--	--	<0.1	--
Ti	40.	--	--	15.	<10.
V	--	--	--	<0.03	--
Cr	1.	--	--	≤1.	0.2
Mn	3.	--	--	1.	0.3
Fe	30.	3.5	3.	12.	3.
Co	0.3	<2.(T)	--	0.3	<0.1
Ni	10.	--	--	3.	≤0.2
Cu	15.	<3.(T)	--	1.	1.
Zn	20.	--	--	5.	5.
As	--	--	--	1.	--
Br	--	--	--	0.2	--
Sr	--	--	--	≤0.2	--
Nb	--	--	--	<0.1	--
Mo	--	--	--	<0.4	--
Cd	--	--	--	<0.3	--
Sn	--	--	--	<0.4	--
W	--	--	--	<0.1	--
Ag	--	1.	--	--	--
Pb	--	--	--	1.	<0.2

[ ] Sample not baked.
(T) Trace.

TABLE 7. COMPARATIVE ANALYSIS OF SINGLE-CRYSTAL MgO[a]

(ppma)

Element	Battelle Mass Spectrographic Analysis, Run 1, As Received	Battelle Mass Spectrographic Analysis, Run 2, Etched	Chemical	Given Analysis
H	30,000.	10,000.	--	--
H_2	1,000.	300.	--	--
OH	10,000.	100.	--	--
Li	0.2	<2.	--	--
B	2.	2.	--	--
C	600.	600.	70.[b]	--
N	200.	100.	<10.	30.
F	6.	3.	--	--
Na	<2.	<2.	--	2.8
Al	100.	60.	--	62.
Si	20.	20.	--	39.
P	2.	2.	--	2.6
S	200.	25.	3.8	<2.5
Cl	120.	20.	--	--
K	<6.	<6.	--	--
Ca	6.	20.	160.	47.
Ti	20.	20.	--	--
V	<0.6	≤0.2	--	--
Cr	0.6	0.6	--	<2.3
Mn	0.2	0.2	--	0.2
Fe	10.	2.	--	2.
Co	0.6	0.2	--	--
Ni	3.	10.	--	--
Cu	3.	<1.	--	--
Zn	10.	4.	--	4.5
As	≤0.2	≤0.2	--	<1.3
Br	<1.	2.	--	1.
Mo	<0.4	<0.4	--	<0.4

(a) Boule No. 8, from Dr. W. A. Sibley, Oak Ridge; material produced by W. and C. Spicer, Ltd., BMI S-0860.

(b) On chunks; 134. ppma on powder run immediately after crushing; 230. ppma on powder run 15 minutes after crushing.

TABLE 8. MASS SPECTROGRAPHIC ANALYSIS OF OP MgO SAMPLES

(ppma)

Element	Sample						
				OP 243[a]		OP 366[b]	
	OP 14	OP 111	OP 125	Mass	Chemical	Mass	Chemical
Li	15.	10.	≤150.[c]	1.	--	1.	--
B	500.	600.	800.	300.	--	20.	--
C	6,000.	4,000.	2,000.	30,000.	170.	3,000.	400.[d]
N	1,000.	200.	100.	3,000.	--	300.	29.[d]
F	1,500.	600.	2.	2,000.	1,330.	300.	59.
Na	20.	20.	6.	300.	290.	3.	--
Al	800.	150.	60.	100.	--	100.	--
Si	600.	1,200.	500.	300.	--	500.	57.
P	60.	60.	20,000.	30.	--	3.	--
S	500.	400.	100.	300.	85.	500.	70.
Cl	400.	250.	250.	300.	595.	30.	32.
K	15.	60.	30.	300.	8.	10.	--
Ca	700.	1,200.	1,500.	5,000.	2,680.	10.	32.
Sc	≤20.	≤100.	6.	--	--	--	--
Ti	80.	600.	120.	50.	--	3.	--
V	4.	20.	20.	1.	--	0.3	--
Cr	60.	50.	70.	3.	--	1.	--
Mn	100.	60.	30.	30.	--	1.	--
Fe	800.	250.	300.	170.	--	20.	--
Co	20.	6.	4.	10.	--	0.3	--
Ni	100.	120.	100.	10.	--	1.	--
Cu	30.	30.	80.	10.	--	0.5	--
Zn	12.	12.	25.	10.	--	2.	--
As	4.	2.	4.	1.	--	<0.1	--
Br	≤0.4	8.	≤0.4	3.	--	<0.6	--
Sr	4.	6.	≤3.	--	--	--	--
Zr	--	--	--	--	--	<0.5	--
Nb	≤0.2	<0.6	0.6	--	--	--	--
Mo	<1.	≤2.	30.	100.	--	<0.4	--
Pb	4.	1.5	0.4	--	--	<1.	--
Cd	≤6.	<0.8	<0.6	--	--	--	--
Sn	30.	<0.2	≤2.	--	--	--	--
Ba	--	--	--	--	--	<0.6	--
W	0.6	<0.4	6.	--	--	--	--

(a) BMI 91940.
(b) BMI S-0432.
(c) Not confirmed at $^{7}Li^{+2}$.
(d) Combustion and Kjeldahl results.

