Metamorphic and geodynamic evolution of the high-grade units of Mundão – Sátão (Northern Portugal)

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The Mundão – Sátão sector (N Portugal) is composed of syn- to post-D$_3$ Hercynian granitoids and by pre-Ordovician metasediments, belonging to the Schist – Greywacke Complex of the Iberian Central Zone. The metasediments comprise two low-grade sequences (chlorite to biotite zones), Ponte Chinchela and Nelas Units, separated by the exotic high-grade tectonometamorphic sequence of the Casinha Derrubada Unit (CDU) [1] that includes three tectonic slices separated by thrusts, from bottom to top: a) micaschists and mylonites with sillimanite; b) mylonites with porphyroclastic staurolite; and c) biotitic micaschists with garnet.

The CDU is a MP metamorphic sequence associated with the establishment of the metamorphic peak during D$_2$. Late retrograde evolution is evidenced by prismatic andalusite pseudomorphs after porphyroclastic staurolite, and andalusite + biotite coronas around staurolite rims. These textural evidence are coeval with the reorientation of staurolite prismatic crystals from sub-horizontal to sub-vertical and late incipient migmatization by decompression and crossing of the granite wet solidus curve during D$_3$ exhumation phase.

The observed petrological/geochemical features and the paragenetic evolution of the CDU high-grade rocks imply that this area is not a typical contact metamorphic sequence [2] or a complete Barrovian-type sequence arround an anatectic dome [3]. The new data points out the existence of net-tectonic control on the emplacement of the high-grade rocks at this sector and that the CDU is an incomplete Barrovian-type sequence from MT to HT, subsequently exhumed onto a low-grade metamorphic sequence. The evidence suggest that the tectonometamorphic evolution of the CDU rocks is consistent with a clockwise P-T-t path, involving: 1) a metamorphic peak at $T \sim 600 - 700$ ºC and $P \sim 6 - 7$ kbar; 2) significant decompression to 2 – 3 kbar; 3) rapid cooling as the result of thermal readjustment to higher crustal levels.

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Surface transformations and element cycling resulting from interfacial Fe(II)-Fe(III) self exchange

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Biogeochemical iron cycling induces coupled electron transfer and atom exchange between aqueous Fe(II) and Fe(III) oxide surfaces [1-4]. Our recent work [5] has explored the molecular-scale structural transformations of hematite surfaces that result from this process. Under both acidic (pH 3) and neutral (pH 7) conditions Fe(II) induces layer-by-layer dissolution or growth of the hematite (110) and (012) surfaces. In contrast, the hematite (001) surface develops a <1 nm-thick discontinuous film that displays structural relaxations different from the underlying surface. This demonstrates that Fe(II) activates localized growth and dissolution independent of macroscopic Fe(II) adsorption.

We have further explored the effect of this process on the fate of the structurally-compatible trace element Ni. For both hematite and goethite we observe that aqueous Fe(II) induces the incorporation of adsorbed Ni into the iron oxide structure. In addition, pre-incoporated Ni is released into solution by Fe(II). The rates of release and incoporation are orders of magnitude slower than the rate of macroscopic Fe(II) adsorption but comparable to iron isotope equilibration [3]. We propose that Fe(II) catalyzes a thermodynamically-controlled redistribution of Ni among the mineral bulk, mineral surface, and aqueous solution. This work has implications for the validity of proxies for ocean composition on the early Earth and micronutrient and contaminant availability in soil, sedimentary, and aquatic systems.

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