

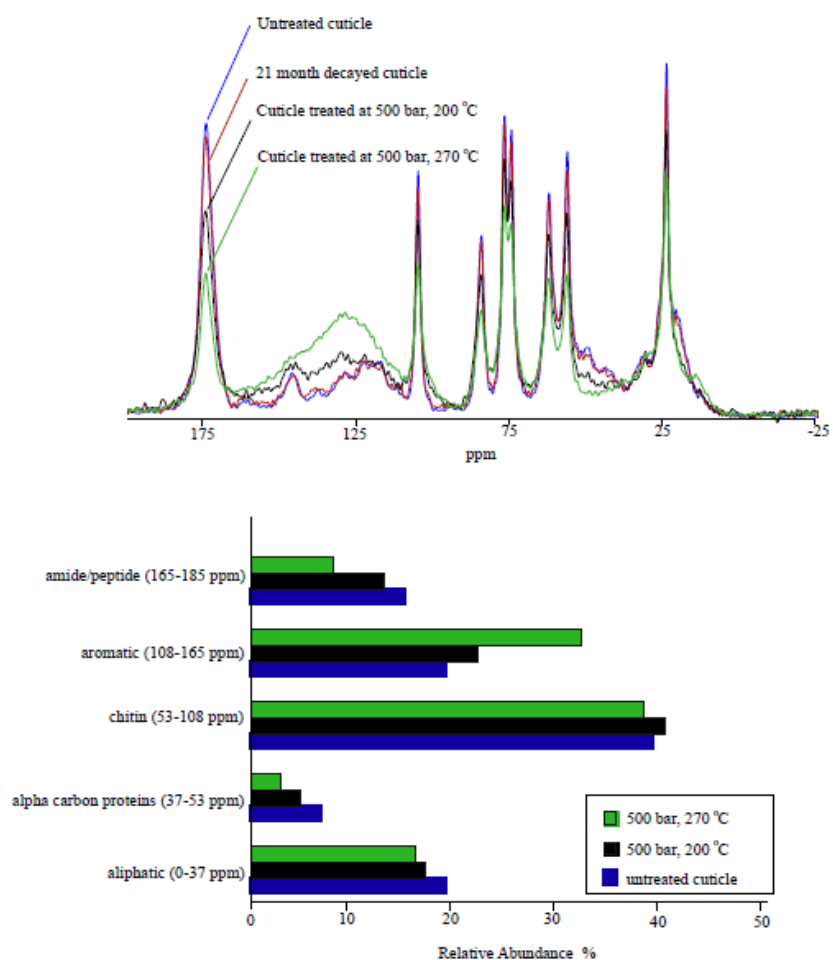


Fig. 1 (a) ¹³C NMR analysis of untreated cuticle and cuticle heated at 200 °C and 270°C, outlining the distribution of chemical moieties from 200 ppm to 225 ppm. (b) Quantitative estimate of changes in the composition of the cuticle with increasing temperature as elucidated using ¹³C NMR. Ranges associated for particular moieties include amide/peptide (165-185 ppm), aromatic compounds (108-165 ppm), chitin (53-108 ppm), α-C proteins (37-53 ppm) and aliphatic compounds (0-37 ppm).

