

# Advanced mineralogical and crystallographical techniques for understanding transformation processes in natural materials and their synthetic analogous

## *Comparison between natural combustion pyrometamorphism and the synthetic analogous process of cement manufacture*

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### INTRODUCTION

Pyrometamorphism is a distinctive type of thermal metamorphism characterized by a wide temperature range and Low-Pressure (LP) conditions, typically occurring at shallower depths compared to regional metamorphism (less than 3-4 km; Bucher & Grapes, 2011).

Combustion Pyrometamorphism (CP) is a complex geological process involving sedimentary sequences and occurs in two stages: (i) 1<sup>st</sup> stage consists of extreme high-temperature and low-pressure conditions resulting from the self-ignition of coal seams or the rise of methane-rich gases from deep reservoirs along fractures; (ii) 2<sup>nd</sup> stage involves low-temperature and low-pressure conditions, characterized by the weathering of previously combusted rocks. CP primarily affects lacustrine sequences (clay-rich protoliths, sandstone, and lacustrine sediments) rather than marine sequences (limestone and marls), which can be attributed to the higher weathering resistance of the former CP protoliths (Grapes, 2010). The mineral assemblages in pyrometamorphosed rocks typically fall within the sanidinite and hornfels facies, indicating the high-temperature and low-pressure conditions (Bucher & Grapes, 2011). Additionally, various high-temperature minerals (such as cordierite, mullite, sapphirine, merwinite, and rankinite), including metastable ones (like larnite, hatrurite, brownmillerite, mayenite, and ye'elimite), are found in both pyrometamorphosed rocks and industrial materials (such as metal slags, ceramics, and cements). Therefore, pyrometamorphosed rocks can be considered as natural analogs of certain human-made materials (Sokol et al., 2014; Vapnik et al., 2007).

CP is an understudied geological process within the uncommon field of petrological experiments (i.e., HT and LP involving limestone). The scarcity of geological information and the relative rarity of CP further complicate the understanding of the processes occurring during CP, particularly in the case of limestone protoliths.

This study focuses on the Hatrurim Basin in Israel, which is the most significant and extensive location where

well-preserved CP rocks and their limestone protoliths are exposed, enabling the observation of geological features and collection of rock samples. Investigating CP rocks and the overall pyrometamorphism process is valuable for both geological purposes (providing deeper insights into microstructure development and stability fields of mineral assemblages under HT and LP) and industrial applications (enhancing production processes and properties of final products).

### GEOLOGICAL FRAMEWORK AND FIELD TRIP

Hatrurim Basin is located in the northern part of the African Plate inside Sinai Microplate (Freund, 1965), representing the southern shelf of Tethys paleo-ocean before the collision with Eurasian Plate (Novikov et al., 2013). The sedimentary sequence is featured by carbonate sediments interrupted by sedimentation breaks and unconformities, later deformed during Late Cretaceous. Tectonic activity led the deposition of phosphorite beds (Mishash Formation) later covered by limestone and marls (Ghareb and Taqiye Fm.) inside synclines; whereas, mainly chalky rocks were formed in anticlines (Novikov et al., 2013). A sea regression and uplifting produced clastic sediments deposition, mainly conglomerates (Hazeva Formation), from Eocene to Oligocene. An intense faulting occurred from Late Oligocene due to the opening of Levantine Transform Fault (Novikov et al., 2013). Hatrurim Basin is a rectangular shaped area (40 km<sup>2</sup>) closely located to Dead Sea in which a sedimentary sequence aged from Late Cretaceous to Paleocene undergone in CP ~ 5 Ma forming a CP sequence up to 190 m from the surface. Hatrurim Basin falls inside a syncline with several minor structures related to the Syrian Arc fold system (Burg et al., 1991; Hirsch & Burg, 2008). CP rocks were formed by means of methane-rich gases combustion coming from deep hydrocarbon reservoirs found in several nearest locations (Sokol et al., 2019, 2007): the combustion occurred at foci reaching HT (1100-1450°C) close to the surface; whereas, LT were reached at greater

