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DEVELOPMENT OF CHEMICAL ANALYSIS TECHNIQUES
FOR ADVANCED MATERIALS

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ABSTRACT

During the 12-month period, emphasis was placed on (1) determining the hydroxyl content of MgO by mass spectrographic and chemical decomposition techniques investigating the effect of several means of causing the decomposition, (2) standardizing the mass spectrograph by suitable cross-check data, (3) studying the effects of storage time, degree of subdivision, and heating on the carbon value as determined by combustion, (4) optimizing the sample preparation for mass spectrographic use, and (5) increasing the accuracy of the mass spectrographic technique by several means. Significant progress has been made in all these areas, but the hydroxyl and carbon determinations remain the most troublesome.

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by

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INTRODUCTION

The determination of impurities in refractory materials is often more difficult than in single-element matrices. In some instances the refractory may be extremely hard or insoluble, leading to problems when chemical or optical emission techniques are employed. Magnesium oxide, the material selected by the former technical representative of this project, Dr. Martin Leipold, presents neither problem. However, it is an insulator and therefore can be sparked directly in the mass spectrograph only with difficulty, if at all. This requires that the samples be briquetted with a conductor or sparked against a conducting counter electrode. The spectra are therefore a composite of the sample and the added conductor. Determination of the relative amounts of these two components is therefore necessary for quantitative work, but this is not easy to accomplish in practice. Early in this program efforts were made to reduce the errors from this source.

Soon after work was begun it became clear that the determination of OH in MgO was a major problem. It is not determined by the usual hot extraction at temperatures above the decomposition temperature of MgOH. Accordingly, a major part of the research effort was put into devising means of obtaining a true value for the OH. Although the problem is not yet solved, at least one technique shows promise of being satisfactory.

Carbon is another problem area, but its importance in MgO is not believed to be so great as is OH. Therefore, less effort was spent on developing reliable techniques for this element.

Other elements are, in general, more easily determined quantitatively by one or more means. The mass spectrograph, because of its sensitivity and universality, is well suited for the task. The major problem is in obtaining quantitative data, and this aspect is proceeding well.

The experimental work and the data obtained are given in the section that follow.

EXPERIMENTAL WORK

General Studies Related to the Mass Spectrographic 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

amounts 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 $^{109}\text{Ag}^+$ and $^{25}\text{Mg}^+$ 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 $0.66 \frac{\text{Ag}}{\text{Mg}}$; 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

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.

Electron Microprobe

Because of the variations in the Ag-to-Mg ion-intensity ratio in the briquettes, a briquette (Fisher M-300 MgO, BMI No. 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.

Hydroxyl Determination

The determination of OH in MgO has proved to be a far more difficult task than anticipated at the beginning of this research program. Previous work by Dr. Leipziger under NASA Contract 950992 showed that low blanks, of the order of a ppmw in refractory and precious metals (equal to a hundred or more ppma), could be obtained on the mass spectrograph. The same investigator reported that hot-extraction techniques were of doubtful value for MgO because they tended to give results higher than those obtained by mass spectrography.

Work performed under the present contract and discussions with the former Technical Representative, Dr. M. H. Leipold, produced conflicting interpretations of the chemistry of OH in MgO. One set of data obtained by heating, but not decomposing, MgO in a graphite crucible showed reproducible and very small amounts of OH in at least one MgO sample (OP243). This same sample, when partially decomposed by reduction with graphite, had an apparent OH concentration about 200 times higher, if extrapolated to complete decomposition. Further, the OH content based on H ($m/e = 1$) as determined by mass spectrography was almost 100 times higher than the thermal-decomposition value.

Another sample, Fisher M-300, calcined in vacuum at 700 C (BMI No. 91938) was studied using a variety of techniques, and again the data presented a confusing picture. It is clear that this sample has considerable loosely bound water and also more tightly bound water (or OH). The experiments conducted to clarify the amount of OH present and the possibility of the existence of different types of OH are described below.

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 $Mg(OH)_2$ is 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. Typical thermograms of brucite and magnesite are shown in Figure 1.

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.

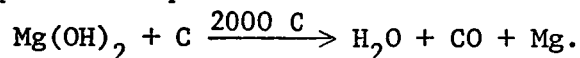
The vacuum-fusion furnace used in this work is a Battelle-fabricated unit similar to the Guldner-Beach design except that the crucible is supported from the bottom of the furnace instead of by platinum wire from the top. The conventional carbon-crucible, graphite-packing, sample-loading system, and degassing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

Run 1 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 H₂O and CO, suggest the following decomposition equation:



Based on this equation, 9.39 mg of brucite should yield 2.9 mg of H₂O and 4.51 mg of CO. The actual recovery of H₂O 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. Run 2 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 subtracted 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-heater coil. The design for the $Mg(OH)_2$ experiments was quite simple--a quartz tube with a removable base, a stop-cock, and a split graphite tube supporting a graphite crucible.

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 No. 91938). For these experiments the entire reaction vessel and the induction coil were submerged in deionized water to cool the quartz 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.

For Run 1, 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 (Runs 2 and 3) were made on a sample that had been dried at 110 C for 75 minutes. The sample was not redried before Run 3 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 Run 2. Based on the H_2 evolved from MgO in Runs 2 and 3, the $Mg(OH)_2$ content was 5.9 and 6.7 weight percent, respectively, and for the undried Run 1, 4.8 percent. The relative reproducibility was about 11 percent.

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 No. 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 H₂ [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 H₂O.

