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Verification of in-situ K-Ar dating using LIBS

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Knowing the age of planetary surfaces is important. In recent years, *in-situ* dating techniques without sample-return missions have been developed. *In-situ* dating conducted by NASA's Curiosity rover on Mars is the only example of such measurements on another planet. Curiosity obtained the K concentration with an Alpha Particle X-ray Spectrometer (APXS) and the Ar concentration with a quadrupole mass spectrometer (QMS), and obtained the K-Ar age of a mudstone at the Gale crater. However, since this system is very complicated, a large rover is needed for operation. Therefore, we investigated conducting both K and Ar measurements using only Laser-Induced Breakdown Spectroscopy (LIBS). Since our method requires only one detection, the instrument package can be more compact and lighter compared with NASA's method. Furthermore, LIBS enables remote and rapid measurements. However, Ar gas contained in a rock has been never detected with LIBS.

In this study, we conduct verification experiments for detection of Ar in rocks using LIBS.

Temperature and electron density of LIBS plasma under atmospheric pressure are expected to be 1 eV (11600 K) and ?10?ˆ17 cmˆ(-3), respectively. We calculated the Ar line intensity at these values using the Saha equation and found that the neutral emission lines at 104.8 nm and 106.7 nm are the strongest ones. We then conducted spectroscopic experiments in a vacuum ultraviolet range (i.e., 10?200 nm). We used a standard basalt sample with known chemical composition (JB-1a) and a sample with enhanced Ar concentration (Ar concentration is 0.1 cc/g). We used an Nd:YAG laser (λ=1064 nm; pulse width 5?7 ns; pulse energy 50 mJ). The emissions from laser-induced plasma is diffracted by concave diffraction grating. The detector is MCP with a phosphor screen. We captured the spectra images on the phosphor screen with a CCD camera.

In a preliminary experiment using pure silicon as a sample, we detected the Siˆ(3+) emission line at 106.7 nm. This suggests that the temperature of plasma is higher than expected, because the Siˆ(3+) emission line requires high excitation energy. Considering the high temperature, and because Ar is thought to be ionized at such a high temperature, we then tried to detect the Arˆ(4+) emission line at 83.5 nm because this line had higher detectability than the neutral emission lines. However, we found that an Oˆ(2+) emission line at 83.4 nm interfered with the Arˆ(4+) line. In our study, we detected a number of multiply charged ion emission lines and found that the Siˆ(3+) emission line at 106.7 nm and Oˆ(2+) emission line at 83.4 nm overlapped with the Ar emission lines. Since the plasma temperature drops rapidly with time, our results indicate that a gate pulse to detector is effective for removing the emission lines of multiply charged ions.

Keywords: LIBS, in-situ dating, K-Ar method