

Application of Raman spectroscopy for understanding the mineralogical composition of ancient copper slags (Timna, Israel)

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Introduction

- Prehistoric slags (Late Bronze Age to early Iron Age, ca. 1300 – 1000 BC) from copper metallurgy were sampled at the archaeological site no.2 in Timna, Israel. Classical combination of analytical methods used for this kind of samples: optical and scanning electron microscopy, electron microprobe analysis (chemical composition), X-ray diffraction analysis (bulk phase composition) was complemented with
- Raman microspectroscopy.

Raman microspectroscopy provides information about the phase composition on the micrometric scale and thus document the complex phase distribution. Due to the fast cooling of the slag samples, these are generally composed of both crystalline and amorphous glass-like phases and include metals, intermetallic compounds and alloys, sulfides, oxides, silicates, silicate glasses and carbonaceous

- fuel residues. With the exception of pure metals and their respective alloys, all these phases can be analyzed using Raman microspectroscopy.
- Laser-induced fluorescence can become a major issue, owing to a presence of many different metallic elements and therefore the selection of appropriate excitation is crucial, and may be very sample specific (fluorescence characteristics reflecting the composition).

Conclusions

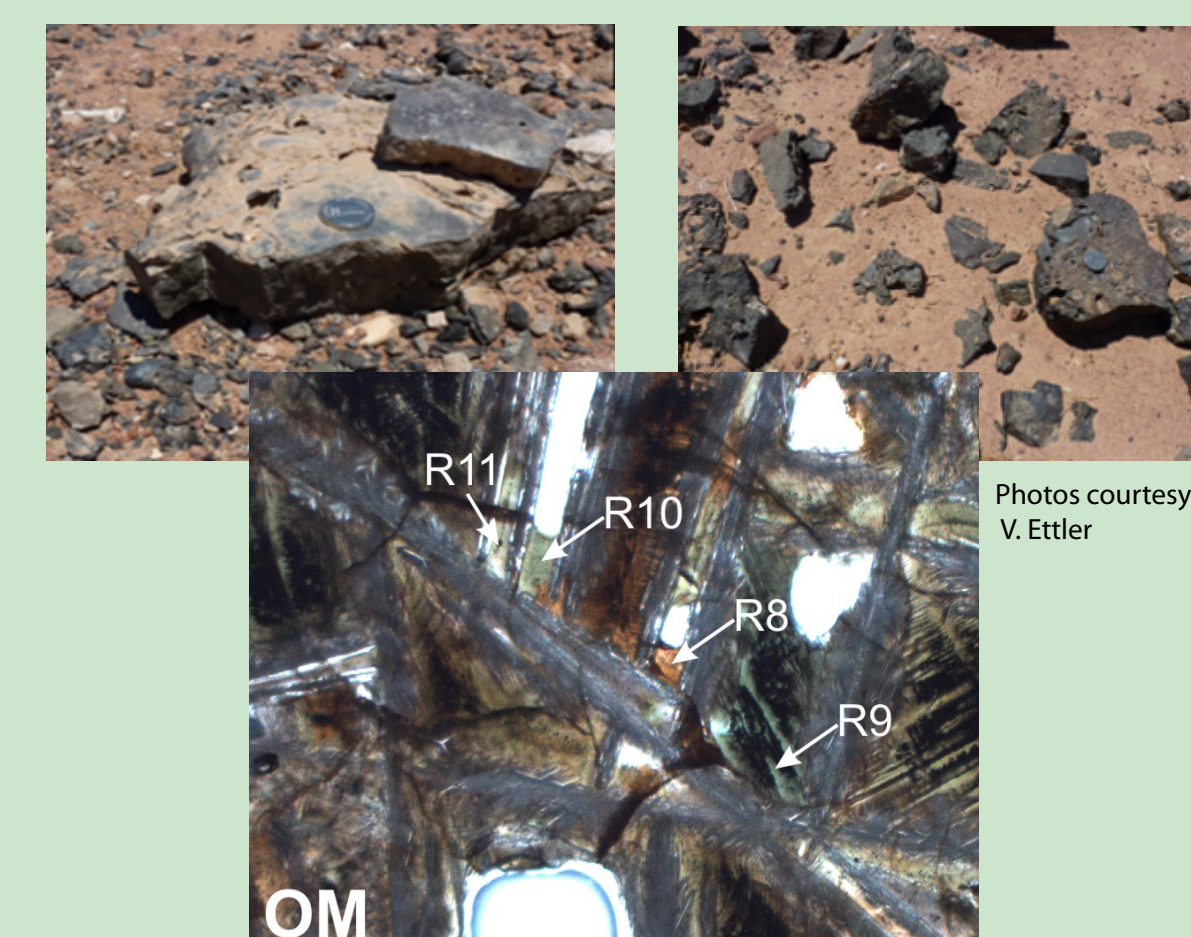
- Raman spectroscopy is a powerful technique for phase identification in the samples of ancient metallurgic copper slags
- Microcrystalline or even glassy character of present phases were revealed by Raman microspectrometry
- Identified phases include: silicates fayalite and clinopyroxenes of various compositions, silicate glasses, sulphides digenite and covellite, iron oxides hematite and goethite, residue of amorphous carbon

