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## Fe-Si oxides tracing the ongoing low-T° hydrothermal alteration of exhumed serpentinites at the ultraslow-spreading Southwest Indian Ridge

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#### Abstract

On the smooth seafloor of exhumed mantle-rocks of the slow-spreading Southwest Indian Ridge, the secondary oxide and carbonate mineralizations record specific chemical signatures of the alteration of serpentinites by low-temperature hydrothermal seawater-dominated fluids. The uncommon characteristics of Fe-oxides forming nodule cortex or thick encrustments are their high Si, low Mn contents, trace elements (e.g. Cr) and REE behavior. Oxides composition evolves through time. Associated to oxides, carbonates (aragonite, calcite, dolomite) characterize the matrix of young indurated serpentinite breccias found at ridge axis. Such mineralogical and geochemical sequences trace, as proxies, the ongoing mantle-exhumation and serpentinization process linked to the detachment faults, and the late alteration reactions that impact on crust–ocean transfers and oceanic budget. © 2017 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license

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#### 1. Context

At slow-spreading ridges, the seafloor is partially and locally formed by detachment faults leading to the exhumation of mantle-derived rocks. Such detachments occur at magma-starved segments of Mid-Atlantic Ridge, and Ocean-Continent Transitions of magma-poor rifted margins<sup>1-3</sup>. Small amounts of melt into the upper lithosphere and magmatism initiation may enhance the hydrothermal circulation, leading to more efficient and gradual serpentinization reactions<sup>2,4</sup>. Tectonic and hydrothermal related processes may leave an imprint in the

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exhumed serpentinized rocks exposed at the seafloor and in first overlying sediments<sup>5,6</sup>. The further post-exhumation interaction between low-temperature seawater-derived fluid and serpentinite, that results in authigenesis of specific phases such as carbonates, silicates and oxides, extends the chemical transfers and may impact the oceanic mass budget<sup>6,7</sup>. The specific signature derived from alteration of exhumed mantle rocks may be recorded in the first sedimentary deposits and could be a good proxy for the identification and understanding of such processes in ancient analogue domains. The study focuses on the peculiar sedimentary facies, Fe-encrusted highly altered serpentinites which often form centimetric nodules and breccias found on the young (<10 Ma) exposed smooth seafloor of the Southwest Indian Ridge (SWIR). The aim is to define their mineralogical and chemical specificity and to evidence the late fluid-rock reactions linked to the serpentinization and rocks exhumation along active detachment systems.

#### 2. Geological setting and sampling

In the Indian Ocean the ultra slow-spreading SWIR revealed up to 100 km long sections of non volcanic seafloor in their deepest parts with active and relict detachment faults, with no equivalent in other ridge systems<sup>8</sup>. In easternmost part of the SWIR, such so-called "smooth seafloor" zones with rare volcanic activity were extensively mapped and dredged during the MD183 cruise of *RV Marion Dufresne* (Fig. 1). Detachment faults dip both toward and away from the ridge axis evidencing cross-cutting relationships and flipped polarities. Former detachments are cut by new faults bringing up mantle-derived rocks on each axis sides. Dredges reveal that the smooth seafloor is made of prevalent highly to fully serpentinized peridotites and scarce gabbros; very few altered basalts have been recovered. Serpentinization and veining fluid-rock reactions are due to reducing, mildly alkaline seawater-derived fluids<sup>9</sup>. The determined fluid pathways draw a large-scale fluid circulation in the footwall of the detachment faults<sup>9</sup>.



Fig. 1. (a) bathymetric map and dredge locations of the two corridors investigated during the Smoothseafloor cruise<sup>8,9</sup>; (b) simplified section of the western corridor from site DR21 to site DR23<sup>8</sup>.



Fig. 2. Deposits overlying SWIR smooth seafloor. (a) nodules with a core of altered serpentinite and cortex of Fe-Si-Mn oxides (DR15); (b) thick botryoidal crust covering residual highly altered serpentinite (DR34 far from ridge axis); (c) indurated serpentinite breccia with carbonated matrix (DR29, near ridge axis).

At many sites the serpentinites display very altered features becoming highly muddy, brownish red and Feoxyhydroxide rich. Abundant nodules and often thick, massive Fe-oxide crusts, as well as indurated carbonated serpentinite breccias, similar to serpentinite gouges, are found at most sites (Fig. 2) and were analyzed (conventional XRD and SEM at CNRS Strasbourg; ICP-OES and ICP-MS data by CNRS-SARM, Nancy). In the area, the sedimentary cover is thin given the seafloor age <10 Ma and a deep CCD (~ 5000m), and pelagic calcareous oozes mixed with fine and silty debris of altered mantle rocks were recovered in all dredges.

# 3. Characterisitics of the oxide deposits, breccia cements and sediments: imprints and paths of the mantle seafloor alteration

The nodule cortices and crusts are thin in samples near the ridge axis and display increasing thickness in older samples, recording successive episodes of oxide accretion (Figs. 2, 3a,b). Oxides are poorly crystallized as ferrihydrite, goethite and birnessite-like phases. SEM data specify that Si is bonded to Fe-phases. Authigenic association of aragonite and calcite is abundant in most oxide encrustments and indurated breccia cements and veins from near axis dredges (e.g. DR15, 17, 06, 01 from W-corridor, DR20, 29 from E-corridor). An unusual late cogenetic mineral association of authigenic dolomite and new globular serpentine, fitted in oxides layers, is found in samples close to the ridge axis (e.g. DR15; Fig. 3c).