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 (Run M-1) showed a total of 147 cc-atm of gas with the following composition, in volume percent: H₂, 17.9; CO, 33.4; H₂O, 46.5; and CO₂, 2.19. The H₂ amounted to 26.3 cc-atm, which is equivalent to 12.82 weight percent Mg(OH)₂ in the MgO (the H₂O 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 Run M-1 was so low as to be insignificant. This analysis, designated Run M-2, showed a total of 152 cc-atm of gas containing 16.7 percent H₂. This is equivalent to 25.4 cc-atm of H₂, or 12.85 weight percent of Mg(OH)₂.

The sample used in Run M-2 was unloaded from the apparatus and allowed to stand unprotected from the atmosphere for 64 hours. For Run M-3 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.

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

The apparatus containing the sample for Run M-3 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 used for Runs M-1 and M-2 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, OP243 (BMI No. 91940) was analyzed twice by the procedure outlined above for Runs M-1 and M-2. These analyses are reported as Runs M-6 and M-7. 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 (Run M-6). 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 (Run M-7) 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 M-6 and M-7. Each lost 0.4 percent of its original weight. This compares with a 23.9 percent weight loss for Run M-2. 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 Runs M-1 and M-2 was water.

A sample of pressed MgO designated as Kanto MgO, OP366 (BMI No. 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 (OP243, BMI No. 91940). All subsequent experiments were run with this same sample. 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 blanks were obtained for H₂ 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, which is in agreement with previous results.

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-minute 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 (Run C-1-3); 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 (Run C-1-4) 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 material was on the bottom of the quartz tube or on the side walls. Less than 10 percent total conversion was obtained.

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 pre-fired 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 $\text{Mg}(\text{OH})_2$ 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 $\text{Mg}(\text{OH})_2$.

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 Run C-2 (with no blank data having been obtained), there is 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 $\text{Mg}(\text{OH})_2$ for Run C-1 would be 423 ppmw and 539 ppmw for Run C-2, or 465 ppmw if the assumed MgO loss is considered.

Intimate contact of the sample and graphite is very important for decomposition and retention of the sample in the crucible. This can be seen by comparing Run C-1-4 at approximately 3300 C, in which most or all the powdered graphite placed in the crucible was lost, and Run C-2-1 at 2000 C with the mixture in pellet form. 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. The loss of part of the pellet in Run C-2 appeared to be caused by a violent reaction within the pellet.

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, a Lepel Model T-5-3-DF-E-S, 12.5-kva input, was used. This unit 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 the Lepel unit could decompose the MgO more efficiently and completely than could the 10-kva Westinghouse unit used previously.

The material used for these experiments was Fisher M-300 B-3, calcined at 700 C in vacuum (BMI No. 91938). Previous work using this material had shown about 5.8 weight percent $\text{Mg}(\text{OH})_2$. 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 H₂. 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 H₂, this is equivalent to 40 ppma as H₂ [55 ppmw as Mg(OH)₂]. This relatively small amount of H₂ 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 H₂ 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 H₂ 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 No. 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 H₂ was detected.

The results obtained using the Lepel unit do not agree with the data obtained using the Westinghouse unit. The Lepel unit operates at about 0.375 mHz and the Westinghouse at about 0.450 mHz. Although this is not a large difference, it is possible that the different frequency accounts for the lack of H₂ when the Lepel 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 No. 91938) weighing 0.0555 g was loaded into the graphite crucible capped as before. The sample was heated with the Westinghouse 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 H₂ 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 H₂ 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 CO upon prolonged heating, an effect mentioned above. Also, H₂ was found while using the Westinghouse unit, but not with the Lepel unit.

Laser-Beam Heating. Because so many problems arose using inductive heating, and because the data were not reproducible or easily interpreted, 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 No. 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 Å 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 H₂, with a total gas content of 0.06 cc-atm. Some hydrocarbons were also present, and the amount of H₂ 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 H₂.

This encouraging performance indicated that ruby-laser heating might be the 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 No. 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 H₂O and CO₂ 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): H₂O, 52; CO₂, 10; H₂, 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 out-gassed 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.

It is interesting to note that in this sample, BMI No. 91938, the $\text{Mg}(\text{OH})_2$ equivalent of H_2 found by induction heating in five cases varied from 4.8 to 20.4 weight percent. The higher values were obtained at lower temperatures and (usually) over shorter times. It is also interesting, and perhaps coincidental, that the $\text{Mg}(\text{OH})_2$ found in the last three runs reported above was 20.1 ± 0.36 (standard deviation). Also, in one case the induction heating appeared to have removed all the OH, but other experiments pointed to incomplete OH removal by this means. Clearly, more work is needed to get reproducibility in the induction technique, if that technique is used. Alternatively, it appears that the laser is capable of giving a reliable OH value, based on quite limited data.

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 $^1\text{H}^+$, $^1\text{H}_2^+$, and $^{16}\text{O}^1\text{H}^+$ at m/e 1, 2, and 17, respectively. In spectra of briquetted MgO powder and Ag (1 MgO:2 Ag) the $\frac{\text{OH}^+}{\text{H}^+}$ and $\frac{\text{H}_2^+}{\text{H}^+}$ 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 $^{17}\text{O}^+$ contribution. But in some compacts the m/e 17 line gives results approaching or below the expected $^{17}\text{O}^+$ 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 $^{17}\text{O}^+$ from $^{16}\text{O}^1\text{H}^+$ (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. Leipzig, 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.

