

## Supplemental online material

### Europium binding to humic substances extracted from deep underground sedimentary groundwater studied by time-resolved laser fluorescence spectroscopy

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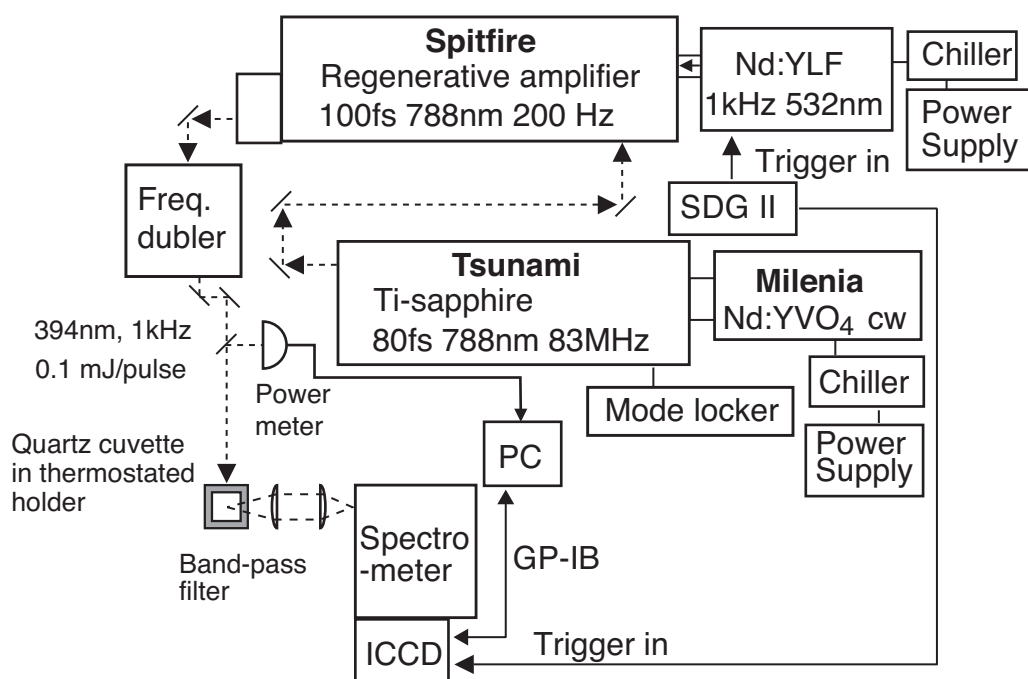
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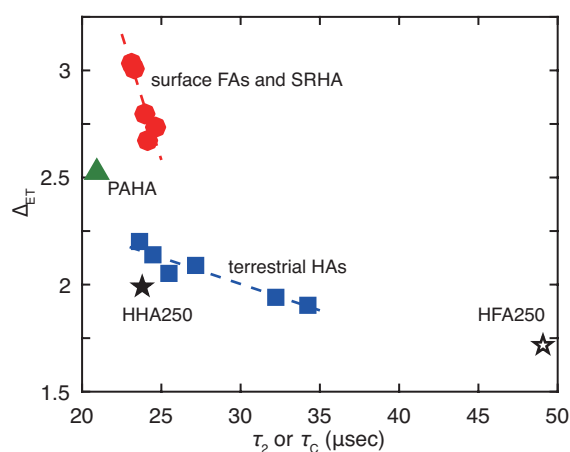
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## TRLFS measurements

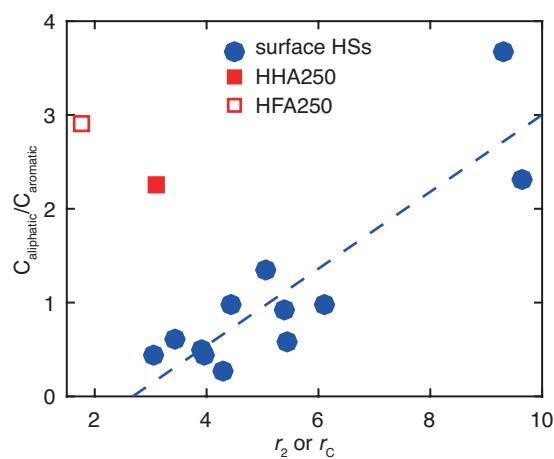
A schematic of the TRLFS setup is given in Figure S1 below. The excitation source was second harmonic generation of 130-fs Ti:sapphire laser (Tsunami, Spectra-Physics) coupled with a regenerative amplifier (Spitfire, Spectra-Physics) and a frequency doubler/pulse selector (model 3890, Spectra-Physics) to increase the output power and to convert the wavelength to 394 nm. A beam splitter was put on the path of the laser light to monitor the variation of the laser power during sample measurements. Typical laser power and the repetition rate were 0.1 mJ/pulse and 1 kHz, respectively. The fluorescence from a sample was collected at 90° to the excitation beam into the entrance slit of a Czerney-Turner spectrograph (Shamrock RS 303i, 300 lines/mm, Andor Technology) through two plano-convex fused silica lenses. The width of the slit was 200  $\mu\text{m}$ . The fluorescence spectra were measured by a time-gated ICCD camera (iStar, Andor Technology). Fifty temporal scans were collected with the gate width and step of both 19  $\mu\text{s}$  and initial delay of 10  $\mu\text{s}$ . Two hundred measurements were accumulated for each sample.



**Figure S1.** Schematic of the setup of the TRLFS measurements used in this study.



**Figure S2.** Relationship between the lifetimes of Factor 2 ( $\tau_2$ ) of HHA250 and HFA250 or Factor C ( $\tau_C$ ) of the surface HSs in ref. 30 at 0.01 M NaClO<sub>4</sub> and the half-width band of electronic transition (ET) absorbance  $\Delta_{ET}$  of the HSs. The dashed lines are the regression lines for the surface FAs and SRHA and for the surface HAs with terrestrial origins.



**Figure S3.** Relationship between the peak ratios of Factor 2 of HHA250 and HFA250 ( $r_2$ ) or Factor C ( $r_C$ ) of the surface HSs in ref. 30 at 0.01 M NaClO<sub>4</sub> and the ratio of aliphatic and aromatic carbon contents ( $C_{aliphatic}/C_{aromatic}$ ) deduced by <sup>13</sup>C NMR.