APPLYING IN SITU K-AR AND RB-SR GEOCHRONOLOGY TO ORDINARY CHONDrites. J. Olsson1, F. Cattani2, K. Almas3, B. A. Cohen1, T. Zack1. 1University of Gothenburg, Sweden (gusolsjie@student.gu.se); 2NASA Goddard Space Flight Center, Greenbelt MD, USA; 3University of Maryland, MD, USA.

Introduction: In situ dating techniques by laser ablation are developed to obtain ages of rocks with minimum sample preparation. They are promising tools for analyzing samples directly on a planetary surface, like Mars or the Moon, with a robotic lander or rover. Applying radiometric in situ geochronology on other planets or moons offers the possibility of studying planetary processes and solar system evolution with higher precision compared to crater counting of terrains and without relying on returned samples. Among the various approaches, this work overviews two methods: Potassium (K) - Argon (Ar) and Rubidium (Rb) - Strontium (Sr). Both lend themselves to in situ dating and could be suitable for hybrid dating on a rover or lander to interpret absolute ages and provide geological context. Two chondritic meteorites, Pultusk and Bjurböle, in addition to one Martian analog sample, AMP 3.8, have been used to investigate in situ methodology on extraterrestrial material.

Techniques: The K-Ar Laser Experiment (KArLE) is currently being developed at NASA Goddard Space Flight Center using flight-heritage instruments such as laser-induced breakdown spectroscopy (LIBS) and quadrupole mass spectrometry (QMS). Rock samples are ablated under high vacuum with a 300 µm UV laser beam. The LIBS technique measures K and other elements within 450-800 nm wavelength from emitted light in the plasma plume when they transition from a state of high energy to lower energy. Argon is measured from the liberated particles sent to the QMS, and the two measurements are correlated by optical profilometry that measures the volume of ablation pits [1].

At University of Gothenburg in situ Rb-Sr has been developed for LA-ICP-MS/MS. Interferences and isobaric overlap of 87Rb on 87Sr have been completely removed by a combination of reaction cell technology and tandem mass spectrometry (MS/MS). Nitrous oxide (N2O) as a reaction gas shows >85% reactivity with Sr to form SrO, while no reaction with Rb occurs. This allows for chemical separation of the two isotopes. Interfering species on the same m/z ratio as the mass shifted analyte ions are filtered out in the first MS, permitting the reaction product to be measured alone in the second MS [2, 3].

For this study, KArLE analyses focused on laser-sample interaction and retrieving major element spectra from chondrites, while LA-ICP-MS/MS was used for meteorite dating.

Samples: Pultusk and Bjurböle are ordinary chondrites classified as H5 and L/LL4 respectively and have been dated using conventional dating techniques by other investigators. Rb-Sr dating of Bjurböle was conducted by Shields et al. [4] who determined the age of chondrules as 4450 Ma. The matrix fell far off the isochron and interpreted to be contaminated by terrestrial weathering. Ar-Ar plateau ages of the same sample provided two chondrule ages; 4479.8 ± 7.7 Ma, and the other a disturbed age spectrum bracketed between 3500-4400 Ma [5]. U-Pb dating provided a whole-rock age of Pultusk at 4550 Ma [6]. An amphibolite sample, AMP 3.8 from Nuvvuagittuq, was used for volume and mass measurements of KArLE ablation pits. AMP 3.8 consists of coarse-grained plagioclase and amphibole and has well-defined K-Ar ages of 2052 ± 29 Ma (plagioclase) and 2649 ± 38 (amphibole) [7].

Results: Ablation pits on AMP 3.8 exhibited distinctively different morphology as a result of density differences of the ablated minerals [7]; ablation of plagioclase generated deep, conical-shaped pits (Figure 1a), while amphibole pits were shallower and bowl-shaped (Figure 1b). Ablated masses were derived from mineral densities and pit volumes. On average, 30 seconds of ablation with a repetition rate of 20 laser shots/s excavated 29.3 µg from plagioclase and 18.0 µg from amphibole.

Figure 1. Different shapes of ablation pits in AMP 3.8. a) Plagioclase pit, b) amphibole pit.

Determining ablation rate for KArLE analyses. Quantities of 40K and 40Ar in the chondrite samples were calculated from published literature values of K2O to further estimate the number of atoms per 10 µg. Between 3.3x10^10 to 2.9x10^11 Ar atoms were estimated in 10 µg, with the higher concentrations found in chondrules. To retrieve 10 µg from the chondrites an ablation time of 15 s and a repetition rate of 20 laser shots/s was estimated to generate the desired mass, based on ablations of AMP 3.8. Accordingly, it demonstrated that 300 laser shots in total would be sufficient for both QMS and LIBS analyses. A low
Ablation rate is preferred to avoid mixed signals and matrix effects [7].

**LIBS spectra.**

Figure 2 and 3 show major element composition of chondrules from representative spectra. The spectra confirm an ultramafic composition dominated by pyroxene and olivine in all obtained spectra. No emission lines of K were detected at 769.89 nm.

**In Situ Rb-Sr isochrons.** The results of the first in situ Rb-Sr measurements on chondrites are presented in figure 3. Only 11 ablation spots were initially shot on each sample with a 40 μm laser spot size. Plagioclase was targeted in both matrix and chondrules. Ages were calculated by the revised $^{87}\text{Rb}$ decay constant of 1.3972 x 10$^{-11}$ a$^{-1}$ [8]. Using the canonical initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.699 [9] a best-fit isochron yield ages of 3974±767 Ma for Bjurböle and 3533±710 Ma for Pultusk.

**Discussion & Conclusions:** An adequate number of laser shots for chondrites was established to 300. It is proposed to be used as a reference to retrieve sufficient signal for in situ K-Ar analysis with KArLE. LIBS spectra of chondrules displayed abundant Na and Mg but no K peaks could be observed. Ar-Ar dating of Bjurböle chondrules [5] indicate that there is sufficient K for dating, but several explanations for the lack of K in the LIBS spectra are possible: there might not have been enough K at the ablated spots; chondrules were not easy to identify in the camera which might have led to mistargeting; the fine grain sizes of chondrites make ablations of a single mineral difficult with a 300 μm spot size. Ablating one phase with K and another without will result in an average and an underestimation of K concentrations [7]. The lower limit of detecting K is currently at 0.3% but technical progress is being made on KArLE to observe even lower concentrations. A chemical map combined with BSE images of the samples made before ablations would aid in finding suitable ablation spots and guide the laser to the right target.

All data points for the in situ Rb-Sr tests statistically form one age population (MSWD of 0.48 and 0.96 for Bjurböle and Pultusk respectively, within errors of reported ages [4, 5]. Given the minute amount of analyzed material (a few ng per ablation spot), age uncertainties can be significantly reduced by upscaling the analyzed sample material. It is noted that highest $^{87}\text{Rb}/^{86}\text{Sr}$ ratios in both chondrites were found in plagioclase, justifying our approach of using as small spot sizes as possible in order to maximize the spread in $^{87}\text{Rb}/^{86}\text{Sr}$ ratios in each sample.

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