TABLE 9. ANALYSIS OF UNIVERSITY OF WASHINGTON MgO SAMPLES

(ppmw)

Element	Cube		Chip	
	Mass	Emission	Mass	Emission
Li	0.01	--	0.06	--
Be	<0.02	--	<0.02	--
B	0.2	--	0.2	--
F	<0.5	--	<0.5	--
Na	<2.	--	<2.	--
Al	20.	30.	60.	180.
Si	5.	<6.(T)	50.	120.
P	<1.	--	1.	--
S	3.	--	6.	--
Cl	4.	--	4.	--
K	1.	--	1.	--
Ca	200.	450.	200.	450.
Sc	0.2	--	3.	--
Ti	<0.4	<5.	10.	5.
V	1.	<3.(T)	3.	3.
Cr	7.	6.	15.	15.
Mn	20.	15.	50.	40.
Fe	100.	100.	600.	450.
Co	0.1	--	0.2	--
Ni	2.	<6.(T)	12.	15.
Cu	1.	<3.	2.	<3.(T)
Zr	0.5	<20.	70.	150.
Mo	0.2	<3.	0.4	<3.(T)

(T) Trace.
-- No data.

Note: Elements not reported (except H, C, N, O, and Mg) were not detected. The detection limints are 0.1 ppma, divided by the isotope fraction of the most abundant isotope of the element.

TABLE 10. RECOVERY DATA FOR SYNTHETIC MgO STANDARDS

Element	Standard A[a] Present	A[a] Found	B[a] Present	B[a] Found	C[b] Present	C[b] Found	D[b] Present	D[b] Found	E[b] Present	E[b] Found
Li	600.	500.	140.	300.	--	--	--	--	--	--
F	900.	100.	360.	50.	400.	60.	200.	60.	100.	60.
Na	840.	100.	360.	30.	1000.	400.	500.	200.	10,000.	6000.
Si	470.	700.	230	300.	--	--	--	--	--	--
S	560.	500.	330.	200.	--	--	--	--	--	--
Cl	360.(c)	6000.	80.(c)	4000.	1500.(c)	24,000.	500.(c)	8000.	200.(c)	8000.
K	820.	500.	100.	100.	--	--	--	--	--	--
Ca	200.	100.	66.	30.	--	--	--	--	--	--
Br	32.	20.	3.	2.	--	--	--	--	--	--
Rb	110.	100.	11.	10.	--	--	--	--	--	--
Sr	100.	180.	20.	15.	--	--	--	--	--	--
Cs	32.	30.	3.	3.	--	--	--	--	--	--
Yb	110.	100.	110.	100.	100.	40.	100.	80.	100.	70.

(a) Base: Kanto MgO, BMI S-0430.
(b) Base: Kanto MgO, BMI S-0429.
(c) Plus an unknown amount from HCl in Yb solution.

TABLE 11. ANALYSIS FOR Cu IN KANTO MgO USING Yb AS AN INTERNAL STANDARD

Line Pair	Intensity Ratio[a]	ppma Yb	ppma Cu
$^{63}Cu^{+}$-$^{172}Yb^{+}$	0.274	29.	8.
$^{63}Cu^{+}$-$^{174}Yb^{+}$	0.33	29.	9.6
$^{63}Cu^{+}$-$^{172}Yb^{+}$	0.33	29.	9.6
$^{63}Cu^{+}$-$^{174}Yb^{+}$	0.39	29.	11.4
$^{63}Cu^{+}$-$^{170}Yb^{+}$	0.04	350.	14.
$^{63}Cu^{+}$-$^{170}Yb^{+}$	0.06	350.	21.

(a) Corrected for isotopic abundances.