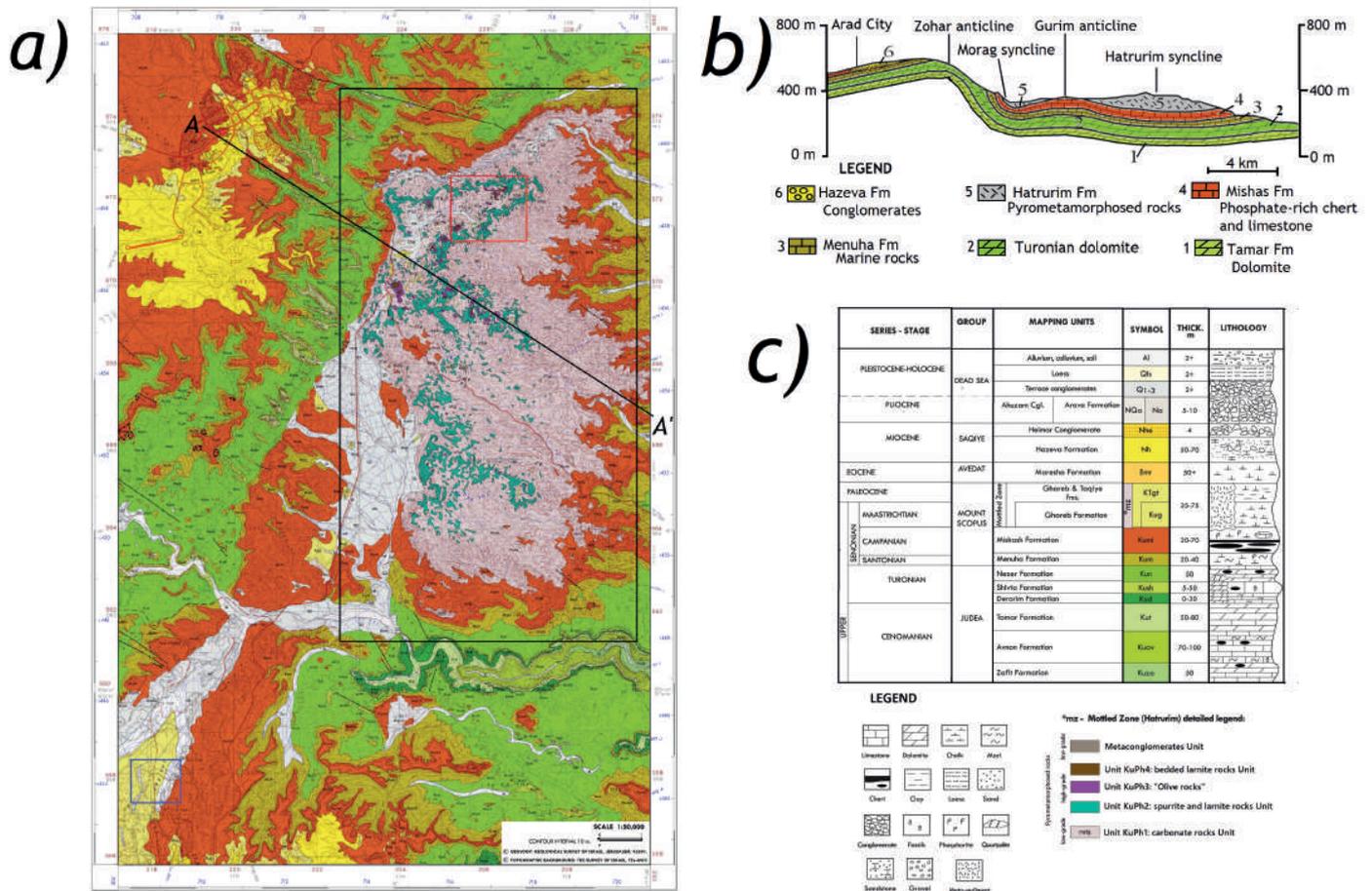


Figure 1 a) Geological map (1:50'000 scale) of Arad, reporting in grey (retrograde CP rocks), cyan, purple and brown (prograde HT CP rocks), black, blue and red squares represent Hatrurim Basin, Rotem Amfort Mine and Larnite-Rocks sampling areas, respectively (Hirsch & Burg, 2008); b) geological section passing through Hatrurim Basin area (Novikov et al., 2013b); c) Legend of geological map (Hirsch & Burg, 2008).

