FIRST RESULTS OF THE INVESTIGATIONS ON THE SYSTEM Fe2O3-CaO-Al2O3-MgO (FCAM): THE PHASES FCAM-I AND FCAM-III, TWO NEW HOMOLOGUES OF THE AENIGMATITE STRUCTURE-TYPE (SFCA)

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In analogy with the so-called SFCA series, our investigation in the chemical system FCAM (Fe₂O₃-CaO-Al₂O₃-MgO) showed the existence of a stoichiometric homologous series $M_{14+6n}O_{20+8n}$, where M = Fe, Ca, Al, Mg and n = 1 or 2. In more detail, the two previously unknown compounds Ca₃MgAl₆Fe₁₀O₂₈ or FCAM-I (isostructural with SFCA-I, ZÖLL et al., 2017) and FCAM-III (ZÖLL, unpublished data) Ca_{2.38}Mg_{2.09}Fe³⁺_{10.61}Fe²⁺_{1.59}Al_{9.33}O₃₆ have been synthesized.

Two experimental series in air and under controlled oxygen fugacity using the hematitemagnetite buffer were conducted. Pure polycrystalline FCAM-I formed at 1190 °C in air. Increasing the temperature from 1300 °C to 1400 °C, the FCAM-I phase breaks down forming a variety of new compounds depending on *T* and fO_2 .

Basic crystallographic data of FCAM-I (Ca₃MgAl₆Fe₁₀O₂₈) are: space group $P \ \overline{1}$, a = 10.2940(3) Å, b = 10.4393(3) Å, c = 11.5977(6) Å, $\alpha = 94.342(6)^{\circ}$, $\beta = 111.611(6)^{\circ}$, $\gamma = 109.617(3)^{\circ}$, V = 1069.81(7) Å³, Z = 2.

In air, the FCAM-III phase forms and co-exists with FCAM-I at 1400 °C. Increasing the temperature up to 1425 °C, FCAM-I disappears completely and FCAM-III co-exists with magnesium ferrite and a variety of calcium iron oxides. At 1450°C FCAM-III breaks down.

Small single crystals of FCAM-III were characterized using electron microprobe analysis and synchrotron X-ray single-crystal diffraction (X06DA beamline at the Swiss Light Source, Paul Scherrer Institut, Villigen, CH). The basic crystallographic data of FCAM-III (Ca_{2.38}Mg_{2.09}Fe³⁺_{10.61}Fe²⁺_{1.59}Al_{9.33}O₃₆) are: space group $P \bar{1}$, a = 10.223(22) Å, b = 10.316(21) Å, c = 14.203(15) Å, $\alpha = 93.473(50)^{\circ}$, $\beta = 107.418(67)^{\circ}$, $\gamma = 109.646(60)^{\circ}$, V = 1323.85(2) Å³, Z = 1.

Using Schreinemaker's technique to analyse the phase relations in the system Fe₂O₃-CaO-Al₂O₃-MgO as a function of T and fO_2 it was possible to obtain the semi-quantitative stability relations between the participating phases and to construct a topologically correct phase sequence as a function of temperature and oxygen fugacity.

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