
Silicate melt electrolysis ("magma electrolysis") is one of the processes currently under study as a means of extracting oxygen from lunar regolith. In addition to oxygen, several by-products of the process are also of potential value. These by-products include a metal phase or phases, spinel, and a residual silicate melt of altered composition. Characterization of the composition of these products is important in evaluating the potential value of the products, in evaluating how the products would react or interact with proposed container and electrode materials, and in evaluating the details of the reduction reactions during actual electrolysis that may not have been apparent from theoretical analyses or studies under conditions different from actual electrolysis.

Product composition may be a function of original composition of the melt, voltage applied between the electrodes, activity of oxygen in equilibrium with the melt, temperature, and various kinetic factors such as diffusion rates, mixing rates, and reaction rates. In this abstract, I report electron microprobe analyses of metal compositions derived at fixed initial composition, temperature, and oxygen fugacity but at variable voltage between the electrodes. The initial composition is similar to an Apollo 12 soil (12001) in which 1/2 of the Fe, Mn, and Cr and 1/4 of the Si and Ti have been removed (simulating a preceding electrolysis step). Temperature is 1350°C, \( f_{O_2} \) is \( 6.5 \times 10^{-4} \) atm, and voltages related to cation reductions for three experiments are 1, 1.5, and 2 volts.

The total voltage for the experiments is equal to the "reducing" voltage, that portion that goes toward reducing the cations and producing oxygen, plus I-R voltage, where "I" is the current and "R" is the intrinsic resistance of the cell. The I-R voltage corresponds to that portion of the energy lost to resistance heating of the melt. By continuously monitoring "I" and "R" and controlling total voltage by means of an IBM-PC-type computer connected to the instruments by an IEEE-488 bus, the "reducing" voltages were maintained at the values reported above for each of three experiments even though the values of "R" and "I" changed throughout the experiments.

Average values for analyses of several product metal grains in each experiment are reported in Table 1 (in wt%). Presence of Ir in the analyses results from the use of Ir as the cathodic material. Immediately apparent is the tendency for an increase in the concentrations of Si, Ti, and Cr in the metal produced at the higher potentials. Qualitatively, this is expected since Fe is more easily reduced than the other cations. However, based on the composition of the silicate melt and the known free energy of reduction for the various cations, we can predict "expected" metal compositions and compare them to observed metal concentrations. This is done in Fig. 1, illustrating that, quantitatively, the change in metal composition with potential does not match expectations, with Si content being much lower than expected.

Based on known or estimated reduction potentials, virtually all Fe, Si, Ti, and Cr should be reduced at 2 volts potential between the electrodes. Therefore, ratios of these elements in the metal should match those in the original melt. As already shown in Fig. 1, and illustrated further in Fig. 2, this is not the case. Fig. 2 demonstrates that the deviation of observed from expected metal compositions is a function of relative reduction potential of the element, with the elements that are more difficult to reduce being increasingly depleted in the metal. Therefore, I suggest that the low (e.g. Si/Fe) ratio in the metals produced at the higher voltages results from the metal reacting with the melt as follows:
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\[ \text{Si}^+ + 2\text{Fe}^{2+} \rightarrow \text{Si}^{4+} + 2\text{Fe}^0 \]  

(1)

Only about 50-80% of the Fe is removed from the melt in each of these experiments, thus sufficient \( \text{Fe}^{2+} \) is present in the melt for reaction (1) to take place. Also, Si concentrations in the metal are strongly inhomogeneous, varying from 0 to 10 wt% from one metal grain to another in A12_1ch and A12_1ci. These observations, coupled with the trends in Fig. 2, are consistent with the interpretation that the Si metal is reoxidizing by reaction with \( \text{Fe}^{2+} \) in the melt. Reoxidation of Si by oxygen is also a possible explanation, but the high oxygen production efficiency observed in the experiments suggests this is not the case. I conclude that a high-Si product cannot be practically achieved unless the Fe content of the melt is very low. In contrast, relatively pure Fe product is possible because \( \text{Fe}^{2+} \) in the melt will tend to reoxidize Si, Ti, and Cr in the metal.

A single metal blob in experiment A12_1cb (≈1.6 volts) contains three metal phases in a textural relationship that suggests they are in equilibrium. Analyses of these three phases are shown in Table 2 (in wt%). These phases correspond to the phases \( \gamma \)-iron, \( \alpha \)-iron, and melt expected at the Fe rich end of the Si-Fe binary. Deviations of the observed compositions from that expected from the phase diagram can be explained on the basis of the presence of Ir in the metal.

Summary: Three metal phases containing various concentrations of Fe, Si, Cr, Mn, and Ti are produced by the electrolysis of silicate melt. Residual \( \text{Fe}^{2+} \) in the melt tends to reoxidize Si, Cr, Mn, and Ti, leaving metal phases depleted in these metals relative to Fe. At lower concentrations of \( \text{Fe}^{2+} \) in the melt, or where electrolysis is carried to completion, we expect the metal to become richer in Si, Ti, Cr, and Mn.

Acknowledgements: I gratefully acknowledge the partial support of this work by NASA through the UA/NASA Space Engineering Center for Utilization of Local Planetary Resources.