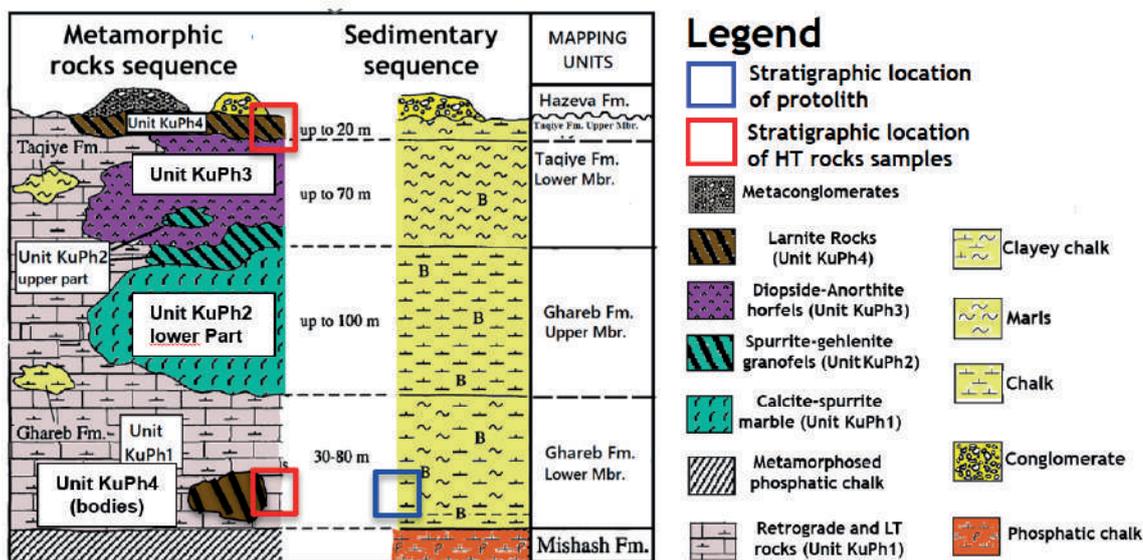


Figure 2 Stratigraphic section of combusted pyrometamorphosed sequence and sedimentary one on left and right respectively (modified from (Burg et al., 1991); red and blue squares highlight the stratigraphic position of sampled HT and sedimentary rocks, respectively).

depths, due to the limited oxygen availability for combustion (Grapes, 2010). The CP sequence is featured by an upward increase of metamorphic grade; however LT and retrograde rocks occur in all parts of the metamorphic sequence. The geological field trip focused on studying CP features and collecting rock samples in the northern part of Hatrurim Basin where the CP sequence is well preserved and exposed along with the sedimentary one (Fig. 1). Highest metamorphic grade rocks were found at top and bottom sequence, representing meta-

morphosed impure limestone (Ghareb and Taqiye Fm.) which are classified as ye'elimite-larnite granofels (also called Larnite Rocks): ye'elimite-larnite granofels rocks are fine and dense rocks always crisscrossed by later hydration veins. Larnite Rocks protolith was sampled from fresh excavation front inside Rotem Amfort Mine close to eastern Hatrurim Basin (Fig. 2): Ghareb Formation rocks were classified as calcimudstone rich in phosphatic pellets and gypsum, very porous and soft.

## MATERIALS

Ye'elimite-larnite granofels both anhydrous and hydrated ones collected at the top and bottom of the CP sequence in Hatrurim Basin area were deeply studied by means of conventional and innovative analytical techniques.

Gypsum-apatite-rich calcimudstone (impure limestone) belonging to Ghareb Formation collected inside Rotem Amfort Mine (Israel), close to the western part of Hatrurim Basin, was studied obtaining microstructural, mineralogical and crystallographical features. Furthermore, this impure limestone was used as starting raw meal for preparing new green-cements doped with  $\text{SO}_3$ , F and  $\text{P}_2\text{O}_5$ .

An industrial fine mixture based on limestone, clays, kaolinite, hematite, and quartz was used as starting raw meal for preparing Belite Cement at laboratory scale.

Sample / Oxide (wt%)	Larnite Rocks	Ghareb Fm.	F-BC raw meal
CaO	56 - 53	47.1 [68.4]	38.5 [57.5]
$\text{SiO}_2$	23 - 25	11.8 [17.1]	14.9 [23.2]
$\text{Al}_2\text{O}_3$	9 - 10	3.3 [4.9]	5.3 [7.4]
$\text{Fe}_2\text{O}_3$	3 - 4	2.5 [3.6]	3.7 [5.5]
MgO	1 - 2	0.2 [0.3]	0.6 [0.9]
$\text{SO}_3$	1 - 4	1.9 [2.7]	2.1 [3.3]
$\text{P}_2\text{O}_5$	1 - 3	1.8 [2.5]	0.1 [0.2]
LOI	1 - 3	31.5	34.8
Tot.	99 - 101	100.4	100.6

**Table 1** X-ray Fluorescence (XRF) of studied materials; esd is lower than 1 wt%; inside square brackets is reported the wt% value normalized to Tot.-LOI.

## METHODS

A multidisciplinary approach based on conventional and innovative techniques was strictly necessary in order to handle the high complexity of studied materials (i.e., low amount of crystal phases, low crystal size, numerous polymorphs and polymorphic transitions during heating), especially for natural ones.

