

Green-clays and the coastal biogeochemical cycles of trace metals

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In New Caledonia, erosion of massive lateritic Ni ores associated with ultramafic rocks have lead to trace metals concentrations in mangrove and lagoon sediments that are up to 1000 times higher than in similar coastal ecosystems worldwide [1,2]. Such a geochemical anomaly represents a unique opportunity to identify early diagenetic processes and mineral transformations that govern biogeochemical cycles of traces metals in modern and ancien coastal ecosystems. In this study, we have followed Ni, Fe, Cr and Mn speciation across a shore-to-reef gradient downstream one of the largest mined lateritic Ni ore in New Caledonia. Our XAS results indicate a major contribution of clays to the speciation of the trace metals investigated with a very minor contribution of sulfide minerals. The clay contribution slightly decreases across the shore-to-reef gradient to the benefit of goethite for Fe, Ni and Cr. This decrease is more pronouced for Mn due to the increasing contribution of carbonates minerals when approaching the coral reef. The clay contribution to trace metals speciation in the lagoon sediments is significantly larger than the one we observed in upstream mangrove sediments where Fe-sulfides equally contribute to Ni speciation [1,2], as well as in surrounding lateritic minerals where Fe and Mn-oxides are also major Ni, Cr and Mn hosts [3,4,5]. TEM-EDX characterization of the Fe and trace metal-bearing clays in the lagoon sediments reveals a mixture of chrysotile, Fe-rich smectite and greenalite/berthierine. The lack of the latter clay specie in the upstream laterite and mangrove sediments supports its authigenic origin in the lagoon environment, while the other clays would be more likely inherited. The significant contribution of this mineral specie to Ni, Cr and Mn speciation suggests that the recently proposed underestimated role of green-clay authigenesis in the coastal/marine biogeochemical cycle of Fe [6] might also apply to these trace metals.

[1] Noël et al. (2014) *GCA* **136**, 211-228. [2] Noël et al. (2015) *GCA* **169**, 82-98. [3] Dublet et al. (2012) *GCA* **95**, 119-133. [4] Dublet et al. (2015) *GCA* **217**, 1-15. [5] Fandeur et al. (2009) *Am. Min.* **94**, 710-719. [6] Baldermann et al. (2015) *Nat. Geosc.* **8**, 885-890