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GEOCHEMISTRY

Gas Fire from Mud Volcanoes as a Trigger for the Appearance of High-Temperature Pyrometamorphic Rocks of the Hatrurim Formation (Dead Sea Area)

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The Dead Sea Transform area hosts more than ten complexes composed of specific rocks of the Hatrurim Formation that is most widespread in the eponymous basin (Fig. 1). They crown the sedimentary sequence and consist of brecciated terrigenous–carbonate, locally bituminous, sediments and high-temperature metamorphic rocks of the spurrite–mervinite facies [1] accompanied by low-temperature hydrothermal veins. In the geological map of Israel, they are designated by the special symbol MZ (Mottled Zone). The MZ complexes are traditionally attributed to areal combustion of bituminous rocks of the Ghareb Formation (Fig. 2) [2–4]. It is believed that the combustion front in near-horizontal continuous sediments reached depths of 80–120 m. Such a scenario of fire development is, however, impossible from the standpoint of the physics of combustion since it precludes oxygen access to fuel particles and their heating up to the spontaneous combustion [5]. The purpose of this work is to substantiate a new model, which would be most adequate to describe this phenomenon. It is based on the systemic analysis of original materials obtained during field observations in 2004–2005 and on published data. The co-occurrence of high-temperature anhydride rocks and low-temperature hydrothermally altered rocks (hereafter, hydrothermalites) is sufficiently well explainable by mud volcanism. This process results in the release of anomalously high formation pressure in petroliferous provinces due to the exhumation of hydrocarbon gases, water, and liquefied rock mass (mud breccia). During the explosion, gases can ignite spontaneously and burn subsequently for a long time [6, 7].

Rock complexes of the Hatrurim Formation are largely confined to axial parts of gentle anticlinal uplifts. The rocks are partly localized in the complicating synclines on near-horizontal Campanian strata (Mishash Formation). The platform cover of this area is crosscut by a young rift valley and is divided by faults into blocks. The Hatrurim basin hosted in one of the blocks associates with the synclinal structure (8×5 km), the eastern limb of which is bordered by listric walls of the Dead Sea Rift valley (Fig. 3). The block is surrounded by anticlines with small gas (Zoar, Kidod, and Haqanaim) and oil (Zuk-Tamrur and Gurim) traps. The rift valley is characterized by salt diapirism (Sdom Dome). Asphaltene, bitumen, and oil occurrences are observed in coastal areas of the Dead Sea [8]. Numerous natural cataclysms related to bitumen burning and gas explosions are mentioned in biblical history.

The landscapes of the Hatrurim, Ma'ale Adummim, Jabel Harmun, and Hyrcania complexes are distinguished in the surrounding cuesta topography characteristic of sedimentary sequences of the Judea Mountains and the Negev Desert. The relief of the Hatrurim basin is marked by several hundred newly formed cones largely composed of mud breccia. In some places, the breccias are characterized by vague bedding discordant with that of host sedimentary rocks. In the southern part of the basin, small individual cones and their chains are located on the eroded surface of the phosphorite and cherty Mishash Formation. In the north, large cones crown the mud breccia. The Ma'ale Adummim and Hyrcania complexes are characterized by a specific relief (truncated cones a few kilometers across at the base and an order of magnitude lower in height). The MZ complexes (particularly, Maqarin) in Jordan are feebly marked.

Breccias are distributed through the entire section of the Hatrurim basin (Fig. 4). Rock fragments are composed of chalk, marl, and dolomite with subordinate cherts and phosphorites of the Mishash Formation.

