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Elemental Analysis of the JSC Mars-1 Soil Simulant using Laser Ablation and Magnetic Separation

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Introduction

Future long-duration missions to Mars require capabilities in terms of manufacture of structures and chemical compounds essential for human habitat and exploratory activities. Currently, it is not feasible to import all the required raw and finished materials from Earth. In fact, essential items such as structural members as well as various gases for human consumption and material processing need to be largely extracted from the available planetary resources. The resources on Mars include its soil and rocks, its atmosphere and the polar caps. Mars atmosphere consists of 95% carbon dioxide and the balance contains small percentages of oxygen, nitrogen, and argon. The Mars regolith contains many metal oxides in various mineralogical forms. Presently, Martian soil samples are not available. However, a closely matched Martian soil simulant developed by the Johnson Space Center has been available for scientific research and engineering studies. The chemical makeup of this simulant is compared with the data from Viking Lander and Path Finder missions in Table 1.

Oxide	JSC Mars-1	Pathfinder	Viking Lander
SiO_2	43.5	40.9	48.4
TiO_2	3.8	0.7	0.74
Al_2O_3	23.3	10.4	8.2
Fe_2O_3/FeO	15.6	21.2	20.8
MnO	0.3	0.5	
MgO	3.4	8.7	6.7
CaO	6.2	6.1	6.6
Na_2O	2.4	3.2	
K_2O	0.6	0.5	<0.17
P_2O_5	0.9	0.9	
SO_3		6	7.4
Cl		0.7	0.8

Table 1: Percent (by weight) chemical composition of the JSC Mars-1 simulant compared to soil data from Pathfinder and Viking Lander – from Allen, C. C., et al, Johnson Space Center [1].

Martian soil, rich in many metal oxides, can be processed to yield various elements such as Si, Fe, Al, Ti and oxygen. Reduction of these oxides to a metallic form with techniques employed on earth is not feasible at this time due the weight and complexity of such processing plants as well as other chemical reagents used in such processes. In this study, it is proposed that Martian soil simulant be irradiated with a high energy source such as a laser and the products of ablation, usually in the form of ions and excited atoms, magnetically separated and collected on substrates as thick films for further processing and packaging.

Laser ablation techniques have been used by others [2] to separate trace elements from geological specimens. Such studies have used quadrupole mass spectrometers which are not suitable for separation and production of any significant amounts of elements for manufacturing purposes. Instead, a magnetic sector in conjunction with an optional ionizing source promises to yield adequate amounts of elements suitable for further processing and forming.

In the proposed process, the soil sample is ablated with a high fluence pulsed excimer laser to produce excited atoms and ions of the elements comprising the soil. Assuming that majority of the ablated material is in ionic form, an applied external magnetic field will divert the path of the ions based on their cyclotron radius which in turn depends on the momentum of the ablated ion. The cyclotron radius is defined as

$$R_c = \frac{mv}{zB}, \qquad \text{where} \qquad v = \sqrt{\frac{2eV}{m}}$$

and m is the mass of the ion, z is the ionic charge, B is the magnetic field strength, V is potential, and v is the ion velocity.

Assuming an ionic ejection energy corresponding to 20 eV, and a magnetic field strength of 1.5 kG, the cyclotron radii for ions of various atomic masses can be calculated and plotted as shown below;

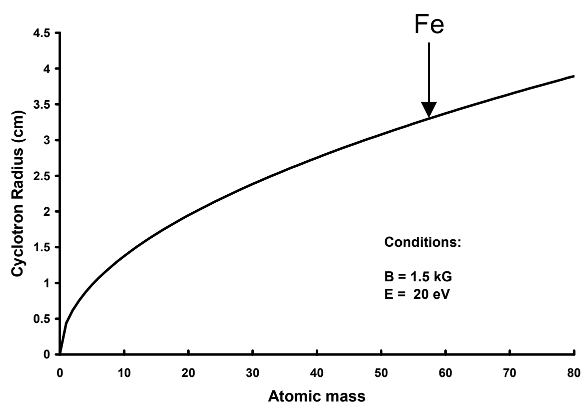


Figure 1: Cyclotron radii of singly ionized elements with various atomic masses

This chart indicates that singly ionized particles of iron traveling with a kinetic energy of 20 eV will follow a circular path with a radius of approximately 3 cm when subjected to a magnetic filed of 1.5 kG.

