CALIBRATION OF THE FLUORINE, CHLORINE AND HYDROGEN CONTENT OF APATITES WITH THE CHEMCAM LIBS INSTRUMENT

P.-Y. Meslin[1], L. Cicutto[1,2], O. Forni[1], C. Drouet[2], W. Rapin[1], M. Nachon[3], A. Cousin[1], J. G. Blank[4,5], F. M. McCubbin[6], O. Gasnault[1], H. Newsom[7], N. Mangold[3], S. Schröder[8], V. Sautter[9], Maurice[1], R.C. Wiens[10]. [1]IRAP, UPS/CNRS/OMP, Toulouse, France; [2]CIRIMAT, Toulouse; [3]LPGN, Nantes, France; [4]NASA Ames, Moffett Field, CA; [5]Blue Marble Space Institute of Science, Seattle, WA; [6]NASA JSC, Houston, TX; [7]U. New Mexico, Albuquerque, NM; [8]DLR, Berlin; [9]MNHN, Paris; [10]LANL, Los Alamos, NM.
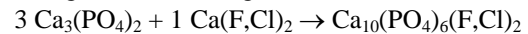
Introduction: Determining the composition of apatites is important to understand the behavior of volatiles during planetary differentiation [1]. Apatite is an ubiquitous magmatic mineral in the SNC meteorites. It is a significant reservoir of halogens in these meteorites and has been used to estimate the halogen budget of Mars [2]. Apatites have been identified in sandstones and pebbles at Gale crater by ChemCam, a Laser-Induced Breakdown Spectroscometer (LIBS) instrument onboard the Curiosity rover [3]. Their presence was inferred from correlations between calcium, fluorine (using the CaF molecular band centered near 603 nm, whose detection limit is much lower that atomic or ionic lines [3, 4]) and, in some cases, phosphorus (whose detection limit is much larger). An initial quantification of fluorine, based on fluorite (CaF$_2$)/basalt mixtures [3, 5] and obtained at the LANL laboratory, indicated that the excess of F/Ca (compared to the stoichiometry of pure fluorapatites) found on Mars in some cases could be explained by the presence of fluorite. Chlorine was not detected in these targets [3], at least above a detection limit of 0.6 wt% estimated from [4]. Fluorapatite was later also detected by X-ray diffraction (with CheMin) at a level of ~1wt% in the Windjana drill sample (Kimberley area) [6], and several points analyzed by ChemCam in this area also revealed a correlation between Ca and F [5].

The in situ detection of F-rich, Cl-poor apatites contrasts with the Cl-rich, F-poor compositions of apatites found in basaltic shergottites and in gabbroic clasts from the martian meteorite NWA 7034, which were also found to be more Cl-rich than apatites from basalts on Earth, the Moon, or Vesta [1]. The in situ observations could call into question one of the few possible explanations brought forward to explain the SNC results, namely that Mars may be highly depleted in fluorine [1].

The purpose of the present study is to refine the calibration of the F, Cl, OH and P signals measured by the ChemCam LIBS instrument, initiated in [3] for F, in [7,8] for Cl in soils, in [9] for P, and estimate their limit of detection. For this purpose, different types of apatites and mixtures of basalt powder and apatites were analyzed using ChemCam Engineering Qualification Model (EQM) at IRAP, Toulouse. The present abstract presents the initial results from the laboratory analyses. Differences between the response function of the EQM and the Flight Model of ChemCam are still to be refined to apply these new results to the Martian dataset.

