Low Power Plasma Ion Source for Trace Element ICPMS on Future Planetary Missions

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Introduction: Argon (Ar) or Helium (He) plasma sources effectively atomize and ionize ablated solid particulates and aspirated solutions for chemical analysis. Inductively Coupled Plasma Mass Spectrometry (ICPMS) is a commonly used technique for measuring element abundances below 1000 ppmw concentration [1]. Analyses of key trace element abundances and their ratios provide critical data needed to constrain processes involved in planetary accretion, core formation, crust-mantle differentiation, weathering, and biologically driven chemical fractionation.

Commercial ICPMS instruments typically require high power (> 1000 W) and high gas flow rates (>10 L/min) to reach temperatures up to 10,000 K, metrics that are prohibitive for spaceflight applications. In contrast, recently demonstrated low power/low temperature plasmas that needed only limited gas flow may serve as practical ion sources for planetary mass spectrometers, as these technologies present an opportunity for their miniaturization with limited resource requirements [3, 4].

We have characterized low power Ar and He microwave plasmas and modeled their abilities to ionize elemental analytes. Using a Langmuir probe and varying the forward power, gas flow rate, and gas composition, we determined electron temperatures (T_e), electron densities (N_e), and ion/neutral ratios via IV-curve measurements. These measurements were then used to estimate the ionization efficiencies of the plasmas for a suite of trace elements with a range of first ionization energies [5–7].

Methods: Here, we investigate low power/low flow microwave plasmas produced at 1 Torr (10^3 Pa). The torch box was evacuated to a pressure $<10^{-3}$ Torr and backfilled with a controlled amount of plasma gas, either Ar or He (20 – 200 mL/min), until the pressure reached ~1 Torr. The plasma was generated at 2.4 GHz using a signal generator coupled to an Evanson microwave cavity [8, 9]. After the plasma conditions were tuned and reflected power was minimized to <1W, the forward power was adjusted between 2 - 25W. A custom Langmuir probe with a 0.05 mm diameter, 2 mm long tungsten probe tip was inserted into the plasma. Voltage on the probe was swept from -20 to +20 V; the measured plasma current vs. probe voltage (IV-curves) were used to calculate T_e, N_e, and plasma potential.

Results: The results of T_e and N_e calculations are shown in Fig. 2. Compared to the He plasma, the Ar plasma shows higher sensitivity in N_e and T_e values as a function of plasma power. Specifically, N_e increases by a factor of 3.5x over a range of 10 W in the Ar plasma, but only by only a factor of 2x over 20 W in the He plasma. T_e also increases more rapidly in Ar plasma than in He plasma, confirming that Ar plasma is more easily influenced by forward power. The temperature increase is attributed to the increased kinetic energy of electrons in higher power microwave plasmas. Increasing N_e promotes a greater probability of collision events and higher kinetic energy electrons. Differences in N_e and T_e profiles between these plasmas are due primarily to differences in the ionization energies of the gases; Ar has a lower first ionization potential (15.8 eV) than He (24.6 eV).

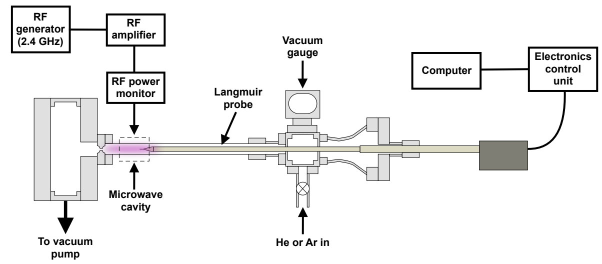

Fig. 1: Schematic diagram of experimental plasma setup.

