

Mn-Fe CRUSTS FROM THE SOUTHERN TYRRHENIAN SEA

by

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Abstract. Dark crusts and concretions dredged from W of the Aeolian Islands mainly contain amorphous Fe-Mn hydroxides with some torodokite, birnessite and goethite. Chemically they are composed of ferric iron (60%), MnO (5%) and traces of Zn, Ni, Co, Cu. The REE patterns conform to those of the Pacific Ocean nodules, but for the negative Ce anomalies. A derivation from hydrothermal waters is suggested.

Resumé. Des incrustations et des concrétions noires sur des roches volcaniques et calcaires ont été draguées à profondeurs moyennes à l'ouest des îles Eoliennes. Elles se composent surtout de hydroxides amorphes de Fe-Mn et en sous-ordre de torodokite, birnessite et goethite. Leur composition chimique est caractérisée par des teneurs élevées de fer (60%) et manganèse (5%) et par des traces remarquables de Zn, Ni, Co, Cu. La distribution des terres rares est semblable à celle des nodules de l'Océan Pacifique, mais il n'y a pas d'anomalie négative du Ce. Ces matériaux dérivent probablement de solutions hydrothermales ou de fluides circulants à l'intérieur de roches volcaniques de composition d'intermédiaire à acide.

Glossy black crusts, coatings and impregnations on massive limestones or altered volcanic rocks have been dredged from the area between Alicudi and Ustica, to the west of the Aeolian Islands. The 18 investigated samples were taken from the flanks of submarine volcanoes at depths of -700 to -2000 m. Outer appearance, shapes and weights of the samples depend entirely on the traits of their sedimentary or volcanic cores. The crusts themselves are rather

thin (max. 2 cm), evenly distributed with concentric layering and the surface occasionally spread with small black grains cemented by white clays. Their mineralogy is monotonous: besides obviously detrital material or the relics of altered volcanic minerals they contain torodokite, birnessite, goethite, hauerite?, and unidentified oxide. The main component is a black to deep red waxy stuff, amorphous and strongly absorbant to the x-rays, which, after optical and thermal experiments, was considered to be a mixture of Fe-Mn hydroxides.

Chemical analyses of 10 samples gave the following results: SiO_2 13-25%, Al_2O_3 <1-15%, Fe_2O_3 10-53%, MnO 0.24-10.7%, TiO_2 0.04-0.32%, CaO 0.60-3.0%, MgO 0.50-3.2%, ign.loss 13-22%, V 50-400 ppm, Ni 15-3000 ppm, Co tr-800 ppm, Cu 40-900 ppm, Zn <1000 ppm, Cr <150 ppm, significant Mo and Na, absent Cd, Hg, Pb. The Mn/Fe ratios vary extensively and show positive correlations with Ni, Co and V.

The chondrite normalized REE distribution patterns follow two distinctive trends; samples with high Mn/Fe and ΣREE have negative slopes for LREE and horizontal slopes for HREE; the others have negative LREE slopes but distinctly positive HREE slopes. When normalized to shales the first type is therefore horizontal, the second one is again V-shaped. Within each type Mn/Fe correlated positively with ΣREE . Although devoid of the typical Ce negative anomaly, the first type of pattern strongly resembles that of a Pacific Ocean nodule analyzed at the same time.

Such REE distributions are not consistent with genetic models implying absorption of the REE from marine water or from altered basaltic rocks. They could satisfy a model of scavenging of clays but, as a whole, the data can be best interpreted assuming that the formation of the crusts is related to waters circulating through volcanics of andesitic, dacitic and rhyolitic compositions, as described both in the subaerial and in the submarine volcanoes of the area.