The kinetic energy of the ablated particles is not well known for these conditions. Other investigations [3] performed under conditions from which our conditions can be extrapolated estimate the ion energies to range from 10 eV to 100 eV. A separate investigation is required to map the energy distribution of the ablated particles.

As part of the general ISRU experiments, we also studied the effect of annealing and external magnetic fields on glass prepared by melting of the simulant constituents as listed in Table 1 in reagent form. It is desirable to form glasses with significant magnetic properties for use in many applications such electric motors, heat production, and radiation shielding.

Experiments

The JSC Mars-1 soil simulant, provided by the Johnson Space Center, was processed in different ways to study its chemical and physical transformations under various conditions. The following sections describe the four separate experimental activities that contributed to improved understanding of our abilities to extract elements of interest from the Martian soil simulant by in-situ techniques.

Experiment 1- Laser Ablation of Soil

In the following series of experiments which constituted the majority of the efforts undertaken as part of the SFFP program, JSC Mars-1 soil simulant was heated in a vacuum furnace at 120 °C for 24 hours and pressed under 10,000 psi to form a pellet of approximately 1 in. diameter and 1/8 in. thickness. The pellet form was preferred to loose soil form due to its ability to retain its shape when undergoing the laser ablation process. An excimer laser (Lambda Physik LPX-100) with 200 mJ pulse energy, 20 ns pulse duration, and 248 nm wavelength (with Kr-F gas mixture) was used for these experiments. The laser radiation was focused using a magnesium fluoride lens on the surface of the soil sample which was centrally placed in a 30-cm cylindrical vacuum chamber. The excimer laser was operated at 10 Hz which provided an average power of 2.0 W with peak powers of 10.0 MW per pulse.

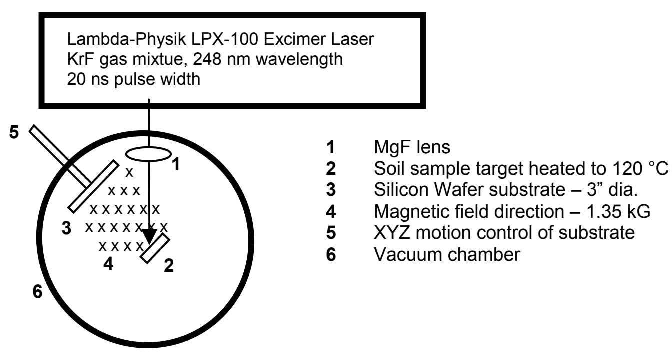


Figure 1: Schematic of the experimental setup

Silicon wafers (3 in. dia.) were used as substrates for their sub-nanometer surface polish which facilitated film thickness measurements as well as for their purity which helped in isolation and identification of the deposited material. Carbon tapes were used to mask a small area of the silicon wafer to provide a reference plain for film thickness measurements. A resistance coil heater using AERO-COAX 1HR063F6.5 wires was manufactured and placed directly behind the soil sample holder and used to heat the soil to 120 °C for several hours under vacuum conditions to ensure any water vapor absorbed from the environment would be vaporized and evacuated before laser ablation resumption. The heating of the sample continued during the laser ablation process.

The pressure in the chamber was maintained at about 4×10^{-5} Torr using a roughing pump (Edwards-18-Two Stage) and a turbomolecular pump (Leybold TurboVac 151C) to provide mean free paths much longer than the radius of the chamber. Chamber pressure was monitored by a thermocouple gauge (Teledyne DV-6M) and a Penning gauge (Edwards CP-25-EK). To investigate the extent of ionization in the plasma produced by laser ablation, two permanent magnets with dimensions of 4 cm by 6.5 cm were placed on opposite sides of the plasma generated by laser ablation. The magnets were separated by 20 mm. The field strength of the magnets was measured to be 1.35 kG at the center which uniformly decreased to 1.1 kG near the edges. If considerable fraction of the plasma were ionized, the path of the ionized particles would be deflected under the influence of a magnetic field perpendicular to the direction of motion of the ionized particles.

