Non-Innocent role of electron-mediating ligands in reductive dissolution of hematite

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Reductive iron (III) oxide dissolution is a primary source of soluble ferrous ions in environment [1]. It can be mediated biotically (e.g., by dissimilatory metal reducing bacteria) or abiotically (e.g., by organic reductive pollutants in anthropogenic environment) [1]. The reductive dissolution is promoted by surface protonation, adsorption of chelating electron-donating ligands (e.g., ascorbate, hydroquinone. sulfide) [2,3,4,5] and chelating electron-mediating ligands (e.g., dicarboxylic acids) [1,6]. Despite the decades of research, we still do not fully understand mechanism of iron(III) oxide reductive dissolution on a molecular level. For instance, in some cases addition of the Fe(II) ions facilitates dissolution (e.g., in the presence of oxalate, ascorbate, EDTA) [7,8], whereas in others it inhibits iron reduction (e.g., AH_2DS, microbial systems) [9-11]. The same appears to be true for surface-bound ligands, that is, some are able to promote surface dissolution by assisting Fe(II) detachment (e.g., oxalate, citrate) [9], while others block surface sites (e.g., chromate, arsenate) [1,11]. Surface protonation plays also an important, synergestic role in hematite dissolution [1].

Here we report the molecular modelling and electrochemical studies of the non-innocent role of the electron-mediating ligands bridging the surface ferric ions with the external reductants.

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LA ICP-MS Trace element and oxygen isotope variation of vanadium-rich Ruby and Sapphire within Mogok Gemfield, Myanmar

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Rubies and sapphires attract scientific and commercial interest, e.g. the renowned Mogok, Myanmar gem field. These gemstones are corundum colored by transition elements within the alumina crystal lattice: sufficient Cr^{3+} gives red in ruby and Fe^{2+}, Fe^{3+} and Ti^{4+} ionic interactions color sapphires; a minor ion, V^{3+} introduces slate to purple colors and color change effects in some sapphires, but its role in coloring rubies remain enigmatic. Trace element and oxygen isotope values provide genetic signatures for natural corundum and assist geographic typing. Precise LA-ICP-MS analysis of ruby and sapphire from Mogok placer and *in situ* deposits reveal V can exceed 5000 ppm, giving V/Cr, V/Fe and V/Ti ratios up to 26, 78 and 97 respectively. Such values significantly exceed those elsewhere and are focused on a specific area, suggesting a geological control on V-rich ruby distribution. Our results demonstrate that detailed geochemical studies of ruby suites can reveal new gemmological, gem grading and gem exploration insights. They give V a greater role as a ruby tracer, encourage comparisons of V/Cr-variation between ruby suites and widen modelling of ruby genesis.

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