

## TRACE ELEMENTS IN BRAZILIAN OILS: INDICATIONS FOR A SERPENTINIZING MANTLE SOURCE

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We have determined the trace element compositions of 68 Brazilian and nine foreign oils by ICP-MS and compared them to the UB-N serpentinitized fertile mantle reference material, as well as to mantle, crust, and seawater compositions in the Earthref database. 24 trace elements were analysed (in order of atomic numbers): Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, Mo, Ag, Ba, La, Ce, Pr, Nd, W, Pb and U. The 77 oils show good correlation with chondrite ( $r^2=0,77$ ) and serpentinitized fertile mantle ( $r^2=0,76$ ); moderate correlation with continental crust ( $r^2=0,35$ ), and none ( $r^2=0,02$ ) with seawater (Szatmari et al., 2005).

The 77 oils are high in Ni, Fe, and V, and their median composition correlates well with serpentinite (Fig. 1).

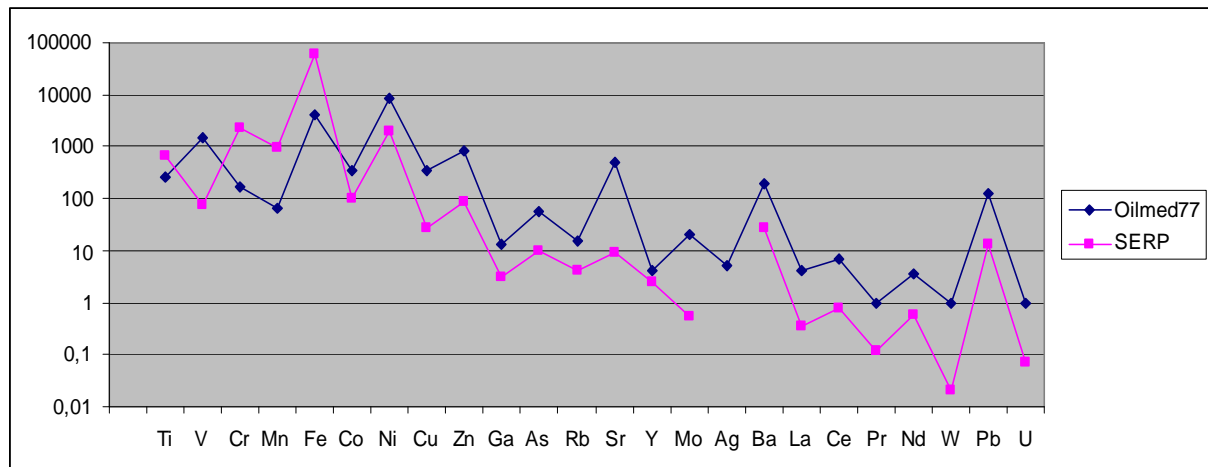


Figure 1. Trace elements in median of 77 black oils (ppb, blue) and UN-B serpentinite (ppm, red).

The median values of the trace elements in the oils are  $10^2$  times below those of serpentinite. But, relative to serpentinite, Fe, Cr, Mn and Ti are lower: Ti is  $10^3$  times, Fe, Cr, and Mn are  $10^4$  times below serpentinite values. We attribute both the serpentinite-like composition of the oils and these lower values to synsedimentary serpentinitization of the continental lithospheric mantle by infiltrating water below sedimentary basins (Szatmari, 1989; Szatmari et al, 2005) where the crust is tectonically thinned or partially unroofed (as on the Iberian margin). Magnetite (and related oxidized minerals) forming during serpentinitization immobilize Fe, Cr, Mn, and Ti decreasing their concentrations in the fluids.

Massive oxidation of the  $\text{Fe}^{2+}$  ion by the dissociating water generates hydrogen during serpentinization, forming the most reducing environment on the earth's surface (Janecky & Seyfried, 1986). Hydrocarbons may form in this highly reducing environment by Fischer-Tropsch synthesis (Szatmari, 1989; Holm and Charlou 2001) with the hydrogen generated during serpentinization reacting with dissolved or gaseous  $\text{CO}_2$  as in the Lost City hydrothermal field over the Atlantis high (Früh-Green, G.L, 2003; Kelly et al., 2005). The hydrocarbons formed are fed upon by archaea and bacteria, making the proportion of chemogenic to biogenic hydrocarbons hard to determine. Talc-stevensite deposited in the lower Cretaceous pre-evaporitic sequence of Brazil's Atlantic margin together with organic-rich source rocks, may be derived by from partially unroofed serpentinizing peridotites.

While Ni concentrations in the black oils are fairly constant at about  $10^4$  ppb, V concentrations and V/Ni ratios vary in our dataset by seven orders of magnitude and are characteristic of each basin, being lowest in the lacustrine Recôncavo basin. V enriched in petroleum from sea water and perhaps ultimately from basalts. V/Ni ratios form a well-defined mixing line from chondrite to seawater values, with the lacustrine Recôncavo oils at the chondritic end of the line.

Pb/Ni ratios are seawater-like. Sr is contained in residual formation brines retained in the oils. Sr/Ni - Ba/Ni ratios in the oils form a straight mixing line between chondrite and continental crust, with the Recôncavo oils occurring at the crustal end of the line.

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