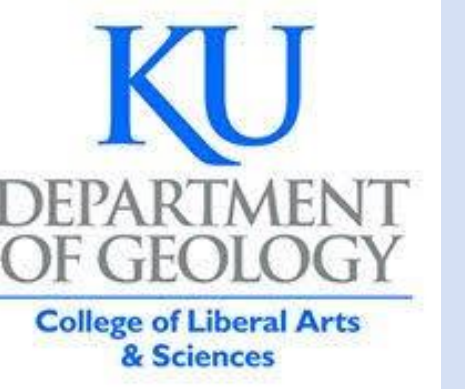




RAMAN SPECTROSCOPY OF OOLITIC HEMATITE: EVIDENCE OF BIOSIGNATURES IN IRON OXIDE RICH ROCKS



Allison Dowling¹, Carson Ruffledt¹, Scott Brande², Craig Marshall^{1,3}

¹Department of Geology, University of Kansas, Lawrence KS, 66045, ²Department of Chemistry, University of Alabama, Birmingham AL, 35294, ³Department of Chemistry, University of Kansas, Lawrence KS, 66045

Objective

Despite the extensive distribution of oolitic hematite, the origin and conditions of their formation is still under considerable debate. Currently, it is postulated that these enigmatic deposits are mineralogically composed of hematite, chamosite, or iron oxyhydroxides. Likewise, little is known about the temperature of the fluids, and whether biological or non-biological processes occurred to induce the precipitation and hence formation of these extensive deposits. Therefore, in order to shed light on the formation conditions of these deposits, we undertake a systematic approach to elucidate the mineralogy and chemistry of oolitic hematite samples located in the USA.

