	Experiment title: A comparison study between cement materials and their natural analogous by ex-situ and in-situ high-temprature Synchrotron X-ray Powder Diffraction	**Experiment number**: ES-964

Beamline:	**Date of experiment**: from: 02/06/2021 to: 05/06/2021	**Date of report**:
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REPORT:

Introduction

The experiment aimed to compare the Combustion Pyrometamorphism (CP) of limestone, which represents the natural analogous process of cement production, and Cement Manufacture (CM), by means of *ex-situ* and *in-situ* High-Temperature Synchrotron X-Ray Powder Diffraction (*ex-situ* and *in-situ* HT-SXRPD). CP is a complex geological process usually involving sedimentary rocks (limestone, marls, clays, among others) in a first stage of HT combustion (up to 1450 °C), followed by a later hydration stage featured by the hydration, sulfation and carbonation of previous HT rocks. Therefere, limestone-rich rocks (impure limestone and marls) involved in CP result in the formation of natural analogous of anhydrous (CP first stage products) and hydrated cement (CP later stage products).

The main focus of this experiment was to get extremely accurate data related to: (i) crystal phase composition; (ii) crystallographic parameters (cell parameters, coherent domain size and microstrain); (iii) chemical reactions and (iv) phase transitions during heating of limestone from *in-situ* results.

Results were crucial for a better understanding of CP, revealing metamorphic reactions and geological feature changes, and improving CM, particularly finding new cement types (i.e., *green-cements* also called *eco-cements*) and thermal treatent able to reduce the energy consumption hence limiting CM environmental impact.

Results

Ex-situ SXRPD were performed on both natural CP rocks (hydrated and anhydrous) and synthetic (laboratory prepared) cement materials (anhydrous and hydrated cements). Anhydrous CP rocks (ye'elimite-larnite granofels, also called larnite-rich rocks, were collected in Hatrurim Basin in Israel)) are composed of larnite (β-Ca_2SiO_4), ye'elimite ($Ca_4Al_6SO_{16}$), spinel ($Mg(Fe, Al)_2O_4$), shulamite ($Ca_3Ti(Al, Fe)_2O_8$) and fluorapatite-ellestadite ($Ca_5(P_{1-x/2}S_{x/2}Si_{x/2}O_4)_3F$) as main constituent, plus minor amount of brownmillerite ($Ca_2(Al, Fe)_2O_5$), mayenite ($Ca_{12}Al_{14}O_{33}$) and ternesite ($Ca_5(SiO_4)_2(SO_4)$). Whereas, hydrated CP rocks (calcite-rich rocks) are composed of calcium carbonates polymorphs (calcite, vaterite and aragonite), ettringite ($Ca_6Al_2(OH)_{12}(SO_4)_3 \cdot 26H_2O$) and tobermorite 11Å ($Ca_5H_2Si_6O_{18} \cdot 4H_2O$) as main crystal phases, associated with minor gypsum ($CaSO_4 \cdot 2H_2O$), thaumasite ($Ca_3(SO_4)[Si(OH)_6CO_3] \cdot 12H_2O$), bulfoteinite ($Ca_2SiO_2(OH, F)_4$), apophyllite ($KFCa_4Si_8O_{20} \cdot 8H_2O$) and aluminium hydroxes (bayerite, gibbsite and nordstrandite). Two different samples of synthetic cement (*green-cements*) were prepared and investigated: (i) sample BC represents a Belite Cement with high Fe₂O₃ and SO₃ doped, heated at 1200 °C at laboratory scale; (ii) sample RM represents the pristine impure limestone of ye'elimite-larnite granofels before CP process, which was sampled in Israel in Rotem Amfort Mine, later laboratory heated at 1200 °C. Crystal phase composition is

