IN-SITU K-AR DATING OF ROCK SAMPLES BY A COMBINATION OF LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) AND NOBLE-GAS MASS SPECTROMETRY.

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Introduction: Radiometric dating using a combination of K and Ar is one of the common method for rock samples. In order to date a specific microscopic portion, it is necessary to determine K and Ar simultaneously. Ar-Ar method is the best solution for this, but it is not easy because handling of neutron-irradiated materials is restricted to controlled areas. In this study, we have developed a measurement system combining a laser-extraction noble gas analysis with an elemental analysis using plasma emission spectroscopy (LIBS). We have applied the system to determine K-Ar ages of lithic clasts in a brecciated H-chondrite [1], Willard (b). Chondrules and matrix of the host chondrite have also been analyzed. Here we present the analysis system and report the in-situ K-Ar ages obtained.

Experimental: The system consists of an Nd: YAG pulse laser (wavelength: 1064 nm; pulse width: 7-8 nsec; original beam diameter: 5 mm), a visible light spectrometer (spectral resolution: ~0.5 nm), and a noble gas mass spectrometer. Polished sections (about 100 μm in thickness) were prepared from mineral standards and Willard (b). Laser ablation was carried out by focusing the beam with energy of 0.1 uJ to a diameter of 20 μm on the polished samples. Typical ablated mass is about 1 μg (10 holes with 20 μm diameter and 100 μm thickness). The K concentration with the LIBS was calculated based on the area ratio of emission lines of K (767 nm) and oxygen (777 nm). Mineral standards were orthoclase (K_2O = 15.226 wt%), albite (K_2O = 0.255 wt%), and wollastonite (K_2O = 0.466 wt%). The noble gas extraction efficiency was corrected based on the orthoclase analysis using the K concentration determined by EPMA and the K-Ar age of 461 Ma [2-3]. The sensitivity correction of the noble gas mass spectrometer was performed with a known amount of the earth atmosphere.

Results and Discussion: Reproducibility of the LIBS analysis for the standard minerals was obtained by using the above condition of laser ablation. The detection limit for K was estimated to be about 1000 ppm for 1 μg samples based on the result for the albite standard sample, and is similar to the typical chondritic values. Hence, we should apply our system to K-rich phases at this stage. Our SEM/EPMA observation revealed that most lithic clasts in Willard (b) have CI-like mineralogy and contain K of ~1000-3000 ppm, which is higher than the typical CI chondrite value of 550 ppm [4].

The K concentrations determined by the LIBS analysis for two CI-like clasts, W2CLT2 and W2CLT3, are 2950 and 1880 ppm, respectively. The ^{40}Ar concentrations for the clasts are 8.6 and 4.9 × 10^{-5} cm^3STP/g, respectively. Based on these K and Ar concentrations for the clasts, we obtained K-Ar ages of 3.0 and 2.8 Ga. These values are longer than CI chondrites and in the range of CM chondrites [5]. Isotopic ratios of He and Ne for the clasts and matrix portions are indicative of the presence of solar wind gases. Higher concentrations of ^4He and ^{20}Ne are consistent with this interpretation. The light noble gas compositions suggest that Willard (b) and also the lithic clasts have not experienced any heating event after lithification of the regolith material of the Willard (b) parent body. The younger K-Ar age for the lithic clasts are due to either the recent heating before arrival to the Willard (b) regolith layer, or due to ^{40}Ar loss caused by recoil [6] and low gas retentivity of phyllosilicate that is the major component of the clasts. In the case of the former, the timing of the lithification of the regolith material should be later than 2.8 Ga.

For chondrules and matrix of Willard (b), concentrations of K are typically lower than 1000 ppm, which is difficult to determine quantity with our LIBS system. Based ^{40}Ar concentrations of two bulk samples (6.36 and 6.57 × 10^{-5} cm^3STP/g) determined using pyrolysis extraction method and the typical K content of 782 ppm [4], the K-Ar age of Willard (b) is calculated to be 4.6 Ga. The laser extraction analysis revealed that ^{40}Ar concentrations in the chondrules vary from 0.5 to 7 × 10^{-5} cm^3STP/g. Higher concentrations of ^{40}Ar (6-10 × 10^{-5} cm^3STP/g) were determined uniformly in matrix, suggesting heterogeneous distribution of K-rich phases in the matrix. However, it is difficult currently to calculate K concentrations in most of the matrix and chondrules based on the LIBS spectrum. In the case of K concentration lower than 1000 ppm, the uncertainty of the multi-function fitting calculation exceeds 100%. In the future, we will improve the limit of quantification by reviewing the measurement conditions of the LIBS system and improving the accuracy of background correction and function fitting of LIBS spectrum.

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