TABLE 12. MASS AND EMISSION SPECTROGRAPHIC ANALYSIS OF UNIVERSITY OF WASHINGTON Al_2O_3

(ppmw)

Element	Mass	Emission	Given	Element	Mass	Emission	Given
Li	0.004			Ag	<0.2	<3.(N)	0.5-1.5
Be	<0.03			Cd	<0.3		
B	0.1		0.6-1.5	In	<0.1		
C	(a)			Sn	<0.3		8.-16.
N	50.(b)			Sb	<0.3		
F	<0.6			Te	<0.3		
Na	2.			I	<0.1		
Mg	6.	5.	0.6-1.2	Cs	<0.1		
Si	20.	15.	7.-12.	Ba	≤0.5		
P	0.3			La	<0.1		
S	6.			Ce	<0.1		
Cl	15.			Pr	<0.1		
K	10.			Nd	<0.4		
Ca	15.	10.	0.0-0.35	Sm	<0.6		
Sc	<0.05			Eu	<0.3		
Ti	3.	3.		Gd	<0.6		
V	<0.2	<3.(N)		Tb	<0.2		
Cr	0.3	<10.(N)	0.0-0.35	Dy	<0.7		
Mn	0.5	<3.(T)	10.-20.	Ho	<0.2		
Fe	6.	10.	7.-15.	Er	<0.6		
Co	<0.1			Tm	<0.2		
Ni	2.	<10.(T)		Yb	<0.7		
Cu	1.	<3.(T)	0.8-1.6	Lu	<0.2		
Zn	<0.3			Hf	<0.6		
Ga	<0.2	<10.(N)		Ta	<6.(c)		
Ge	<0.2			W	<0.6		
As	<0.1			Re	<0.4		
Se	<0.2			Os	<0.4		
Br	<0.2			Ir	<0.4		
Rb	<0.2			Pt	<0.6		
Sr	<0.1			Au	<2.(d)		
Y	<0.1			Hg	<0.6		
Zr	<0.2	<10.(N)		Tl	<0.2		
Nb	<0.1			Pb	<0.4		
Mo	<0.4	<10.(N)		Bi	<0.2		
Ru	<0.6			Th	<0.2		
Rh	<0.1			U	<0.2		
Pd	<0.4						

(a) Graphite binder.
(b) Source not baked - value may not be valid.
(c) High "less than" value due to contamination from Ta source parts.
(d) TaO^+ interference.
(N) Not detected.
(T) Trace.

TABLE 13. CARBON AS DETERMINED BY COMBUSTION IN MgO (FISHER M-300) SAMPLES AS A FUNCTION OF HEATING AND STORAGE

(ppma)

Treatment	Original[a]	2nd Lot Calcined[b]	2nd Lot As Received[c]	2nd Lot Hot Pressed[d]
As received	27,000	14,000	6,700	170
1 hr @ 100 C	--	14,000	--	170
16 hr @ 140 C	--	14,000	--	170
1 hr @ 1100 C	--	4,700	--	<17
190 hr @ 930 C				
1st sample [1 hr][e]	--	2,600	--	--
2nd sample [2 hr][e]	--	4,000	--	--
3rd sample [3 hr][e]	--	4,700	--	--
21 days in air	--	19,700	--	--
24 hr @ 975 C	--	--	1,000	--
$\frac{1}{4}$ hr in desiccator	--	--	1,200	--
$\frac{3}{4}$ hr in desiccator	--	--	1,600	--
3 hr in desiccator	--	--	2,100	--
$\frac{1}{4}$ hr in CO_2	--	--	4,000	--
$\frac{1}{2}$ hr in CO_2	--	--	4,000	--
1 hr in CO_2	--	--	4,300	--
2 hr in CO_2	--	--	5,300	--
3 hr in CO_2	--	--	6,000	--

(a) Small plastic bottle, labeled Batch 2; BMI 90940 (powder).
(b) Large plastic bottle, labeled B3 Calcined 700 C Vac; BMI 91938 (powder).
(c) Large plastic bottle, labeled B3 As Received; BMI 91939 (powder).
(d) Small plastic bottle, labeled OP 243 (hot pressed); BMI 91940 (solid).
(e) Taken successively from same ignited MgO sample stored in desiccator.