Materials and Methods: Phospho-calcium apatites are calcium phosphates with general formula Ca$_{10}$(PO$_4$)$_6$X$_2$ with X being a monovalent anion (also called the X-site), typically OH$^-$ (hydroxyapatite), F$^-$ (fluorapatite) and Cl$^-$ (chlorapatite), or a combination of those. Pellets were prepared from the mixing of finely grained β-Tri Calcium Phosphate (β-TCP) (obtained from amorphous TCP calcinated at 900°C for 24h) and fluorite (CaF$_2$) or (CaCl$_2$) powders, weighted according to the following formula:

$$3 \text{ Ca}_3(\text{PO}_4)_2 + 1 \text{ Ca(F,Cl)}_2 \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{F,Cl})_2$$

These pellets were calcinated at >900°C for 1 hour. Synthetic chlorapatite (ClA), fluor-hydroxyapatite (FHA – 50%-50%) and hydroxyapatite (HA) were also analyzed. Initial analyses of these samples using the ChemCam EQM showed no significant difference between the synthetic apatites and the pressed pellets in terms of LIBS spectral signatures (for a similar stoichiometry of F and Cl). The method was thus used to prepare a large set of samples (184 pellets, 2 pellets for each sample), covering a large range of compositions. This technique also allowed to prepare samples with compositions outside the natural range of apatites, to cover for example the possible presence of both fluorite and fluorapatite at the scale of ChemCam LIBS analyses (300-500 μm). Mixtures with a powder of basalt from Skajldbreidur, Iceland, were also prepared, as ChemCam analyses on Mars are rarely probing pure phases at the above scale. These mixtures also allowed us to vary the hydrogen and phosphorus abundance and calibrate these elements. The following series were prepared (with n giving the mole fraction):

- (1) 3 β-TCP + n CaF$_2$ (n = 0.1 to 5), n =1 being equivalent to fluorapatite (FA) (1)
- (2) 3 β-TCP + n CaCl$_2$ (n = 0.1 to 3)
- (3) 3 β-TCP + n SrCl$_2$ (n = 1.5 to 5), to increase the range of Cl concentrations (pellets with large fractions of CaCl$_2$ powder had a poor cohesion)
- (4) 3 β-TCP + n CaO (n = 1, 1.5)
- (5) 3 β-TCP+n CaCl$_2$+(1-n) CaF$_2$ (n=0.25,0.5,0.75)
- (6) n FA + (1-n) HA (n = 0 to 1)
- (7) ClA + basalt (from 0% to 100%)
- (8) FHA + basalt (from 0% to 100%) (in progress)
- (9) n_{mass} HA+(1-n_{mass}) basalt (n_{mass}=0.5, 0.6, 0.7, 1)

Natural apatites from Durango (pressed powder pellet) and from the Neoproterozoic Mud Tank carbonatite complex, Australia were also analyzed for comparison.

The ChemCam EQM, operated at -10°C, was used to acquire the LIBS spectra in conditions similar to Mars (i.e., the samples were placed in a vessel filled with 8 mbars of CO_2). 2 to 7 points on each pellet were analyzed, with 30 laser shots (i.e., 30 spectra) on each point, and were averaged together.

The lines processed in this study were the CaF molecular band centered at 603 nm [3,4] (Fig. 1) (integrated over [595-607 nm]), the P line at 255.4 nm (not shown), the P lines at 602.6, 604.5, 605.95 nm (in the absence of the CaF band, i.e., in the absence of F) (visible below the CaF band in Fig. 1), and the Cl line at 837.6 nm. The raw spectra are processed in the same way as data from Mars [10]. The emission line at 656.5 nm was used for hydrogen and processed according to the method described in [11].
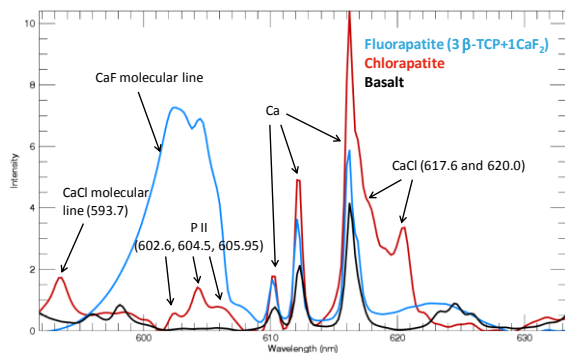

Figure 1 : Laboratory LIBS spectrum of fluorapatite, chlorapatite and basalt near the CaF band @ 603 nm.