Materials and Methods

Samples

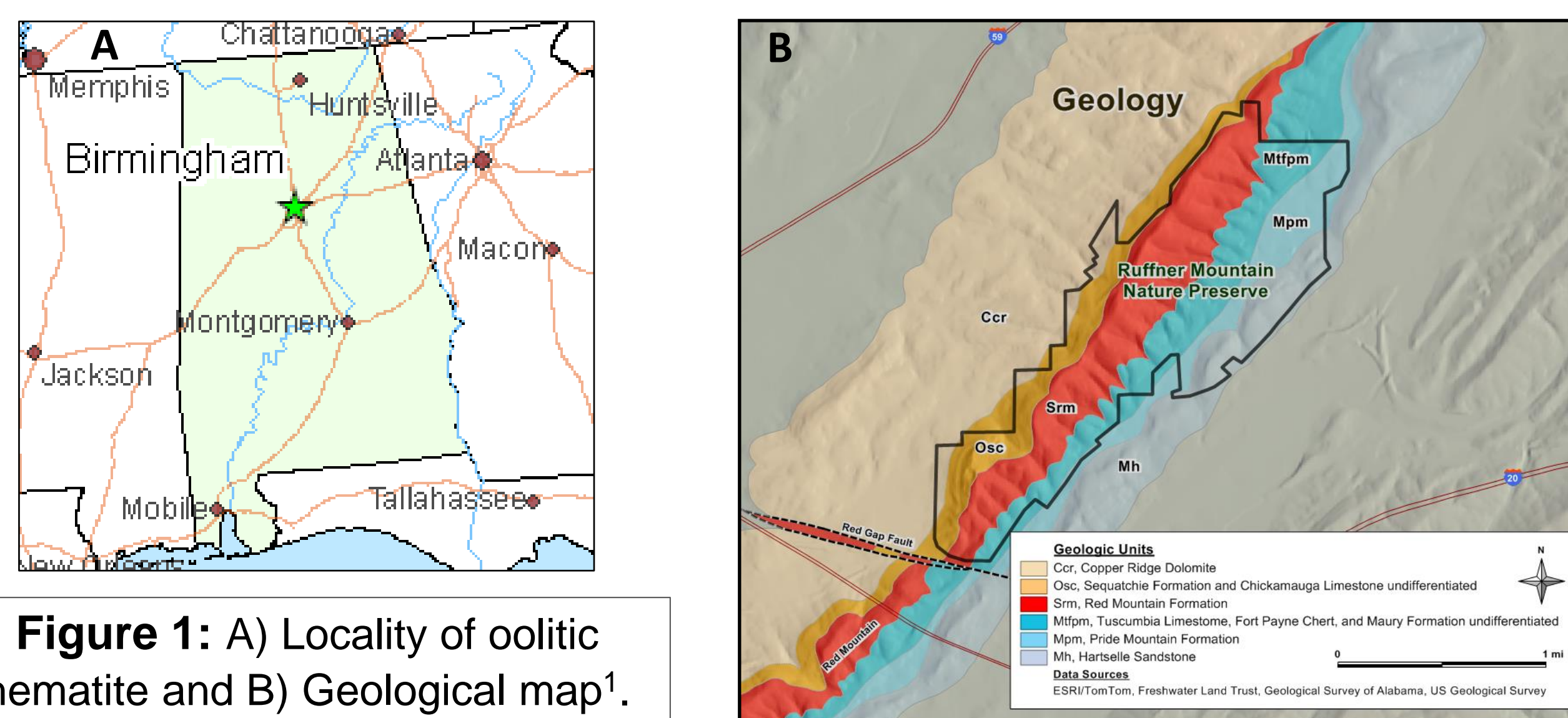


Figure 1: A) Locality of oolitic hematite and B) Geological map¹.

The Lower Silurian Red Mountain Formation consists of fossiliferous material, fine to medium grained sandstone interbedded with shale and lesser siltstone, oolitic ironstone, pebbly sandstone, and fossiliferous limestone^{1,2} (figure 1). During the Silurian^{1,2} the depositional environment forming these rocks is attributed to a shallow tidal delta².