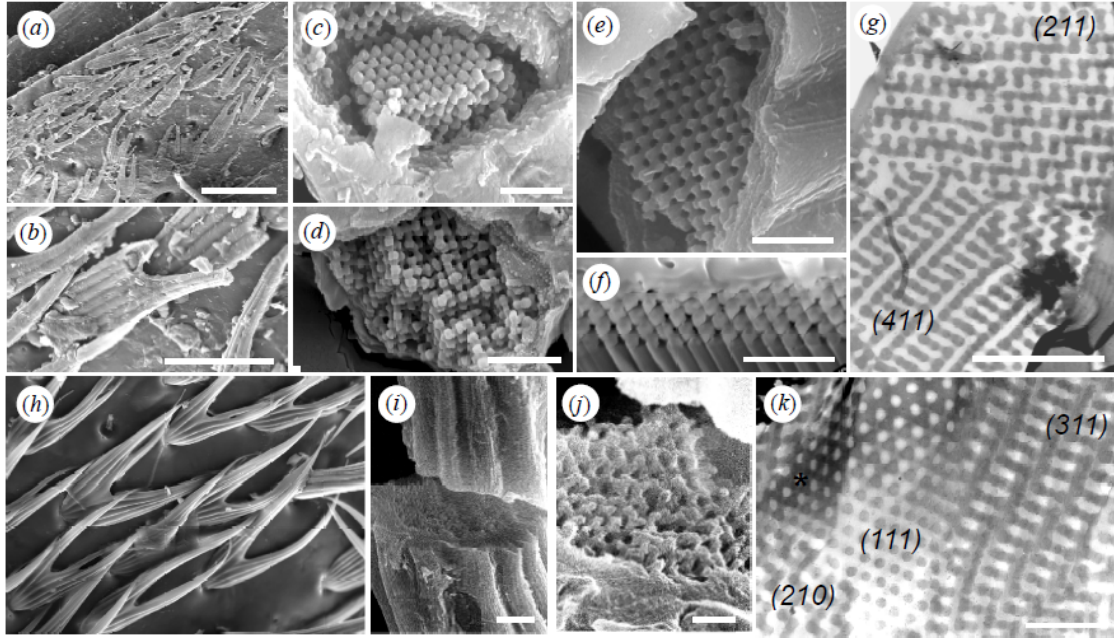


Figure 2. Electron micrographs of fossil (a-g, k, l) and modern (h-j, m, n) scales. (k-n) are transmission electron micrographs; all other images are scanning electron micrographs. (a, h) Surface of the fossil cuticle showing alignment of scales. (b-f, i, j) Detail of fractured scales showing 3DPC in the scale lumen; (f) is an ion milled vertical section. (g) Fractured section through the cuticle of the fossil weevil showing fine lamination in the exocuticle (ex) and bundles of chitin microfibrils in the endocuticle (en); sc, scale. (k-n) Transmission electron micrographs of vertical sections of fossil (k, l) and modern (m, n) scales showing photonic polycrystallite domains. Numbers in parentheses denote distinctive motifs characteristic of specific planes of the single diamond morphology. Scale bars: a, 50 μm ; b, 10 μm ; c-f, j, k-n, 1 μm ; g, i, 5 μm ; h, 25 μm ; j, 2 μm .

