



TEM/EELS DETECTION OF WATER IN EXTREMELY DRY PHOSPHATES FROM ORDINARY CHONDRITES

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INTRODUCTION

- Metasomatic fluids played an important role during metamorphism on the ordinary chondrites parent bodies and were instrumental in forming and late-stage equilibration of secondary phases, including phosphate minerals [1-2].
- This study focuses on phosphates since they are highly susceptible to various fluid-induced chemical and textural changes and retain volatiles more effectively than bulk rock materials during thermal or shock events (Fig. 1).
- Additionally, phosphates can help interpret the metamorphic environment of the S-type Itokawa asteroid since their occurrence has been documented in the samples returned by the Hayabusa spacecraft [3].
- Phosphate minerals preserve a record of their interactions with parent body fluids, and they are useful indicators of the metamorphic conditions on small Solar System bodies. However, previous studies showed that phosphates in equilibrated ordinary chondrites (EOCs) are extremely dry, contain water with an upper limit of <100 ppm H₂O [1].
- In this study, we examine phosphates with variable water amounts (0-5500 ppm [1, 4]) using electron energy-loss spectroscopy (EELS) in combination with transmission electron microscopy (TEM), which is a method suitable for the small phosphates (2-5 μm, [3]) identified in the Hayabusa samples.
- The goal of this study is to determine the detection limit of water.

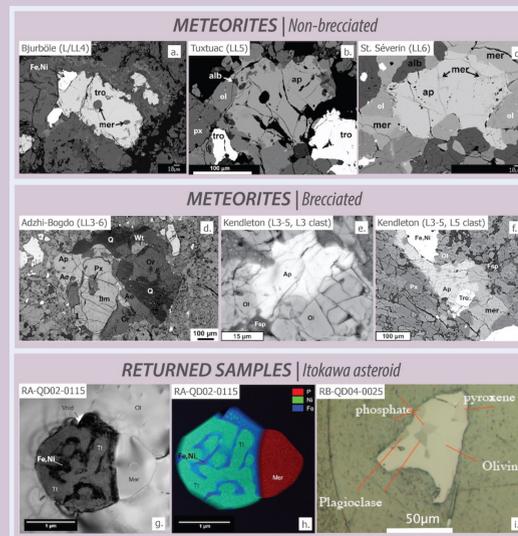


Figure 1. Backscattered electron (a-f), bright-field TEM (g), energy dispersive X-ray composite map (h), and optical microscope (i) images showing the texture, minerals associations, crystal shapes, and sizes of apatite and merrillite in non-brecciated (a – Bjurböle, L/LL4; b – Tuxtuac, LL5; c – St. Séverin, LL6, from Jones et al. 2014) and brecciated (d – Adzhi-Bogdo, L/LL4; e – Kendleton, L3-5, L5 clast; f – Kendleton, L3-5, L5 clast, from Bischoff et al. 2006; Lewis and Jones 2016) meteorites, and the returned samples from the Itokawa asteroid (g-h – RA-QD02-0115; i – RB-QD04-0025, Harries and Langenhorst 2018; Terada et al. 2018). Mineral abbreviations: Ap = apatite, Fe,Ni = metal, Fsp = feldspar, Mer = merrillite, Ol = olivine, Px = pyroxene, Tro = troilite, Tt = tetraenaite.

METHODS AND SAMPLES

As a test of our methods, we first analyzed focused ion beam (FIB) sections of terrestrial serpentine of known water content (12.1 wt.% H₂O) [5] and synthetic fayalite with an unknown water content [6]. Imaging and analyses were carried out at 300 kV using the Titan3 G2 60-300 scanning TEM (STEM). Furthermore, we analyzed FIB sections of phosphates from two terrestrial standards and a meteorite using the same technique. The terrestrial standards are apatite crystals from the synthetic chlorapatite, Atlas Mountains, Morocco, and from an unknown pegmatite locality in India [1, 4]. They contain 0, 300, and 5500 ppm of H₂O, respectively [4]. The meteorite apatite crystal extracted from the LL6 St. Séverin, previously described as extremely dry, contains only 28-38 ppm H₂O [1].