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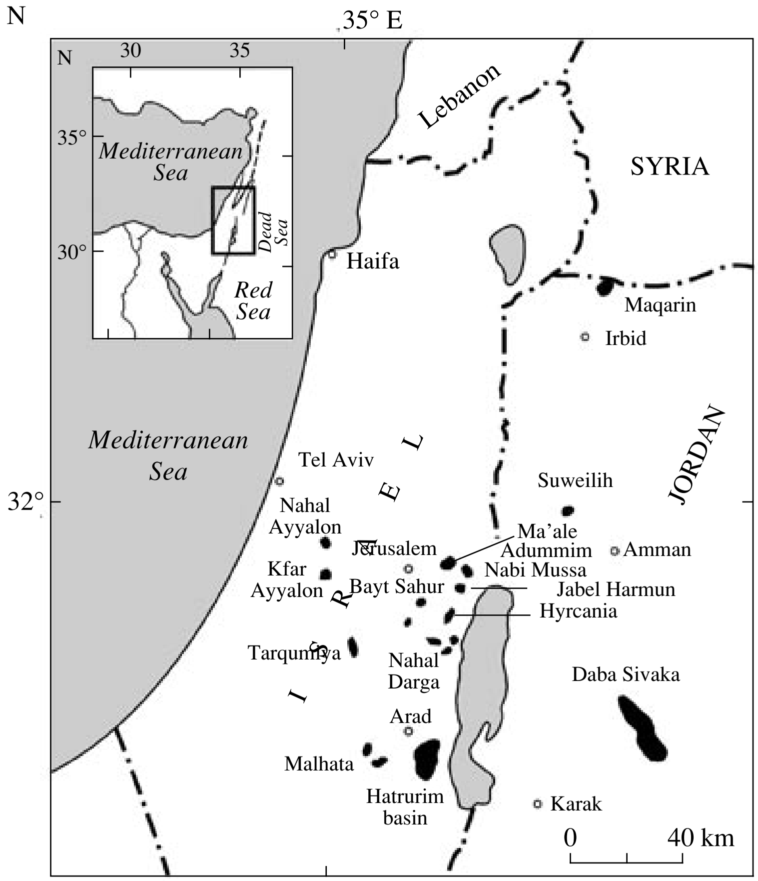

Fig. 1. Outcrops of the MZ Complex of the Hatrurim Formation (shown in black). Based on materials from [2, 3].

Combustion metamorphic (hereafter, pyrometamorphic) rocks are relatively diverse [2–4] (table). Monolithic larnite and spurrite marbles ($T = 700–900$°C) are usually localized close to the surface always above breccia horizons. Their outcrops are up to 10 m thick and hundreds of square meters in size. Garnet–melilite rocks (2–5 m thick) form outcrops tens of square meters in size. In sections of large cones, fragments of pyrometamorphic rocks occur locally at intermediate levels alternating with breccia layers. Eight such horizons are observed in the section of Mt. Yeelim, the highest edifice in the Hatrurim basin.

Pyroxene–anorthite hornfelses are formed frequently in the concentric collars up to 2 m high and 5–40 m across. The breccia of hornfels fragments (up to 0.7 m across) is monolithic. Bodies fringed by these rocks become sharply narrower downward to form conical funnels filled with altered fragments of sedimentary and pyrometamorphic rocks cemented by calcite and zeolite. Contacts between such bodies and host mud breccia are sharp. The peripheral part of funnels contains veins of anomalously high-temperature (up to 1250°C) pyrometamorphic pyroxene–anorthite rocks (paralavas). Based on geological observations, the mineral composition of rocks, and reconstructed metamorphism parameters ($T = 900–1250$°C, $P_{tot} < 120$ bar), conical collars of hornfels breccia are interpreted as markers of the eruptive apparatus of mud volcanoes [9]. Their explosive eruptions were stimulated by the discharge of hydrocarbon gases and accompanied by gas burn-offs above the Earth's surface, which promoted pyrometamorphism of rocks.