Figure 2: Experimental setup showing the excimer laser and the vacuum chamber

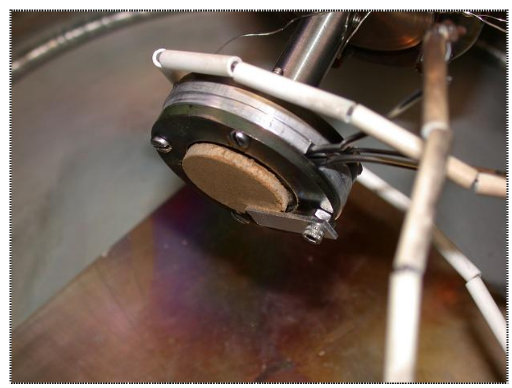


Figure 3: Soil sample mounted on an electrically heated target holder

In each case, the soil sample was ablated for 35 minutes at 10 Hz with approximately 200 mJ per pulse. The silicon wafer substrate was placed parallel to the soil sample at a distance of 5 cm from the soil sample. Experimental facilities and the target holder are shown in figures 2 and 3.

The deposited film on the silicon wafer was examined using a stylus profilometer (Tencor Alpha-Step 200) which has a vertical resolution of 5 angstroms.

<u>Experiment 2 – Ionization Extent of Silicon</u>

In order to investigate the ionization stage of the ablation plasma, an experiment was set up using the facilities at University Alabama, Huntsville under the direction of Dr. Andrew Pakhomov. In these experiments a glycol cooled array detector (Princeton Instruments IRY-512G/RB) was used in conjunction with a 1200 lines/mm grating spectrometer to study the atomic as well as ionic emission lines of silicon which was the dominant constituent of the soil. The radiation from a pulsed Nd:YAG laser (Molectron MY32-10) was focused on a small piece of high purity silicon wafer. The emission from the plasma generated as a result of the surface ablation of the silicon wafer was focused on the spectrometer which was set to observe the 500.6059 nm line of the atomic silicon and the 504.1024 nm emission line of the ionic silicon. . As of the writing of this document, the emission data has not yet been collected on the silicon wafer nor the soil sample. However, it is planned that the emission data be collected at various delay times relative to the laser pulse generation. Emission spectrum will be collected at delay times of 20, 30, 50, 100, and 1000 nanoseconds to observe the relative particle densities of the silicon ions compared to the atomic silicon. Once such preliminary data is processed, the JSC Mars-1 simulant will undergo the same experiments to observe the emission lines belonging to other elements such as iron and aluminum. The ultimate goal of these set of experiments is the study of the ionization extent of some of the elements comprising the soil simulant.

Experiment 3 – Oven Melting of Reagents

The sample under study in these series of experiments was prepared by mixing the oxide constituents of the JSC Mars-1 soil as reagents and heated at 1500 °C for 6 hours. The molten mixture was then cooled down to room temperature. The provided sample has a dark gray color similar to an iron magnet. The sample is also slightly magnetic and responds to an applied magnetic field. Three pieces from the provided sample were cut to study the effect annealing and applied external magnetic field on this sample. The cut pieces had dimensions of 4 mm by 14 mm with a typical thickness of 2 mm. One of the pieces was subjected to resistive heating in an oven which was continuously purged by argon for the entire duration of the heating and cooling processes. The oven temperature was raised to 800 °C at a rate of approximately 20 °C/min. The maximum temperature of 800 °C was then maintained for 4 hours before the oven was cooled at a rate of 50 °C/hr to 100 °C. In a separate experiment, another piece of the sample was heated in the oven as described above except that in this case an external magnetic field of nearly one Tesla was applied for the entire duration of heating and subsequent cooling of the specimen. A summary of the processed pieces and their respective labels are shown below,

