Targeting the OH's within Bone's Bioapatite by Neutron and Optical Vibrational Spectroscopy

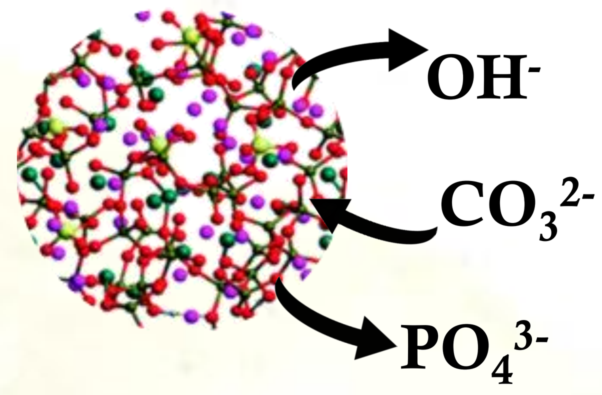
Mamede AP, Vassalo AR, Piga G, Cunha E, Parker S, Marques MPM, Batista de Carvalho LAE and Gonçalves D

Introduction

In vivo

Carbonates substitute phosphate and hydroxyl groups

Bioapatite



Post mortem alterations

- Increase in Crystallinity
- Organic material degradation
- Changes in the content of carbonates, phosphates and hydroxyls

Similar chemical alterations are seen as a consequence of fire/heat exposure

Aims The current study focuses on the vibrational signature of bioapatite´s hydroxyls, through FTIR-ATR and INS spectroscopies in order to distinguish whether archaeological skeletal remains were subjected to heat or not and to differentiate burned remains from fossils, which tend to present the same postmortem changes.

Experimental

- Experimental burnings were performed in an electric muffle for 120min. at 400 to 1000ºC (100ºC increment)
- INS analyses were performed on modern unburned and burned samples of human femur and humerus
- FTIR-ATR was measured for a large set of samples (modern human bones comprising 638 unburned and 623 experimentally burned samples (400-1000 ºC) with an emphasis on different OH/PO_4^{2-} ratios: **630/603 cm^{-1}, 3572/603 cm^{-1} and 3572/1035 cm^{-1}**
- 25 samples of archaeological cremated human remains (Bronze/Iron Ages)
- Fossil remains (Middle Triassic-Eocene) were also analysed

Results and Discussion

FTIR-ATR - modern bone

- Organic material lost up to 600ºC
- OH_{lib} (630 cm^{-1}) and $\nu(OH)$ (3572 cm^{-1}) seen in samples burned above 700ºC
- Experimentally burned human bone at 1000ºC revealed being the same compound as HAp from NIST, as corroborated by INS (Figure 1)