Results: The calibration curve obtained for F using the CaF molecular band (Fig. 2) does not appear to depend on the type of samples used (series 1, 5, 6 above), indicating limited chemical matrix effects. The curve is non–linear, exhibiting a steep initial increase at low F abundances, consistent with a low detection threshold (detection threshold against false negatives at 95% confidence level < 0.5 wt%), followed by a progressive saturation. The initial offset, which makes a more precise estimate of the limit of detection difficult with the present dataset, results from the presence of a "triple peak feature" resulting from the underlying P peaks (Fig. 1). This feature should induce a difference between the F calibration curves derived using F-apatites or fluorite (CaF_2), which remains to be evaluated. In the presence of apatites free of F, and possibly other phosphates, however, these P peaks can be used to estimate the P content with a much smaller detection threshold (< 3.5 wt%) than the P line at 255.4 nm (~10 wt%). Quantification of Cl using the 837.6 nm line was found to be challenging, as the detection threshold was

found to be ~5 wt% Cl. This is somewhat lower than the 6.8 wt% Cl for pure chlorapatite, which should therefore be detectable. Additional lines of Cl, in particular the CaCl molecular line at 593.5 nm, will be analyzed in the future. Its detection threshold when mixed with basalt (series 7), however, was found to be ~2.5 wt%, which is significantly larger than the limit found by [4]. The natural apatites fall well within the 95% prediction limits for all these elements (e.g, fig.2).

The hydrogen signal is found to vary linearly with the OH content over the range investigated here (e.g., 0 to 3.4 wt% OH for series 8 and 9), and no significant matrix effect is observed between FHA, HA and their mixtures with basalt (Fig. 3). An offset is observed, possibly explained by the presence of residual water in the basalt (but the LOI was <0.2 wt%), or by the fitting method (difficulty to fit the H line properly in the presence of the C triplet near 658.0 nm from atmospheric CO_2, when H is low). This result makes the estimation of the OH content of martian apatites possible if they are mixed with anhydrous phases at the scale of the laser spot. If the surrounding matrix is hydrated (as often found in Gale rocks at the depth of analysis of ChemCam), the OH content may still be disentangled using mixing trends between the matrix and the apatite phase, and using F or Ca as a discriminator. This, however, should be further tested.
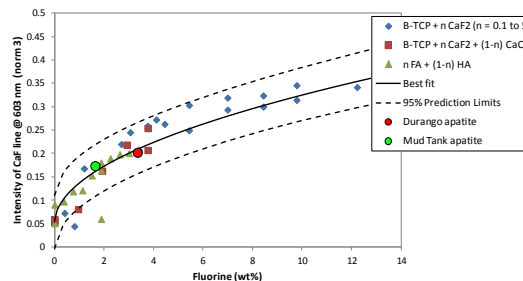

Figure 2 : Calibration curve obtained for F using the CaF band @ 603 nm. The Durango apatite (pressed powder pellet) and Mud Tank apatite (section) are superposed (the size of the circles gives their standard deviation along the Y-axis).
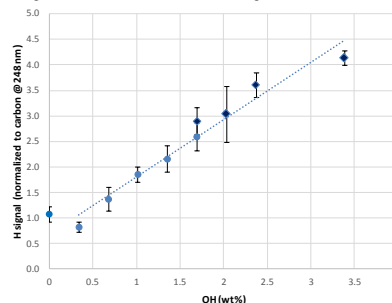

Figure 3 : Calibration curve for OH using series 8 (light blue circles) and 9 (blue diamonds).

References: [1] McCubbin et al. (2013) *44th LPSC*. [2] Patiño Douce et al. (2011) *Chem. Geol*. [3] Forni et al. (2015) *GRL*. [4] Gaft et al. (2014) *Spectrochim. Acta B*. [5] Forni et al. (2015) *46th LPSC*. [6] Treiman et al. (2015), *JGR Planets*. [7] Cousin et al. (2015), EMSLIBS, P-37. [8] Anderson et al., (2016) *47th LPSC,* this conf. [9] Blank et al. (2015), *46th LPSC*. [10] Wiens et al. (2013), *Spectrochim. Acta B*. [11] Rapin et al. (2016) *47th LPSC,* this conf.