Sample label	**Oven max. T**	**Ext. Mag. Field**	*Notes*
Re-Cont	n/a	n/a	*Control piece*
Re-A	800 °C	0.0	*Annealed with no applied magnetic filed*
Re-B	800 °C	1.0 Tesla	*Annealed with applied magnetic field*

Table 2: List of specimens processed for magnetic property studies

The magnetic properties of each of the specimens as labeled above were measured using a Vibrating Sample Magnetometer (VSM) system. The VSM produced the Hysteresis curves for each sample. The samples were further examined by polishing their surface to 1 μm and applying a small quantity of a ferrofluid (FerroTec EMG 909) to their surface. The ferrofluid used in this case had particle sizes of 10 nm and viscosity of less than 5 cp. The ferrofluid is generally used to reveal the possible magnetic domain structure of a sample. This method is a well recognized tool in the field of magnetic domain analysis and is known as the Bitter method.

Experiment 4 – Laser Melting of Soil

Experiments involving the melting of JSC Mars-1 were previously conducted by the author at Middle Tennessee State University. In these experiments the Martian soil simulant was placed in a metal container with dimensions of approximately 2 in. by 4 in. and 1 in. deep. A CO_2 laser was used to melt a 0.25 in by 0.5 in. area in central area of the sample. The laser light, with a spot size of 0.005 in. was focused at the surface level of the soil. The soil was at room temperature and atmospheric pressure. The experiments were performed in air. The laser scan rate was set at 0.3 in/min. In one experiment the soil as received from JSC was processed using the procedure outlined above. In another experiment 10% (by weight) graphitic carbon was added to the soil to study its effect on the reduction of iron oxides present in the soil to metallic iron. The use of the surrounding soil as the crucible in these experiments alleviated the problems associated with selection of suitable containers which could tolerate the temperatures and high rates of heating and cooling encountered in theses cases. The processed soil samples were sectioned, mounted in epoxy and polished at NASA-MSFC and submitted to Mr. Paul Carpenter of BAE Systems for electron beam microanalysis. The discussion of these analyses is included in the next section.

Results

Energy deposited by the excimer laser on the soil sample caused ablation of neutral and ionic particles from the sample surface. Since the ablation process is temporally separated from absorption of the laser radiation energy, the ablation materials are ejected in the direction normal to the surface of the sample, regardless of the direction of the incident beam as shown in figure 4. There is, however, a certain degree of asymmetry which is believed to be caused by the shape of the cavity formed by laser ablation after a few hundred pulses. Figure 5 shows that the cavity becomes increasingly deeper at the distal location which forms a wall which in turn inhibits the plasma from expanding in that direction.

It is further noted that under adequate magnification, a cone-like structure is observed to from in the ablated area of the soil sample (Figure 6). The cones are about 100 microns in width and generally point in the direction of the incident beam. We believe that these cones are similar to those observed by many researches [4, 5] in the field of thin film coating using laser ablation. Foltyn, *et al* [5] suggest that vaporization-resistant impurities are responsible for the cone formation. They demonstrated that the cone tips are much richer in certain elements compared to other parts of the sample.

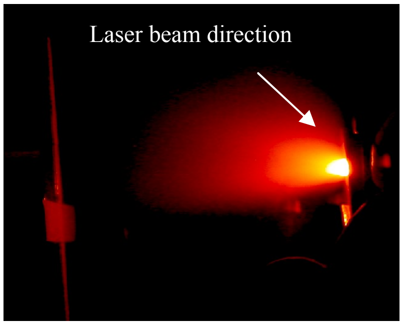


Figure 4: Formation of plasma by the ablated material. Silicon substrate is shown on far left

