

A new procedure to synthesize fulvic and humic acids. Determination of their physico-chemical properties using XRD, LC-APCI-MS, and optical spectroscopy

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In order to better understand the role played by fulvic acids (FA) and humic acids (HA) in low temperature geochemical processes, FA and HA model compounds are routinely synthesized in the laboratory, although under high oxidation conditions ($fO_2 \approx 0.1$ MPa). As a result, the products obtained may not be representative of the FA and HA which form in the environment. This study reports the synthesis of FA and HA in four aqueous systems of (1) catechol ($C_6H_4(OH)_2$), (2) catechol and acetic acid (CH_3COOH), (3) catechol and glycine (NH_2CH_2COOH), and (4) catechol and cysteine ($NH_2CH(CH_2SH)COOH$) as a function of pH (5.5-10.0) as well as functional groups ($-OH$, $-COOH$, $-NH_2$, and $-SH$) under atmospheric oxidation conditions at 25°C and 0.1 MPa.

Equilibrium in all four systems was reached after eight weeks. Determination of the reaction products was performed by X-ray diffraction, ATR-FTIR, and UV-visible spectroscopies, and LC-APCI-MS. All solid products (i.e. FA and HA) appear to be amorphous. Synthesized FA and HA belonging to three groups of m/z ratio (m = molecular mass, z = charge) of 317, 759 and 1566 have been obtained. In system (1), synthesized FA and HA correspond to assemblages of 2 to 6 catechol molecules with two functional groups: alcohol and ether. In addition, ester functional groups were observed in systems (2)-(4). Elemental analysis also indicated that some nitrogen was incorporated into the FA and HA of systems (3) and (4). In contrast, the use of cysteine in system (4) did not allow to synthesize FA and HA with thiol groups.

These synthetic model fulvic and humic acids are currently being used as reference compounds in experiments devoted to quantifying the complexation and transport of inorganic and organic pollutants by these species in natural aqueous systems.

The HFSE budget of post-collisional high-K basalts and shoshonites

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High-K basalts and shoshonites are an important trace element-enriched endmember among subduction zone rocks. They mainly occur in post-collisional settings or in arc systems with a high flux of subducting sediments. Ancient lithospheric mantle is another possible source explaining the unusual trace element enrichment. Previous studies (e.g. [1, 2]) have reported extremely elevated Nb/Ta ratios (up to 30) in high-K basalts from Indonesia and New Zealand. There is also some evidence for elevated Nb/Ta ratios in basalts originating from the continental lithosphere [3]. Hence, high-K basalts and shoshonites might probe a high-Nb/Ta reservoir in the Earth's mantle that may significantly contribute to the global element budget of Nb and Ta.

In order to elucidate the HFSE inventory of K-rich subduction-related rocks, we obtained high-precision HFSE concentration (Nb, Ta, Zr, Hf) and Sr-Nd-Hf isotope data for a suite of syn- to post-collisional lavas from the Eo-Oligocene Eastern Rhodope province, SE Bulgaria. The compositional spectrum of these volcanic rocks comprise mafic high-K lavas, shoshonites and absarokites. The data were obtained using a mixed Zr-Hf-Ta-Lu tracer and the Neptune MC-ICP-MS at Bonn university. With respect to their HFSE ratios, the high-K basalts and shoshonites lie well within the MORB array ($Zr/Nb = 11.3 - 20.5$, $Nb/Ta = 12.8 - 15.1$ and $Zr/Hf = 39.5 - 41.7$). However, absarokites yield significantly higher Nb/Ta than MORB (16.2 – 19.8) at Zr/Hf of 34.6 – 37, which is possibly related to the fractionation of phlogopite.

In ϵHf - ϵNd space, the samples broadly define the expected positive trend but are offset from the mantle array towards more unradiogenic ϵNd (ϵHf -0.4 to +3 and ϵNd -5 to -1.5). $^{87}Sr/^{86}Sr$ compositions range from 0.7070 to 0.7085.

These isotope systematics together with the HFSE indicate a relatively young, possibly Tertiary, overprint of the mantle source region by melts rather than fluids, involving no significant HFSE fractionation. Collectively, there is no evidence from the Bulgarian lavas for the presence of a volumetrically important high Nb/Ta reservoir in the sources of high-K magmas.

[1] Stolz *et al.* (1996) *Geology* **24** 587-590, [2] Münker *et al.* (1998) *Chem. Geol.* **144** 23-45, [3] Pfänder *et al.* (2002) *Geochim. Cosmochim. Acta* **66** 15A