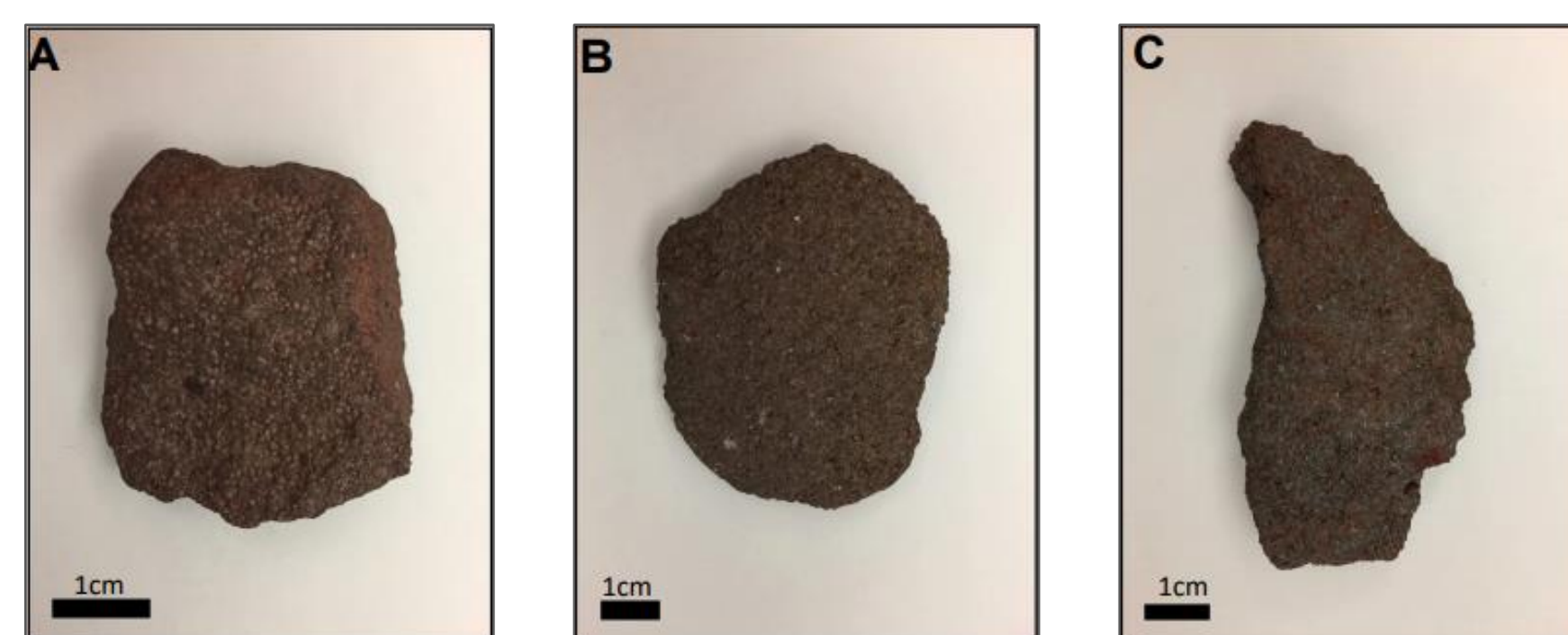


Figure 2: Oolitic hematite hand samples. A) Lower Silurian Red Mountain Formation, where samples B) and C) were obtained from the mineralogy teaching collection.

Raman spectroscopy

Backscattered Raman spectra were collected at room temperature with a Renishaw *in Via* Reflex Raman Microprobe. The Raman scattered light was dispersed by a diffraction grating with 2400 grooves/mm, and the signal was analyzed with a Peltier-cooled CCD camera (1024 x 256 pixels). Spectra were collected over the Raman shift region 100 – 1800 cm⁻¹ with spectral resolution of ca. 2 cm⁻¹. Sample excitation was achieved with an argon ion laser emitting at a wavelength of 514.5 nm. The laser was focused onto a 1.6 μm spot size through a 20X (NA = 0.40) microscope objective. The attached microscope is a Leica DMLM. Spectra were summed over five 30s accumulations.

Results and Discussion

Raman spectroscopy reveals the presence of hematite, quartz, apatite, rhodochrosite, siderite, magnesite, low Mg calcite, and calcite (table 1).

Mineral Identified	Diagnostic phonon modes (cm ⁻¹)
Hematite (α -Fe ₂ O ₃)	225 245 294/298 (doublet) 412 500 610 660 1320
Quartz (α -SiO ₂)	206 464 511
Apatite (Ca ₅ (PO ₄) ₃ (Cl/F/OH))	Only band present was a weak mode at 960
Rhodochrosite (MnCO ₃)	185 292 720 1088 1417 1729
Siderite (FeCO ₃)	184 287 735 1087 1728
Magnesite (MgCO ₃)	215 333 738 1094 1445 1762
Calcite (CaCO ₃)	154 280 711 1085 1434 1747
Low Mg calcite (CaMg(CO ₃))	154 280 711 1088 1434 1747

Table 1: Diagnostic phonon modes. Relative wavenumbers obtained from representative Raman spectra of each mineral present within the oolitic hematite. These spectra were identified by comparison with the literature³⁻⁵. The bold wavenumbers represent the most intense diagnostic phonon mode for identification.

Moreover, the hematite composing this formation varies from very poor crystallinity, and poor to moderate crystallinity, which is demonstrated by the Raman spectroscopic analysis (figure 3). The single-crystal hematite shows all the 7 group theoretically predicted phonon modes and the 2LO line. While the moderate crystallinity hematite shows reduced intensity and line-broadening. And finally, the poor crystallinity hematite displays fewer and broader phonon modes. This is expected for poor crystallinity hematite³.