This area also hosts numerous small eruptive apparatuses (0.5 to 2.0 m across) fringed by low (up to 30 cm high) concentric collars composed of fragments of Mishash Formation cherts cemented by the carbonate–zeolite matrix. No metamorphic rocks are associated with them. These structures are interpreted as gryphons discharging mineralized water. They are accompanied by a system of clastic dikes containing 20–70% quartz sand and microclastic material of sedimentary rocks, hydrothermalites, cherts, and rare spurrite and larnite rocks. Cement (20–40 vol %) in dikes is either calcite or fluorapatite–apophyllite in composition.

Thus, conical hills of the Hatrurim basin, mud flows at their bases, flat MZ cones in Judea, and topograpically obscure MZ complexes in Jordan represent different morphological types of mud volcanoes. Their shapes and sizes are determined by the viscosity of explosion products and intensity of eruptive processes,

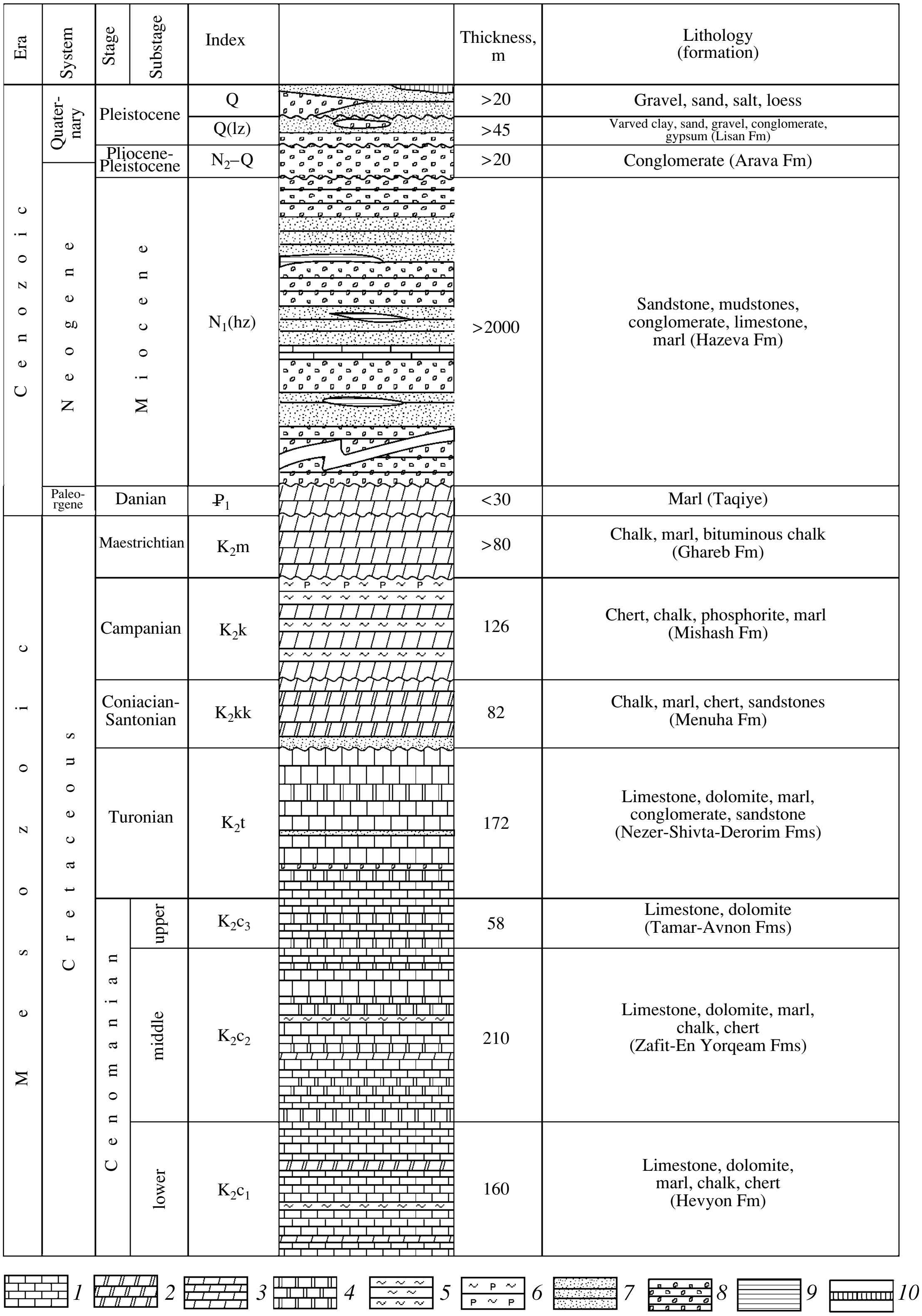

Fig. 2. Stratigraphic column of the Meso–Cenozoic sedimentary section exposed in the northern Negev Desert. Based on materials from [12, 15]. (*1*) Limestone; (*2*) marl; (*3*) chalk; (*4*) dolomite; (*5*) chert; (*6*) cherty phosphorite; (*7*) sandstone; (*8*) conglomerate; (*9*) kaolinite clay; (*10*) loess.

