

Summary

The Hatrurim Complex is located in Jordan, Israel and the Palestinian Authority. It consists of separate outcrops spread over the Dead Sea rift valley, located between 10 and 100 km from the Dead Sea Transform Fault. The rocks of the complex were formed as a result of pyrometamorphism (so-called combustion metamorphism), which corresponds to high-temperature and low-pressure conditions of rock transformations. The largest outcrop of pyrometamorphic rocks in Israel is the Hatrurim Basin, a stratotype of the complex. It is characterized by a great variety of high-temperature metamorphic rocks. Intensive studies over the last decade have enabled a better understanding of the mineralogy of the Hatrurim Complex, leading to the discovery of many new natural phases. These investigations have focused mainly on high-temperature rock-forming minerals, whereas the low-temperature mineralization has remained essentially unexplored.

The objective of the present doctoral dissertation has been to characterize the zeolite mineralization of the pyrometamorphic rocks of the Hatrurim Basin. Samples originating from the collection of Prof. Galuskin's research group were used for the study. In addition, samples collected during fieldwork in 2022 were analyzed. In order to achieve the desired objective, the following methods of instrumental analysis were applied: scanning electron microscopy, electron microprobe analysis, Raman spectroscopy, and single-crystal X-ray diffraction. In total, nearly 120 thin sections and dozens of rock samples were examined.

The most abundant zeolite in the pyrometamorphic rocks of the Hatrurim Basin is flörkeite, $K_3Ca_2Na[Al_8Si_8O_{32}] \cdot 12H_2O$. It is a rare zeolite with **PHI**-type structure. To date, flörkeite has been known only from the type locality – the Bellerberg volcano in Germany. In Israel, flörkeite has been found in several types of rocks in association with the following minerals: thomsonite-Ca, minerals of the gismondine series, minerals of the tobermorite supergroup, and vertumnite. It is important to note that flörkeite crystallises at the end of the low-temperature mineralization sequence, overgrowing previously formed minerals or filling the remaining space in the cavities. The structural investigation confirmed the triclinic symmetry and a fully ordered structure. In addition, the comparison of the Raman spectra of flörkeite and minerals of the phillipsite series revealed that the main band at 470 cm^{-1} , characteristic for the **PHI**-type structures, is independent of the Si/Al ratio and the arrangement of cations in the framework.

During the work on the project, a new mineral – gismondine-Sr, $Sr_4[Al_8Si_8O_{32}] \cdot 9H_2O$, was discovered. It is the strontium analog of gismondine-Ca with a **GIS**-type structure.

Gismondine-Sr was found in partially melted hornfels, which is mainly composed of wollastonite, gehlenite and minerals of the grossular-andradite garnet series. A number of zeolites characterized by low Si/Al ratios were identified in the low-temperature mineralization, similar to the flörkeite association. Interestingly, only the new mineral was rich in Sr, whereas the surrounding zeolites were not enriched. Chemical composition analyses revealed that gismondine-Sr differs from gismondine-Ca not only by the dominant cation, but also by the significant substitution of monovalent cations (mainly potassium), which was not observed in the calcium counterpart. The structural investigation enabled the solution and refinement of the new zeolite structure in the $B22_12$ space group with the following unit cell parameters $a = 14.0256(2) \text{ \AA}$, $b = 10.45900(10) \text{ \AA}$, $c = 13.79360(10) \text{ \AA}$, $V = 2023.44(4) \text{ \AA}^3$. Contrary to the monoclinic gismondine-Ca, gismondine-Sr crystallizes in the orthorhombic crystal system. Both minerals have an ordered aluminosilicate framework. The extraframework cations of gismondine-Sr are disordered, a feature which contrasts with the ordered cation arrangement of gismondine-Ca. In addition, a comparison of both frameworks showed significant deformations of the eight-membered rings in the structure of the strontium analog. The spectroscopic study of minerals with **GIS**-type structure showed that the main band is located about 460 cm^{-1} regardless of the elliptical deformation of the eight-membered rings.

Insightful analyses of obtained results and literature data on minerals with **GIS**-type structure enabled to distinguish two mineral series varying in Si/Al ratio. The series with a ratio equal to 1, including gismondine-Sr, gismondine-Ca, and amicitite, can be represented by the following general formula $(M_y D_{0.5(8-y)})[Al_8 Si_8 O_{32}] \cdot n H_2 O$, wherein $y \leq 8$ and represents the stoichiometric coefficient of the monovalent cations. Additionally, a Ba-rich mineral of this series has been found in pyrometamorphic rocks, and can be considered as a potentially new mineral. The second series includes minerals with a Si/Al ratio greater than 1.66. The general formula of this series can be written as $(M_y D_{0.5(x-y)})[Al_x Si_{(16-x)} O_{32}] \cdot n H_2 O$, where $x \leq 8$ and $y \leq 8$ denote coefficients of trivalent Al cation and monovalent cations, respectively. Accordingly, garronite-Ca, gobbinsite, and garronite-Na belong to this series. However, the distinction between gobbinsite and garronite-Na is disputable, as they have been distinguished based on slightly different hydration levels and differences in Si/Al ratios, resulting in various Na contents.

In summary, the occurrence of flörkeite in various types of pyrometamorphic rocks indicates the regional character of relatively uniform conditions for zeolite formation in the Hatrurim Basin. The formation of this mineralization can be divided into two stages.

Ca played a major role in the first stage, and rarely Na-enriched minerals may be found. However, monovalent cations (Na and K) were dominant in the second stage, resulting in the formation of flörkeite at the end of the crystallization sequence. Generally, zeolites from the pyrometamorphic rocks of the Hatrurim Complex are characterized by a low Si/Al ratio implied by a high Al content in the crystallization environment and consequently, high alkalinity. Such conditions resulted from the interaction of meteoric water and clinker-like minerals, which induced Al release into the system. Also, local enrichment in Sr and Ba is a result of their release from minerals such as barium feldspar or minerals of the fluorapatite-fluorellestadite series.

The abovementioned results were published as three contributions to mineralogical journals.