Dissolution kinetics of Pd and Pt from automobile catalysts by naturally occurring complexing agents

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Powder samples prepared from gasoline (Pt, Pd, Rh, new GN/old GO) and diesel (Pt, new DN/old DO) catalysts and recycled catalyst NIST 2556 were tested by kinetic leaching experiments following 1, 12, 24, 48, 168, 360, 720 and 1440-hour interaction with solutions of 20 mM citric acid (CA), 20 mM $Na_2P_4O_7$ (NaPyr), 1 g L^{-1} NaCl (NaCl) and a fulvic acid solution (FA- DOC 50 mg L^{-1}). The mobilization of Pt metals into solution was fastest through the effect of CA and NaPyr. In the other interactions (NaCl, FA), the release of PGE is probably followed by immobilization processes and the interactions cannot be considered to correspond to simple release of Pt metals into solution. Because of their low concentrations, the individual complexing agents did not have any effect on the speciation of Pd and Pt in the extracts; both metals are present in solution as complexes (Me $(OH)_2$, Me $(OH)^+$). Immobilization can take place through the adsorption of the positively charged hydroxyl complexes or flocculation of fulvic acid complexing the Pt metals on the surface of the extracted catalysts. The calculated normalized bulk released NRi values are similar to the reaction rate, highest in solutions of CA and NaPyr.

$^{87}Sr/^{86}Sr$ isotope ratios in single benthic foraminifera by LA-MC-ICPMS

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$^{87}Sr/^{86}Sr$ analysis of foraminifera is usually performed from solution samples using either TIMS or MC-ICPMS techniques. With increasing precision offered by recent advances of laser ablation instrumentation, the LA-MC-ICPMS approach rivals solution work in terms of precision, and outperforms conventional solution techniques in terms of sample throughput and time needed per analysis.

Within an ongoing paleoclimatic study, we have determined $^{87}Sr/^{86}Sr$ isotope ratios from single tests of the benthic foraminifera *Quinqueloculina* sp. from a Neogene hyperhaline paralic sequence in Central Anatolia, Turkey. The analytical setup used consists of a RESOlution M-50 excimer LA instrument (λ=193 nm) including a factory-built Laurin two-volume sample cell, coupled to a Thermo Neptune MC-ICPMS. During 60 seconds of data acquisition a 200-300 μm long line was ablated (8 Hz, 3.5 J/cm^2) with pit diameter varying between 53 to 140 μm. After correction for interferences from Rb, Kr, Ca-dimers and doubly-charged REE, all Sr isotope data were corrected for mass fractionation ($^{86}Sr/^{88}Sr = 0.1194$) and normalized to NIST SRM987 using $^{87}Sr/^{86}Sr$ of 0.71025. Repeated measurements on a recent coral from the Red Sea (~3000 ppm Sr) yielded $^{87}Sr/^{86}Sr$ ratios of 0.709235 ± 0.000023 (2σ s. d.).

For the *Quinqueloculina* sp. tests, pit diameter were adjusted to 80 or 120 μm and the ablation path was located at the topmost part of the curved, quasi-globular test surface. $^{87}Sr/^{86}Sr$ ratios cover a range from 0.707174 ± 0.000032 to 0.707255 ± 0.000027, with calculated net reproducibilities being in the range of as low as ±0.00004 (2σ s. d.).

Overall, the LA-based analysis of $^{87}Sr/^{86}Sr$ in foraminifera is likely most suitable in cases where low sample amounts (e.g. high-resolution stratigraphic work on drillcores) and/or high sample numbers are dealt with; i.e. for material otherwise not providing the necessary Sr concentration in the final solution, or requiring time-consuming Sr separation and solution work.