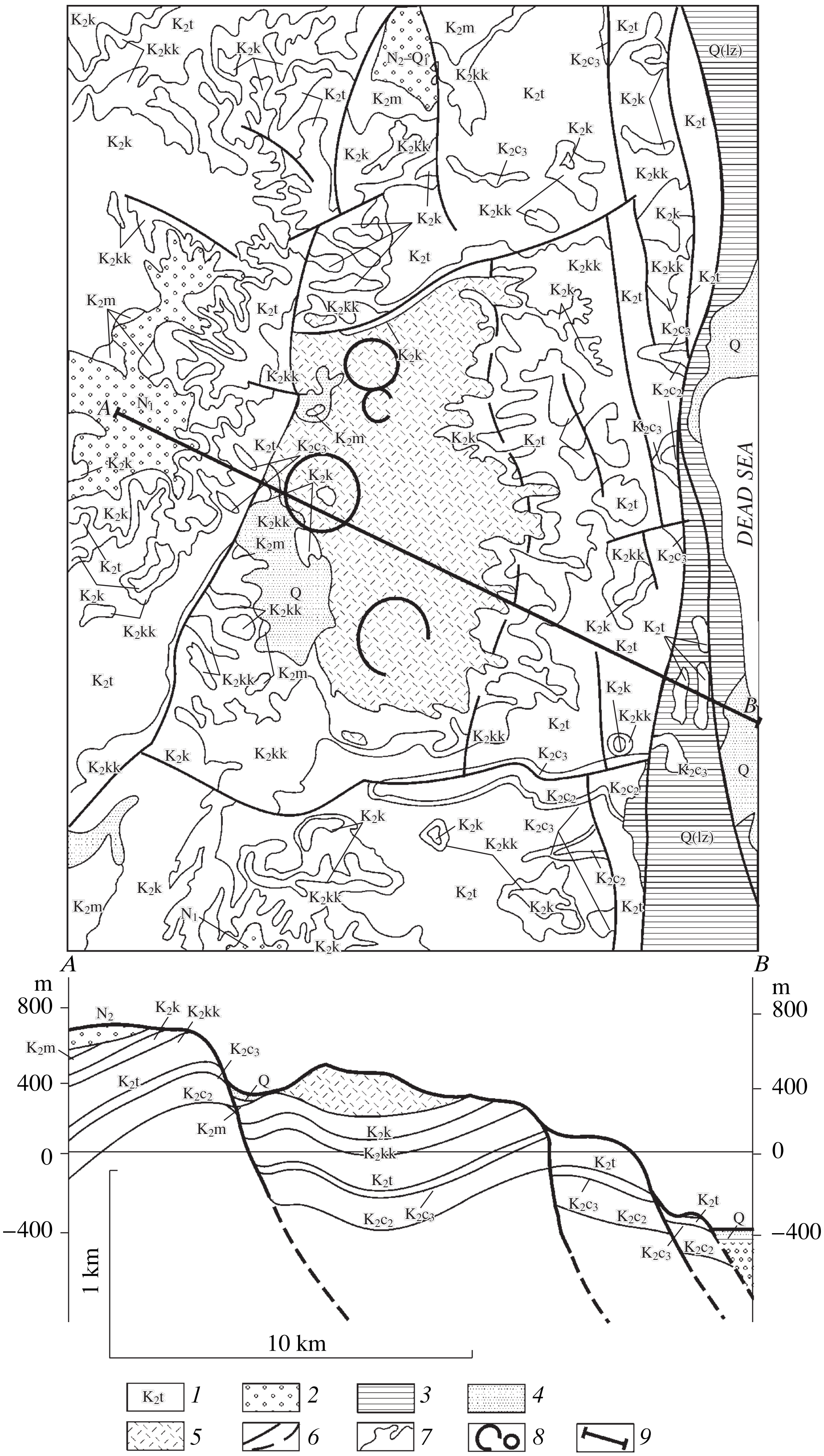

Fig. 3. Geological map and section of the southwestern part of the Dead Sea Rift valley. Based on geological materials of the Geological Survey of Israel and data from [3, 4]. (*1*) Upper Cretaceous rocks (symbols hereinafter are as in Fig. 2); (*2*) Neogene and Neogene–Quaternary conglomerates; (*3*) Pleistocene sediments; (*4*) Pleistocene–Holocene sediments; (*5*) Hatrurim Formation; (*6*) faults; (*7*) stratigraphic boundaries; (*8*) ring structures; (*9*) profile.

