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High-precision potassium measurements using laser-induced breakdown spectroscopy under high vacuum conditions for in situ K–Ar dating of planetary surfaces

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ABSTRACT

We conducted a series of laser induced breakdown spectroscopy (LIBS) experiments for K measurements under high vacuum conditions (10^{-6} Pa) for the purpose of developing in-situ isochron type K–Ar dating instruments for planetary missions. Unlike whole rock measurement methods, isochron measurements require LIBS experiments in a vacuum chamber because simultaneous Ar isotopic measurements are necessary. However, detailed examination of detection limits and accuracy of this method at low pressures has not been examined extensively before. In this study, the capability of K measurements under high vacuum conditions was examined using LIBS. A compact Czerny-Turner type spectrometer equipped with a charge-coupled device (CCD) as a detector was employed. Twenty-three geologic standard samples were measured using the LIBS method. The second strongest K emission line at 769.89 nm was used for calibration because the strongest emission line at 766.49 nm may suffer from strong interference from another emission line. A calibration curve was constructed for K using internal normalization with the oxygen line at 777 nm and well fitted by a power-law function. Based on the prediction band method, the detection limit and the quantitation limit were estimated to be 300 and 800 ppm, respectively. The 1σ relative uncertainty of the K calibration was 20% for 1 wt.% K_2O and 40% for 3000 ppm K_2O. If the amount of Ar is measured with 15% error for the 3.5 billion years rocks containing 1 and 0.3 wt.% K_2O, the K–Ar ages would be determined with 10% and 20% 1σ errors, respectively. This level of precision will significantly improve the current Martian chronology, which has uncertainty about a factor of two to four. These results indicate that the concentration of K can be measured quantitatively under high vacuum conditions using a combination of instruments that have previously been carried in planetary missions, which suggests the viability of building in situ isochron K–Ar dating instruments with LIBS.

1. Introduction

Surface retention age is a key observable to achieve an understanding of the history of planets. A technique known as crater chronology is often used to estimate the age of a planetary surface [e.g., 1,2]. Crater chronology can estimate the ages of geologic units by measurement of the crater number density from image data, based on higher crater number densities on older surfaces. Crater chronology models have been constructed based on the correlation between the radiometric ages of returned samples obtained by Apollo and Luna missions, and the crater number density where the samples were collected [e.g., 1–3]. These calibration curves enable conversion of the crater number density to the absolute age of the surface, thereby allowing investigation of the surface evolution of the Moon [e.g., 4–6].

The lunar crater chronology has been applied to other planets including Mars [7,8]. However, Doran et al. [9] pointed out that the chronology model of Mars is so poorly constrained that the surface age of Mars would differ by as much as 1 billion years depending on the assumed model. Hartmann et al. [10] pointed out that the true age of a lava unit estimated to be around 2 Ga could range from <1 Ga to ca. 3.5 Ga due to a factor two to four uncertainty in Martian cratering ages. The radiometric ages of Martian rocks are necessary for calibrating

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the crater chronology on Mars. However, we do not have radiometric age data from Mars, of which the original geologic unit is known. The NASA Curiosity (Mars Science Laboratory) mission most recently conducted the first in situ dating experiments on Martian rock and obtained 4.21 ± 0.35 Ga for a mudstone on the floor of Gale crater [11], demonstrating that K–Ar dating is actually possible on Mars. The interpretation of the obtained radiometric age, however, is very difficult. Because the measured sample is a sedimentary rock, it would contain both minerals (perhaps volcanic rock fragments) formed before the rock and minerals (perhaps clays and carbonates) formed simultaneously with the rock. Their mixing ratio is unknown. The whole-rock K–Ar age of such a rock would be a K-weighted average of the age of the parent volcanic rock possibly reset by the Gale-forming impact and the age of the authigenic components that occurred during subsequent sedimentation. Because of the ambiguous age of the sedimentary components, the whole-rock K–Ar age of the mudstone cannot be readily tied to the cratering age of the floor, which is based on the timing of the sedimentation. The lack of a robust absolute age model thus prevents an accurate understanding of the major issues of Martian evolution, such as the nature of climate transition and volcanic history.

Sample-return missions from other planetary bodies including Mars and the Moon and comprehensive analyses of the returned samples thus provide far more accurate and precise data on age. However, both technical difficulties and high cost severely limit the opportunities of sample-return missions. Thus, in situ dating missions to planets without sample return are very important. In addition to the lower cost, in situ dating is advantageous because of the ability of iterative and multiple measurements while traversing the planetary surfaces.

Many scientists have been active in the development of in situ dating methods for future planetary missions [12–18]. Many of these efforts are focused on potassium–argon (K–Ar) dating because measurements of these elements are relatively straightforward compared with other methods; K is relatively abundant in rocks (100 ppm-10 wt.%) and Ar is easily extracted and measured because it is a noble gas. K–Ar dating uses the decay of ^{40}K to ^{40}Ar with a half-life of 1.25 billion years [19]. The amount of ^{40}K is calculated from the total amount of K assuming 1.167×10^{-4} as the present ^{40}K/K ratio, and ^{40}Ar is measured by mass spectrometry.