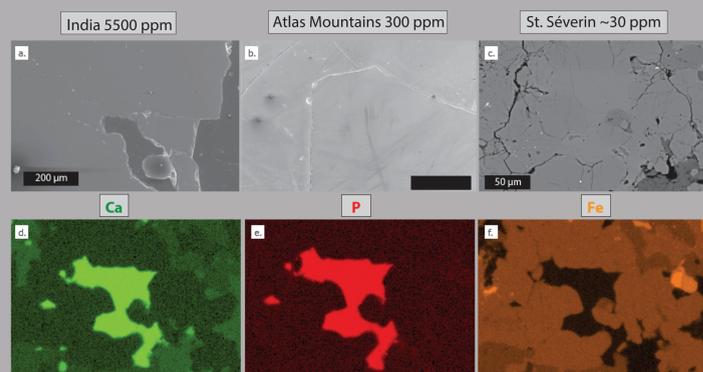
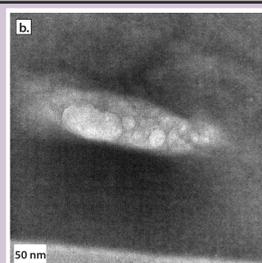


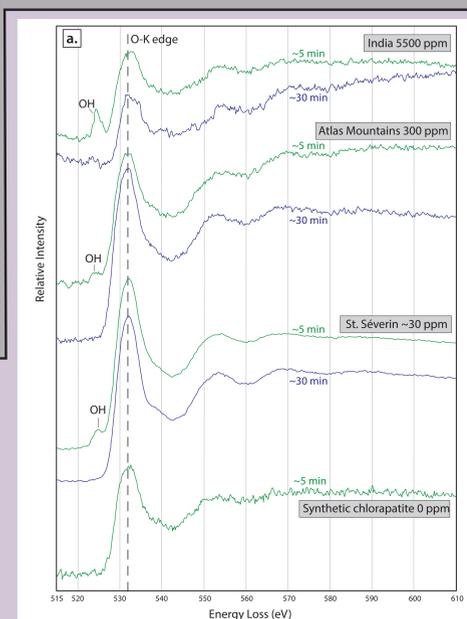
Figure 2. Secondary electron (a-b), backscattered electron (c), and energy-dispersive X-ray maps (d-f) of the apatite crystals analyzed in this study. FIB sections were prepared in two terrestrial standards (India and Atlas Mountains) and one meteorite (St. Séverin).

Figure 3. EELS spectra of phosphates from India, Atlas Mountains, St. S verin, and synthetic chlorapatite with different amounts of water. The spectra show the presence of OH- peak in the phosphates that contain water (~30-5500 ppm). The peak is at about 528 eV prior to the onset of the O-K edge at 532 eV. This OK pre-edge feature (~528 eV) gradually appears after ~5 minutes (green lines) and disappears after ~30 minutes of the exposure of the sample to the electron beam (blue lines). No OH- peak was identified in the water-free synthetic chlorapatite. b) Bright-field TEM image showing the occurrence of vesicles due to electron-beam induced radiolysis.



RESULTS AND DISCUSSION

- Valence electron energy-loss spectroscopy (VEELS, low-loss) and core-loss EELS contain specific features at 4.3, 8.5 eV, 13.5, and ~528 eV, corresponding to the presence of water in minerals [7-9].
- We searched for these features in:
 - phosphate
 - serpentine => to determine the detection limit of water
 - fayalite
- Since phosphates have a complex low-loss region dominated by the collective excitations (plasmons) and several Ca peaks [10], the low-loss spectra were only recorded in the silicates (serpentine and fayalite) in this study.
- In the serpentine mineral, we identified all low-loss and core-loss features corresponding to the ionization threshold energy and the energy gap of water and the hydrogen (H-K) core scattering edge [7]. No water characteristic features were detected in the synthetic fayalite.



- For phosphates, we collected a time-resolved series of O-K core-loss edges using a non-monochromated electron probe (10-15 nA screen current over an area of ~3 μm²). The spectra were recorded every ~5 minutes by cumulative acquisition.
- No OH- peak was identified in the water-free synthetic chlorapatite.
- We observed an O-K pre-edge feature (~528 eV), which gradually appears after ~5 minutes and disappears after ~30 minutes of exposure (Fig. 3). This feature was detected in each phosphate analyzed, including the apatite crystal containing only 28-38 ppm OH/H₂O.
- In several regions analyzed, we observed the nucleation and growth of nanoscale vesicles (Fig. 3) due to electron-beam induced radiolysis.
- Previous studies have shown that radiolysis plays an important role in the interaction between high-energy electrons and water [11-13]. Water molecules exposed to high-energy electrons become excited and ionized, and transient radiolytic breakdown products, including OH, are formed with continuing irradiation [13].
- Our study demonstrates that the electron-beam irradiation of water-bearing minerals can locally concentrate these breakdown products in the irradiated area, facilitating their detection before they are dissipated and released over long exposure times. However, reliance on the O-K pre-edge feature alone is not a definitive indicator of water because it may also be due to O₂ formation resulting from the radiolytic decomposition of the phosphates, although this feature was not observed in the olivine analyzed [14].

CONCLUSION

This study suggests that electron energy-loss spectroscopy is a useful tool for detecting tens of ppm-level water on a scale of a few microns (>28 ppm H₂O) by radiolysis and local concentration of the breakdown products.