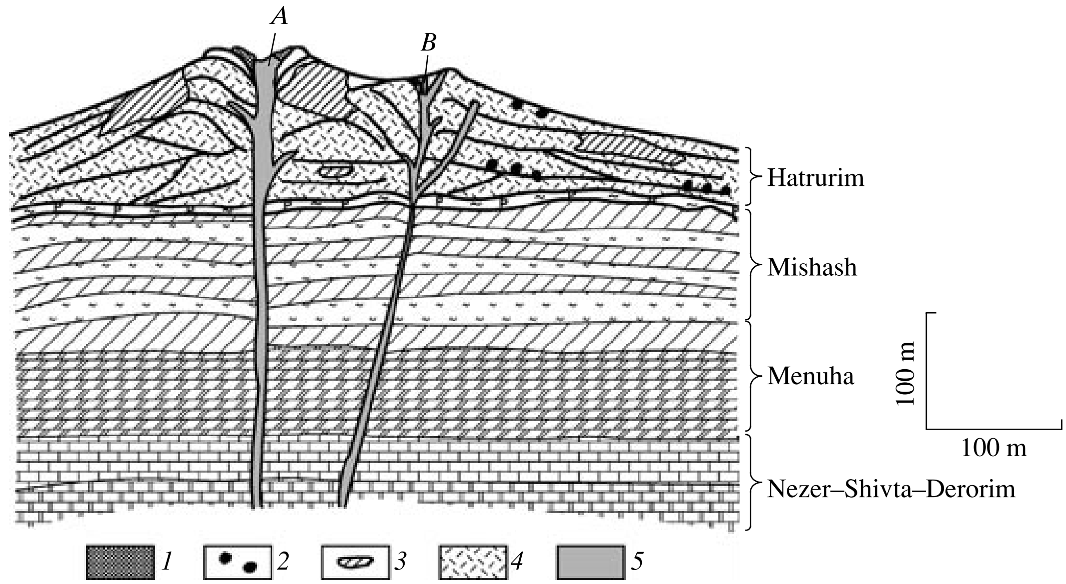

Fig. 4. Generalized geological section of the northwestern part of the Hatrurim basin. (*1*) Anorthite–clinopyroxene hornfels; (*2*) melilite hornfels; (*3*) spurrite- and larnite-bearing marbles; (*4*) breccia of sedimentary, pyrometamorphic, and hydrothermally altered rocks; (*5*) clastic material cemented by calcite and (or) zeolite in conduits of (*A*) mud volcanoes and (*B*) gryphons.