The important question, and the one not yet answered, is, "Can the intensities of the lines at m/e 1, 2, and 17 be related to the true OH content of the sample?" Dr. Leipziger, in his work at Sperry Rand, tentatively concluded that it was possible. 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 OP14 and OP111, 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.

Thermal (quartz-tube graphite-crucible) and mass data for OP243 were 650 and 50,000 ppma H, respectively. For another sample, Fisher M-300 isostatically cold-pressed B-3 (BMI No. S-0460), the agreement was good, with the thermal and mass values being 180,000 and 200,000 ppma H, respectively. Sample OP366 showed 200 and 3,000 ppma H by the thermal and mass techniques.

When the MgO residues from the thermal analyses were examined mass spectrographically, the H value increased to 30,000 ppma in the case of OP366, and decreased to 10,000 ppma for OP243. It is difficult to understand why H or OH should increase in MgO during or after the thermal treatment, as appears to have occurred in OP366. Adsorption from the atmosphere alone could scarcely account for such an increase, especially since the samples were protected from long exposure to the atmosphere and were baked in the spectrograph prior to analysis.

The Fisher M-300 B-3, calcined in vacuum at 700 C (BMI No. 91938), which had given values, in weight percent of $Mg(OH)_2$, of 11.3 to 20.2 by laser and from 4.8 to 20.4 by induction heating, gave about 2.7 by the mass spectrograph.

Until a material can be analyzed with certainty by another technique, it is impossible to determine whether or not the mass spectrographic technique is valid for MgO, and which ion specie is most suitable.

Optical Emission Spectrograph

Dr. Leipold pointed out a recent article that described an emission-spectrographic technique to determine H₂O or OH.* A ground sample is mixed with silica and arced in a large, necked electrode with a cap similar to the "boiler cap" electrode system. The OH bandhead at 3063.6 A is the analytical line.

Preliminary experiments using this technique for Mg(OH)₂ and two samples of MgO (Fisher M-300 B-3 isostatically cold pressed and OP366) were quite unsuccessful. The intensity of the bandhead was weak, even with a drop of water added to the sample. The response was very poor and there was a factor of only four between the ratio $\frac{\text{intensity of OH line}}{\text{weight of sample}}$ for Mg(OH)₂ and OP366, yet the difference in OH content is a factor of at least several hundred. The minerals used by Quesada and Dennen were arced in special electrodes fabricated to the dimensions given in the article. All specified conditions were followed exactly except that a portable oven was not used. Again, very poor response was noted at the OH bandhead, and no correlation of intensity versus OH content was found. Even the minerals having high OH gave only a weak bandhead. There may be some operating parameter in the reported technique that is being overlooked in the present work. In any case, the technique is not suitable for the determination of OH in MgO and will not be pursued further.

Interpretation of Thermal Data

Considering the data presented above, a possible explanation of the variations in OH content with the method of determination was proposed

* Quesada, Antonio, and Dennen, William H., "Spectrochemical Determination of Water in Minerals and Rocks", Applied Spectroscopy, 21 (3), 155 (May-June, 1967).

by Dr. Leipold. Loosely bound (physically adsorbed) water can be removed simply by pumping. The isostatically cold-pressed Fisher M-300 B-3 reported above apparently contained this type of water. This sample gave off so much water when pumped at room temperature that a good vacuum could not be reached.

The second type of water may be considered to be that present as $Mg(OH)_2$. As has been reported above, this water is quantitatively removed at temperatures between 300 and 400 C. Brucite analyzed by thermogravimetric analysis showed a sharp weight loss at about 350 C, confirming the decomposition temperature given in handbooks.

A third type of water may be present, although the experimental evidence is unclear. Perhaps the water released by the heating of MgO to around 2000 C, without decomposition, is a more tightly bound water than adsorbed water or $Mg(OH)_2$ water; on the other hand, it may be either or both of these kinds of water diffusing from the interior of the solid material. This point could be clarified by a time-temperature study, but such a study seems rather unnecessary inasmuch as whichever type of water this is, it apparently is not the water of primary interest.

The water of interest, and that which is proving so difficult to determine, is the water presumed to be present in the crystal structure as OH substituting for O. If this is true, and if the thermodynamics of the MgO-MgOH system are such that the OH cannot be removed without rupturing the other Mg-O bonds, then it follows that only in a few induction and laser-beam heating experiments described above did the OH liberation (as H_2) approach the true value. Certainly the data cited in these experiments tend to confirm Dr. Leipold's contention that there is hydroxyl in MgO that cannot be determined using conventional techniques.

There is evidence that excessive heat or time reduces the quantity of gas evolved. In one experiment almost half of the gas evolved disappeared after an additional heating period of 2 hours. Because it was not present as a gas phase after this heating, it must have reacted to form some non-volatile compound in the cooler portions of the vessel. Such a reaction is difficult to imagine, even assuming that reactive Mg metal is available. A study of where the CO and H_2 went would be interesting, but hardly in line with the objectives of this program.

In summary, the problem of OH determination is still unsolved. Evidence has been cited which shows that induction heating is not satisfactory, and again that it is quantitative. The laser may be the answer, and work so far has been encouraging, but reproducibility and accuracy must be established. In some experiments the induction heating released significant amounts of H_2 , but in other experiments almost no H_2 was formed. It is not clear at this time whether carefully controlled induction heating of MgO in contact with C will remove all the OH as H_2 , whether laser-beam heating will be a quantitative technique to accomplish this purpose, or whether neither technique can be developed satisfactorily. The mass spectrographic technique probably could be developed to give reliable data, but only if one or more MgO samples, whose OH content is known accurately, are available. Further, these standards must not change under reasonable storage conditions.