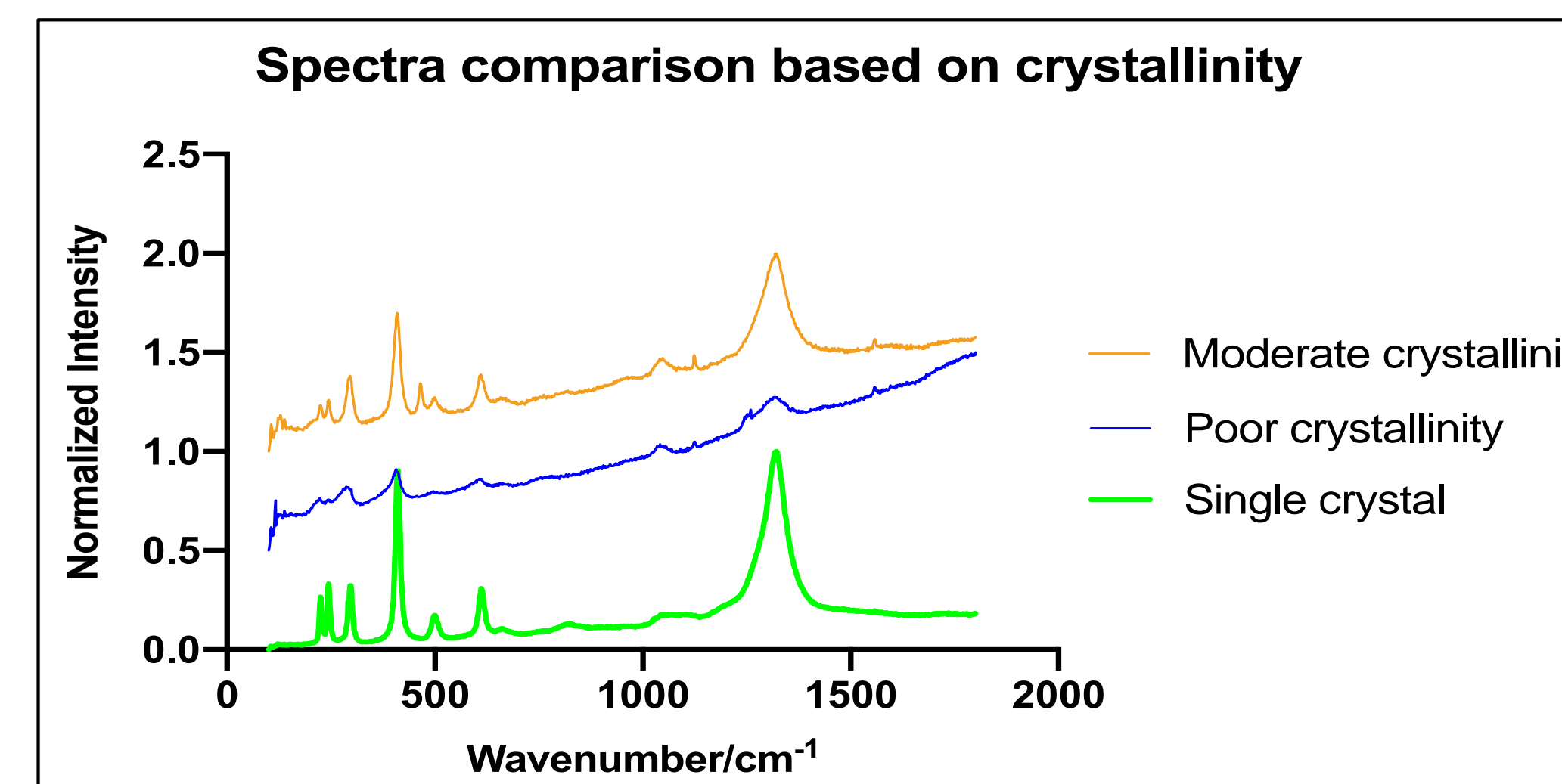


Figure 3: Stack plot of single-crystal (purchased Wards Scientific), oolitic hematite of poor-crystallinity, and poor- to moderate-crystallinity.

Interestingly, the Raman spectroscopic analyses showed the presence of *sp*² carbonaceous materials, associated with the larger size ooids and with dark brown coloring (figures 4 and 5).