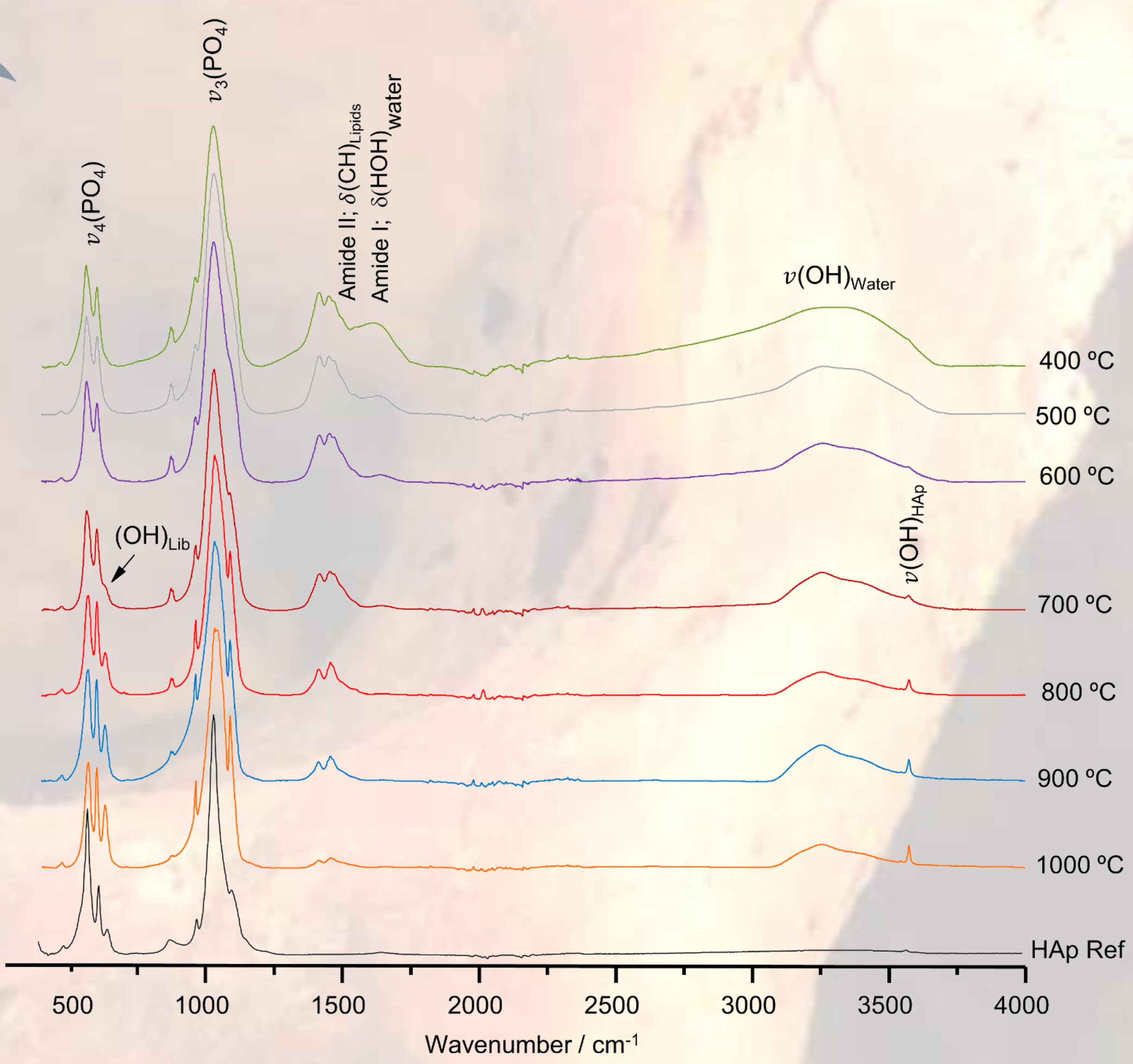


Figure 2. FTIR-ATR spectra of human femur experimentally burned from 400 to 1000 ºC and hydroxyapatite reference spectrum.

INS - modern bone

- OH_{lib} band (630 cm^{-1}) clearly seen in all samples
- $\nu(OH)$ (3572 cm^{-1}) being observed only above 600ºC along with 1st OH_{lib} overtone and the $(OH_{lib})+\nu(OH)$
- Experimentally burned human bone at 1000ºC revealed being the same compound as HAp from NIST