respectively [6, 7, 10]. Fragments of sedimentary rocks represent a main constituting material of mud breccia. The MZ mud volcanoes are characterized by high content of carbonate rocks in their breccia. Pyrometamorphic rocks are distributed in some places among mud breccias and are associated with different-age areas of hydrocarbon burning. The concentric hornfels collars mark sites of the explosive emission of gases and surround caldera-type craters formed around conduits. The pyrometamorphic spurrite, larnite, and garnet–melilite rocks are related to long-term high-temperature diffuse fluid flow of burning gases. Similar large-scale baking of rocks due to the burning of gases in contraction fractures is described in the Apsheron Peninsula, Azerbaijan [6]. Mud volcanic eruptions accompanied by gas explosions and burning and formation of pyrometamorphic rocks were numerous in the area. Geochronological data indicate at least three main periods of gas eruption and burning in the Hatrurim basin: 16, 4.2–3.0, and 1.5–1.0 Ma ago [11].

In the Hatrurim basin, pyrometamorphic rocks make up collars of several ring structures with mud breccia and sedimentary rock blocks. One ring structure (ring-shaped depression) is located in the northern part of the basin and fringed by high volcanic cones. It resulted most likely from subsidence of the area with volcanic edifices along a system of concentric faults. The collapse of cones and subsidence of the area around the crater due to removal of large rock volumes from beneath are characteristic of mud volcanoes [6, 7, 11]. The subsidence structures of the regional scale (the so-called subsidence synclines) are typical of mud volcanic provinces. The asymmetrical syncline of the Hatrurim basin represents in fact a subsidence syncline developed at the flank of an anticlinal fold.

The MZ rocks experienced intense hydrothermal alteration [12]. They are filled with veins composed of calcite, zeolite, anhydrite, gypsum, and ettringite and are characterized by unique Cr mineralization (volkonskoite, bentorite, stichtite) and opalization [2]. Mud breccia contains usually tobermorite, aragonite, halite, and subordinate talc and serpentine. Fragments of pyrometamorphic rocks are usually overgrown with crustified calcite and zeolite, which imply activity of low-temperature solutions. Ca–Cl waters took part in the formation of MZ hydrothermalites [2]. Brines of the Dead Sea are precisely of this kind [8]. The Hatrurim rocks are characterized by elevated concentrations of Ti, V, Cu, Zn, Cr, As, Y, Sb, Ba, La, Zr, Nb, Mo, and particularly U [12, 13]. Melt inclusions in the main rock-forming minerals of garnet–melilite paralavas show anomalously high contents of V (1350–2150), U (600–3600), Li (35–515), B (220–100 ppm), and BaO (up to 13 wt %) [9]. The oxygen isotopic composition of pyrometamorphic rocks indicates their relation to the sedimentary protolith [14]. Such a unique combination of geochemical properties is typical of elision basins with genetically associated mud volcanic provinces [10].

Thus, rock complexes of the Hatrurim Formation are characterized by a complete set of features that are typical of mud volcanic provinces [6, 7, 10, 15]. Progressive development of mud volcanism was accompanied by rifting, which is evident from the timing of the main pyrogenic events [4, 11]. The roots of mud volcanoes confined to the Hatrurim Formation are unknown thus far. Nevertheless, finds of Turonian limestones [3] in agglomeratic gryphon collars imply depths of at least

