

Mineralogy of certain pyrite concretions from Israel and their alteration products

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Summary. Pyrite concretions from an arid area of Southern Israel are described. The alteration products include alunite, gypsum, jarosite, baryte, celestine, goethite, hematite, sulphur, and sideronatrite. Sideronatrite is described in detail. The pyrite alteration is considered to be recent and the sideronatrite is preserved owing to climatic aridity. The puzzling appearance of sulphur is tentatively explained by microbiological reduction of the sulphates.

THE Ghareb-Taqíya formations (of upper Campanian to Paleocene age) in the Negev (Southern Israel) are marine sequences consisting mainly of chalk, marl, and shales, frequently bituminous and gypsiferous. They are characterized by the occurrence of sulphide concretions (Bentor, 1960). These concretions, of varying sizes and structure, are found in different stages of alteration leading, in most cases, to the complete disappearance of the original sulphide.

The Ghareb-Taqíya outcrops in the vicinity of Kilometre 146 north of Neve Midbar, on the Eilat-Beersheva road, were found to contain concretions displaying different stages of alteration within a restricted area; this area has been chosen for more detailed mineralogical study.

Field relationships. The Ghareb-Taqíya beds locally overlie chert beds of the Mishash formation (Campanian) and underlie chalk of Eocene age. The outcrops are part of a narrow and elongated belt surrounding the Wadi Hyion depression. Lithologically, they are chalky and shaly rocks notably bituminous in the lower part of the section.

Mineralogy. The concretions are of varying shapes, from spherical to tubular, but are mainly ellipsoidal, with a diameter of from a few centimetres up to 20 cm. They are closely associated with gypsum veins, the distribution of the two being sporadic. The following description refers only to the concretions.

While some concretions may consist wholly of sulphide, the larger ones are usually so altered that only a nucleus of the original sulphide remains intact, and even this may be lost. The sulphide has a granular

or radial structure and although formerly reported to be marcasite, it has been shown by X-ray to consist of pyrite. Around the nucleus, or replacing it, a yellow mass is found, frequently in concentric bands; it consists of jarosite or gypsum or both (the jarosite was previously described as limonite).

The jarosite occurs in two forms: the most abundant is yellow, granular or earthy, usually mixed with gypsum; the second is in the form of small (1.5–0.5 mm) hexagonal, amber yellow plates, displaying a division into six segments. Those plates are almost always associated with the remains of original sulphide; they are also mixed with gypsum.

The gypsum is found usually as concentric fibrous veins cutting across the concretion but may be granular when intermixed with jarosite. Sometimes, in the centre of the concretions, there are cavities partly or completely filled with large gypsum crystals up to a centimetre across. Many other minerals are found together with the jarosite, including alunite, baryte, celestine, sideronatrite, sulphur (as a powdery mass together with gypsum and jarosite, or as minute euhedral crystals) and, as yet unidentified, iron-aluminium sulphates.

The outer part of the concretions is usually composed of red to deep violet hematite and dull-brown goethite. Sometimes a coating of gypsum scales is found on the outside.

Both jarosite and sideronatrite are here reported for the first time from Israel.

Sideronatrite has hitherto been reported from a few localities:¹ Tarapaca, Chile (the type locality; Raimondi, 1878); Cheleken Island, Caspian Sea ('urusite'; Frenzel, 1880); Sierra Gorda, Chile (Frenzel, 1890; Genth and Penfield, 1890); Chuquicamata, Chile (Palache and Warren, 1908; Bandy, 1938); Potosi, Bolivia (Lindgren and Creveling, 1928); and coal-mines in the Ruhr (Seeliger, 1950) and in Belgium (Van Tassel, 1956). It is noteworthy that at the Cheleken Island occurrence the mineral was accompanied by sulphur, as it is in Israel.

In the concretions of the Israeli occurrence, the sideronatrite appears either as veins or aggregates or as discrete prismatic crystals disseminated in masses of jarosite. The crystals are soft, straw-yellow in colour, and of elongated prismatic habit, up to 5 mm in length.

Crystals were hand picked under a binocular microscope and analysed after solution in HCl (1+2): Fe₂O₃ 21.57, CaO 0.15, MgO 0.07, Na₂O

¹ The imperfectly characterized bartholomite is possibly sideronatrite (Dana, Syst. Min., 7th edn, p. 604). It occurs as an alteration product of pyrite on St. Bartholomew island, West Indies.

16.75, K_2O 0.15, SO_3 42.77, H_2O+ 8.49, H_2O- 9.01, insol. 0.20, total 99.16 %. X-ray powder photographs agree well with Van Tassel's (1956), and the optical data (α 1.506, colourless; β 1.524, pale yellow; γ 1.586, yellow; $2V_\gamma$ (calc.) 59°) also agree well with previous determinations (Van Tassel, 1956; Larsen and Berman, 1934).

Discussion. The occurrence of secondary sulphates on oxidized pyrite is well known. The kind of minerals formed depends mainly upon climatic and hydrological factors and the type of the country rock. Pyrite is usually converted into hydrated ferric oxide, the so-called 'limonite', but locally jarosite is found. In the concretions described here, the alteration products are thought to be of very recent origin. Their mode of formation is simple and relatively well known, and it is thought that the sulphuric acid produced by the inorganic oxidation of the pyrite reacts with the calcite of the country rock leading to the formation of gypsum. Where calcite is relatively scarce, the acid will attack the clay, leaching out the alkalis and alumina, to form jarosite or natrojarosite. The restriction of jarosite to the central part of the concretion and of goethite to the outer part agrees with the conclusions of Merwin and Posnjak (1937) who considered that jarosite is formed in the low pH section of their phase equilibrium diagram, an increase in the pH resulting in the formation of iron oxides.

The preservation of so ephemeral a mineral as sideronatriite can be explained by the peculiar aridity of the region (Ashbel, 1951). The scarcity of rain would prevent the leaching of the soluble sulphates, yet the occasional floods would supply enough moisture to oxidize the sulphide. Similar conditions are found in other places from which ephemeral sulphate minerals have been reported (Miroshnikov and Shcheglova, 1959). The climatic factor will also explain why similar concretions from the more humid regions of Israel are found almost completely oxidized to gypsum and iron oxides.

The occurrence of elemental sulphur is more puzzling as it is not, under ordinary conditions, intermediate in the oxidation of pyrite. It is probable that the sulphur has been formed by sulphate-reducing bacteria.

Investigation of the isotopic composition of the sulphur and its possible biogenic origin is to be undertaken shortly.

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