roughly different between BC and RM samples: (i) BC is mainly composed of larnite, representing > 60 wt.%, brownmillerite and ye'elimite, plus minor srebrodolskite ($Ca_2Fe_2O_5$), mayenite and k-feldspar ($KAlSi_3O_8$); (ii) RM is mainly based on larnite, ternesite, lime (CaO), fluorapatite-ellestadite and brownmillerite associated with minor mayenite and ye'elimite.
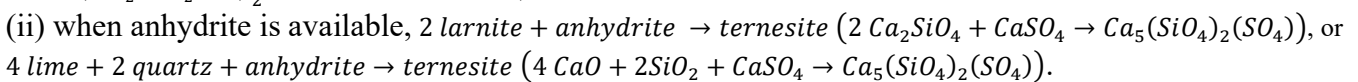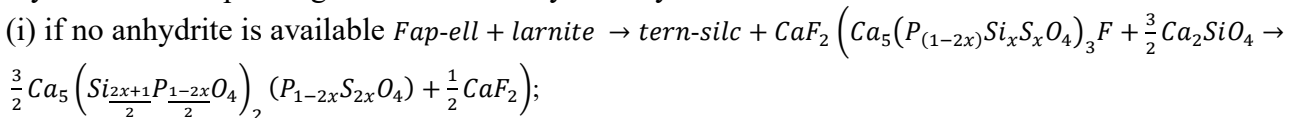
In-situ HT-SXRPD was performed on impure limestone (RM) representing the pristine rock of ye'elimite-larnite granofels before CP process. Two different experimental set-ups were emploied: (i) heating at different selected T (916, 966, 1029, 1040, 1077, 1095, 1111, 1133 and 1182 °C) with an increasing rate of 15 °C/min till 900 °C and 5 °C/min from 900 to 1182 °C and a stabilisation time of 10 min before data collection; (ii) continuos step-by-step T increase of ~ 13 °C without stabilisation time before data collection with an increasing rate of 15 °C/min till 900 °C and 5 °C/min from 900 to 1250 °C. In-situ experiment performed with the stabilising time pointed out four main features (Fig. 1a): (i) fluorapatite-ellestadite solid solution (Fap-ell) highlighted a first steep decrease from 966 to 1029 °C related to ternesite and ye'elimite formation, followed by a gradual reduction till 1182 °C; (ii) ternesite, after its crystallisation at T > 966 °C, increased up to 1111-1133 °C consuming Fap-ell and C2S, after which decomposed even during cooling (~ 1182 °C) halving its wt.%; (iii) α'L-Ca2SiO4 decreased during the grow of ternesite and turned into α'H-Ca2SiO4 from 1111-1150 °C, whereas at T > 1150 °C only α'H-Ca2SiO4 and α-Ca2SiO4 were stable; (iv) flamite (α'H-Ca2SiO4) was found even after quenching from HT; (v) no brownmillerite and mayenite reduction occurred over the temperature window investigated, confirming the lack of main melting event. Whereas, in-situ experiments performed without a stabilisation time before data collection highlighted six remarkable features: (i) till 1098 °C the mineral assemblage is composed of lime, mayenite, brownmillerite, Fap-ell, α'L-Ca2SiO4 and minor amount of anhydrite (CaSO4); (ii) ternesite crystallised at T 1098-1123 °C and fastly increased till 1170 °C, following a gradual reduction ending with the total decomposition at 1232-1235 °C; (iii) ye'elimite appeared at 1123-1146 °C leading mayenite consumption; (iv) Fap-ell strongly decreased after stabilisation of ternesite and ye'elimite, completely disappeared when hatrurite (Ca3SiO5) occurred at T 1235-1244 °C, and finally re-crystallised during cooling; (v) α'L-Ca2SiO4 firstly turned into α'H- Ca2SiO4 from 1123 to 1146 °C, at T > 1189 °C definitly changed in α- Ca2SiO4, and after queching only α- Ca2SiO4 occurred with no α'H or β- Ca2SiO4 modifications; (vi) hatrurite started crystallising from 1235-1244 °C and remained stable during cooling.