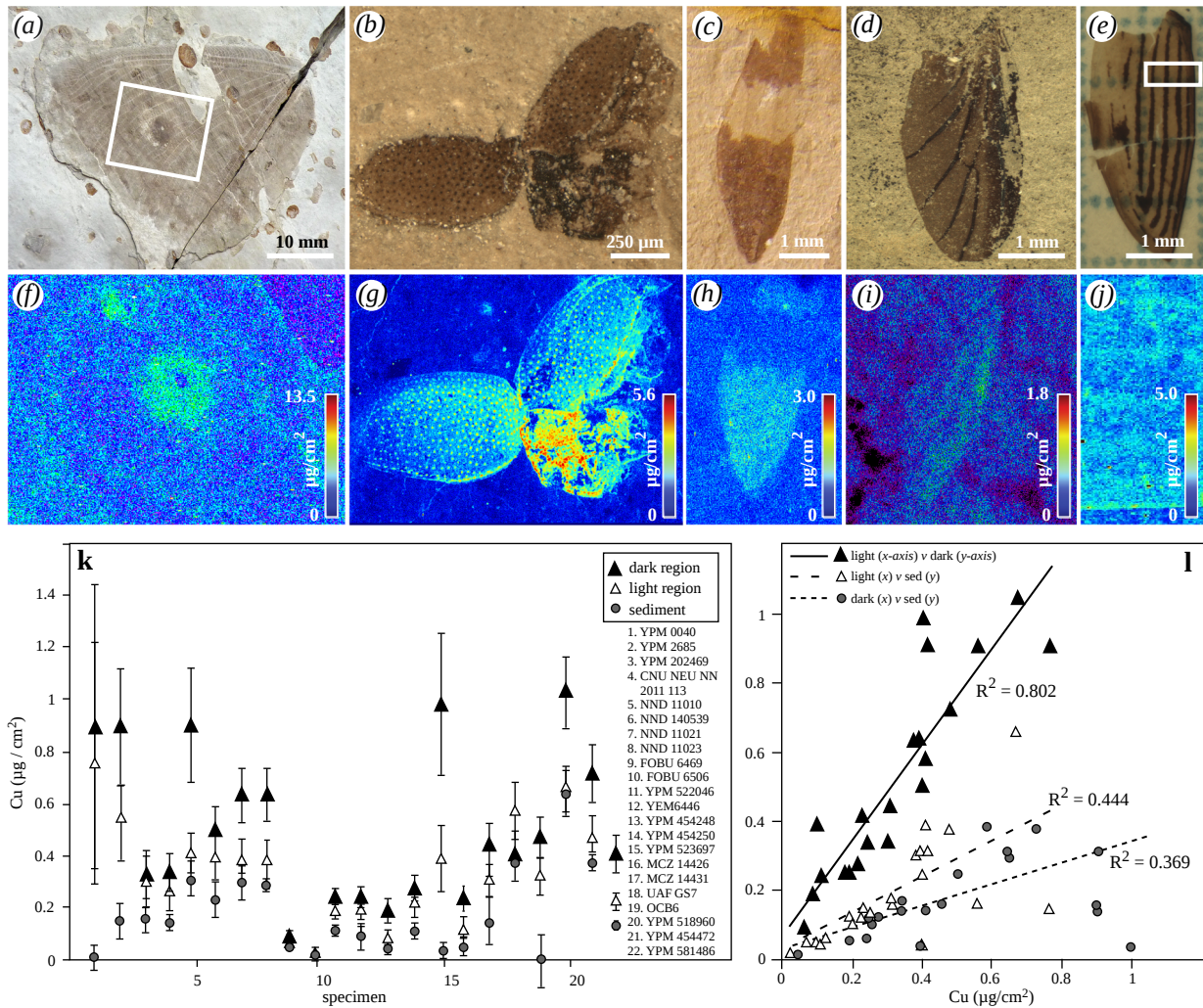


Figure 3. Cu in the cuticle of fossil insects. Light micrographs (a-e) and synchrotron X-ray fluorescence maps (f-j) for Cu for selected fossil insects used in this study. (a, f) NIGP NND 11021 (Neuroptera: Kalligrammatidae; Jiulongshan Formation, Middle Jurassic, Inner Mongolia, China); (b, g) UCM 1311 (Coleoptera: Chrysomelidae; Green River Formation, Middle Eocene, Colorado, USA); (c, h) YEM 518960 (insect indet.; Ruby Paper Shale, Late Oligocene, Montana); (d, i) UAF GS7 (Hymenoptera: Bibionidae; Grubstake Formation, Late Miocene, Alaska, USA); (e, j) LIS OD 105-110 (Coleoptera indet.; Lobigdensee, Pleistocene, Switzerland). (k) Mean and standard deviation of Cu concentrations in light and dark cuticle regions and adjacent sedimentary matrix for all specimens studied. (l) Cu concentrations in dark- versus light-toned cuticle regions and in each cuticle region versus the sediment. Note consistently lower concentrations of Cu in the sedimentary matrix relative to the fossils (b-d, g-i).

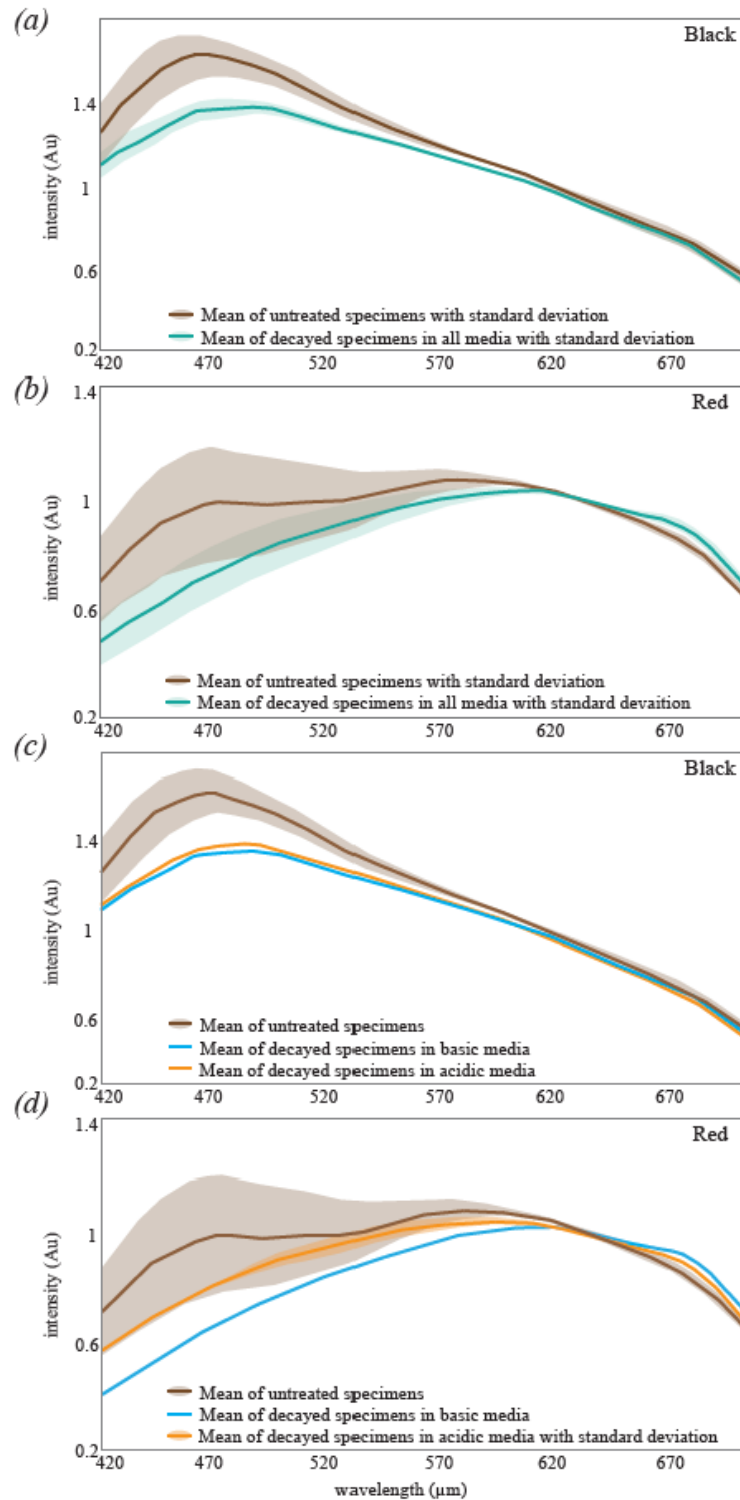


Fig. 4. Microspectrophotometry of black and red coloured regions of the cuticle of *Harmonia axyridis* before and after decay for two months in acidic and basic media.