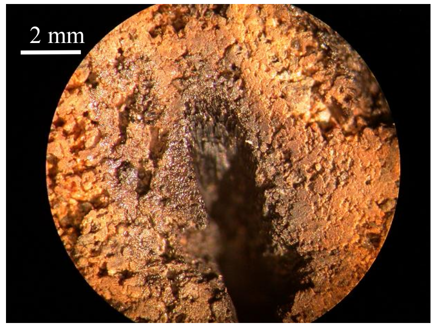


Figure 5: Crater formed by mass removal from the soil sample by laser ablation

Figure 6: Cones formed in the direction of incoming laser radiation

The thin film formed on the surface of the silicon wafer shows a ringed color pattern which is believed to be caused by interference of light from the film surface and the reflective substrate. This is not unlike the colors observed from a thin film of oil on water. The colors observed on the substrates are consistent with film thickness measurements using a stylus-based instrument. It is also noted that more than one order of interference is present.

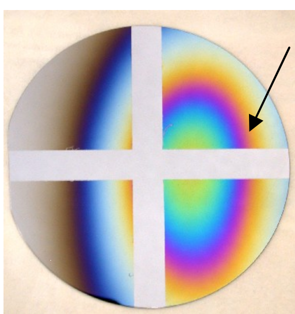


Figure 7: Thin film deposit on silicon wafer showing interference patterns

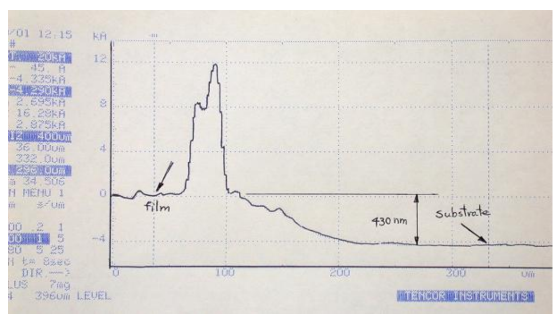


Figure 8: Film thickness measured at the point marked in figure 7

The film shown in figure 7 has a maximum thickness of approximately 500 nm which is consistent with the film thickness measurements conducted by the stylus profilometer. The film demonstrates some level of graininess not unlike those observed for crystals of table salt (Figure 9). It is our intention to analyze the deposited film to determine its composition. We believe that the majority of the film consists of silicon dioxide since silicon is the most abundant element in the soil sample. Moreover, film of other elements such as iron, aluminum, or titanium would have created an opaque film and not caused the interference pattern observed on the substrate. Experiments conducted with an applied magnetic filed of 1.35 kG in the direction perpendicular to the direction of particle motion resulted in similar deposited films and film thicknesses as shown in figure 10.

The presence of the magnets above and below the plasma and the presence of magnet housing on the sides of the plasma created a cold wall confining the plasma to the center portion of the passage formed by the magnet and the magnet housing. The resulting pattern is not conclusive concerning the deflection of the plasma by the applied magnetic field. Even though, there seems to be a more convex shape to the pattern towards the right direction, which would be consistent with deflection of positive ions to the right, the effect could as well be due to the wall confinement.

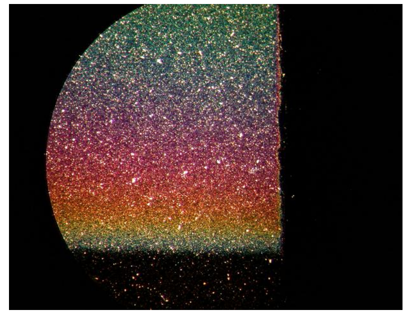


Figure 9: Grain-like structure of the thin film deposit

We plan to devise an experiment where the effect of magnetic filed on the pattern formed on the substrate could be demonstrated on the same substrate. This could be accomplished by coating an area of the substrate in the presence of external magnetic field and then masking the coated area and coating an adjacent area with ablated material in the absence of the magnetic field. We are also planning to take advantage of electromagnets for this purpose to fix the experiment geometry and only alter the field strength.