Carbon Determination

Mass Spectrographic and Combustion Analyses

Carbon is one of the impurities whose value in the Fisher M-300 MgO varied by more than one magnitude, depending on the technique employed to determine it. The mass results were scattered, but as low as 300 ppma was observed in the original powder, Batch 2 (BMI No. 90940). Combustion C determinations were made on four samples of Fisher M-300, and several were subjected to various heating and storage conditions. It was apparent that the three powder samples gave higher C values than did the hot-pressed material. Assuming the accuracy of the combustion determination (i.e., if complete recovery of C is realized with the solid hot-pressed material and if no pickup of C occurs in the powdered material), it was observed that in no case studied was the powdered material lowered in C content to the level of the as-received solid. The powders have C contents from 1000 to 27,000 ppma, and the hot-pressed compact (OP243) about 170 ppma. Furthermore, the powdered material very quickly picks up C, even when stored for brief periods in an Ascarite-containing desiccator. When stored in a

desiccator over solid CO_2 , the pickup is even more rapid and shows no sign of leveling off after 3 hours. When stored in air with the usual humidity present, the pickup of C after 21 days is in the percent range.

The conclusion that can be reached from these experiments is that C values obtained in powdered samples, no matter how carefully stored, are probably of little value. Only with compact samples such as the hot-pressed material, OP243, can one expect to get reproducible and valid results. This sample was analyzed mass spectrographically, and 30,000 ppma were found. Another solid, OP366, showed 400 ppma C by combustion and 3,000 ppma C by mass spectrography. A single-crystal MgO from Oak Ridge gave 70 and 600 ppma C by combustion and mass, respectively. In powders, the agreement was even poorer. Three Kanto samples, BMI Nos. S-0429, S-0430, and S-0431 gave 2200, 570, and 7400 ppma C by combustion, respectively, and 60, 2000, and 60 ppma C by mass, in the same order. With few exceptions, the mass results are higher than combustion for the compact samples, and lower than combustion for the powders.

Monitoring of Released Gases

The wide variance between the combustion and the mass spectrographic results for C suggested that the source of C (MgCO_3 ?) was being depleted by thermal decomposition during the first few exposures, giving a fictitiously low C result when read from the later exposures. This hypothesis was checked by monitoring the gases given off in the source during the sparking of a Kanto MgO sample. A partial-pressure analyzer, attached to the source pumping system, was set to follow the amount of H, H_2 , CO, and CO_2 being produced at any given time. During sparking these peaks increased greatly over the nonsparking background but, rather surprisingly, they remained essentially constant from the initial sparking to the last. This fact suggests that uniform amounts of these gases (and their precursor compounds) are being sparked during the analysis. Carbon is read at m/e 6-1/2 ($^{13}\text{C}^{+2}$) to minimize the contribution from ^{26}Mg --this contribution from $^{26}\text{Mg}^{+4}$ can

be estimated by noting the intensity of m/e 6-1/4 ($^{25}\text{Mg}^{+4}$). The $\frac{\text{C}^{+1}}{\text{C}^{+2}}$ factor was assumed to be 10, as this factor has been found to be reasonably valid in other analyses.

To summarize the C data, it has been shown that powdered MgO rapidly picks up CO_2 from the atmosphere, and therefore the combustion value obtained may be high. The mass spectrographic data are much lower as a rule; it is not clear whether this indicates a very large sensitivity drop for C as compared with other elements, or whether the bake and the prespark employed in the mass spectrographic technique remove some C (as CO_2 ?). In solids, the higher mass spectrographic results (relative to combustion) suggest that either the combustion technique does not quantitatively liberate the CO_2 from solids, or that the effects of the bake and prespark in the mass spectrograph are not effective for solids. In metals it has been shown that blanks of the order of 1 ppma C are possible with a bake and prespark. Therefore, there seems no valid reason to assume that the mass results are grossly in error. The tentative conclusion is that the combustion technique does not determine the total C, even though the temperature reached with the Fe accelerator is well above the decomposition temperature of MgCO_3 .

Cross-Check Analysis for Other Elements

In addition to the mass spectrographic technique, which essentially is universal in that every element can be detected with only a minor instrumental adjustment, other techniques were employed to standardize specific impurity elements in MgO. The techniques described below are considered more accurate than the mass spectrograph; standards can be prepared, blanks can be run, and in many cases the sample can be handled as a solution, thus completely eliminating physical differences between samples and standards. The limitations of the techniques vary, but in general three problems are noted: large amounts of sample are sometimes required for a single element determination, the detection limits may not be sufficiently good to analyze the purer samples, and the physical form of the sample may produce spurious effects in the analysis, as in optical emission analysis.

The results of these analyses are shown in the tables following the text of this report. Only selected elements were analyzed--primarily elements of specific interest or elements whose accuracy by mass spectrography was questionable.

Emission Spectrograph

Three techniques were employed for the emission spectrographic analysis of MgO. For impurities above several hundred ppm, the solution spark was used because it is accurate and is easily standardized. Most lower level impurities were determined by arcing a 15-mg mixture of MgO:C (1:1) in a Stallwood jet with flowing Ar-O₂. This is essentially the same technique used by Dr. Leipziger. Refractory impurity elements was determined by arcing a mixture of MgO:Ge:C = 1:9:10. In all cases synthetic standards were used and the impurity elements in the sample were determined by visual or microphotometric comparison with the standards.