Discussion

SXRPD results on Combusted Pyrometamorphosed rocks (CP rocks) and their synthetic corresponding cement materials highlighted relevant outcomes for geological and industrial purposes.
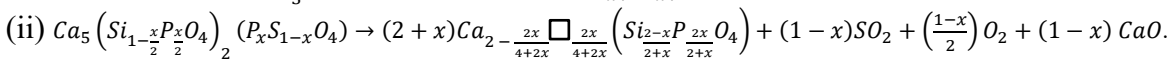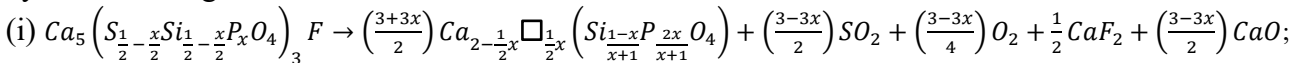
Ex-situ results on CP rocks were fundamental in higlighting the variability of crystal phase assemblage of ye'elimite-larnite granofels (anhydrous CP rocks), which differs mainly in minor phases, such as brownmillerite, mayenite and ternesite occurrence, which the latter could be used to better constrain the formation temperature (geothermometer). Whereas, hydrated CP rocks revealed higher variability of mineral assemblage compared to anhydrous samples and the ubiquitarius occurrence of minor fluorapatite-ellestadite, spinel and shulamitite, confirming different hydration condition from a location to another (i.e., temperature, pH and chemical compostion of water) and the genesis from direct in-situ weathering of anhydrous rocks (i.e., percolation of water or rains) mainly running along fractures, cracks and weather exposed surfaces.

In-situ HT-SXRPD on RM samples (impure limestone from Israel) clarified all main changes occurring during heating of impure limestone, helping in estimating formation temperature and metamorphic reactions of ye'elimite-larnite granofels. Experiments confirmed the involvement of Fap-ell, anhydrite and larnite during ternesite crystallisation starting at 966-1029 and 1098-1123 °C for experiments with and without the stabilisation time before data collection, respectively. This outcome pointed out two different reactions of ternesite crystallisation depending on the availability of anhydrite:

(i) if no anhydrite is available $Fap\text{-}ell + larnite \rightarrow tern\text{-}silc + CaF_2$ $\left(Ca_5(P_{(1-2x)}Si_xS_xO_4)_3F + \frac{3}{2}Ca_2SiO_4 \rightarrow \right.$

$\left. \frac{3}{2}Ca_5\left(Si_{\frac{2x+1}{2}}P_{\frac{1-2x}{2}}O_4\right)_2(P_{1-2x}S_{2x}O_4) + \frac{1}{2}CaF_2 \right)$;

(ii) when anhydrite is available, $2\ larnite + anhydrite \rightarrow ternesite$ $\left(2\ Ca_2SiO_4 + CaSO_4 \rightarrow Ca_5(SiO_4)_2(SO_4) \right)$, or $4\ lime + 2\ quartz + anhydrite \rightarrow ternesite$ $\left(4\ CaO + 2SiO_2 + CaSO_4 \rightarrow Ca_5(SiO_4)_2(SO_4) \right)$.

The partial involvement of Fap-ell in ternesite crystallisation always releases CaF2 which should be partially hosted in mayenite [1] and the excess forms a melt at T > 1054 °C: Ca2SiO4-fluorellestadite-CaF2 assemblage at T ~ 1054 °C reaches a peritectic point incongruently melting (Ca2SiO4-fluorellestadite-Liq.) [2]. Later, the breakdown of tern-silc (occurring at 1111-1133 °C and 1170-1189 °C for in-situ with and without stabilisation time, respectively) and Fap-ell (starting at 1150-1182 °C and 1170-1189 °C for in-situ with and without

stabilisation time, respectively) released significant amount of phosphorous, which could be hosted inside larnite by the following two breakdown reactions:

(i) $Ca_5\left(S_{\frac{1}{2}-\frac{x}{2}}Si_{\frac{1}{2}-\frac{x}{2}}P_xO_4\right)_3F \rightarrow \left(\frac{3+3x}{2}\right)Ca_{2-\frac{1}{2}x}\square_{\frac{1}{2}x}\left(Si_{\frac{1-x}{x+1}}P_{\frac{2x}{x+1}}O_4\right) + \left(\frac{3-3x}{2}\right)SO_2 + \left(\frac{3-3x}{4}\right)O_2 + \frac{1}{2}CaF_2 + \left(\frac{3-3x}{2}\right)CaO;$

(ii) $Ca_5\left(Si_{1-\frac{x}{2}}P_{\frac{x}{2}}O_4\right)_2(P_xS_{1-x}O_4) \rightarrow (2+x)Ca_{2-\frac{2x}{4+2x}}\square_{\frac{2x}{4+2x}}\left(Si_{\frac{2-x}{2+x}}P_{\frac{2x}{2+x}}O_4\right) + (1-x)SO_2 + \left(\frac{1-x}{2}\right)O_2 + (1-x)CaO.$

Dicalcium silicate highlighted during *in-situ* experiments all polymorphic transitions at temperatures lower than ones reported for stoichiometric dicalcium silicate [3]–[5]: dopants, especially Na^+, K^+, Sr^{2+}, P^{5+}, B^{3+}, S^{6+} and Al^{3+}, usually reduce polymorph transition temperatures. More specifically, P^{5+} alone or coupled with Na^+ and/or K^+ increase the stability field of HT polymorphs (α'_L, α'_H, α- Ca_2SiO_4) [6]–[12], as occurring in RM heated samples.