X-Ray Fluorescence (XRF), Reflected and Transmitted Light Microscopy (RLM & TLM), Scanning Electron Microprobe and Electron Microprobe microAnalyser (SEM/EMPA), Laboratory X-Ray Powder Diffraction (LXRPD) and Single Crystal X-Ray Diffraction (SC-XRD) were used as conventional techniques obtaining relevant information for microstructural, crystallographic, mineralogical and chemical information.

Whereas, Synchrotron X-Ray Powder Diffraction with in-situ High Temperature and ex-situ experiments (in-situ HT and ex-situ SXPDP), Neutron Diffraction (NXRD), Single Crystal Synchrotron X-Ray Diffraction (SC-SXRD)

and Computed MicroTomography with in-situ High Temperature and ex-situ experiments (in-situ HT and ex-situ  $\mu$ -CT) were used to gain relevant microstructural and mineralogical changes occurring during heating and overcoming limitations of ordinary techniques.

HT and LP experiments were performed at laboratory scale to synthesize Belite Cement and S-P-F-doped Cement using industrial raw meal and Ghareb Fm., respectively. A laboratory oven with SiC resistors was used for HT experiments up to 1350°C with an increasing rate of 2°C/min and slow cooling.

Furthermore, Isothermal Calorimetric Analysis (ICA), Thermal Gravimetric Analysis associated with Differential Scanning Calorimetry (TGA-DSC) and Specific Surface Analysis (SSA) were used during hydration study.

## RESULTS

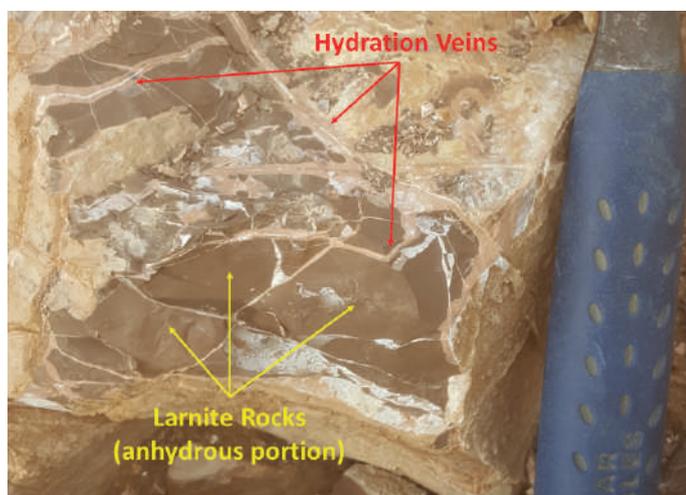
Results were presented in four sections considering (i) the study of Larnite Rocks (i.e., natural cement) sampled in Hatrurim Basin (see section 5.1), (ii) investigation and synthesis of S-P-F-doped Cement using Ghareb Fm. rocks (see section 5.2), (iii) synthesis of Belite Cement at laboratory scale (see section 5.3) and (iv) hydration experiments between synthetic Belite Cement and natural Larnite Rocks (see section 5.4).

### Ye'elimite-larnite granofels investigations

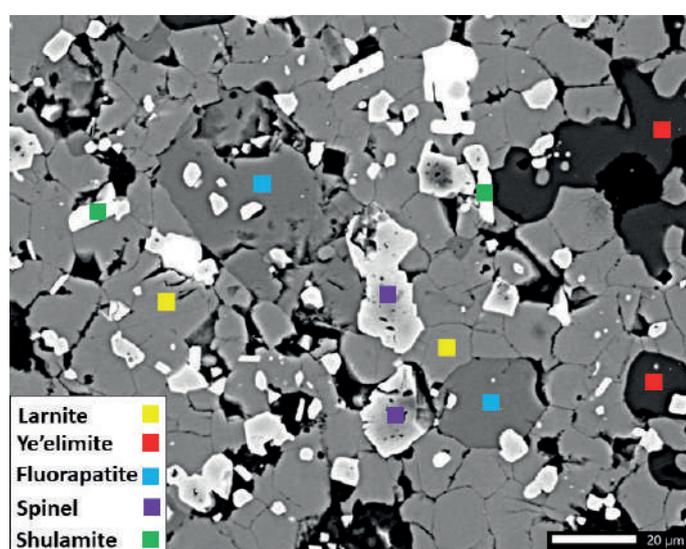
Ye'elimite-larnite granofels were collected at bottom and top of Hatrurim Basin, highlighting similar features:



**Figure 3** Irregular metric outcrops of Larnite Rocks at the bottom of CP sequence in Hatrurim Basin, surrounded by retrograde LT rocks.



