

MINERALOGY AND U/Pb PHOSPHATE DATING OF THE LOS ANGELES MARTIAN DIABASE. B. J. Wilson¹, C. R. M. McFarlane¹, and J. G. Spray², ¹Earth Sciences, ²Planetary and Space Science Centre, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3, Canada (bennett.wilson@unb.ca)

Introduction: The Los Angeles (LA) Martian meteorite was discovered in 1999 by Robert Verish in a pre-existing rock collection. LA is a slightly to negligibly weathered medium-grained shergottite consisting of two stones: LA001 (453 g) and LA002 (245 g) [1]. They primarily comprise pyroxene and maskelynitized plagioclase (>80%), with phosphates contributing ~2.5% in both stones [2]. These phosphates contain uranium, allowing in situ Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) to be performed for the first time on LA. Three spectroscopy techniques were deployed to characterize the phosphates: A Field Emission Scanning Electron Microscope (FESEM) equipped with an Energy Dispersive Spectrometer (EDS), a Raman Spectrometer, and an Electron Microprobe equipped with a Wavelength Dispersive Spectrometer (WDS). LA-ICP-MS was deployed to determine the phosphate age, and to appraise the ability of the LA phosphates to resist shock resetting due to impact, and ejection at ~3 Ma [3].

Mineralogy: Modal analysis indicates that Los Angeles is composed chiefly of maskelynitized plagioclase and pyroxene, totalling ~89 wt% for stone 1, and ~81 wt% for stone 2. Los Angeles has significantly more maskelynite (~45%) than many other Martian shergottites, such as Shergotty (~23%) and Zagami (~22%) [1]. Modal abundances for other minor phases exhibited are silica (~3-4%), ulvospinel (~3%), fayalite (~3%) K-rich feldspathic glass (~2%), ferromerrillite (~1.5%), apatite (~1%), pyrrhotite (~0.6%), and ilmenite (~0.3%) [2]. About 5-10% of LA displays a symplectitic texture of ~50-200 μm -sized vermicular intergrowths of fayalite, ferroan clinopyroxene (hedenbergite), and silica in a 2:2:1 ratio, termed “pyroxferroite breakdown material” (PBM) [1]. The conversion of pyroxferroite to PBM indicates that LA cooled from igneous temperatures (~1100-900°C) in a period exceeding 3 days, otherwise metastable pyroxferroite would be expected [1]. Stone 1 and stone 2 exhibit minor differences. Stone 2 contains more late-stage melt products (fayalite, silica, and K-rich feldspathic glass) and is mainly subophitic [1]. Stone 1 texturally more closely resembles a plagioclase-pyroxene orthocumulate [1]. It was inferred that 95-97% of LA had crystallized before phosphates crystallization, which is borne out by textural relations in our samples [4]. The phosphates occur as relatively large crystals (>>100 μm), which are amenable to laser ablation.

They are dominated by ferromerrillite with minor apatite. In the crystallization sequence, merrillite typically precedes apatite [2], but in some instances, merrillite and apatite crystallized simultaneously.

Results: A Micro-XRF was used to map phosphates within 5 available thick sections (LA001–T1 through LA001–T5) pertaining to stone 1. Data collection focused on the most phosphate-rich thick sections: LA001–T2 and LA001–T5 (Figure 1), except for the Raman. The Raman was deployed on a separate Los Angeles polished thin section (loaned from the Smithsonian Institute: sample 7059-1) due to limited optical resolution of the Raman microscope in reflected light when using the thick sections.

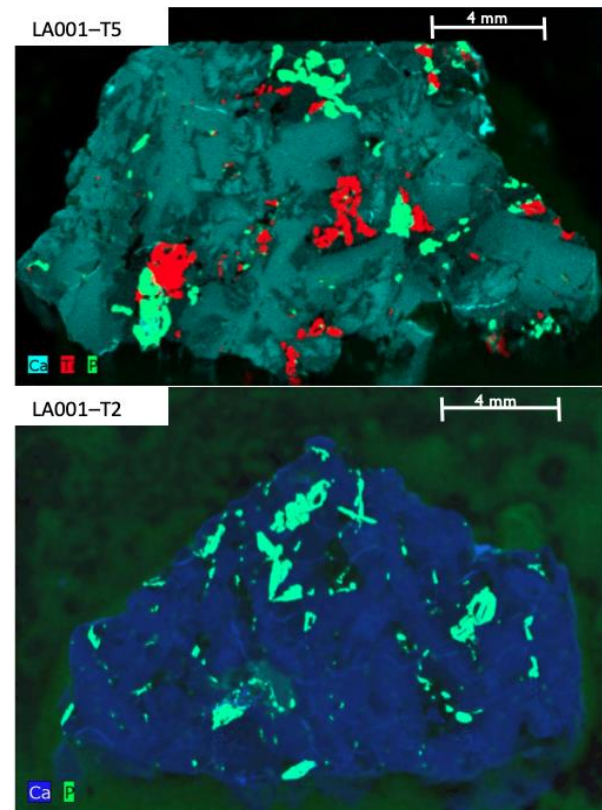


Figure 1: Micro-XRF images for thick sections LA001–T5 (top) and LA001–T2 (bottom). Phosphates are indicated by the green/turquoise colour for both samples. Red areas are Ti-rich.