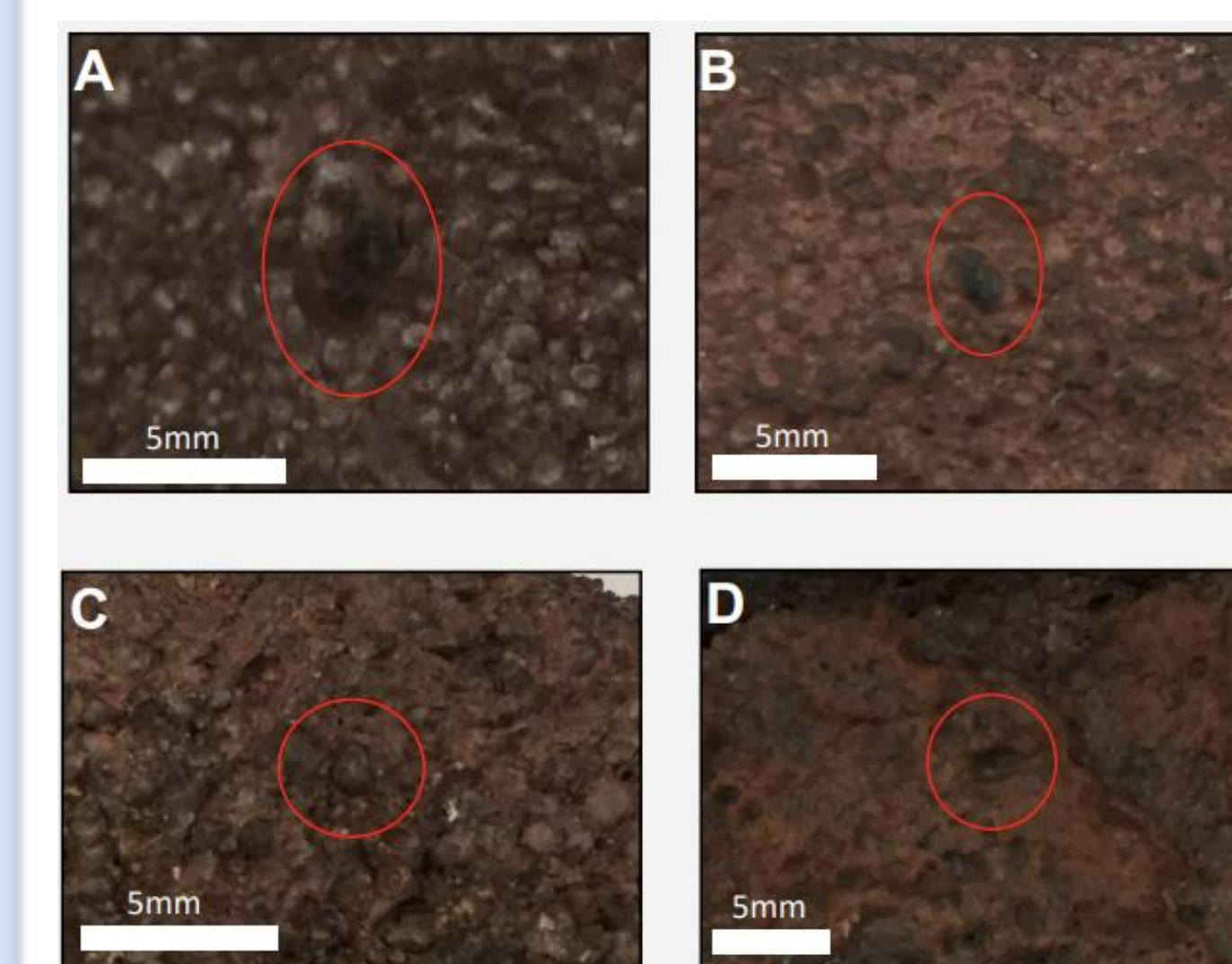


Figure 4: Different ooids located on various oolitic samples where higher concentrations of *sp*² carbonaceous materials are found. (A and B) Ooid of interest located on Red Mountain formation sample seen in figure 2A. (C) Ooid of interest located on sample seen in figure 2B. (D) Ooid of interest located on sample seen in figure 2C.