Chemical Analysis

The techniques employed for the chemical determinations were as follows:

Carbon:	Combustion in oxygen using an Fe accelerator; conductometric readout
Nitrogen:	Kjeldahl using Devarga's alloy; titrimetric readout
Silicon:	Dehydration with HClO ₄ ; gravimetric readout
Calcium:	Atomic absorption
Fluorine:	Winter's method; titrimetric readout
Chlorine:	Turbidimetric readout with AgNO ₃
Sulfur:	Luke's method and combustion
Potassium:	Flame emission spectrophotometer
Sodium:	Flame emission spectrophotometer

Analysis of Samples

During the course of this research project, many samples were analyzed mass spectrographically. All but one sample was from JPL via Dr. Leipold. The exception was a single-crystal MgO from Dr. Sibley of Oak Ridge. All samples were nominally MgO except a Mg(OH)₂ powder sample and the brucite and magnesite samples used to establish thermal characteristics of these compounds.

Some samples also were analyzed at Battelle by techniques other than mass spectrographic, and a few had been analyzed previously by other laboratories. The agreement between techniques was good for some elements, less satisfactory for others. But in almost no case was the spread as great as for the OH and C, discussed above.

The data given in the tables have, for the most part, appeared in previous reports under this contract. In a few cases additional data have been added to tables previously reported. Not all tables previously reported are included in this report, although they have been summarized in the text.

The data from other laboratories were produced prior to the beginning of this research and were taken from Dr. Leipziger's reports, from JPL reports, from sample containers (vendor's analyses) and, in the case of the single crystal, from an analysis supplied by Dr. Sibley. In the mass spectrographic data, the notation "sample not baked" indicates that the sample may have contained air, H₂O, or CO₂ that might have been removed by baking under vacuum at about 150 C. Therefore, the H, C, and possibly N values may be high. The amounts of these elements found in most samples are considerably higher than the blank of the mass spectrograph's source. Thus, it is believed that any error introduced by not baking is primarily caused by the sample condition, not by residual gases in the unbaked source. Elements other than H, C, and N should not be affected by baking.

CONCLUSIONS AND RECOMMENDATIONS

The research reported above shows that most elements in MgO can be determined with fair accuracy and to good detection limits using the mass spectrograph. Cross-check data obtained by other techniques are useful; fortunately, chemical and optical emission procedures are available to perform this task. Two problems remain partially unsolved: satisfactory procedures for determining C and OH. More research is needed before these determinations can be considered satisfactory, but it is believed that, with sufficient work, good techniques can be developed. The laser-beam and the induction heating produce H₂ from MgO. Some evidence indicates that lower temperatures (1000 C) are better than the higher temperatures (2000 to 3000 C) because the quantity of H₂ seems to decrease as the temperature is raised. On the other hand, the decomposition of MgO in the presence of C is quite slow at the lower temperature; if decomposition is required before complete H₂ evolution takes place, then a compromise between the two factors must be reached.

It is recommended that this program be extended to other advanced materials of importance to NASA and JPL. The growing use of oxide and carbide systems for extreme service could be aided were the materials fully characterized chemically. Before this can be done, however, considerable development work on the analytical chemistry of these materials must be done. As refractories are made more pure, and as the importance of trace and difficult-to-determine impurities is recognized, it will not be adequate merely to apply classical methods of analysis. This fact has been recognized by researchers in the pure metals, and is beginning to be recognized by ceramic research personnel. If this current program, and others of a similar nature, can be continued and even enlarged, the useful applications of advanced materials can be expected to increase.

NEW TECHNOLOGY

No reportable items of new technology have been generated under this contract to date.

FUTURE WORK

The problem areas pointed out in the experimental work section of this report will be studied in future research on this project. Specifically, the mass spectrographic technique will be modified by means of an internal standard, spiked samples, and sensitivity-coefficient determinations so as to give greater accuracy. The determination of OH and perhaps C will be pursued with the objective of a reliable technique. If time and funds permits, some of the other refractories including the Zr-C-O system may be studied.

TABLE 1. COMPARISON OF ANALYTICAL RESULTS FOR FISHER M-300 AND JPL 49 MgO

(ppma)