**Figure 4** Larnite Rocks outcrop highlighting a fine microtexture and anhydrous dark brown portions crisscrossed by internally structured hydration veins.



**Figure 5** SEM of Larnite Rocks revealing the fine microtexture based on polygonal larnite (medium grey, yellow square), anhedral ye'elimite (dark grey, red square), subhedral spinel (light grey, purple square), prismatic shulamite (white, green square) and euhedral peciloblastic fluorapatite (darker medium grey, light blue square).

dark brown to black rocks with fine microtexture, dense and hard to brake rocks (Figs.3,4). Mineral assemblage is always based on larnite (Larn,  $\beta$ - $\text{Ca}_2\text{SiO}_4$ ) and ye'elimite (Yel,  $\text{Ca}_4\text{Al}_6\text{SO}_{16}$ ) as major phases, and shulamitite (Shul,  $\text{Ca}_3\text{Ti}(\text{Al},\text{Fe})_2\text{O}_8$ ), fluorapatite-ellestadite (Fap-ell,  $\text{Ca}_5(\text{P}_{1-x}\text{S}_{x/2}\text{Si}_{x/2})\text{F}$ ) and spinel (Spin,  $\text{Mg}(\text{Al},\text{Fe})_2\text{O}_4$ ) as minor ones; whereas differences among samples are related on ye'elimite abundance and trace phase occurrence such as brownmillerite (Brw,  $\text{Ca}_2(\text{Al},\text{Fe})_2\text{O}_5$ ), ternesite (Tern,  $\text{Ca}_5(\text{SiO}_4)_2(\text{SO}_5)$ ) and mayenite (May,  $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ). Microtextural investigations showed high density and low porosity of samples, revealing larnite as main mineral with polygonal shape (i.e., granoblastic texture), anhedral ye'elimite, prismatic shulamitite and peciloblastic euhedral fluorapatite crystals (Fig. 5).

Ye'elimite-larnite granofels are always crisscrossed by later hydration veins that often reveal an internal structural made of a white core and brown rims: white core is mainly composed of calcium carbonate polymorphs

(calcite, aragonite and vaterite) and minor gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) ettringite (Etrr,  $\text{Ca}_5\text{Al}_{12}(\text{OH})_{12}(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$ ) and tobermorite (Tob,  $\text{Ca}_5\text{H}_2\text{Si}_5\text{O}_{18} \cdot 4\text{H}_2\text{O}$ ); whereas, brown rims are composed of low water reactive phases (Shul, Spin and Fap-ell), calcium carbonates, Ca-Si-H phases, hydrogarnet (Hydrg,  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ ) and aluminium hydroxides (i.e, gibbsite, nordstrandite and bayerite).

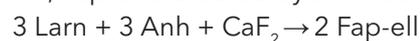
### Ghareb Formation HT experiments (S-P-F-doped Cements)

Ghareb Fm. samples were collected at Rotem Amfort Mine (Fig. 2a) and were classified as calcimudstone rich in gypsum and apatite as fish bone fragments and phosphatic pellets (Lewy, 1990; Schneider-Mor et al., 2012). The selection of Ghareb Fm. as starting raw material for synthesizing new green-cements was based on the following reasons: (i) Ghareb Fm. represents a voluminous waste generated from the operations of the Rotem Amfort Mine (Israel), allowing the chance of waste management as alternative raw material promoting Circular Economy; (ii) Ghareb Fm. possesses a high concentration of dopant elements (P, S and F) which are common in several different wastes (phosphogypsum, bottom and fly ashes) that can even boost clinkering reactions (calcium silicate phases formation at HT) if are used as alternative raw materials (Kurdowski, 2014); (iii) Ghareb Fm., along with Taqiye Fm., represents the protolith of ye'elimite-larnite rocks, allowing for the reconstruction of the transformation processes (i.e., metamorphic reactions, microstructural changes, polymorphic transitions and melting) during CP by means of HT laboratory experiments.

Despite Ghareb Fm. samples showed a homogeneous and fine microtexture, three different inhomogeneities locally occurred at larger observation scale: (a) millimetric black, soft and porous nodules composed of calcite, goethite ( $\text{FeO}(\text{OH})$ ), quenstedtite ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 11\text{H}_2\text{O}$ ), bernalite ( $\text{Fe}(\text{OH})_3 \cdot 0.25\text{H}_2\text{O}$ ), titanite ( $\text{CaTiSiO}_5$ ) and minor clays; (b) millimetric gypsum-rich veins (> 90 wt%) with decimetric lateral continuity showing no preferred orientation; (c) submillimetric goethite-rich layers with decimetric later continuity revealing no preferred orientation.

