Fe-gehlenite formation in ancient ceramics: a firing or a primary composition indicator?

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Recently, in the ruins of Roman Napoca city (present day Cluj-Napoca, in Romania), dated back to 2nd century A.D., more than one hundred sherds of fine and semifine household pottery were found. In the voids left by the decomposition of carbonate aggregates and foraminifera tests, various firing phases such as glass, 'ceramic melilite', clinopyroxene and Fe-gehlenite were identified. The latter is an important marker for the temperature reached when producing ancient ceramics. Due to usually low amount and very fine grains, its presence is generally difficult to document. Most of the proofs are provided by X-ray powder diffraction (XRPD), electron microprobe analysis (EMPA) and classical scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDX). The overwhelming strong X-ray diffraction peak of quartz masks the weak peaks which may be assigned to Fe-gehlenite. Additionally, the solid solution among gehlenite and åkermanite may change the position of the indicative XRPD lines. The EMPA and SEM-EDX chemical data are biased by the diameter of the electron beam, much larger than the individual grains/crystals.

We describe here in greater details Fe-gehlenite formed in the Roman sherds having a vitreous matrix, based on the analyses provided by cold field emission scanning microscope coupled with an energy dispersive X-ray spectrometer (CFE-SEM-EDX). With a very fine focused electron beam, CFE-SEM-EDX enables to visualize phases ~10 nm in size, and to measure a surface as small as 100 nm^2. The aim of the study is to find how Fe-gehlenite looks like, its chemistry and its relation with firing temperature.

Fe-gehlenite forms flat, leaf-like dendrites, maximum a few µm in length and 50 to 100 nm in width, showing often a divergent 'blow-up' orientation. The arms of the dendrites are polycrystalline and consist of 10 nm-sized tabular grains arranged in a rod-like manner. The chemistry is variable, with ~45 to 57 mass% CaO, ~15 to 27 mass% SiO_2, ~6 to 29 mass% FeO_{TOT}, and ~6 to 9 mass% Al_2O_3. Only K_2O and MgO show a constant and low amount, around 2 mass%. Fe-gehlenite contains a significant amount of Fe-åkermanite, as part of a solid solution.

The Fe-gehlenite dendrites have formed by the reaction between the Fe-rich illite-like groundmass and lime resulting from calcite decomposition. Its highly variable composition reflects mainly the local inhomogeneity of the ceramic paste and the time too short to reach a chemically balanced material. The mixed environment, both vitreous and crystalline, in the Roman ceramics indicates the formation of Fe-gehlenite between ~850 °C and ~950 °C, with a maximum around 900 °C.

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