The Curiosity rover measured a whole-rock K–Ar age of the mudstone using an alpha particle X-ray spectrometer (APXS) and a quadrupole mass spectrometer (QMS). The whole rock measurement was conducted because the mudstone was powdered by the rover's drill. The whole rock analyses require that the contribution of trapped ^{40}Ar is negligible compared to that of in situ radiogenic ^{40}Ar, or at least, the contribution of trapped ^{40}Ar must be removed from the amount of total ^{40}Ar based on the isotope ratio measurements. Martian rocks, however, may not satisfy this requirement; the noble-gas analyses of shergottites have revealed significant excess ^{40}Ar of unknown isotopic ratio derived from the Martian mantle [20]. In addition, old sedimentary rocks could contain atmospheric ^{40}Ar because ancient Mars, such as Noachian, may have had an atmosphere as thick as 1 bar [21]. When the whole rock measurement is carried out, these initially trapped ^{40}Ar would cause a large error in age particularly for low-K rocks and young rocks. To establish the Martian crater chronology for a wide range of ages, initially trapped ^{40}Ar needs to be distinguished from radiogenic ^{40}Ar. An isochron dating method, in contrast, requires no assumptions about the isotopic ratio or the amount of the initially trapped ^{40}Ar; the contribution of trapped ^{40}Ar can be evaluated by isochron plots. Furthermore, if a sample was partially degassed in terms of ^{40}Ar, the isochron data would scatter and do not yield a single isochron age because different minerals have different closure temperatures. Thus, isochron-dating method is very advantageous for reliable in situ K–Ar dating on planetary explorations.

The precision of isochron measurements depends on the range of measured K concentrations. Bogard estimated that when the range of K concentration is a factor of two or greater, the uncertainty in K–Ar isochron ages would be comparable to the measurement errors in K and Ar of a single measurement [20]. Basaltic rocks, for example, would have such a variation in K concentration because they have different phases with discrete K contents, such as feldspar, pyroxene, and small K-rich glasses in mesostasis. Although measuring these pure minerals is preferable for isochron dating, their grain sizes are sometimes smaller than the typical laser spot size. In such cases, nevertheless, we can still measure isochron ages by separately analyzing K-rich and K-poor portions of a rock. In fact, a series of ChemCam analyses revealed that the Jake_M rock is heterogeneous at the laser beam scale [22], suggesting the feasibility of isochron measurements with the laser ablation technique. Furthermore, chemical zoning within large feldspar grains, if any, would be used as well.

The authors have been developing an in situ K–Ar dating instrument that uses laser-induced breakdown spectroscopy (LIBS) and quadrupole mass spectrometry (QMS) to realize isochron-based dating in planetary missions [23–25]. LIBS is an elemental analysis method with which the atomic/ionic emissions from plasma generated by high-intensity pulsed laser are observed [e.g., 26]. QMS is used to obtain the abundance of isotopic species by measuring the ion current for different mass-charge ratios. An advantage of the proposed system is the ability to construct an isochron for each rock sample by spot-by-spot analyses. Focused laser pulses (spot size ca. 500 μm) are used to measure K-to-Ar ratios within a rock sample for several minerals to obtain an isochron. Isochron measurements significantly enhance the reliability of age determination because the contribution of excess ^{40}Ar and the partial loss of ^{40}Ar can be evaluated. Another advantage of the LIBS-QMS approach is its high feasibility; an experimental system can be constructed using commercially available instruments that have analytical performance comparable to those flown in previous planetary missions. For example, both LIBS and QMS have already been operated on Mars in the Curiosity mission [27–30].

Unlike the method used in Curiosity, our LIBS measurements must be conducted in a vacuum chamber for simultaneous Ar measurements. The pressure is maintained low (ca. 10^{-6} Pa) for the detection of small amounts of Ar extracted from samples by laser irradiation. Accurate and precise measurement of the K abundance under high vacuum conditions (i.e., 10^{-6} Pa) is critical for in situ K–Ar dating. One of the problems associated with such low-pressure measurements is that the emission from laser plasma becomes weak when the ambient pressure is lower than 10^{-2} Pa [31]. Thus, one technical challenge is to achieve accurate and precise measurement of the K concentration with suppressed K emissions. Accurate measurements of K under atmospheric pressure (i.e., 1 bar) have been previously demonstrated. In an attempt to develop an in situ K–Ar geochronology method using LIBS, Stipe et al. [32] showed that K can be measured with a precision of 0.5–5.5% over 3.63–0.025 wt.% K_2O using a UV pulse laser (wavelength = 266 nm), an Echelle spectrometer with a resolving power of $\lambda/\Delta\lambda = 1700$, and an intensified charge-coupled device (ICCD) camera with an optimized gate delay of 1.5 μs. Five standard basaltic glasses were measured using the non-weighted and weighted calibration methods, which gave limits of quantitation (LOQ) of 920 and 66 ppm, respectively. They also measured four equivalent basaltic rocks and reported LOQs of 2650 and 328 ppm using the non-weighted and weighted calibration method, respectively. However, the considerable pressure dependence of the LIBS signal intensities must lead to much poorer analytical performance (i.e., higher detection limits with lower accuracy and precision) when LIBS measurements are conducted under high vacuum conditions. The capability of LIBS under vacuum was studied by Lasue et al. [33]. They briefly reported the limit of detection (LOD) and limit of quantitation (LOQ) for K from an evaluation of LIBS performance for future lunar explorations. The concentrations of major and minor elements in a simulated lunar regolith were measured using a multivariate regression analysis known as the partial least squares regression (PLSR). An LOD of 1577 ppm was determined by comparing the K line intensity and the noise level of the spectrometer. An LOQ of 1705 ppm