Samples and instruments

Raman microspectrometer: Renishaw InVia Reflex spectrometer coupled to a Leica microscope (50x), excitation 514.5 nm argon laser, spectral resolution $< 2\text{ cm}^{-1}$, spectral range for this study 100 - 1800 cm^{-1} .



Samples: Fragments of ancient copper slags at Timna metallurgic site

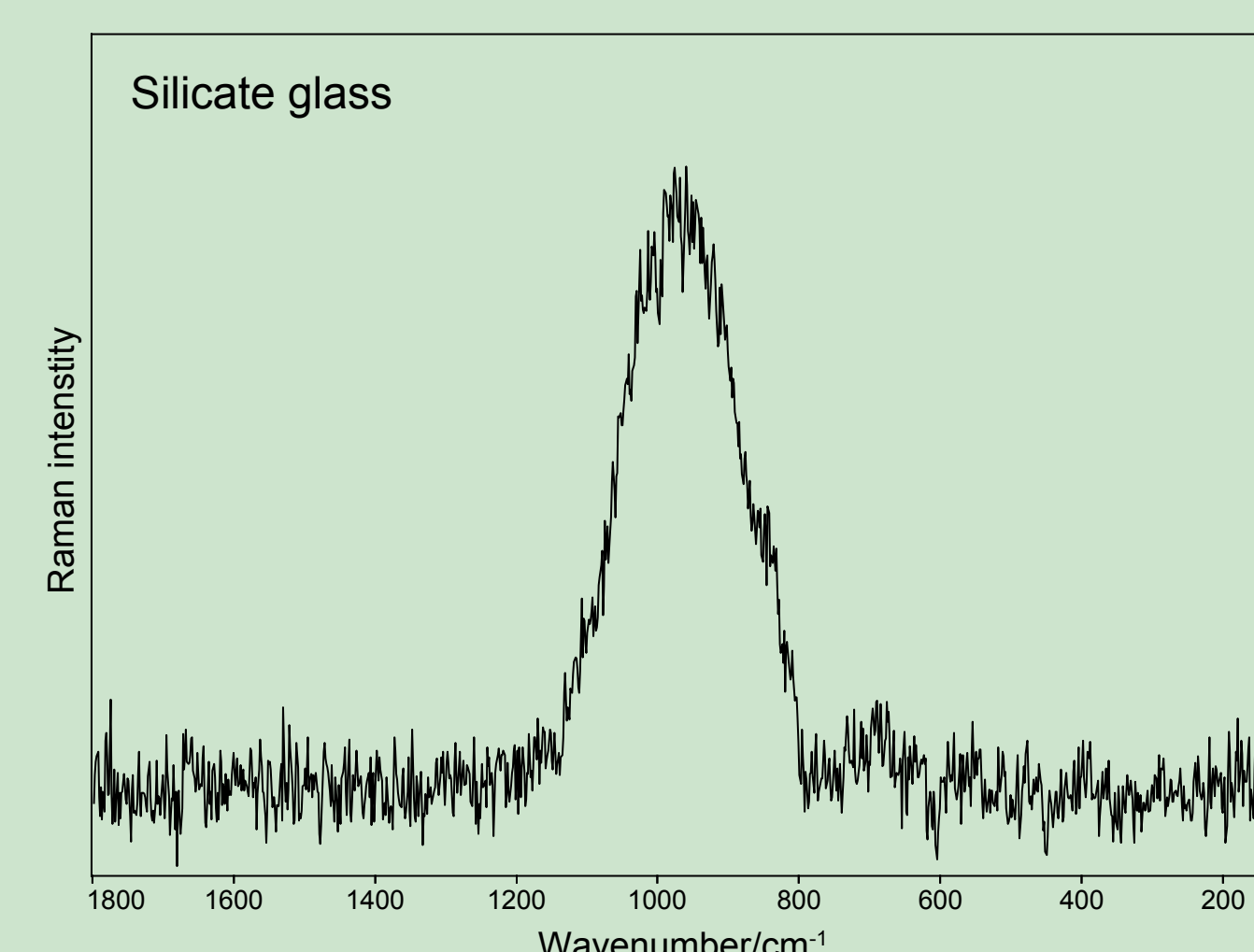
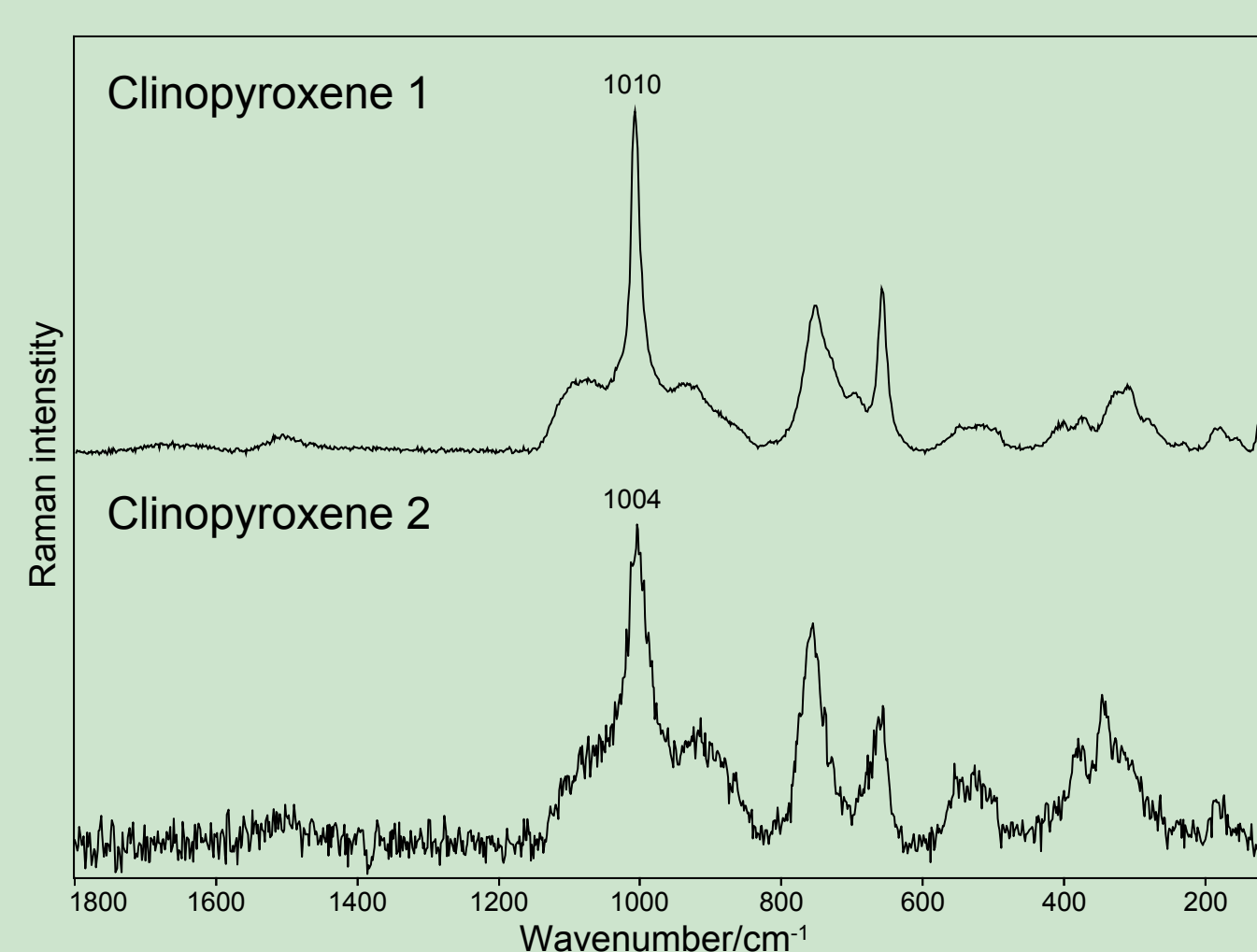
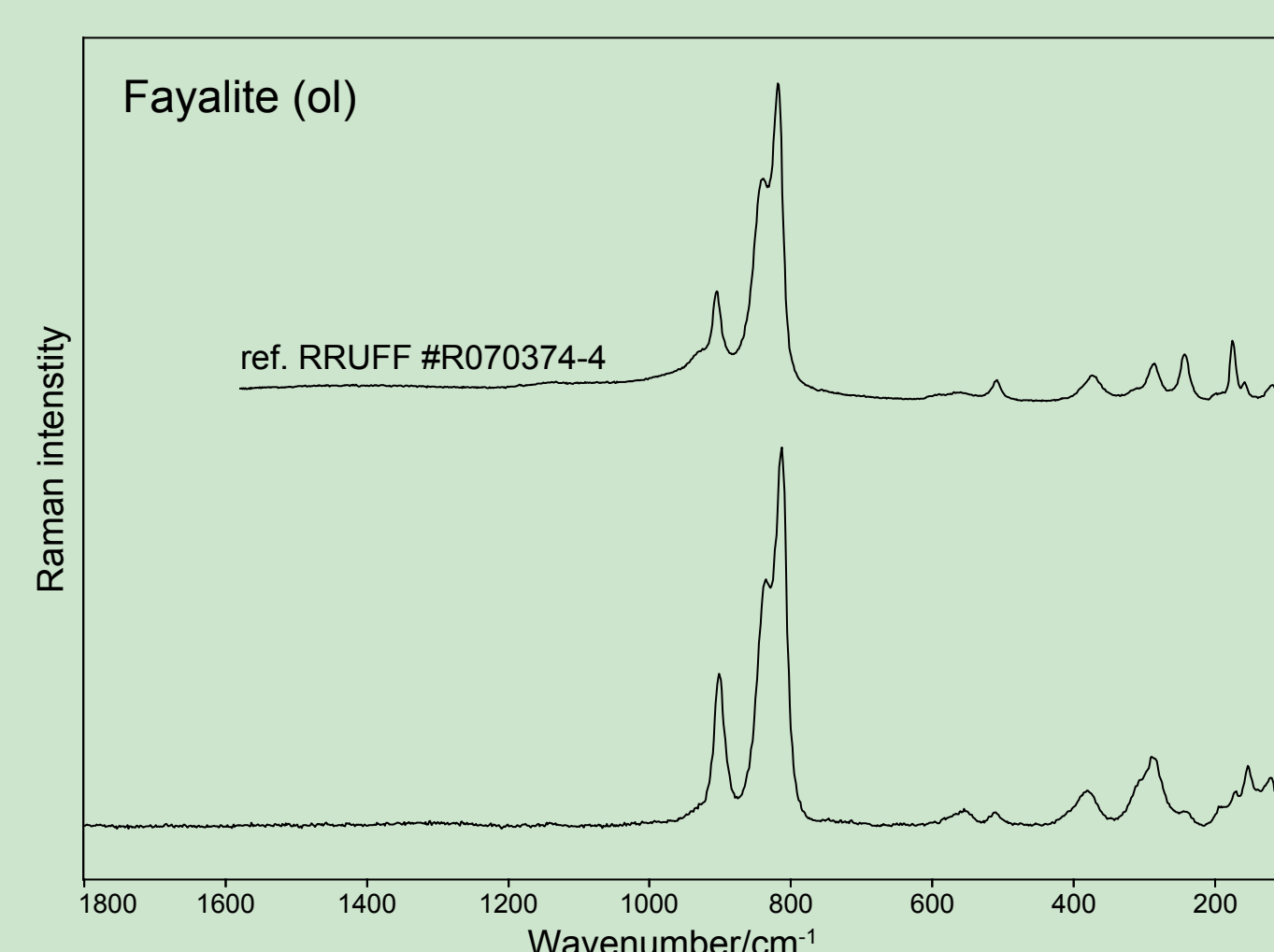


