Invited keynote lecture:

Recent advances in Raman spectroscopy of graphitic carbons in the Earth Sciences

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Graphitic carbons are widespread in terrestrial and cosmochemical samples, where they span a wide range of structure/chemistry from amorphous-like compounds to crystalline graphite *sensu stricto*. They have unique and original properties controlled by their structure, they carry important geological or biological legacy, and they buffer the chemical composition of fluids in equilibrium with rocks. They are also used as advanced materials or energy sources. Carbon can vary the combination between its valence orbitals (2s, 2p) to form hybrid orbitals (sp^1, sp^2, sp^3). This hybridation ability makes carbon unique and allows it to form various kinds of atomic bonds which constitute the foundation for the infinite structural and chemical variety of graphitic carbons. In terms of chemical composition, graphitic carbons are relatively simple as they are mostly composed of C and heteroatoms such as H and O with possible traces including N and S. During graphitization, they tend to simplify their chemistry by releasing heteroatoms to converge toward the pure C composition of graphite. In Natural systems, graphitic carbons exhibit an infinite range of structure, from amorphous-like compounds (soots, charcoals, low-grade coal) to crystalline graphite through a myriad of turbostratic structures (coals, kerogens…). Graphitic carbons are turbostratic with an infinity of possible arrangements for the aromatic layers by opposition to the true crystalline structure of graphite defined by the ABAB sequence of aromatic planes in the hexagonal structure. Importantly, the multiscale structure of graphitic carbons determines their physico-chemical properties but also reveals their geological history.

Raman spectroscopy is widely used to characterize graphitic materials of geological interest with implications in cosmochemistry, geobiology or geology. The Raman spectrum of graphitic materials has actually unique specificities with the presence of the so-called defect bands, and these specificities may be (cautiously) used to characterize their structure and retrieve some information of geological relevance. Over the last years, there has been a considerable research effort not only in terms of theory on the Raman spectrum of graphitic carbons, but also in terms of methodology as these compounds are highly sensitive materials when exposed to a laser. A short review on the theoretical knowledge of the Raman spectrum of graphitic carbons with an emphasis on the defect-activated peaks will be given. These peaks have unique specificities that are described and explained in the frame of the double-resonance theory. Then latest methodological developments will be reviewed and a reference methodological protocol for a reliable analysis of natural graphitic carbons by Raman spectroscopy will be provided. Limits of the method will be discussed and some information will be given on complementary methods to Raman for the study of graphitic carbons, such as X-ray diffraction, (XANES) X-ray Absorption Near-Edge Spectroscopy or Transmission Electron Microscopy (TEM).

There is a huge diversity of studies in the Earth Sciences that use Raman spectroscopy of graphitic carbons. Some recent studies will be presented and discussed. These studies deal with thermometry with application to terrestrial and extraterrestrial metamorphism and are based on the extreme sensitivity of graphitization to temperature. Alternatively, graphite may