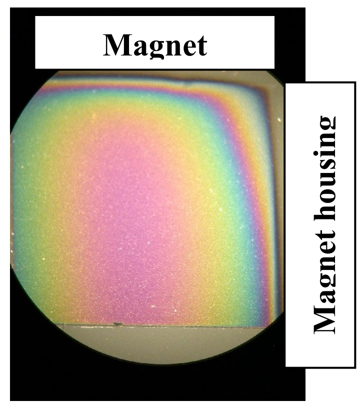
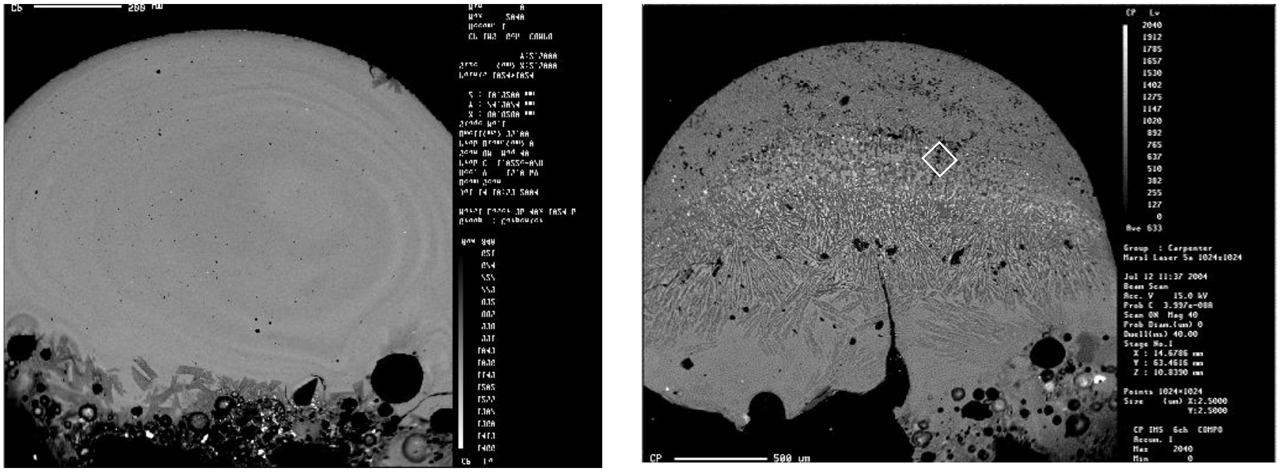


Figure 10: Interference pattern of the film in the presence of a magnetic field

Lack of detailed knowledge of the plasma constituents and their average kinetic energy remains the biggest obstacle in the progress of these experiments. Experiments being conducted at UAH are not completed as of the writing of this report.

Studies of the magnetic properties of the cast pieces from oxide reagent are also in progress at this time. The specimens listed in Table 2 have been polished to 1 micron and observed at magnification of 1000X after the surface was treated with a thin film of ferrofluid. No domain structure has been observed from our preliminary analysis as of this writing. We plan to conduct detailed susceptibility and domain analysis studies on these specimens.

Soil samples which were processed by a CO_2 laser at MTSU were analyzed using a microprobe. The two samples that were studied in detail were the laser-processed sample as received (sample a) and the soil sample with 10% by weight graphitic carbon (sample b). As shown in figure 11 sample (a) does not display any granular structure which is an indication of a homogeneous glass structure with some uniform convection lines apparent. On the other hand, sample (b) exhibits many features such as various grains and crystal growth.



(a) (b)

Figure 11: BSE images of the laser-processed samples. (a) JSC Mars-1 soil as received, (b) JSC Mars-1 with 10% (wt) graphitic carbon added.

Further element-specific analysis of various areas of the cross section shown in figure 12 points out the presence of metallic iron at some intermediate locations within the cross sections.

The addition of solid carbon has apparently caused reduction of iron oxides present in the soil to metallic iron. Figure 12 shows the elemental analysis of the area indicated in figure 11(b) for iron. Other prominent structures shown in figure 11(b) were found to be mostly glass, plagioclase, FeTi oxides, CaTiFeAl oxides, as well as several other oxides.