Optical microscope image of a thin section illustrating the heterogeneity of clinopyroxene minerals and glasses

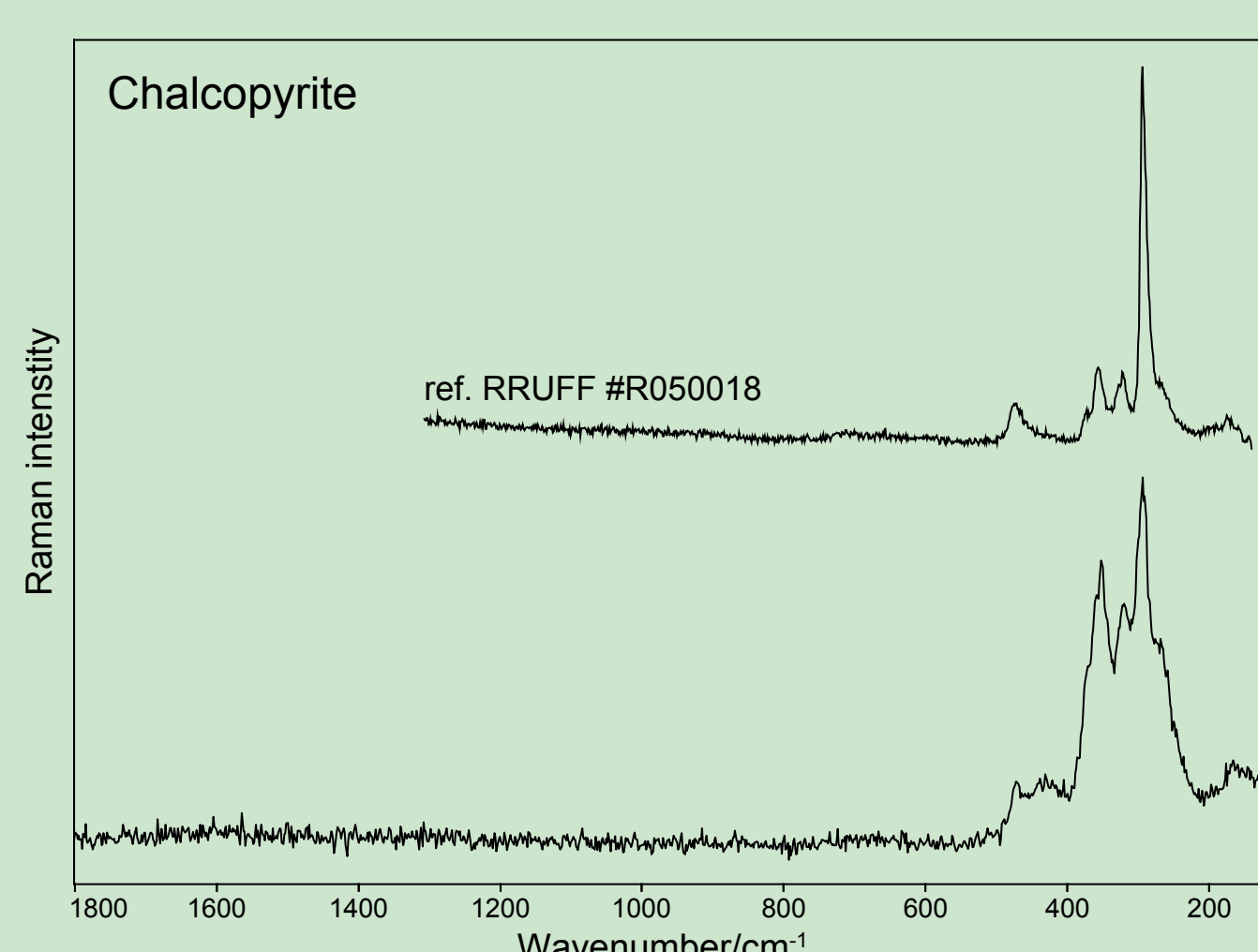
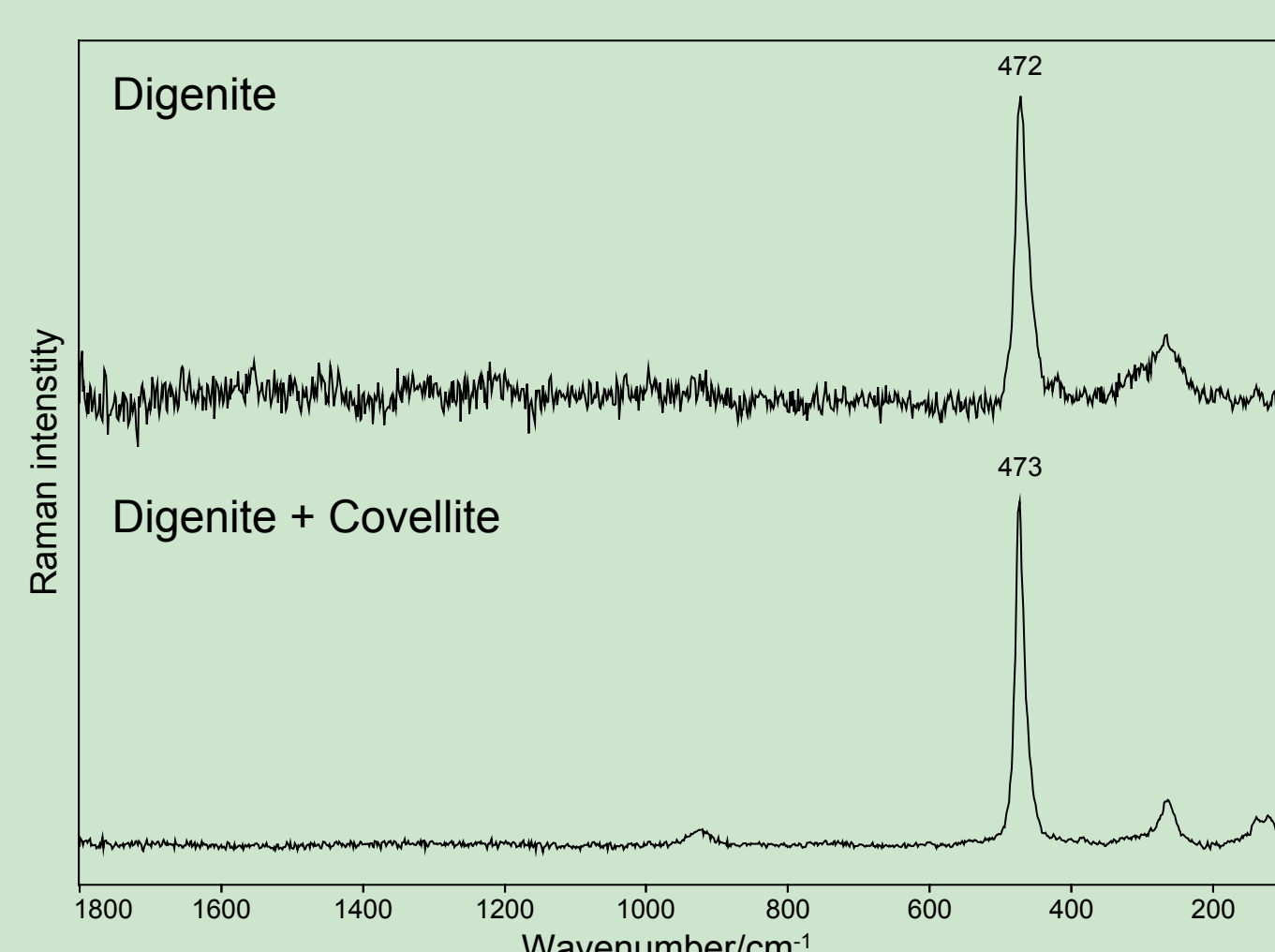
Results