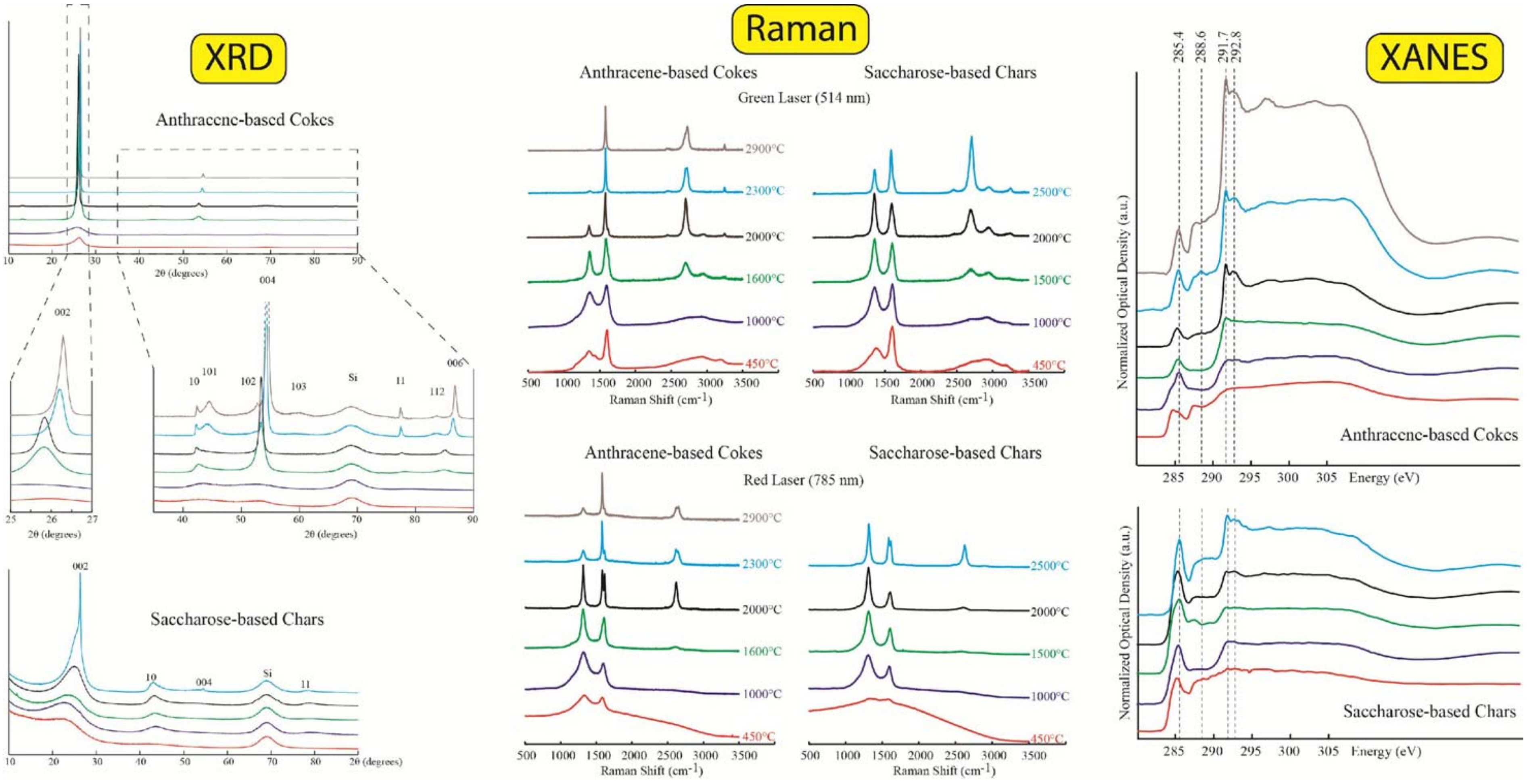

Fig. 1. *X-ray diffraction, Raman spectroscopy and XANES spectroscopy data for two reference cokes pyrolyzed at various temperature conditions: the graphitizing anthracene-based coke and the non-graphitizing saccharose-based coke (Bernard et al. 2010).*

form through the saturation of a COH fluid due to a change in chemical composition and/or P-T conditions. Raman spectroscopy performed in situ in rocks can be an efficient tool to distinguish between both types of graphite, issued from graphitization or from fluid-deposition. Raman spectroscopy is also extensively, sometimes abusively, used to investigate the structure of graphitic carbons in putative organic fossils or biological fingerprints in ancient rocks: this has for instance triggered some considerable controversies about the oldest traces of life in the geological record. This example emphasizes the limits of Raman spectroscopy to characterize the structure of poorly ordered graphitic carbons and the necessity to combine it with other structural or geochemical tools. Due to its non-destructive character and relatively high-resolution, Raman spectroscopy has also become one of the main techniques to investigate the structure of organics in meteorites yielding information on their thermal histories but also, more generally, on cosmochemical processes. These different examples will be presented based on latest studies from the literature. Altogether, advantages/limits of Raman spectroscopy of graphitic carbons point to the necessity for multiscale and interdisciplinary studies to properly characterize graphitic carbons and retrieve optimal geological information.

The interested reader will find a recent bibliography on the theoretical, methodological and scientific aspects around Raman spectroscopy of graphitic carbons in Beyssac and Lazzeri (2012).

References:

Bernard S, Beyssac O, Benzerara K, Findling N, Tzvetkov G, Brown Jr GE (2010) XANES, Raman and XRD signatures of anthracene-based cokes and saccharose-based chars submitted to high temperature pyrolysis. Carbon 48:2506–2516

Beyssac O, Lazzeri M (2012) Application of Raman spectroscopy to the study of graphitic carbons in the Earth Sciences. In: Applications of Raman Spectroscopy to Earth Sciences and Cultural Heritage (Dubessy J, Caumon M-C, Rull F, Eds). EMU Notes in Mineralogy 12, European Mineralogical Union and the Mineralogical Society of Great Britain & Ireland, p 415–454