

INTEGRATED HALOGEN, MAJOR, TRACE, AND ISOTOPIC MICROANALYSIS OF PLANETARY APATITES BY FEMTOSECOND-LA-LIBS-ICP-MS

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Introduction: Apatite is widely used to evaluate the origin, abundance, and evolution of volatile species in planetary bodies [1], provide thermochronological constraints on geological processes and meteorite impact events [2, 3] and track magmatic evolution through trace element and isotopic studies [4]. This is due to the incorporation of volatile species in apatite group minerals, hexagonal $\text{Ca}_5[\text{PO}_4]_3[\text{F}, \text{Cl}, \text{OH}]$, and the fact that it is a principal carrier of a wide-range of trace elements such as rare earth elements, uranium, and thorium in many planetary crustal rocks.

Despite this wide-ranging importance, the *in-situ* measurement of many of these chemical records in apatite remains challenging. Specific analytical issues include the migration of volatiles (including halogens), and related crystallographic orientation effects, during electron beam interaction, and the requirement to integrate data from several approaches with different analytical volumes (e.g. major elements by EPMA, halogens, and isotope ratios by SIMS, NanoSIMS, LA-ICP-MS, etc.).

Here we report on the development of a new approach to the concurrent acquisition of halogens, major & trace elements, and U-Th-Pb isotope ratios in apatite group minerals at the 20 to 30 μm scale, using tandem femtosecond laser ablation (LA) and laser-induced breakdown spectroscopy (LIBS) coupled with ICP-MS.

Analytical approach: Analyses are being performed at the University of Portsmouth, using an Applied Spectra J200 Tandem LA-LIBS system that is equipped with a 343 nm femtosecond laser source, novel two-volume ablation and LIBS cell design, and two intensified CCD spectrometers.

Terrestrial apatite reference materials with a wide-range of chlorine and fluorine compositions are being used to optimize laser and spectrometer detection conditions for the measurement of the major elements Ca and P, along with F by LIBS, and concurrent analysis of Cl, a wide-range of trace elements, and U-Th-Pb isotope ratios using an Agilent 8900 ICP-MS/MS system (building on the LA-ICP-MS protocols of [5, 6]). Analyses are being performed with the laser-focused to either 20 or 30 μm on the sample, fluences between 5 and 10 Jcm^{-2} , and laser repetition rate of 10 Hz (200 shots total).

Progress and opportunities: Although previous LIBS studies have determined F contents in phosphates using the 685.6 nm atomic emission line [7], we find only weak emission of halogen atomic lines using our analytical setup. This is not particularly unexpected, as these emissions require high excitation energies (and hence laser conditions) that are not well suited to LA-ICP-MS analyses. Alternatively, alkali earth-halogen molecular emission can be used to quantify F contents by LIBS [8]. Here, we focus on CaF molecular emission at ~ 532 nm.

The dual ICCD spectrometer setup of the LIBS system allows for optimization of P and Ca atomic emission lines at a relatively short gate delay (~ 0.1 μs ; length of time between the laser pulse and the spectrometer detection), and separation of CaF molecular emission from potentially interfering atomic and ionic emission lines using longer gate delay (> 0.3 μs). As a result, background-corrected count rates for CaF are in the Mcps range from terrestrial fluorapatite, and we report on the accuracy and detection limits of LIBS calibration of F, along with Ca and P for use as independently determined internal standard elements for LA-ICP-MS trace element measurements. Initial results from terrestrial reference materials show the tremendous potential of the technique to enable concurrent halogen, major, trace, and U-Th-Pb geochronology from terrestrial and planetary apatite.

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