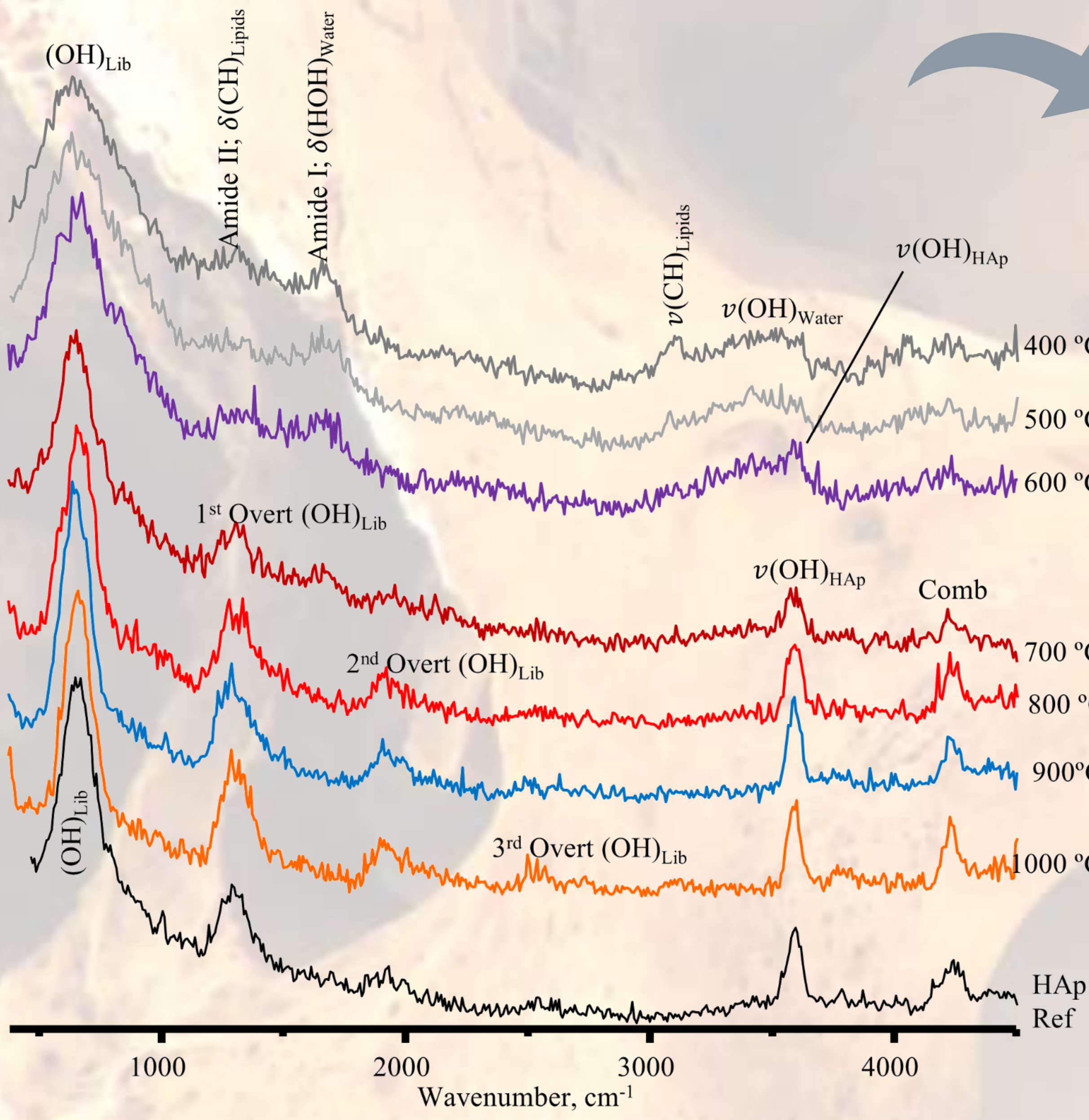


Figure 1. INS spectra recorded on MAPS (with 5240 cm^{-1} incident energy) for human femur, experimentally burned from 400 to 1000 ºC and hydroxyapatite reference spectrum.

FTIR-ATR - up: fossil; bottom: archaeological

- Absence of organic material in both fossil and burned archaeological remains
- Increased crystallinity in both fossil and burned archaeological remains ($\nu_4(PO_4^{3-})$ signal)
- **Presence of the OH vibrational modes in the archaeological burned bones**
- **Absence of the OH vibrational modes in the fossil bones**