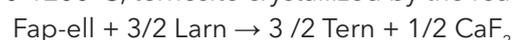
HT experiments and in-situ HT SXRPD on Ghareb Fm. powders highlighted microstructural, metamorphic reactions, polymorphic transition, crystal phase assemblage changes occurring upon heating of impure limestone. Ghareb Fm. powders (i.e., S-P-F-rich impure limestone) were heated up to 1350°C revealing four main features occurring at different temperatures:

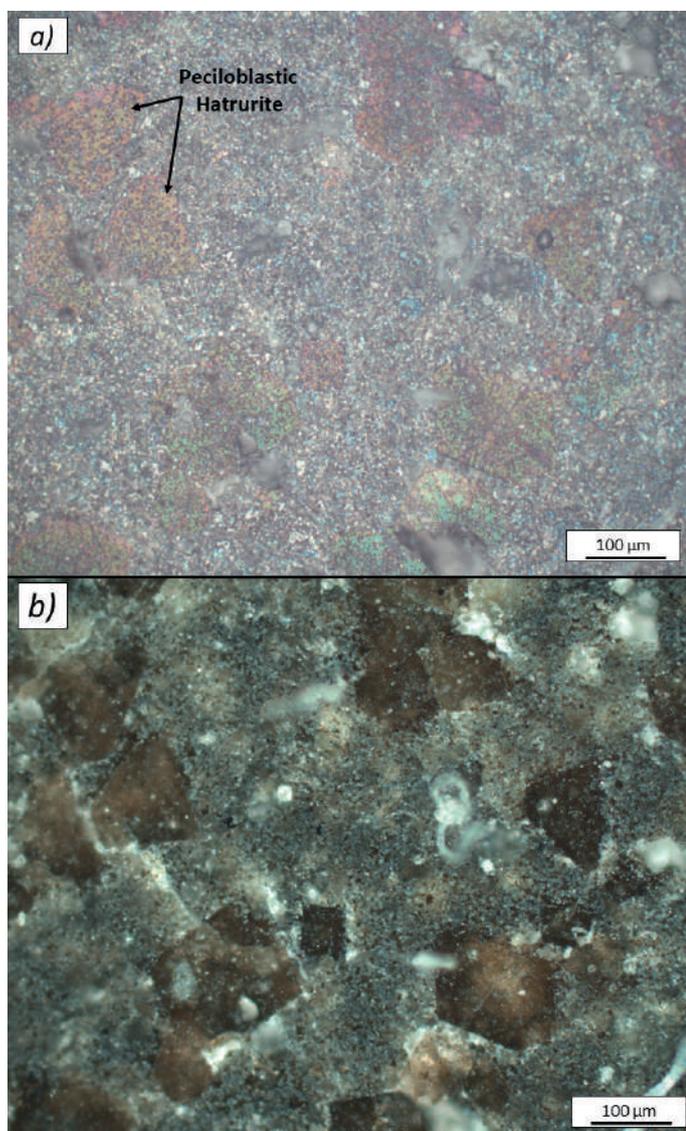
(i) 800-1000°C, Fap-ell increased by the reaction



which leads larnite consumption;

(ii) 1000-1200°C, ternesite crystallized by the reaction:





**Figure 6** RLM of Ghareb Fm. powders heated at 1250°C after Nital etching at (a) parallel nicols and (b) crossed nicols, revealing peciloblastic pseudo-hexagonal hatrurite.

which released fluorite;

(iii) 1200-1250°C (Fig. 6), 1<sup>st</sup> melting event (LT melt) due to the incongruent melting of:

$\text{Larn} + \text{Fap-ell} + \text{CaF}_2 \rightarrow \text{Larn} + \text{Fap-ell} + \text{Liquid}$

(iv) 1250-1280°C, 2<sup>nd</sup> melting event (HT melt) featured by the melting of Ca-Al-Fe-rich phases (i.e., brownmillerite, mayenite and part of ye'elimite) revealed by the change from euhedral to xenomorphic texture.

Furthermore, hatrurite (also called alite,  $\text{Ca}_3\text{SiO}_5$ ) crystallized at T of 1200-1250°C forming coarse peciloblastic pseudo-hexagonal crystals (Fig. 6), which later breaks down at  $T > 1250^\circ\text{C}$ . At  $T > 1250^\circ\text{C}$  hatrurite turned from euhedral crystals (100-200 µm) to rounded crystals with lesser inclusions that are made of May+Brw. All these outcomes are relevant for cement manufacture because Ghareb Fm. represents the starting raw material for producing a S-P-F-doped Cement (i.e., new type of green-cement).