Fig. 3. SEM images. (a) Si-Fe-(Mn)-oxide of DR11 crust; (b) cauliflower-like Fe-(Mn) oxide of DR15 nodule cortex; (c) new formed globular serpentine and dolomite in oxide layer, DR15 nodule cortex – SEM-BSE; (d) aragonite formed within altered serpentine sheets, DR29 breccia.



Fig. 4. Geochemical behavior of oxides, breccia cements and sediments overlying exhumed mantle. (a) Bonatti's diagram showing the hydrothermal signature of oxides; (b) Cr-Y-La relationships: changes of oxides with sources and time; (c) Ce/Ce\* vs Nd<sub>n</sub>/Yb<sub>n</sub>: tracing the imprint of fluids and oxidative evolution of oxides.

The composition of carbonated matrices of serpentinite breccias evidences both the signature of SWIR mantle source, which is higher in aragonite samples, and the seawater contribution (e.g. REE, Fig. 4). Stable aragonite formation at depth in mantle-rocks is assigned to moderate to low-T<sup> $\circ$ </sup> hydrothermal reactions<sup>10,11</sup>. The composition of sediments is due to the mixing between seafloor silty components and the pelagic biogenic calcite (Fig. 4).

The oxides record specific geochemical signatures of the alteration progress of the SWIR serpentinites. The oxides are Fe-Si-rich (Fe<sub>2</sub>O<sub>3</sub>: 27-43%; SiO<sub>2</sub>: 9-20%; MnO: 5-20%) and have very low Al and Ti contents. Such

compositions fall in the hydrothermal field of conventional diagram [Fe-Mn-(Ni+Co+Cu)\*10] (Fig. 4a). The oxides evolve through time, as encrustments nearest to the SWIR axis, and youngest cortex layers show the highest contents in Cr (Fig. 4b), Cu, Ni, Mg. The oxides from the more volcanic sites, on basalt fragments differ with higher Mn, La, Th and Mo contents but also record low-T° hydrothermal imprint (Fig. 4a). The REEs content of oxides is correlated to Fe content and the negative Eu anomaly (0.75-0.72) unvaries. The Nd<sub>n</sub>/Yb<sub>n</sub> ratio (>3.5) is related to a deep hydrothermal fluid contribution while positive Ce anomaly (Ce/Ce\*) marks an oxidative evolution (Fig. 4c).

According to their composition (low Mn/Fe, high Si, Cr, Th, REE...) the oxides on SWIR serpentinized seafloor clearly differ from oxides found in basalt-seated hydrothermal sites (e.g. EPR, JDFR sites), and from deep-sea hydrogenetic concretions. Si-rich Fe-oxide crusts form after the carbonatation of serpentinite breccias (aragonite, calcite), their growth appears relatively rapid and allows peculiar mineral cogenesis (e.g. dolomite and secondary serpentine) to occur. These mineralogical sequences strongly differ from those due to the long-term cold seawater alteration of abyssal serpentinites that forms Mg-clay phases<sup>7</sup>. The mineralogical sequences relate the progress of an active fluid-rock reaction under moderate T° conditions<sup>10,11</sup>, and implying a gain of Ca, Mg, Fe, Si, and Cr. The mixed end-members fluids are the low-T° mantle-derived upward flow and the seawater (isotopic data in progress). The conditions near axis at seafloor surface are fairly oxidative. At investigated SWIR segment no hydrothermal vent was detected, and therefore the intense alteration reactions should be driven by a convective flow along faults that was initially related to the exothermic serpentinisation process as well as local magmatic activity.

#### 4. Implications and conclusion

On the SWIR smooth seafloor, the carbonate-oxide parageneses record the late serpentinization by-products from hydrothermal fluid upward circulation along detachment faults, as well as the progress of subsequent alteration by seawater-dominated fluid on the young seafloor. The mineralization sequence of imbricated carbonates and Si-rich oxides, overlying the young brecciated serpentinized seafloor, is still rarely investigated and seems to firstly reflect specific alteration conditions at ridge axis, with a slight influence of localized bedrock heterogeneities. The surficial fluid convection, with oxidizing seawater infiltrating along shallow parts of detachment faults and that mixes with deep fluids, enhances the fluid-rock reactions near surface and the mineral authigenesis.

However the peculiar chemical trap of elements mobilized by the moderate to low-temperature reactions (e.g. Fe, Si, Mg, Cr, Mn) makes that these sequences are good proxies of mantle exhumation processes at ultra-slow spreading ridges, similar to those occurring in core complexes of mid-oceanic ridges or magma poor rifted-margins. Such proxies could be particularly important for understanding the fossil and/or embryonic oceanic domains settings as well as the evolution of crust-ocean transfers and fluxes through time.

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