Iron oxidation state in serpentine during subduction: implications on the nature of the released fluids at depth

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Serpentinites may be present in more than 40% of the oceanic lithosphere that formed at slow to ultra-slow spreading centers. Serpentine could thus be one of the most abundant hydrated minerals recycled into the mantle in subduction zones. Prograde metamorphism in subducted serpentinites is characterized by the destabilization of lizardite into antigorite, and then into secondary olivine. The nature of the released fluid (e.g. H_2O vs H_2) during those phase transitions is controlled by redox reactions and can be inferred from Fe oxidation state of serpentine. We used whole rock analyses, magnetic measurements, SEM observations and μXANES to establish the evolution of Fe_{total} and magnetite content in serpentinite as well as Fe speciation in serpentine minerals from the ridge to the subduction setting.

At the mid-ocean ridge, during the alteration of peridotite into serpentinite, the iron is mostly redistributed between magnetite and oceanic serpentine (usually lizardite). The Fe^{3+}/Fe_{total} ratio in lizardite and the modal magnetite progressively increase with the local serpentinization degree to reach 0.8 and 7 wt% respectively in fully serpentinized peridotites.

During subduction, the Fe_{total} of serpentinite remains constant (=7-10 wt.%, depending on the primary mode of the peridotite) while the magnetite mode decreases from greenschist to eclogite facies to reach less than 2% under the eclogite facies. Also, the Fe^{3+}/Fe_{total} ratio in serpentine progressively decreases down to 0.2 during the transition from lizardite to antigorite.

Our results show that, in the first 70 km of subduction, the transition from lizardite to antigorite is accompanied by a global reduction of Fe in serpentinite and in serpentine. This redox reaction allows the oxidation of reduced oceanic phases such as sulfurs, and the formation of oxidized fluid. At greater depths, the beginning of antigorite dehydration leads to an increase of Fe^{3+}/Fe_{total} in the remaining antigorite implying the formation of reduced fluids (e.g. H_2, CH_4).

The National Geochemical Survey of Australia (NGSA) project

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The National Geochemical Survey of Australia (NGSA) project (www.ga.gov.au/ngsa), part of Geoscience Australia's Onshore Energy Security Program 2006-2011, was carried out in collaboration with all state and territory geological surveys. It delivered Australia's first national geochemical atlas, the underpinning geochemical database, and a series of reports and papers.

Catchment outlet sediments (mostly similar to floodplain sediments) were sampled in 1186 catchments covering ~6.2 million km^2 or ~81% of the country (on average one sample per 5200 km^2). Samples were collected at two depths (0-10 cm and ~60-80 cm), each sieved to two grain size fractions (<2 mm and <75 μm) and analysed for total, aqua regia, and Mobile Metal Ion® element contents; other analyses (pH, electrical conductivity, grain size distribution, spectroscopy, etc.) were also performed.

Results to date have been used to: (1) investigate first-order controls on the geochemical makeup of Australian regolith in comparison to Europe; (2) compile preliminary, multi-continental, empirical 'Global Soil' reference values; (3) produce continental-scale soil pH maps; (4) map Fe oxide mineralogy and soil colour; (5) investigate the level and distribution of bioavailable elements in Australia; (6) determine element associations by multivariate statistical methods and compare resulting patterns to independent geoscience datasets; (7) model the distribution of soil carbonate using multiple environmental covariates; (8) assess the potential of the dataset for mineral prospectivity analysis (e.g., for base metals, U, Au and REEs); (9) select salt lakes to be investigated for their potential to host potash, Li and B resources; (10) ground truth, infill and 'correct' airborne radiometric concentration data for K, U and Th; and (11) shed light on the phenomenon of disequilibrium in the radioactive decay chain of U by comparing actual to estimated U concentrations at the continental scale.

The NGSA project was Australia's first national-scale geochemical survey, requiring certain strategic decisions to be taken about sampling medium, density, etc. The resulting atlas and dataset have proven useful and applicable to many end-uses, but limitations and challenges exist as in every geochemical survey.

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