The strong increase of dopants in dicalcium silicate, mainly in phosphour, as claimed by previously reported breakdown reactions, justify the transition to α-Ca_2SiO_4 at lower temperatures, promoting the formation of R-Ca_3SiO_5 at 1235-1244 °C, thanks to the higher reactivity of α-Ca_2SiO_4 with lime (CaO+α-$Ca_2SiO_4 \rightarrow Ca_3SiO_5$) compared to α'_H-Ca_2SiO_4 and even the occurrence of low-T melt [3], [4]. Furthermore, both α-Ca_2SiO_3 and hatrurite were found at room temperature after quenching from 1244 °C, representing an extremely important outcome useful for improving CM: hatrurite associated with α-Ca_2SiO_4, instead of other lower polymorphs, improves hydration reactivity and reduces energy expenditure by the lower T formation compared to Ordinary Portland Cement (OPC) conditions (T ~ 1450 °C).

Ex-situ SXRPD experiment on Belite Cement (BC) slightly doped in sulphur with higher Fe_2O_3 prepared at 1200 °C showed up a crystal phase assemblage similar to common BCs plus minor ye'elimite and higher brownmillerite content. Therefore, results confirmed to chance of producing BC using alternative raw materials (i.e., impure natural raw materials and wastes) and reducing CO_2 emission thanks to lower combustion T (~ 150-100 °C).

Conclusions

Results were crucial in better constraining combustion temperature of ye'elimite-larnite granofels, describing metamorphic reactions occuring during heating: (i) ye'elimite-larnite granofels should have formed at T higher than ternesite breakdown T (1111-1133 °C) and lower than fluorapatite-ellestadite ones (1150-1182 °C); (ii) ye'elimite-larnite granofels estimated temperature formation (~ 1111 to 1182°C) excluded the reaching of main melting point (1250-1270 °C, high-T melt) during CP process.

Furthermore, *in-situ* studies on RM samples, representing the pristine rocks of ye'elimite-larnite granofels before CP, pointed out several benefits of reusing impure limestone as alternative raw material for designing new *green-cements* with better hydration properties compared to standard Belite Cement (BC) thanks to simultaneous minor elements effects (F-P-S-doping): occurrence at lower T of hatrurite and HT dicalciumsilicate polymorphs (α-Ca_2SiO_4 and α'_H-Ca_2SiO_4) compared to Ordinary Portland Cement conditions, boost the reduction of CO_2 emission and improves hydration reactivity. This study confirmed the availability of wastes valorisation (e.g., phosphogypsum, solid urban wastes, F-rich sludges, P-S-F-rich rock wastes, etc.) as partially replacing raw materials in cement manufacture being able to cope with the aim of managing waste-related problems (dangerous elements pollution, reducing land use for landfills and waste treatment costs) and reducing CO_2 emissions (lowering combustion T, grinding energy expenditure, fuel and natural raw materials consumption).

Experiments on synthetising Belite Cement with slightly doped in sulphur and high in Fe_2O_3 (BC sample) prepared at 1200 °C showed the same stable crystal phase assemblage of ordinary BCs with minor ye'elimite and higher brownmillerite: final mineral assemblage was obtained at 1200 °C, excepted for minor amount of k-feldspar; (ii) β-Ca_2SiO_4 was always stable at room temperature without γ-Ca_2SiO_4 retrograde polymorphic transition even with a slow cooling. These outcomes allow (a) a strong reduction of energy expenditure and CO_2 emission for cement plant, thanks for the lower temperature combustion; (b) the positive reuse of Fe-S-rich wastes as alternative raw material, helping in handling raw materials supply (i.e., shortages of bauxite deposits and availability of limestone) and landfill related problems.

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