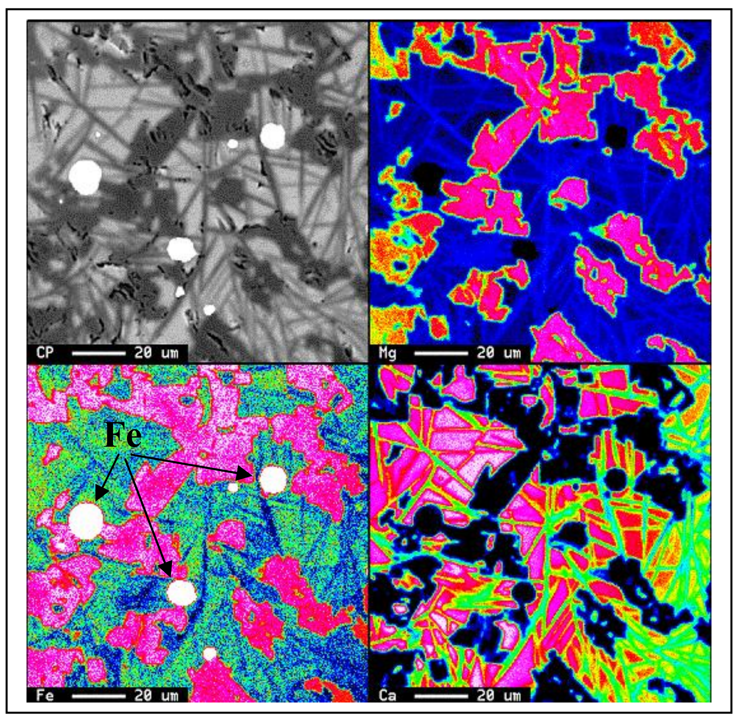


Figure 12: BSE images of the area shown in fig. 11 (b) for Mg, Fe, and Ca.

Conclusions

Martian soil stimulant JSC Mars-1 was ablated by an ultraviolet excimer laser in order to separate the constituent elements for *in-situ* resource utilization purposes. It was found that applied external magnetic field had some effect on the path of the ablated particles which could indicate that some of the excited particles forming the plasma are in ionic form. This aspect of the study will be further investigated to determine the extent of ionization in the laser induced plasma. The thickness of the ablated material on a silicon substrate followed the cosine relationship which is typical for film deposition by laser ablation.

The electron beam microanalysis of the soil samples processed by a 30 W CO_2 laser revealed that some iron oxides had reduced to elemental iron in the presence of carbon. Samples with no carbon added did not display any iron oxide reduction.

Study of the magnetic properties of the samples processed under various annealing and external magnetic field condition are still in progress and have not produced any results as of this writing.

Future Directions and Recommendations

Many aspects of the preceding investigations remain unresolved requiring further experimentation and analysis. In particular, the laser-supported plasma formed due to laser ablation of the soil simulant needs to be characterized more precisely in terms of ionization extent and the identification of the major constituents of the plasma at various times and distances from the target. The results of such studies will guide efforts in designing supplemental ionization chambers as well as specification for the magnetic sector stage. It is recommended that an emission spectrometry system with a time delay controller be an integrated part of future laser ablation experiments. Such a system will provide continuous, time resolved and detailed information about the laser-supported plasma.

Experiments that utilized a CO_2 laser to melt the soil sample would benefit from construction of a controlled environment where cover gases and their pressures could be varied. Others have noted that presence of CO during the melting process of iron oxides leads to production of metallic iron. It is recommended that experiments in CO environments under pressures representative of the Martian atmosphere be conducted to study the effect of such environments on the yield of various elements.

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Jeff Quick provided machining and other support services, and Drs. Laurent and Sen of BAE Systems participated in project discussions with the author. Dr. Narayaran Ramchandra guided the experiments involving the magnetic characterization of the sample produced from reagents.

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