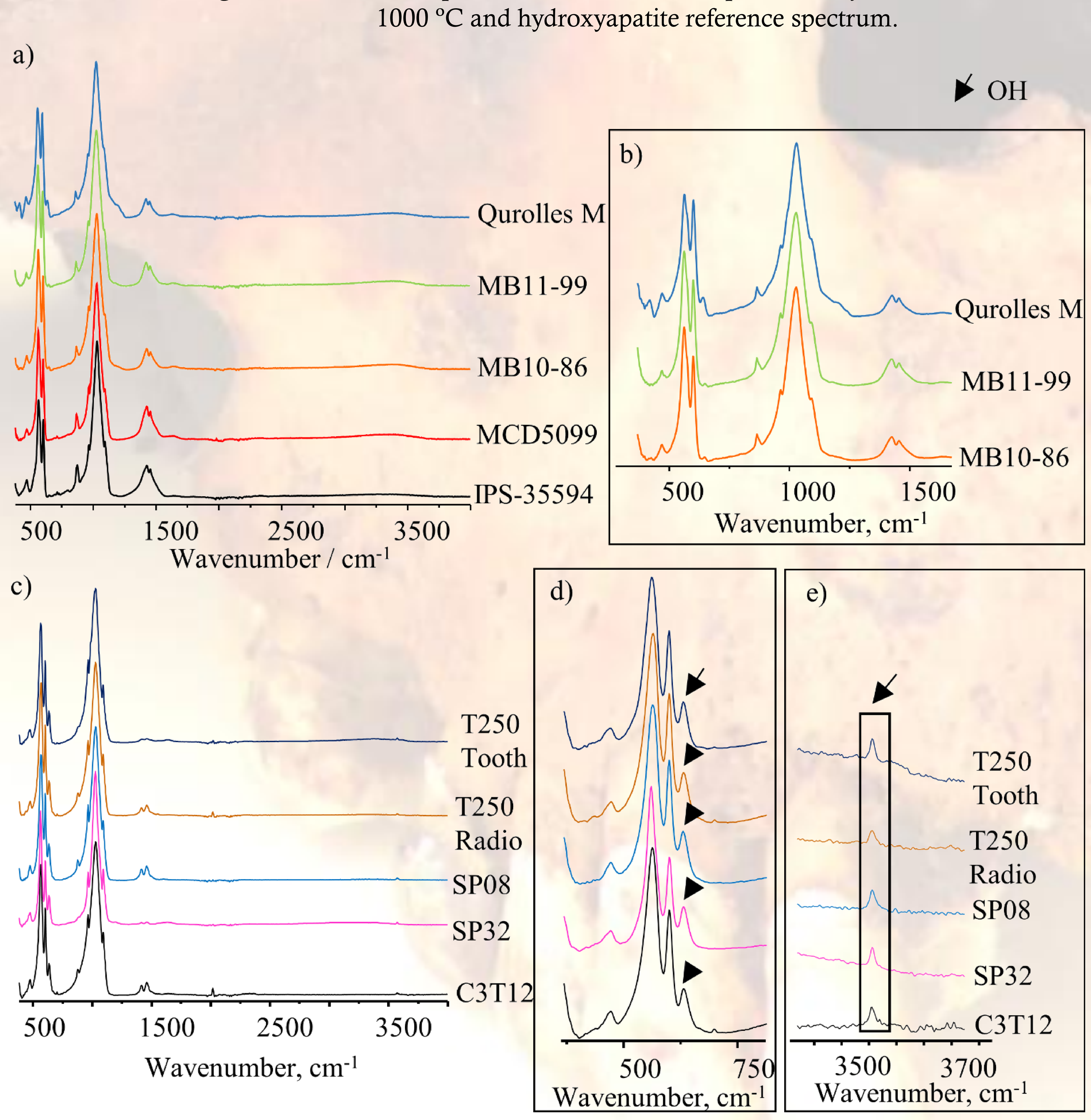


Figure 3. a) FTIR-ATR spectra of five **fossil** samples (Qurolles M, MB11-99, MB10-86, MCD5099 and IPS-35594) in the 380 - 4000 cm^{-1} range; b) in the 380 - 1750 cm^{-1} range; c) in the 380 - 4000 cm^{-1} range; d) FTIR-ATR spectra of five **archaeological** burned samples (T250-Tooth, T250-Radio, SP08, SP32 and C3T12) in the 380 - 800 cm^{-1} range, highlighting the OH libration band; e) in the 3000 - 3700 cm^{-1} range, highlighting the OH stretch signal.

Table 1. OH/P average and standard deviation values for the bone samples experimentally burned at 800 (n=83), 900 (n=97) and 1000 ºC (n=83).

Temperature (ºC)	630 cm^{-1}/603 cm^{-1} $OH_{lib}/\nu(PO_4)$	3572 cm^{-1}/603 cm^{-1} $\nu(OH)/\nu(PO_4)$	3572 cm^{-1}/1035 cm^{-1} $\nu(OH)/\nu(PO_3)$
800	0.5168 ± 0.0536	0.5502 ± 0.0281	0.5443 ± 0.0110
900	0.1528 ± 0.0838	0.1527 ± 0.0396	0.1425 ± 0.0173
1000	0.0588 ± 0.0600	0.0597 ± 0.0345	0.0555 ± 0.0145

Conclusions

- The INS spectroscopy provided very valuable information, corroborating the FTIR data, validating the second for a daily analysis
- **The OH_{lib} and $\nu(OH)$ bands were observed in all the burned samples, both modern and archaeological, but not in the fossils.** Their presence, combined with high crystallinity, can therefore be used as a criterion to differentiate them .
- Statistical analysis of FTIR data from experimentally burned bones showed that **the 630/603 cm^{-1} index provides a different information from that yielded by the other two ratios**, which justifies its combined use with one of the latter in future attempts to accurately estimate the maximum temperature affecting a burned bone.

References

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