Mineral composition of main rock types of the Hatrurim Formation

Rock type	Distribution area	Rock-forming minerals	Accessory minerals
Chalk of the Ghareb Formation (Maestrichtian)	Layers at the base of the Hatrurim Formation	Calcite, aragonite, kaolinite, boehmite, nontronite	Francolite, magnetite, hematite
Mud breccia	Flows at the base of volcanic cones. Occupy up to 60–70% of the Hatrurim basin area	Calcite, gypsum, aragonite, tobermorite, halite, and hydrogrossular in matrix. Sedimentary and, rarely, spurrite, larnite, and garnet–melilite rocks in fragments. Gypsum, calcite, halite, and volkonskoite complex of veins	Jennite, afwillite, ettringite, apatite, hydrogrossular, hematite, and portlandite in matrix; fluorapatite in fragments of pyrometamorphic rocks
Garnet–melilite rocks and associated paralavas	Single outcrops (up to a few m^2) near the section base	Gehlenite, schorlomite, wollastonite, rankinite, nagelschmidtite, larnite	Calcite, tobermorite, pseudowollastonite, fluorapatite, perovskite, magnetite, hematite, ellestadite
Spurrite and larnite marbles	Outcrops (up to 1 km^2) usually above mud breccia cover. Channels up to several meters across and tens of meters long	Calcite, spurrite, larnite, gehlenite, brownmillerite, mayenite, yeelimite. Calcite, volkonskoite, and bentorite veins. Barite and hematite concretions	Ferropericlase, Cr–Mg–Al spinel, perovskite, fluorapatite, ellestadite, nagelschmidtite, cuspidine, hatrurite, portlandite, hydrogrossular, tobermorite, greigite
Anorthite–diopside hornfels and paralavas	Top of cone volcanoes, collar around caldera-type craters	Anorthite, diopside	K-feldspar, apatite, Ti magnetite, hematite, ilmenite, fayalite, troilite, zeolite, calcite
Hydrogarnet–zeolite–calcite rocks	Products of hydrothermal alteration of hornfels	Calcite, esseneite–diopside, tomsonite, phillipsite, and hydrogrossular. Maghemite and hematite veins. Barite and hematite concretions	Aragonite, serpentine, vaterite, maghemite, gismondine, chabazite, andradite, grossular, apatite
Collars of gryphons	Middle and upper hypsometric levels	Calcite, apophyllite, and quartz sand in matrix. Pebbles and fragments of chert, phosphorite (Campanian), limestone (Turonian), spurrite, and larnite rocks	K-feldspar and zircon in matrix
Clastic dikes	Associate with gryphons	Calcite, apophyllite. Quartz sand. Fragments of sedimentary, spurrite, and larnite rocks	Tobermorite, fluorapatite, plombierite, wollastonite, reinhardbraunsite

Note: Minerals were determined by the XRD analysis, optical microscopy, and microprobe measurements. Based on original materials and data from [2].

300 m. Micropaleontological studies may help in solving this problem. Analysis of sand from eruptive craters may promote the identification of aquifers that transported hydrocarbons and water. It is conceivable that explosive processes in the vicinity of the rift depression could be initiated by deep gas flows ascending along listric faults. This assumption is confirmed by the first data on the Ar and He isotopic compositions in vapor inclusions from vein calcite: $^{40}Ar/^{36}Ar = 1096$, $^3He/^4He = 2.1 \cdot 10^{-6}–3.4 \cdot 10^{-5}$.

The formation of the mud volcano system in areas surrounding the Dead Sea Rift proceeded in the course of neotectonic reactivation of the region, which resulted in its draining in the Miocene and formation of the Hazeva molasse in response to the intense opening of the rift basin. It was accompanied by repeated powerful explosive discharges of gas, waters, and water-saturated clastic material. Combustion of hydrocarbon gases provided high-temperature metamorphism, while extrusion of mineralized waters promoted the hydrothermal alteration of materials in mud volcanoes. Thus, the Hatrurim Complex represents a specific type of pyrometamorphic rocks. Wide distribution of similar rocks should also be expected in other provinces of surface mud volcanism, such as the Apsheron, Turkmen, and Kerch–Taman regions.

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