Element	Bell and Howell Mass	Fisher M-300 (BMI No. 90940)						JPL 49			
		Sperry Rand Mass	Sperry Rand Emission	Battelle Emission ^a	Battelle Emission ^b	Battelle Emission ^c	Battelle Chemical	Battelle Mass	Sperry Rand Mass	Battelle Emission ^a	Battelle Mass
H	--	--	--	--	--	--	--	--	--	--	--
Li	1.2	--	--	--	--	--	--	--	--	--	--
B	300.	3.	<10.	80.	--	--	--	--	<1.	<0.1	<4.
C	--	--	--	--	--	40.	27,000.	300.	--	100.	3.
N	100.	100.	--	--	--	--	--	50.	65.	50.	--
F	4700.	110.	--	--	--	--	1,330.	100.	8.	100.	--
Na	61.	100.	500.	200.	--	--	400.	30.	<1.	30.	<50.
Al	100.	75.	50.	75.	--	--	--	10.	11.	10.	10.
Si	1800.	2400.	>1000.	450.	500.	430.	400.	350.	40.	350.	14.
P	120.	130.	--	--	--	--	--	10.	--	10.	10.
S	420.	510.	--	--	--	--	100.	300.	--	300.	200.
Cl	80.	285.	--	--	--	--	200.	400.	45.	400.	400.
K	64.	<1.	<1.	--	--	--	10.	30.	<0.1	30.	30.
Ca	310.	150.	350.	>500.	2300.	>500.	1,500.	2000.	13.	2000.	30.
Ti	66.	10.	<10.	100.	85.	16.	--	15.	--	15.	40.
V	<1.	--	--	--	--	--	--	0.3	--	0.3	<0.2
Cr	16.	5.	<5.	2.5	--	--	--	10.	--	10.	1.
Mn	22.	2.	<5.	30.	15.	<8.	--	10.	--	10.	3.
Fe	510.	85.	65.	110.	90.	220.	--	120.	3.	120.	30.
Co	<1.	10.	5.	2.	--	--	--	2.	--	2.	<2.(T)
Ni	10.	10.	<5.	3.5	--	<7.	--	4.	--	4.	0.3
Cu	12.	5.?	<5.	<3.(T)	--	3.	--	2.	--	2.	10.
Zn	97.	11.?	5.	<6.	--	--	--	4.	--	4.	15.
As	<1.	--	--	--	--	--	--	1.	--	1.	20.
Br	<1.	--	--	--	--	--	--	1.5	--	1.5	--
Sr	<1.	--	--	2.5	--	--	--	--	--	--	--
Zr	<1.	--	--	7.	--	--	--	--	--	--	--
Ag	<1.	--	--	1.	--	1.	--	--	--	--	--
Cd	15.	--	--	--	--	--	--	--	1.	--	--
Pb	<1.	--	--	--	--	--	--	0.4	--	0.4	--

(T) Trace.

a 1:1 graphite, enclosed Stallwood jet, 70% Ar, 30% O₂.

b Germanium matrix (MgO:Ge:C = 1:9:10).

c Solution spark.

d Sperry Rand method.

e 100,000 at m/e 1; 30,000 at m/e 17; sample not baked.

-- No data reported, element not sought, or element not detected.

[] Sample not baked.

34-A

34-B

TABLE 2. ANALYSIS OF KANTO MgO
(ppma)

Element	Mass	Emission	Element	Mass	Emission
H	10,000	--	S	200.	--
Li	2	--	Cl	350.	--
B	10	4.	K	10.	--
C	1,000	--	Ca	120.	10.
N	100	--	Mn	1.	<0.7
F	20	--	Fe	10.	4.
Na	3	--	Ni	2.	14.
Al	3	15.?	Cu	2.	0.6
Si	60	140.	Zn	4.	--
P	30	--			

TABLE 3. MASS SPECTROGRAPHIC ANALYSIS OF
OP111, OP14, OP125, and JPL #56
MgO

Element	(ppma)			
	OP111	OP14	OP125	#56
H	600.	2000.	(a)	10,000.
Li	10.	15.	≤150. (b)	1.
B	600.	500.	800.	1.
C	4000.	6000.	2,000.	250.
N	200.	1000.	100.	3.
F	600.	1500.	2.	1.5
Na	20.	20.	6.	0.3
Al	150.	800.	60.	3.
Si	1200.	600.	500.	35.
P	60.	60.	20,000.	3.
S	400.	500.	100.	50.
Cl	250.	400.	250.	200.
K	60.	15.	30.	1.
Ca	1200.	700.	1,500.	20.
Sc	≤100.	≤20.	6.	<0.1
Ti	600.	80.	120.	15.
V	20.	4.	20.	<0.03
Cr	50.	60.	70.	≤1.
Mn	60.	100.	30.	1.
Fe	250.	800.	300.	12.
Co	6.	20.	4.	0.3
Ni	120.	100.	100.	3.
Cu	30.	30.	80.	1.
Zn	12.	12.	25.	5.
As	2.	4.	4.	1.
Br	8.	≤0.4	≤0.4	0.2
Sr	6.	4.	≤3.	≤0.2
Nb	<0.6	≤0.2	0.6	<0.1
Mo	≤2.	<1.	30.	<0.4
Cd	<0.8	≤6.	<0.6	<0.3
Sn	<0.2	30.	≤2.	<0.4
W	<0.4	0.6	6.	<0.1
Pb	1.5	4.	0.4	1.

(a) m/e 1 not on photographic plate by mistake.

(b) Not confirmed at ${}^7\text{Li}^{+2}$.

TABLE 4. MASS SPECTROGRAPHIC ANALYSIS OF MgO
(ppma)

Element	Sample				
	BMI-3				JPL 63
	1(a)	2(b)	3(c)		
		Run 1	Run 2		
H	30,000.	5,000.	1,000.	--	[100,000.]
OH (d)	3,000.	300.	100.	[1,000.]	[30,000.]
Li	0.3	0.3	≤1.	2.	0.5
B	10.	25.	≤1.	2.	≤0.1
C	2,000.	1,000.	1,000.	[10,000.]	[5,000.]
N	300.	100.	50.	[1,000.]	[300.]
F	10.	20.	1.	5.	<1.
Na	10.	≤1.	<1.	10.	<1.
Al	10.	3.	30.	10.	30.
Si	100.	100.	400.	500.	<3.
P	5.	3.	2.	5.	0.3
S	100.	100.	100.	500.	10.
Cl	100.	12.	40.	130.	40.
K	30.	≤1.	10.	30.	10.
Ca	20.	10.	50.	100.	30.
Ti	<4.	<1.	40.	40.	<10.
Cr	1.	4.	10.	15.	0.2
Mn	≤0.3	1.	10.	3.	0.3
Fe	10.	10.	400.	50.	3.
Co	1.	<0.1	1.	≤1.	<0.1
Ni	1.	1.	15.	15.	≤0.2
Cu	15.	15.	15.	5.	1.
Zn	10.	10.	70.	15.	5.
Pb	1.	3.	1.	<0.4	<0.2

(a) As pressed.

