European Mineralogical Conference
Vol. 1, EMC2012-142-1, 2012
European Mineralogical Conference 2012

Natural analogues of sulfate-bearing cement clinkers: mineralogy and mineral chemistry

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Brownmillerite-ye'elimite-larnite (BYL) rocks have been found in the lower and uppermost parts of a peculiar sequence of ultrahigh-temperature ambient-pressure calcareous combustion metamorphic rocks in the Hatrurim Basin, Israel. In the lower section they are dark gray or brown cobbles coated with multimineral rhythmic crusts of Ca carbonates and silicate hydrates, gypsum, ettringite, hydrogarnets, and halite. On hilltops, microcrystalline, dark grey or greenish larnite-bearing rocks form massive bodies akin to hornfels. All rocks are compositionally similar and contain (in wt%) 21-26 SiO_2, 0.4-0.5 TiO_2, 10-12 Al_2O_3, 4-5 Fe_2O_3, 0.5-1.1 MgO, 52-56 CaO, 0.1-0.5 Na_2O, and 1.3-2.3 wt% P_2O_5, with K_2O from 0.1 to 2.3 and SO_3 from 1.3 to 5.0 wt%, and with rather high enrichment (ppm) in V (40-110), Cr (95-380), Ni (130-240), Zn (250-430), Sr (1400-3000), Ba (130-440), Se (up to 95), and U (up to 23). The BYL rocks consists of 30-40% larnite, 20-40% ye'elimite, 5-15% brownmillerite-perovskite$_{ss}$ + spinel; and 15% fluorellestadite or fluorapatite. Minor phases are barite, periclase (Fe-Ni-Zn-bearing), and gibbsite as a decomposition product of ye'elimite. Hatrurite (Ca_3SiO_5), α'- Ca_2SiO_4, eucairite (CuAgSe), and Cu_2Se occur as single grains. Crystals in all minerals are subhedral and rather uniform in size (10-30 μm).

Larnite (β-Ca_2SiO_4, an analogue of type II belite) is a predominant polymorph of Ca_2SiO_4. It forms colorless rounded grains with one set of parallel lamellae. The α'-Ca_2SiO_4 (analogue of type I belite) modification has distinct two sets of lamellae crossing at 60°. The two modifications have similar compositions (in wt%): 63.57-65.26 CaO, 30.20-34.68 SiO_2, 0.20-0.57 Na_2O, 0.05-0.80 K_2O, up to 0.22 FeO, 0.17 BaO, and 0.10 MgO. The empirical formula is $Ca_{1.96-1.98}Na_{0.01-0.02}Si_{0.96}P_{0.03}Al_{0.01}O_4$. β-Ca_2SiO_4contains 0.45-2.12 wt% $P_2O_5$and 0.03-0.34 wt% Al_2O_3 whereas α'-Ca_2SiO_4 is richer in P_2O_5 (0.51-4.67 wt%) and Al_2O_3(0.02-0.66 wt%).

Ye'elimite is brownish and bears numerous inclusions of Ca_2SiO_4. Ye'elimite differs compositionally from $C_4A_3\overline{S}$, with (in wt %) 45.84-47.91 Al_2O_3, 35.05-36.73 CaO, 11.54-13.64 SO_3, 1.80-2.41 Fe_2O_3, 0.64-0.83 SiO_2, 0.26-0.37 BaO, 0.10-0.20 K_2O, 0.07-0.47 P_2O_5, 0.06-0.23 MgO, and 0.05-0.15 Na_2O. Its empirical formula is $Ca_{3.99}Mg_{0.02}Ba_{0.01}Na_{0.02}K_{0.02}Al_{5.73}Fe^{3+}_{0.16}Si_{0.10}S_{0.97}P_{0.02}O_{16}$.

Fluorapatite and fluorellestadite crystals (up to 200-400 μm) are stuffed with inclusions of the other minerals. They are series of solid solutions with nearly constant CaO (54.20–56.21 wt%) and variable P_2O_5 (10.15–25.55), SO_3 (7.36–15.66), SiO_2 (6.81–12.64), and F (2.90–3.45), all in wt.%. The main impurities are V_2O_5 (0.10-0.51) and FeO (0.03-0.58); Cl has not been detected ($<$ 0.03 wt.%). The empirical formula is $(Ca_{9.84-9.99}Fe^{2+}_{0.01-0.03}V_{0.01-0.03}P_{1.73-3.62}Si_{1.14-2.06}S_{1.11-1.95}O_{24}F_{1.54-1.85})$.

The compositions of brownmillerite $Ca_2(Fe_{1-x}Al_x)_2O_5$ range as x= 0.20–0.27 and contain (in wt.%): SiO_2 (0.57-0.81), TiO_2 (2.12-2.54), Cr_2O_3 (0.19-0.25), and MgO (0.71–0.86). It coexists with a phase close to $Ca_3Ti(Fe,Al)_2O_8$ containing up to 15.11 wt % TiO_2.

BYL rocks form mineral assemblages similar to calcium sulfoaluminate cement (CSA). They are derived from slightly phosphatic chalks and marls annealed by burning methane at 1200-1350°C, under both oxidizing and reducing conditions. The rocks have been exposed for at least several hundred thousand years and thus are less active than industrial CSA.