TABLE 14. OH FOUND IN MgO BY VARIOUS TECHNIQUES

Conditions	Temperature, C	OH, Expressed as $Mg(OH)_2$
OP 366 (BMI S-0432), ppmw		
Graphite, Induction	2000	133, 144
Mass Spectrograph	--	2600
O_2 Reaction	500	632
O_2 Reaction	900	3387, 3454, 3421, 3831
OP 243 (BMI 91940), ppmw		
Graphite, Induction	1000	1700
Graphite, Focused Laser	--	85
Graphite, Induction	1000	1600
Graphite, Defocused Laser	--	3300
Graphite, Focused Laser	--	37
Mass Spectrograph	--	1300, 5200
Graphite, Induction	2000	2, 2.7
Graphite, Induction	2000	24
Graphite, Induction	2800	346
Graphite, Induction	3300	0
M-300 (BMI 91938), weight percent		
Graphite, Induction	2200	5.9, 6.7, 4.8
Graphite, Induction	2500	0
Graphite, Induction	2700	0
Graphite, Induction	2700	0
Graphite, Induction	2000	0.0055
Graphite, Induction	2700	0
Graphite, Induction	2800	0.3400
Graphite, Defocused Laser	--	35.8
Graphite, Defocused Laser	--	11.3
Graphite, Defocused Laser	--	20.4
Graphite, Defocused Laser	--	20.2
O_2 Reaction	500	15.5
O_2 Reaction	500	26.9
Mass Spectrograph	--	$\geq$ 2.7
Cold Pressed Fisher M-300 (BMI S-0460), weight percent		
Graphite, Induction	2000	12.82
Graphite, Induction	2000	12.85
Graphite, Induction	1700	0
Mass Spectrograph	--	15.

TABLE 15. RELEASE OF OH FROM MgO BY THE MgO-O_2 SYSTEM

Fisher M-300 (BMI 91938)		
OH Expressed as Weight Percent of $Mg(OH)_2$		
Run 1		
100 C	0.4	
500 C	11.1	
500 C, O_2	4.0	
Overall Total		15.5
Run 2		
100 C, 1st	1.1	
100 C, 2nd	0.1	
100 C, 3rd	0.1	
Total		1.3
500 C, 1st	20.3	
500 C, 2nd	0.0	
Total		20.3
500 C, O_2, 1st	5.3	
500 C, O_2, 2nd	0.0	
Total		5.3
Overall Total		26.9
OP 366 (BMI S-0432)		
OH Expressed as ppmw of $Mg(OH)_2$		
Run 1, Crushed, Not Sieved		
100 C, 1st	55.	
100 C, 2nd	0.0	
Total		55.
500 C, 1st	542.	
500 C, 2nd	21.	
500 C, 3rd	2.	
500 C, 4th	0.0	
Total		565.
500 C, O_2, 1st	0.0	
500 C, O_2, 2nd	12.	
500 C, O_2, 3rd	0.0	
Total		12.
Overall Total		632.

TABLE 15. (Continued)

OP 366 (BMI S-0432)
OH Expressed as ppmw of $Mg(OH)_2$

Run 2, Crushed, Not Sieved		
100 C		24.
500 C		3108.
500 C, O_2, 1st	15.	
500 C, O_2, 2nd	24.	
500 C, O_2, 3rd	12.	
500 C, O_2, 4th	0.0	
500 C, O_2, 5th	0.0	
500 C, O_2, 6th	15.	
Total		66.
900 C		188.
900 C, O_2		1.
Overall Total		3387.
Run 3, Crushed, Not Sieved		
100 C	71.	
500 C	3148.	
500 C, O_2	10.	
900 C	222.	
900 C, O_2	3.	
Overall Total		3454.
Run 4, Crushed, Sieved (100 to 150 μ)		
100 C	227.	
500 C	3402.	
500 C, O_2	56.	
900 C	130.	
900 C, O_2	15.	
Overall Total		3831.
Run 5, Sample from Run 4 Exposed to Moist Air 18 hr		
100 C	152.	
500 C	126.	
500 C, O_2	7.	
900 C	0.5	
900 C, O_2	0.1	
Overall Total		286.

TABLE 16. ANALYSIS OF Zr_2CO SAMPLE NO. 28

(weight percent)

	Gas Analysis										
	N_2	CO	CO_2	O_2	H_2	H_2O	CH_4	Ar	C_2H_4	C_2H_6	Total O
Vacuum Fusion											
Run 1 [1900 C]	1.8	(1.21)	(0.02)	0.29	0.013	(0.009)	0.005	0.02	0.002	0.02	1.53
Run 2 [2400 C]	2.3	(1.29)	(0.016)	--	0.009	--	--	--	--	--	1.32
Chlorination	0.13	(0.26)	--	0.008	--	--	--	--	--	--	0.27

	Element Analysis										
	C										
	Residue	Total	Zr	Hf	Sn	Al	Si	Other	O	N	Total
	3.53	9.27	83.5	1.5	0.2	1.7	1.9	0.09	0.27	0.13	98.6

( ) Weight percent as oxygen, not compound.

