

***In situ* measurements of Cu isotopes in Cu sulphides**

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Previous investigations observed Cu isotope fractionation in hydrothermal or porphyry ore deposits in the order of 2‰ [1, 2]. If such Cu isotope variations occur within a single ore body or mineralisation vein, they likely point to changes of the redox conditions or salinity of hydrothermal fluids [2, 3], rather than source heterogeneities. To distinguish these processes we are developing a method of *in situ* copper isotope analyses by femtosecond LA-MC-ICP-MS.

Initial tests were conducted using in-house standards of Cu metal, brass and Cu-sulphide minerals (chalcopyrite, covellite and enargite) that are homogeneous regarding their major elements. For comparison, the copper isotope composition of these in-house standards was also analysed by solution MC-ICP-MS. In both cases in-house standards were measured relative to the Cu (NIST976) standard while Ni (NIST986) was used to monitor instrumental mass bias [3]. For replicated analyses of metal in-house standards relative to NIST976, in both laser ablation and solution modes the precision of <0.05‰ for $\delta^{65}\text{Cu}_{\text{NIST}}$ was achieved. Replicated LA-MC-ICP-MS analyses of minerals relative to NIST976 or in-house standards of the same mineral, revealed reproducibility variations for $\delta^{65}\text{Cu}$ of ~0.2‰. The laser ablation analyses of the in-house mineral standards agreed within 0.15‰ ($\delta^{65}\text{Cu}$) with those obtained by solution analyses. The larger scatter of the mineral standards (relative to metals), obtained by laser ablation, likely indicates Cu isotopic heterogeneities within the analysed minerals.

First *in situ* Cu isotope measurements of samples from the Bor hydrothermal ore deposit (East Serbia) reveals differences of ~0.35‰ in $\delta^{65}\text{Cu}$ between chalcopyrite in veins and those dispersed as small grains. These systematic variations likely imply a change in the composition of hydrothermal fluids.

[1] Zhu, X. K., O'Nions, R. K., Guo, Y., Belshaw, N. S. & Rickard, D. (2000). *Chem. Geol.* **163**, 139-149.

[2] Li, W., Jackson, S. E., Pearson, N. J. & Graham, S. (2010). *Geochim. Cosmochim. Acta* **74**, 4078-4096.

[3] Markl, G., Lahaye, Y. & Schwinn, G. (2006). *Geochim. Cosmochim. Acta* **70**, 4215-4228.

Regeneration of organophilic zeolites after sulfamethoxazole antibiotic adsorption

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The large amount of non-biodegradable sulfonamide antibiotics used in hospitals, feedstocks and in fish farming cause their occurrence in the aquatic environment resulting in the dramatic emergence of antibiotic resistance in fish pathogens and in the transfer of these resistance determinants to bacteria in land animals and to human pathogens [1]. In Italy, it was found that sulfamethoxazole (SMX) is one of the most abundant residual drug in surface waters [2]. Recently, it has been proven that high-silica zeolites (Y, ZSM-5 and MOR) are environmentally compatible adsorbents able to effectively remove sulfamethoxazole when dissolved in aqueous matrix [3]. The effective incorporation of this pollutant inside the zeolite cavities has been demonstrated by combining diffraction and spectroscopic techniques [3].

In this work, the thermal regeneration of hydrophobic high-silica ZSM-5 and hydrophobic high-silica zeolite Y after sulfamethoxazole adsorption was investigated using *in situ* high-temperature synchrotron X-ray powder diffraction (GILDA, ESRF) to monitor the structural modifications induced by heating. The evolution of the structural features was followed both in temperature ramp (25-575°C, heating rate 10 °C/min) and in isotherm mode (120 minutes at 575 °C) by full profile Rietveld refinements.

Structure refinements demonstrate that the thermal regeneration accompanied by the full degradation of SMX is completed at about 575 °C and it does not affect the crystallinity of the sorbing materials. These results indicate that high-silica zeolite Y and high silica ZSM-5 are affordable materials for water clean-up and drug delivery.

[1] Acar *et al.* (2001) *Rev. Sci. Tech.* **20**, 797- 810. [2] Castiglioni *et al.* (2006) *Environ. Sci. Technol.* **40**, 357-363.

[3] Blasioli *et al.* (2011) *Advances in Zeolites Science and Technology*, De Frede Eds., Napoli, 49-52.