Micro-Raman Spectroscopy of low-grade carbonaceous materials and its evolution

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The organic materials trapped in the sedimentary rocks, generally known as carbonaceous material (CM), attain maturity by two main processes, namely carbonization and graphitization during prograde metamorphism (Franklin, 1950; Oberlin, 1984). The first stage of carbonization is characterized by the chemical changes that lead to the relative enrichment of aromatic structures in CM due to the release of heteroatoms such as hydrogen, nitrogen, oxygen, and sulfur and degradation of aliphatic CH groups. In the later stage, solid-state reorganization takes place by the formation of basic structural units with the release of non-condensable gases (e.g., CH_4 and H_2) from the aromatic CH groups (Oberlin et al., 1999). Graphitization is the process by which the aromatic structure is reorganized to form turbostratic to graphitic structures. Micro-Raman spectroscopy is being widely used to assess the thermal maturity and evolution of CM in sedimentary rocks for the past three decades (e.g., Pasteris and Wopenka, 1991). Compared with medium grade CM, the Raman spectra of low-grade CM is more complex with several disordered bands (e.g. D1, D2, D3, D4, D5) as it undergoes the two stages of carbonization. The deconvolution of these disordered bands in the Raman spectra is essential to separate the overlapping bands. However, the number of disordered bands is controversial, and different authors have used a combination of different bands with different functions to define laser Raman parameters of CM that can be applied in maturity studies (Sadezky et al., 2005; Kouketsu et al., 2014). In this study, the peak deconvolution and the metamorphic temperature were estimated following Kouketsu et al. (2014) for the low-grade CM.

As a test case, the maturity of the CM from the Archean medium grade Chitradurga Schist Belt, Dharwar Craton has been evaluated. Following the Raman Spectra of CM thermometry developed by Beyssac et al. (2002) for medium to high-grade CM, using the R2 ratio (Area $_{\text{D1 band}}$ / Area $_{\text{G+D1+D2 bands}}$) a systematic increase in the metamorphic condition from upper greenschist facies to lower amphibolite facies was observed along with the younger to older stratigraphic sequences respectively. To extend our understanding of the carbonization process and evolution of CMs under low thermal maturation additional samples were considered from Archaean (Tumbiana Formation, 2.7 Ga, Pilbara Craton; Malmani Subgroup, 2.5 Ga, Kaapvaal Craton) and Proterozoic (Duck Creek Formation, 1.8 Ga, Pilbara craton) terranes. Preliminary results indicate that the CMs are metamorphosed under prehnite-pumpellyite to lower greenschist facies condition. A recent study by Quirico et al, (2020) used UV Raman spectroscopy that avoids the fluorescence and distinguished immature terrestrial kerogens and coals from those of extraterrestrial kerogens extracted from type 1 and 2 primitive chondrites. Moreover, traces of organic molecules present in the CM can be identified due to the resonance effect of the UV laser and even installed in planetary missions such as Mars 2020 (Bhartia et al., 2021). In this presentation, we will be comparing the visible and UV Raman spectra of CM in low to medium-grade rocks and attempts to understand the maturation process of Archean unicellular organisms and complex multicellular organisms.

References:

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