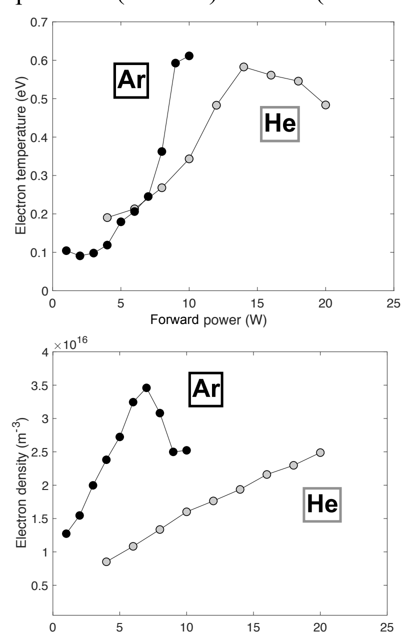

Fig. 2: Variation in plasma electron temperature *(top)* and electron density *(bottom)* with varying forward power, as measured by Langmuir probe

Estimates for analyte ionization. The Saha equation describes the relationship between ions and neutrals in a plasma, and is driven by fundamental plasma characteristics, namely T_e and N_e. The Saha equation is calculated as:

$$\frac{N_i N_e}{N_o} = 2\frac{g_i}{g_o}\left(\frac{2\pi m_e k T_e}{h^2}\right)^{\frac{3}{2}} e^{\frac{-E_i}{kT_e}}$$

where N is the population density of ions (N_i), neutrals (N_o), and electrons (N_e), g is the statistical likelihood of an electron transition, m_e is the electron mass, k is the Boltzmann constant, T_e is temperature, h is Planck's constant, and E_i is the first ionization energy of the element [10–12]. The Saha equation contains variables for T_e and N_e, but electron temperature has a greater impact on ion/neutral ratio than electron density; increasing both N_e and T_e produces a net increase in ionization.

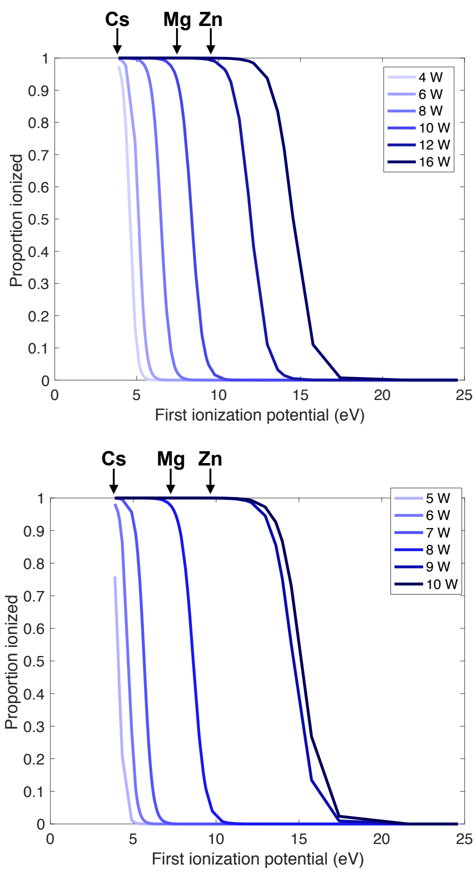

Fig. 3: Estimates of ionization efficiency for He (*top*) and Ar (*bottom*) calculated for a range of first ionization potentials based on measurements by Langmuir probe

N_e and T_e were measured via Langmuir probe, and changes in analyte ionization efficiency as a function of plasma power were calculated using the Saha equation. Fig. 3 illustrates the degree of ionization as a function of first ionization energy for a range of forward power conditions. These plots show that first ionization energy is effectively reached for many elements with a forward power conditions of 10W, regardless of plasma gas composition. For example, elements with a range of first ionization potentials from Cs (3.8 eV) to Mg (7.6 eV) to Zn (9.4 eV) are modeled to achieve up to 99% ionization with an 8 W Ar plasma or a 12 W He plasma. This range of first ionization potentials includes about 70% of the periodic table.

Conclusion: Here, we have measured the fundamental characteristics of low power/low gas flow Ar and He plasmas and estimated their capabilities as ion sources for prospective planetary mass spectrometers. Such plasmas can effectively ionize elemental analytes despite a reduction in power and gas consumption relative to commercial systems. Based on measurements and models of the plasma, Ar and He plasma gasses can achieve up to 99% ionization of elements with high first ionization potential using only 8 – 12 W of power. Either Ar or He plasma gasses can be used with applications to spaceflight mass spectrometry, as we have shown that a significant reduction in resource use does not compromise instrument performance for *in situ* geochemical analysis.

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