TABLE 17. MASS SPECTROGRAPHIC ANALYSIS OF ZrO_2, C, AND Zr_2CO

(ppmw)

Element	Starting Materials		Zr_2CO		
	ZrO_2	C	No. 26	No. 28	No. 29
Li	0.3	<0.02	0.1	0.1	0.1
Be	0.04	<0.08	0.05	0.2	0.05
B	2.	0.3	0.5	5.	0.5
F	<0.1	<0.5	0.2	1.	0.2
Na	400.	10.	100.	300.	100.
Mg	40.	<60.	40.	40.	40.
Al	15.	2.	high	high	high
Si	200.	12.	high	high	high
P	1.	0.5	2.	6.	2.
S	40.	≤15.	15.	50.	15.
Cl	30.	200.	1.	10.	1.
K	10.	15.	100.	100.	100.
Ca	10.	30.	20.	60.	20.
Sc	(a)	<1.	(a)	(a)	(a)
Ti	4.	<4.	5.	20.	10.
V	0.5	<0.1	3.	3.	6.
Cr	2.	<0.1	3.	10.	10.
Mn	2.	<0.1	3.	3.	3.
Fe	30.	0.3	60.	150.	60.
Co	<0.2	<0.2	<1.	<1.	<1.
Ni	2.	<0.3	3.	6.	6.
Cu	30.	<0.3	4.	50.	15.
Zn	1.	≤0.4	1.	5.	1.
Ga	<0.06	<0.3	<0.6	<0.6	<0.6
Ge	<0.1	<0.6	<0.1	<0.1	<0.1
As	<0.02	<0.2	0.1	0.1	0.1
Se	<0.04	<0.4	<0.1	<0.1	<0.1
Br	0.2	<0.4	<0.1	≤0.3	<0.1
Rb	<0.1	<1.	≤1.	2.	≤1.
Sr	<1.	<0.2	<0.5	<0.5	<0.5
Y	100.	<0.2	15.	25.	15.
Zr	--	5.	--	--	--
Nb	3.	<0.2	20.	2.	20.
Mo	<1.	<3.	<0.2	<0.2	<0.2
Ru	<1.	<1.	<0.3	<0.3	<0.3
Rh	<1.	<0.3	<3.	<3.	<3.
Pd	<5.	<4.	<10.	<10.	<10.
Ag	<6.	<0.6	--	--	--
Cd	<2.	<1.	<10.	20.	<10.
In	<1.	<1.	<5.	<5.	<5.
Sn	<5.	<1.	100.	2000.	100.

TABLE 17. (Continued)

Element	Starting Materials		Zr_2CO		
	ZrO_2	C	No. 26	No. 28	No. 29
Sb	<0.2	<0.6	<1.	<1.	<1.
Te	<1.	<1.	<2.	<0.6	<0.2
I	<0.3	<0.3	<0.6	<0.6	<0.6
Cs	<0.3	<0.3	<0.3	<0.3	<0.3
Ba	≤0.5	<0.4	1.	3.	1.
La	0.2	<0.3	0.3	0.3	0.3
Ce	0.4	<0.3	≤0.3	≤0.3	≤0.3
Pr	0.1	<0.3	≤0.3	≤0.3	≤0.3
Nd	1.	<1.	<1.	<1.	<1.
Sm	<0.5	<1.	<0.3	<0.3	<0.3
Eu	<0.2	<0.6	<0.2	<0.2	<0.2
Gd	<0.5	<1.	<0.3	<0.3	<0.3
Tb	<0.04	<0.4	<0.1	<0.1	<0.1
Dy	<0.5	<1.	<0.4	<0.4	<0.4
Ho	<0.1	<0.4	<0.1	<0.1	<0.1
Er	<0.5	<1.	<0.3	<0.3	<0.3
Tm	<0.1	<0.4	<0.1	<0.1	<0.1
Yb	<0.2	<1.	<0.4	<0.4	<0.4
Lu	<0.2	<0.4	<0.1	<0.1	<0.1
Hf	10,000.	<2.	2000.	6000.	2000.
Ta	≤0.2	<5.	≤3.	≤10.	≤3.
W	≤0.2	<2.	1.	0.6	<0.3
Re	<0.1	<1.	<0.2	<0.2	<0.2
Os	<1.	<1.	<0.4	<0.4	<0.4
Ir	<0.5	<1.	<0.3	<0.3	<0.3
Pt	<15.	<2.	<3.	<3.	<3.
Au	<0.2	<0.5	<1.	<1.	<1.
Hg	<0.4	<2.	<0.4	<0.4	<0.4
Tl	≤0.07	<0.6	<0.3	<0.3	<0.3
Pb	2.	<1.	2.	2.	1.
Bi	≤0.07	<0.6	<0.1	<0.1	<0.1
Th	0.1	<0.6	<0.1	0.1	<0.1
U	0.3	<0.6	<0.1	0.1	<0.1

(a) Severe interference from matrix.