FESEM and EDS: 149 analyses were obtained from 37 phosphate crystals via EDS. Based on totals from

99 to 101 wt%, 91 analyses were approved; 78 of which were ferromerrillite ($\text{Ca}_9\text{NaFe}(\text{PO}_4)_7$); 13 were chlor- or fluorapatites. Most existing literature cites merrillite $\text{Ca}_9\text{NaMg}(\text{PO}_4)_7$ or whitlockite $\text{Ca}_9(\text{MgFe})(\text{PO}_4)_6\text{PO}_3\text{OH}$ as the major phosphate phases in Martian meteorites [e.g., 1, 2]. However, due to enriched Na_2O (~1 wt%) and FeO (~5 wt%), combined with depleted MgO (0.8 wt%), ferromerrillite is confirmed here. Ferromerrillite is a trigonal, R3c space group mineral, and is the dominant phosphate phase in LA [5].

Raman Spectroscopy: Due to the inability of EDS and WDS techniques to detect hydrogen, Raman spectrometry was deployed to further distinguish ferromerrillite from whitlockite. Using 50 acquisitions on an assumed ferromerrillite crystal, Figure 2 was produced, ruling out whitlockite. The apatites were also investigated for hydroxylapatite via Raman, but the hydrogen peak was not present in the signature. This shows that both phosphate phases are anhydrous.

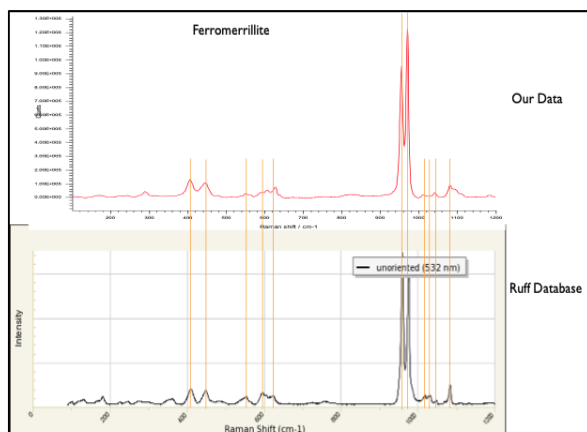


Figure 2: Raman spectrum for ferromerrillite (top) compared to merrillite from the Ruff Database. Acquired data comprise 50 acquisitions with baseline subtracted. No hydrogen peak is apparent.

Microprobe and WDS: As ferromerrillite has not been extensively studied, the microprobe was deployed to obtain higher precision analyses of the phosphates. A total of 110 analyses were obtained; 67 ferromerrillite and 24 apatite analyses, with 24 points rejected for existing outside the 98-102% accepted totals range. Ba, Sr, and Al were found to be trace constituents in both phases of phosphates. In comparison to the EDS results, the largest change in the WDS data corresponds to the average decrease in P_2O_5 and average increase in CaO and MnO . In LA001-T5, 16 phosphate points (9 ferromerrillite and 7 apatite) were tested for LREEs, U and S. Trace amounts of S existed in all 7 apatites; the rest were below detection limit for both phosphates.

LA-ICP-MS: Utilizing the U/Pb system, LA-ICP-MS analysis was performed to obtain an age for the phosphates, and to test their susceptibility to U-Pb resetting during ejection-related shock. Large (~80 μm) craters were utilized by the LA-ICP-MS and were placed to avoid surface fractures as best as possible. The collected points were plotted on an inverse Concordia plot with a data-point error ellipse of 2σ . Utilizing all 117 data points collected, an age of 171 ± 31 Ma was produced. Additionally, to test the shock resistance of the phosphate phases, phosphates within, or neighboring shock melt pockets were separately targeted to evaluate their age. From this, an age of 147 ± 42 Ma was produced, providing evidence that they are robust, and shock resetting has not occurred (i.e., due to ejection at ~3 Ma). After removing outliers, and including phosphate points within the shock melt pockets, a refined age of 170 ± 16 is produced (Figure 2), showing good agreement with previously reported Rb-Sr and Sm-Nd ages [3]. This confirms an igneous crystallization age of ~170 Ma for Los Angeles via in situ LA-ICP-MS.

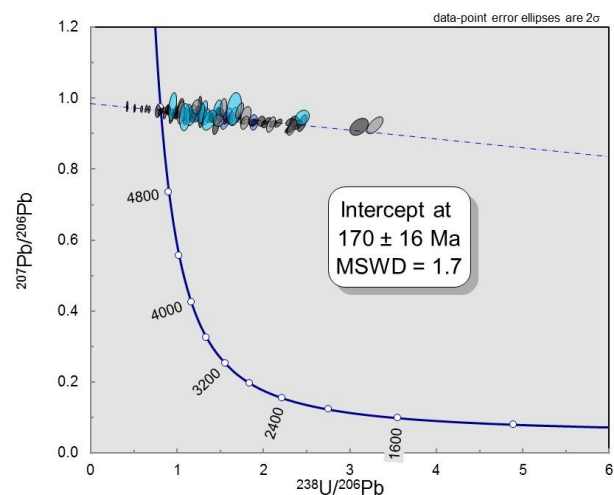


Figure 3: After excluding outliers, an inverse Concordia plot was utilized to produce a refined age of 170 ± 16 Ma.

References: [1] Rubin A. E. et al. (2000) *Geology*, 28, 1011-1014. [2] Warren P. H. et al. (2004) *Meteoritics. Planet. Sci.*, 39, 137-156. [3] Nyquist L. et al. (2001) *Space Science Reviews*, 96, 105-164. [4] Xirouchakis D. M. et al. (2002) *Geochim. Cosmochim. Acta*, 66, 1867-1880. [5] Britvik et al. (2016) *Europ. J. Mineral.* 28, 125-136.