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Why are the yellow bricks yellow?

Защо са жълти жълтите павета?

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During a project led by Prof. Dr. Lyuben Lakov of the IMSETHAC, BAS, a technology for producing yellow bricks, using as raw materials marls of deposits near the town of Popovo, NE Bulgaria has been developed. The technical parameters of the project are described by Lakov et al. (2016) and in a patent № 112274/04.13.2016.

The present investigation discusses the reasons for the colour of both, newly and original old yellow bricks emblematic for the Sofia’s city centre.

The X-ray powder diffraction patterns of both materials were carried out on diffractometer TUR M 62 at the Earth and Man National Museum using U=32 kV, I=15 mA, CuKα radiation. In both cases they indicate the presence of two major crystalline phases: diopside and anorthite, a certain amount of amorphous phase, as well as traces of wollastonite, quartz, and fayalite.

Chemical analyses were carried out using a Scanning Electron Microscope JEOL JSM 6010 Plus/LA&EDS System at University of Mining and Geology “St. Ivan Rilski”, Sofia. Fe^{2+}/Fe^{3+} were determined in the chemical laboratory of Sofia University “St. Kl. Ohridski”. In all bricks the iron is almost entirely trivalent (3.95 wt% Fe_2O_3 and 0.4 wt% FeO for the old bricks, 5.47 wt% and 0.28 wt% for the new ones). Recalculation of the microprobe analyses based on those Fe^{2+}/Fe^{3+} ratios have been done. The chemical composition (average of 3 analyses) of the pyroxenes is shown in Table 1.

The results are represented in a triangular diagram with coordinates: diopside, esseneite and Ca-molecule Tschermak (Fig. 1). The fields of the diagram are according to Cosca and Peacor (1987) and correspond to the dominant cation in position M1 – Fe^{3+} (esseneite), Al^{3+} (CaTs) and Mg (diopside). During recalculation Fe^{2+} and Mn^{2+} have also been added but their amounts are insignificant and hence do not change the positions of the points. Fig. 1 shows that the analysis of the py-

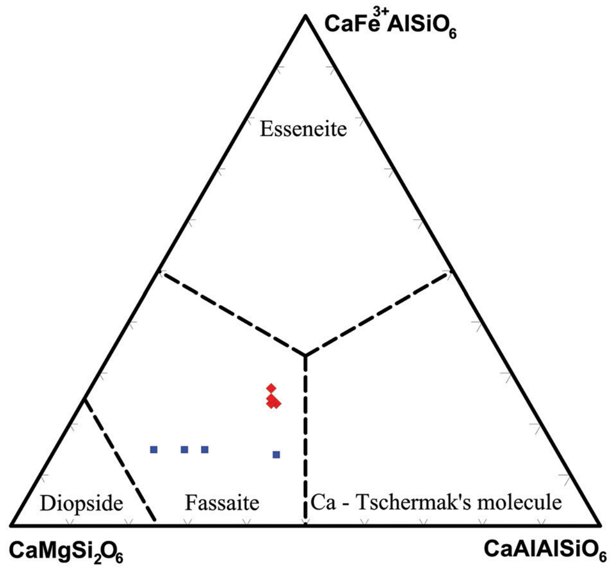

Fig. 1. Clinopyroxene compositions in the system $CaMgSi_2O_6$–$CaFe^{3+}AlSiO_6$–$CaAlAlSiO_6$ (according to Cosca and Peacor, 1987); blue squares, original bricks; red rhombs, new bricks

Table 1.

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	FeO	MnO	MgO	CaO	Na_2O	K_2O	Total
Old bricks	53.19	0.57	8.45	5.71	0.58	0.20	11.15	18.53	0.66	1.02	100.07
New bricks	47.70	1.00	13.52	9.07	0.46	0.00	7.67	19.38	0.50	0.88	100.17

roxenes from the old and the new bricks respectively, falls unambiguously within the “fassaite” field. The old bricks have greater variations in the content of Al^{3+}, whereas the new ones – in Fe^{3+}.

For comparison a determination of the colour using the system of Munsell for the new bricks and for the original ones has been made. The record of colour, specified in the nomenclature of the Munsell Soil Color Charts, is represented by hue, value and chroma. The determination itself is carried out by placing a test sample directly behind the opening which then separates the closest colour determinants in the card (Kulev, 2012). Equivalent colour characteristics for the old and the new bricks were established. A slight difference in hue is only present with respect to the upper surface, due to the fact that the old bricks are partially worn (Fig. 2).

Fig. 2. Old (a and b) and new brick (c) with equivalent colour

The Commission on New Minerals, Nomenclature and Classification of IMA describes fassaite as “subsilitcic aluminian ferrian diopside” (Morimoto, 1988). According to Spiridonov (2014) the definition of IMA is incorrect: “fassaite” is a special clinopyroxene, poor in Si and rich in Ca and Al. It is of particular petrogenetic importance; for instance, it is a typomorphic mineral for high temperature Mg-skarns.

According to experimental studies of Huckenholz, “fassaite” represents a high temperature solid solution of diopside $CaMgSi_2O_6$ (or ferrous diopside – salite), calcium Tschermak’s molecule $CaAlAlSiO_6$ and ferri-Tschermak’s (FTS) molecule $CalFe_2^{3+}SiO_6$. “The colour of synthetic fassaite solid solutions ($fassaite_{88}$) depends on the amount of the ferri-Tchermaks’ molecule dissolved in the structure. Clinopyroxenes close to ideal fassaite composition ($CaFe^{3+}AlSiO_6$) are slightly yellow with a touch of green. They turn to a more brownish yellow when the amount of FTS increases…” (Huckenholz et al., 1974).

It should be noted that the idea of “fassaite” as a reason for the yellow colour of some bricks is also applied by Kreimeyer (1987). According to him: “There is a close relationship between the occurrence of high-temperature crystalline phases and the colour of clay bricks after being fired under oxidizing conditions at 1000 °C. Firing colours in various red shades expected on the basis of the relatively high Fe content (3–7 wt%) may fail to appear due to the incorporation of Fe in specific high-temperature crystalline phases rather than its occurrence as free iron oxide in the form of hematite. X-ray investigations show that these minerals could be one or the other of mullite or metakaolinite and a fassaitic pyroxene in which the iron is present in its trivalent form. Yellow and beige to light brown colours result in the formation of these minerals… Fassaitic pyroxene is formed from $CaCO_3$-rich materials in which the $CaCO_3$ is fine grained and homogeneously dispersed.”

So why the yellow bricks are yellow?

The colour of the yellow bricks refers to the process of oxidation and reduction of the Fe-oxides, which is generally true. However, the most accurate answer is mineralogical – the reason for the yellow colour is that one of the major phases is not just a diopside, but its special variety – “fassaite”.

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