(b) 1010 C.

(c) 1750 C.

(d) Read at m/e 17.

[] Sample not baked.

TABLE 5. MASS SPECTROGRAPHIC ANALYSIS OF MgO
(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. 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 No. 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 No. 91938)							
Battelle (C)	1310.	340.	350.	121.	435.	12.	2750.
Battelle (M)	1300.	50.	800.	100.	300.	10.	2500.
B-3 As Received (BMI No. 91939)							
Battelle (C)	1700.	23.	350.	89.	285.	10.	1450.
Battelle (M)	2000.	12.	4000.	150.	200.	3.	2500.
OP243 (BMI No. 91490)							
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 7. ANALYSIS OF FISHER M-300
(ppma)

Element	OP243(a)		After Heating ^(b) Mass	Isostatic As Received (c)	
	As Received Mass	Chemical		Mass	Chemical
H	50,000.	{ 3. (as H) (d) 650. (as H) (d)	10,000.	200,000.	180,000. (as H) (d)
H ₂	300.		1,000.	10,000.	
OH	300.		500.	30,000.	
Li	1.		0.1	<1.	
B	300.		15.	100.	
C	30,000.	170.	3,000.	10,000.	
N	3,000.		30.	100.	
F	2,000.	1,330.	30.	500.	
Na	300.	290.	<2.	300.	
Al	100.		30.	10.	
Si	300.		3,000.	300.	
P	30.		10.	10.	
S	300.	85.	50.	1,000.	
Cl	300.	595.	10.	300.	
K	300.	8.	<1.	30.	
Ca	5,000.	2,680.	2,000.	2,000.	
Ti	50.		20.	30.	
V	1.		0.4	10.	
Cr	3.		0.5	0.3	
Mn	30.		15.	20.	
Fe	170.		100.	100.	
Co	10.		0.2	3.	
Ni	10.		3.	3.	
Cu	10.		5.	5.	
Zn	10.		0.5	3.	
As	1.		<0.1	2.	
Br	3.		<0.2	20.	
Mo	100.		<0.4	<0.4	

(a) BMI No. 91940.

(b) Average of analyses of residues from quartz-tube, graphite-crucible Runs M-6 and M-7.

(c) BMI No. S-0460; cold pressed at 90,000 psi.

(d) Quartz-tube, graphite-crucible data.

TABLE 8. ANALYSIS OF KANTO SAMPLES

(ppma)

Element	Mg(OH) ₂ (a)		MgO (b)				Calcined MgO (c)			OP366 (d)			
	Mass	Given (e)	Chem	Mass		Chem	Mass		Chem	As Received	Chem	After Heating	
				Run 1	Run 2		Run 1	Run 2				Run M-8	Run M-9
H	--	--	--	--	--	--	--	--	--	--	3,000.	30,000.	30,000.
H ₂	--	--	--	--	--	--	--	--	--	--	500.	300.	300.
OH	--	--	--	--	--	--	--	--	--	--	200.	100.	100.
Li	<2.	--	--	<2.	--	--	<0.2	--	--	--	1.	≤0.1	<0.1
B	100.	--	--	20.	--	--	10.	--	--	--	20	5.	20.
C	60.	--	2,200.	300.	--	570.	60.	7,400.	400	400	3,000.	30,000.	1,000.
N	60.	2,500.	7,500.	300.	195.	86.	20.	500.	29.	29.	300.	10.	3.
F	50.	--	<30.	250.	--	310.	6.	110.	59.	59.	300.	10.	10.
Na	20.	--	--	40.	--	--	<2.	--	--	--	3.	<3.	3.
Al	10.	22.	--	10.	60.	--	20.	--	--	--	100.	10.	10.
Si	200.	55.	83.	200.	29.	71.	100.	130.	57.	57.	500.	500.	500.
P	20.	10.	--	20.	8.5	--	6.	--	--	--	3.	3.	3.
S	200.	17.	42.	200.	--	250.	30.	51.	70.	70.	500.	500.	300.
Cl	600.	17.	26.	600.	45.	52.	20.	19.	32.	32.	30.	30.	10.
K	20.	--	--	20.	--	--	<2.	--	--	--	10.	3.	2.
Ca	20.	15.	12.	50.	30.	30.	20.	18.	30.	30.	10.	10.	20.
Ti	20.	--	--	20.	--	--	20.	--	--	--	3.	10.	10.
V	<1.	--	--	<1.	--	--	0.6	--	--	--	0.3	<0.1	<0.1
Cr	≤2.	--	--	≤2.	--	--	1.	--	--	--	1.	3.	0.1
Mn	2.	1.1	--	2.	3.	--	1.	--	--	--	1.	3.	0.3
Fe	20.	3.5	--	20.	11.	--	20.	--	--	--	20.	20.	5.
Co	<2.	--	--	<2.	--	--	0.6	--	--	--	0.3	1.	0.3
Ni	3.	--	--	3.	--	--	1.	--	--	--	1.	15.	5.
Cu	3.	--	--	3.	--	--	0.3	--	--	--	0.5	10.	0.5
Zn	10.	--	--	10.	12.	--	1.	--	--	--	2.	4.	1.
As	2.	0.4	--	2.	0.2	--	<0.2	--	--	--	<0.1	<0.1	<0.1
Br	<1.	--	--	<1.	--	--	<0.4	--	--	--	<0.6	1.	0.4
Zr	<0.5	--	--	<0.5	<0.25	--	<0.5	--	--	--	<0.5	<0.5	<0.5
Mo	<0.4	--	--	<0.4	--	--	<0.4	--	--	--	<0.4	<0.4	<0.4
Ba	<0.6	--	--	<0.6	6.	--	<0.6	--	--	--	<0.6	<0.6	<0.6
Pb	<1.	1.5	--	<1.	2.	--	<1.	--	--	--	<1.	<1.	<1.