### Fe-rich Belite Cement (F-BC) synthesis

An industrial raw meal composed of a mixture of li-

mestone, clays, hematite and gypsum was used to prepare F-BC at laboratory scale (Table 1), studying microstructural, mineralogical and crystallographic changes occurring during heating up to 1350°C. Commercial BCs are always composed of mainly larnite, brownmillerite, mayenite and/or celite ( $\text{Cel}$ ,  $\text{Ca}_3\text{Al}_2\text{O}_6$ ) plus a variable amount of ye'elimite depending on the selected  $\text{SO}_3$  content (De La Torre et al., 2007). Our F-BC prepared at laboratory scale highlighted Larn-Brw-Yel-May already stable at  $T \geq 1200^\circ\text{C}$ , despite this final mineral assemblage usually occurs between 1300-1350°C (Ghorab et al., 2014): this result represents an important outcome for improving BCs manufacture. Samples heated at  $T \leq 1300^\circ\text{C}$  showed a microtexture based on micrometric crystals of Larn, Yel, May and coarser prismatic Brw with high porosity; whereas samples heated  $T > 1300^\circ\text{C}$  figured out lower porosity, coarse rounded Larn, subhedral Yel and xenomorphic matrix of Brw. This dramatic change in microtextural features is accounted to the main melting event of BCs which usually occurs between 1270-1309°C leading the formation of a melt mainly rich in Ca, Al and Fe (Brw and May melt) improving the growth of crystal phases and reactions (Kurdowski, 2014).

### Hydration experiments

Hydration properties comparison between ye'elimite-larnite granofels and F-BC prepared at 1350°C was made by means of hydration experiments. Cements were prepared by adding 3 wt% of gypsum to ye'elimite-larnite granofels powder and F-BC. Later, cements were mixed with water (0.5 water/cement ratio) and investigated till 28 hydration days. Results highlighted that natural and synthetic Belite Cement have similar heat release and crystal phase evolution during hydration, excepted for the earlier crystallisation of stratlingite ( $\text{Strat}$ ,  $\text{Ca}_2\text{Al}_2\text{SiO}_2(\text{OH})_2 \cdot 3\text{H}_2\text{O}$ ) after 7 hydration days for natural cement.

Furthermore, the natural hydration of ye'elimite-larnite granofels was reproduced at laboratory scale by hydrating (a) rock powders and (b) rock fragments. (a) Rock powders hydration revealed after 4 months a mineral assemblage composed of unreacted larnite, low reactive phases (i.e., Fap-ell, Shu and spinel), stratlingite, ettringite, calcite, aluminium hydroxides and amorphous Ca-Si-H, which the latter comes from larnite hydration starting after 12 hydration weeks. However, the obtained phase assemblage is similar to brown rims one, excepted for the occurrence of stratlingite and amorphous Ca-Si-H instead of crystalline Ca-Si-H phase and hydrogarnet: stratlingite should later breakdown in hydrogarnet and Ca-Si-H phases when  $\text{Ca}(\text{OH})_2$  content increases due to larnite hydration. (b) Rock fragments hydration produced a white precipitate made of calcite, ettringite, gypsum and aluminium hydroxides, which well fits with white core mineral assemblage of natural hydrated veins.

## DISCUSSION AND CONCLUSIONS

This study deeply compared the natural process of Combustion Pyrometamorphism (CP) that involved impure limestones occurring in Hatrurim Basin (Israel) and the synthetic analogous process of cement manufacture by means of a multidisciplinary approach.

The geological field trip in Hatrurim Basin area allowed to collect both CP rocks and protolith of Larnite Rocks, and relevant geological features making a direct comparison with available bibliographic data. Chemical composition differences (i.e., changes inside the  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ ) and microstructural changes observed along the metamorphic sequence are well linked to changes occurring inside the pristine sedimentary sequence: (i) metamorphosed Mishash Fm. corresponds to the base of metamorphosed sequence; (ii) gehlenite-wollastonite and anorthite-diopside hornfels represent brown to black layers corresponding to the metamorphism of marls belonging to Taqiye Fm.; (iii) stratified Larnite Rocks and calcite-spurrite well fit with HT metamorphism of well stratified marly limestone of Hafir Member (Upper Taqiye Fm.). Furthermore, HT rocks usually occur at the metamorphic sequence top or areas featured by high oxygen availability. Therefore, all results confirmed the general hypothesis of in-situ HT and LP metamorphism of a sedimentary sequence by methane-rich gases combustion which came from deep hydrocarbon reservoirs.

