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Modern and Fossil Charcoal: Aspects of Structure and Diagenesis

I. Cohen-Ofri (1), L. Weiner (2), R. Popovitz-Biro (2), E. Boaretto (3), G. Mintz (3) and S. Weiner (1)

(1) Department of Structural Biology, Weizmann Institute of Science, Rehovot 76100, Israel.
(2) Chemical Research Support Unit, Weizmann Institute of Science,Rehovot 76100, Israel.
(3) Radiocarbon Dating Laboratory, Weizmann Institute of Science, Rehovot 76100, Israel.

(ilit.cohen-ofri@weizmann.ac.il/ Tel.:+972 8 9342547)

Understanding the degradation processes of fossil charcoal is of much interest as charcoal is an important component in many ecosystems and in archaeology because it is a common material used in radiocarbon dating. Furthermore, charred plant remains are an important component of the archaeobotanical record. To this end, the structures and compositions of modern charcoal samples produced in camp fires and fossil wood charcoal samples were compared. The examination of modern charcoal samples using various spectroscopic methods (FTIR and Raman), as well as TGA/DTA, ESR and resistivity measurements, is consistent with charcoal containing two major phases: graphite-like microcrystallites and a non-organized phase. High resolution TEM and Electron Energy Loss Spectroscopy (EELS) showed that two different structural types can be recognized in modern charcoal: one comprises the two major phases (graphite-like microcrystallites and a non-organized amorphous carbon phase), and the other has a homogeneous semi-ordered phase. These two structures are present in charcoals of wood derived from different genera. The fossil charcoal samples (Tel Dor, Israel: around 3000 years BP and Kebara cave, Israel: around 60,000 to 30,000 years BP) also contain graphite-like microcrystallites (mainly in an onion-like structure) and a non-organized phase, but with a reduction in the amount of graphite-like microcrystallites. The predominant structure is amorphous carbon. This is consistent with the observations that the fossil charcoals have higher electrical resistivities than modern charcoal, and markedly altered surface electronic states as indicated by ESR. Infrared spectra show the presence of additional carboxylate groups. These groups are the prod-

uct of oxidation. According to electron energy loss spectroscopy (EELS), the oxygen is confined to the non-organized phase. However, the few graphite-like microcrystallites found primarily exist in an onion-like structure. It is possible that their rounded structure is thermodynamically more stable than graphitic microcrystallite sheets, and hence less susceptible to degradation. It appears therefore that the diagenesis of charcoal mainly occurs by a "self-humification" process that reduces the relative proportion of the graphite-like microcrystallites and changes the chemical structure of the non-organized phase.