(a) BMI No. S-0431.

(b) BMI No. S-0430.

(c) BMI No. S-0429.

(d) BMI No. S-0432.

(e) Analysis supplied with sample; other values are BMI.

(f) As H; from quartz-tube graphite-crucible experiments.

41-A

41-B

TABLE 9. COMPARATIVE ANALYSIS OF
SINGLE-CRYSTAL MgO^(a)

(ppma)

Element	Battelle		Chemical	Given Analysis
	Mass			
	Run 1, As Received	Run 2, Etched		
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 No. S-0860.

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

NO. 4510-L 10X10 TO THE INCH

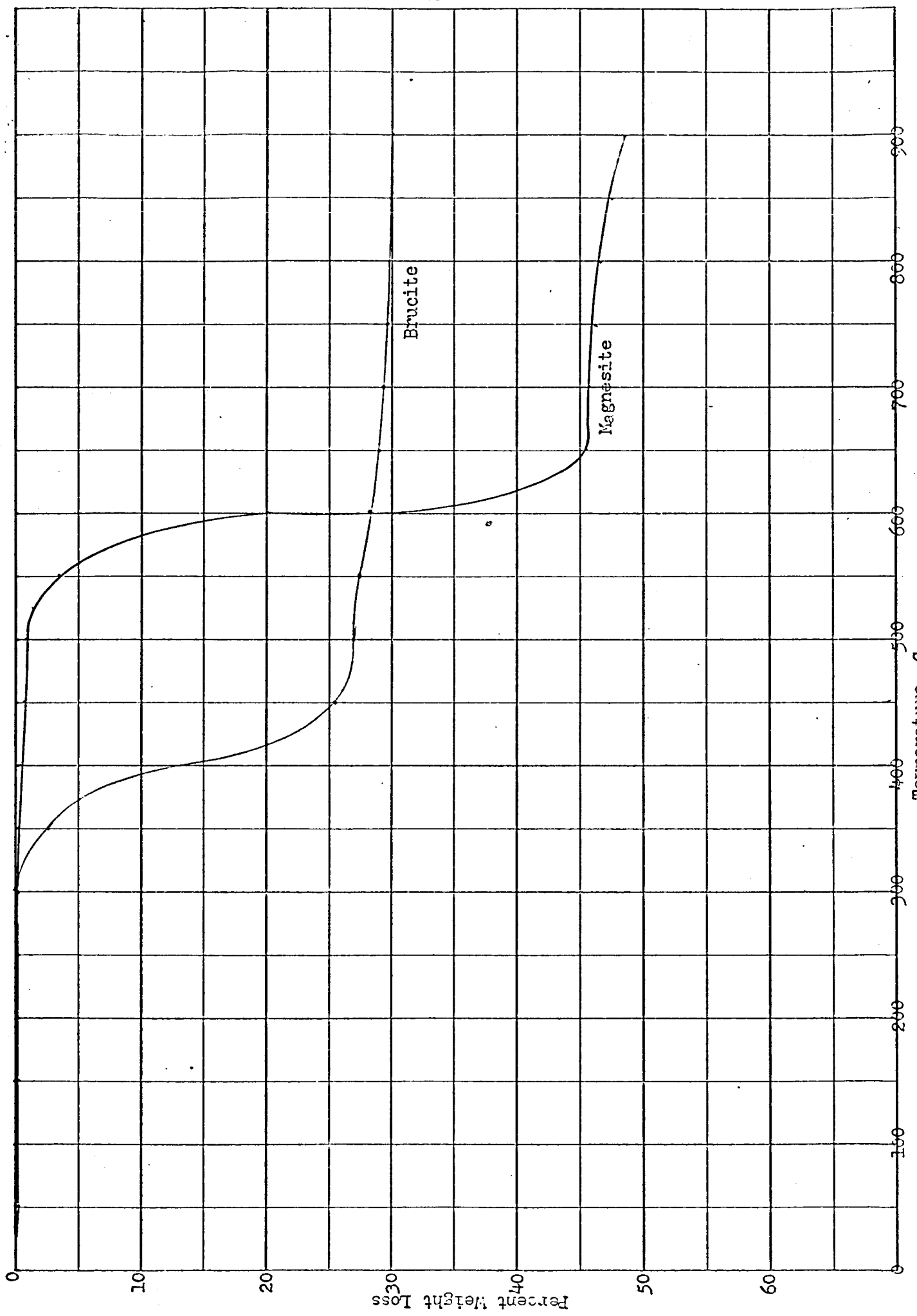


FIGURE 1. TGA THERMOGRAMS OF MAGNESITE AND BRUCITE. 4 C PER MINUTE AND 0.1 mm Hg