The study on protolith of Larnite Rocks (Ghareb Fm.) was crucial to reveal detailed mineralogical and crystallographic information and to highlight natural anisotropies which influence mineral assemblage and microtexture of resulting CP rocks. The link between Ghareb Fm. inhomogeneities and ye'elimite-larnite granofels microtexture was confirmed by: (i) millimetric black nodules rich in spinel and Ti-bearing phases in ye'elimite-larnite granofels should be correlated with millimetric dark nodules rich in Fe-phases and minor titanite occurring inside pristine limestone; (ii) coarse fluorapatite crystals occurring inside ye'elimite-larnite granofels should be linked to the occurrence of phosphatic pellets inside protolith rocks.

Detailed crystallographic and microtextural investigations on ye'elimite-larnite granofels and the equivalent green-cement doped in S-P-F, which was laboratory prepared using ye'elimite-larnite granofels protolith, revealed crystal phase evolution upon heating till 1350°C showing two main melting events: (i) low-T melt rich in Anh-Larn- $\text{CaF}_2$  is produced from  $T \geq 1054^\circ\text{C}$  when  $\text{CaF}_2$  is released during Tern crystallisation and Fap-ell breakdown; (ii) high-T Al-Fe-rich melt occurs at 1250-1270°C, leading microtextural features close to BCs ones. Furthermore, highly doped hatrurite occurred at Room Temperature (RT) after heating Ghareb Fm. at 1244°C even with a slow cooling, representing a relevant outcome for designing new green-cements and advancing cement

manufacture: the simultaneous occurrence of S, P and F in cement raw meal strongly improves hydration properties and reduces combustion T. Therefore, this study figured out the availability of S-P-F-rich wastes reuse (e.g., phosphogypsum, solid urban wastes, F-rich sludges and S-P-F-rich rock wastes) as alternative raw materials in cement manufacture coping with the aim of managing waste-related problems (dangerous elements pollution, reducing land use for landfills and waste treatment costs) and reducing  $\text{CO}_2$  emissions (lowering combustion T, fuel and natural raw materials consumption). Furthermore, results could be employed not only for improving cement manufacture but also for advancing oil fields exploration, due to the vicinity of CP rocks to oil and gas reservoirs: CP rocks could be used as a proxy especially for methane-rich reservoirs exploration.

F-BC samples showed a mineral assemblage and hydration properties similar to commercial BCs. Nevertheless, results highlighted that the BCs final mineral assemblage (Larn-Brw-Yel) was already occurring at 1200°C with high porous and fine microtexture representing relevant outcomes for BCs manufacture allowing: (a) lower energy expenditure and  $\text{CO}_2$  emission reduction thanks for the lower combustion T compared to common BCs conditions (1250-1350°C); (b) lower grinding costs thanks to the advantageous porous-soft microtexture that represents a main item of expenditure in cement manufacture; (c) the positive reuse of Fe-S-rich wastes as alternative raw material helps in handling bauxite supply and landfill related problems.

Natural ye'elimite-larnite granofels figured out similar hydration reactions of F-BC, excepted for earlier stratlingite occurrence in natural cement due the hydration contribution of minor phases such as mayenite and aluminium hydroxides:  $\text{Al}(\text{OH})_3$  that occurs as minor phase in Larnite Rocks and is also produced by mayenite hydration can reacts with Ca-Si-H phases forming stratlingite.

Furthermore, hydration experiments on ye'elimite-larnite granofels clarified the formation of natural hydrated veins better explain their textural features: (i) the weathering of ye'elimite-larnite granofels outcrops caused the water interaction with reactive anhydrous phases (e.g., larnite, ye'elimite, mayenite, brownmillerite and ternsite) leading a circulating pore solution rich in  $\text{Ca}(\text{OH})_2$ ,  $(\text{SO}_4)^{2-}$  and  $\text{Al}(\text{OH})_3$ , and hydration products (i.e., Ca-Si-H phases, Hydr, gibbsite and Ettr); (ii) the resulting pore solution infills cracks and lead the precipitation of calcite, ettringite and gypsum, forming white core of hydration veins; (iii) the hydration products remain in the same position close to anhydrous portions and gradually crystallise as Ca-Si-H phases (tobermorite, jennite and afwillite), hydrogarnet, gibbsite and minor minerals coming from the pore solution (e.g., calcite, ettringite and gypsum), resulting in the brown rims of hydration veins.

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