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Iron and sulfur containing sandy aggregates from the North Sea

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Iron and sulfur containing sandy aggregates, that occur on the German North Sea shore, e.g., on the beach of the island Juist, show grey to black and yellow to red-brown colors. Macroscopically they consist of sand grains and shell fragments with black coatings that oxidize when keeping them for longer time at (humid) air. X-ray powder diffraction and X-ray absorption near edge (XANES) spectroscopy (SUL-X beamline, ANKA) at the S and Fe K-edge have been applied to determine the mineralogical composition and the chemical forms of S and Fe. XANES spectra have been processed with the Athena program [1]. By X-ray diffraction (XRD) quartz (SiO_2), calcite ($CaCO_3$) and calcium sulfate hydrate have been identified. Two sharp reflections could not yet been assigned. And there are no reflections left that indicate an iron oxide, iron oxyhydroxide or an iron sulfide phase because their amounts might be too small for XRD or they are not or not well crystalline. S K XANES spectra of the brown parts have been assigned to sulfate and to elemental sulfur by comparison with reference spectra. Brown-black parts show additionally a feature close to S^{4+}. In the grey-black areas mono-sulfide (S^{2-}) has been identified by comparison with a spectrum of pyrrhotite ($Fe_{1-x}S$) [2]. Fe K XANES spectra are under evaluation. Because of the intergrowth with shells formation of aggregates takes place on the sea floor, for example in the tideland areas where reducing conditions are common [3]. Fe(II) and sulfide might precipitate to from iron sulfides around the quartz grains and shells, and later on partially oxidize to elemental sulfur and sulfate, e.g. during wave transportation and deposition on the beach. Meanwhile some aggregates have been found that contain metallic fractions assuming that at least some of them might have been formed around scrap metal. Further investigations will consider cross sections of a larger amount of samples to look in detail for the metallic parts, and will focus on the binding agent of the sand grains.

[1] Ravel B. & Newville M. (2005). JSR, 12: 537–541

[2] Goettlicher J. & Steininger R. (2012) Goldschmidt Conference, Montreal, submitted

[3] Katoka M. & Matsuo M. (2005) Photon Factory Activity Report 2004 #22 Part B (2005), 7C, 9A, 12C/2004G302