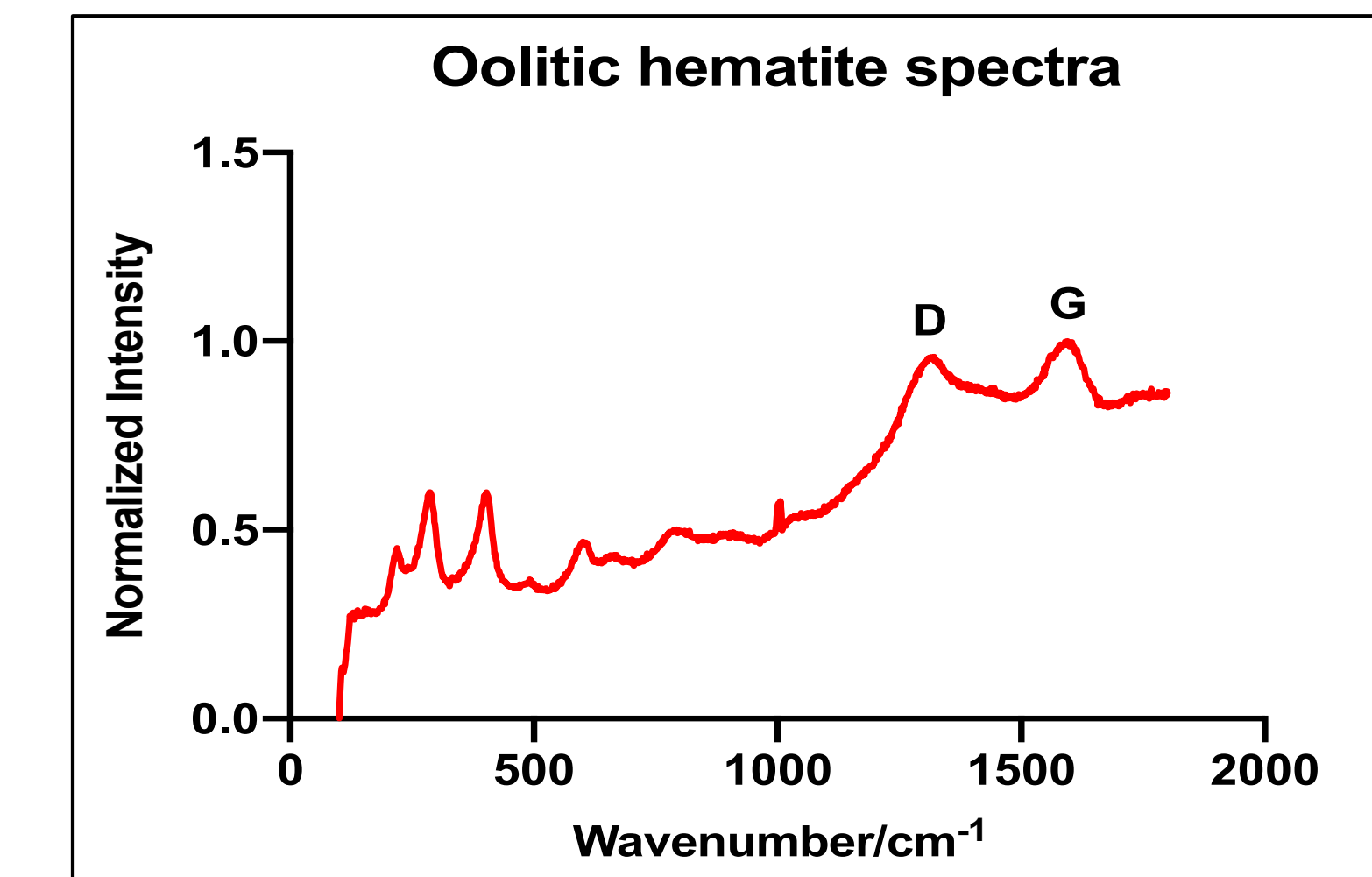


Figure 5: Representative spectrum indicating the presence of kerogen. The G and D bands at ca. 1600 and 1350 cm⁻¹, respectively, are indicative of *sp*² carbonaceous materials. The D band is likely affected by a small contribution from the 2LO line of hematite.

Comparison with the literature⁶ reveals that the representative spectra acquired on the *sp*² carbonaceous materials from various samples of oolitic hematite are representative of the organic material undergoing a thermal mature pathway indicative of 60-140° C which, is consistent with thermally immature diagenetic alteration. This would indicate the preserved remains of biology (i.e. kerogen) and that the fluids of formation of this deposit never exceeded 140°C.

Further evidence to the role of biogenicity in the formation of this deposit is the presence of rhodochrosite. The deposition of rhodochrosite is generally an anaerobic process of Mn^{IV} oxide reduction that is strongly linked to organic degradation in sedimentary systems by microbes⁷.

Conclusions and Implications

For the first time, we demonstrate that the mineralogy of these enigmatic deposits is not as simple as previously supposed, but instead consist of a variety of mineralogy, including: hematite, quartz, apatite, rhodochrosite, siderite, magnesite, low Mg calcite, and calcite. Also, we demonstrate that the hematite occurs in two populations, that is, poor crystallinity and moderate crystallinity. Lastly, taken together, the presence of low temperature kerogen and rhodochrosite are strongly indicative of a biological origin of these deposits.

Future work will concentrate on obtaining a thin section to further document the localization of kerogen with respect to ooid morphology.

Acknowledgements and References

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