Raman spectra of detected crystalline and amorphous phases of materials identified in the samples of ancient copper slags reflect complex mineralogical composition: silicate minerals and silicate glass (I.), sulphides of copper (II.), and iron oxides (III.). A full mineralogical study of ancient copper slags from Timna, Israel, that will contain more detailed Raman data and interpreted together with other analytical methods is in preparation.

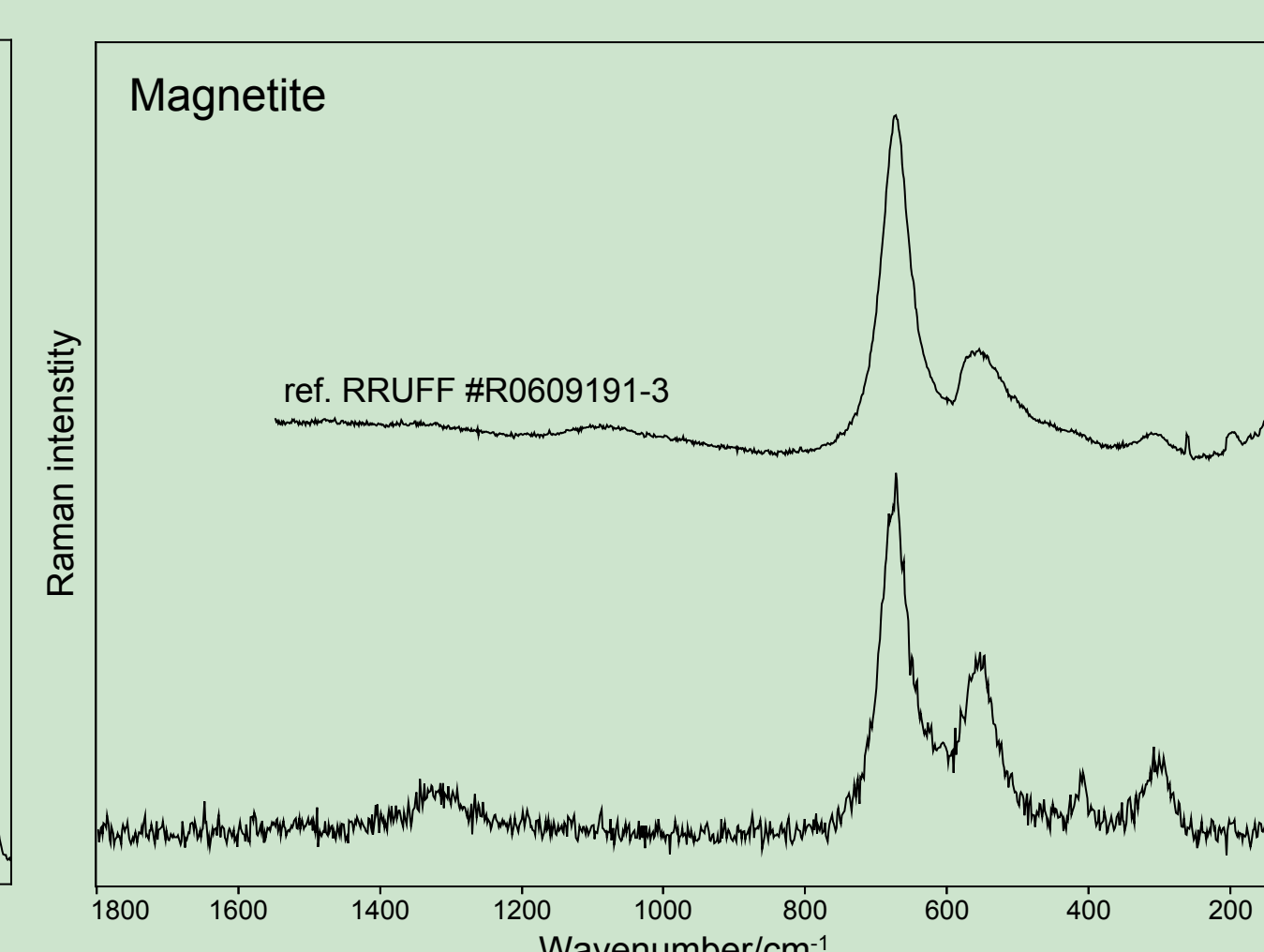
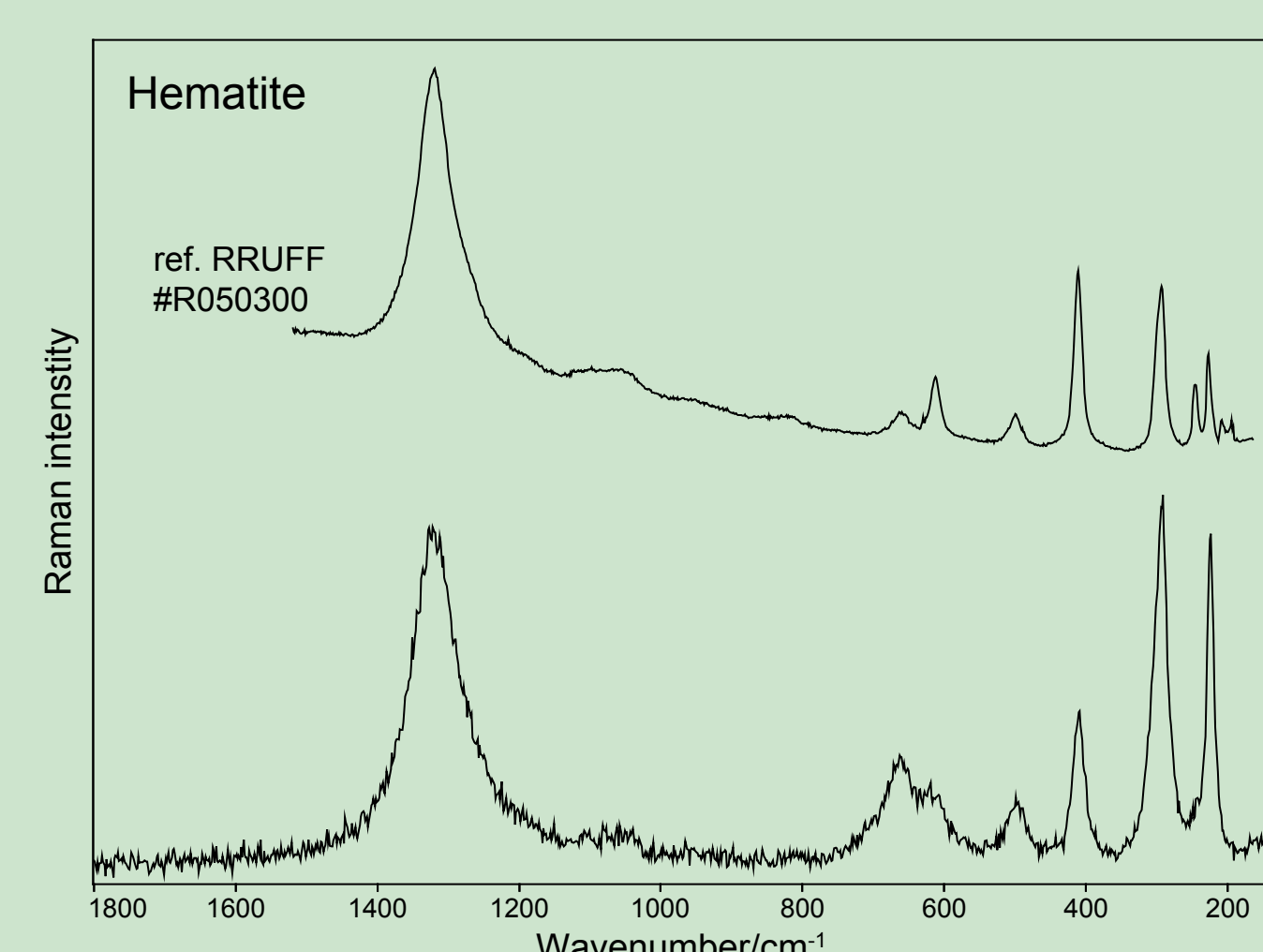
I.



II.



III.



References

RRUFF.info Online database of Raman spectra of minerals
Lafuente B, Downs R T, Yang H, Stone N (2015) The power of databases: the RRUFF project. In: Highlights in Mineralogical Crystallography, T Armbruster and R M Danisi, eds. Berlin, Germany, W. De Gruyter, pp 1-30

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