Harmunite CaFe₂O₄: A new mineral from the Jabel Harmun, West Bank, Palestinian Autonomy, Israel

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ABSTRACT

Harmunite, naturally occurring calcium ferrite CaFe₂O₄, was discovered in the Hatrurim Complex of pyrometamorphic larnite rocks close to the Jabel Harmun, the Judean Desert, West Bank, Palestinian Autonomy, Israel. The new mineral occurs in larnite pebbles of the pseudo-conglomerate, the cement of which consists of intensely altered larnite-bearing rocks. Srebrodolskite, magnesioferrite, and harmunite are intergrown forming black porous aggregates to the central part of the pebbles. Larnite, fluorellestadite, ye'elimite, fluormayenite, gehlenite, ternesite, and calciolangbeinite are the main associated minerals. Empirical crystal chemical formula of harmunite from type specimen is as follows $Ca_{1.013}(Fe_{1.957}^{3+}Al_{0.015}Cr_{0.011}^{3+}Ti_{0.004}^{4+}Mg_{0.003})_{\Sigma 1.993}O_4$. Calculated density is 4.404 g/cm³, microhardness VHN₅₀ is 655 kg/mm². The Raman spectrum of harmunite is similar to that of the synthetic analog. Harmunite in hand specimen is black and under reflected plane-polarized light is light gray with red internal reflections. Reflectance data for the COM wavelengths vary from ~22% (400 nm) to ~18% (700 nm).

The crystal structure of harmunite [*Pnma*; a = 9.2183(3), b = 3.0175(1), c = 10.6934(4) Å; Z = 4, V = 297.45(2) Å³], analogous to the synthetic counterpart, was refined from X-ray single-crystal data to R1 = 0.0262. The structure of CaFe₂O₄ consist of two symmetrically independent FeO₆ octahedra connected over common edges, forming double rutile-type $\frac{1}{2}$ [Fe₂O₆] chains. Four such double chains are further linked by common oxygen corners creating a tunnel-structure with large trigonal prismatic cavities occupied by Ca along [001]. The strongest diffraction lines are as follows [d_{hkl} , (I)]: 2.6632 (100), 2.5244 (60), 2.6697 (52), 1.8335 (40), 2.5225 (35), 2.2318 (34), 1.8307 (27), 1.5098 (19). Crystallization of harmunite takes place in the presence of sulfate melt.

Keywords: Harmunite; calcium ferrite; Raman; structure; Jabel Harmun, Palestinian Autonomy, Israel

INTRODUCTION

The new mineral harmunite $CaFe_2O_4$ (IMA2012-045) was discovered in pyrometamorphic larnite rocks belonging to the Hatrurim Formation (also known as the "Mottled Zone"; Bentor 1960; Gross 1977; Vapnik et al. 2007; Novikov et al. 2013). The name is given after Mt. Harmun (Jabel Harmun in Arabic language) where the rock was sampled, at the Hatrurim Formation complex situated in the Judean Desert, West Bank, Palestinian Autonomy, Israel (31°46′N–35°26′E). Type materials were deposited in the mineralogical collections of the Saint Petersburg University, Russia, catalog number 1/19518, and of the Fersman Mineralogical Museum, Moscow, Russia, catalog number 4398/1.

Natural CaFe₂O₄ was previously described from burned fossilized woody relics of siderite composition enclosed in pyrogenic iron ore in an ancient fire of the Kuzbass, Russia (Nigmatulina and Nigmatulina 2009). This mineral, which the authors called "aciculite," has a significant Mn content (4.64–6.70

wt% MnO) and forms exsolution structures in magnesioferrite (Nigmatulina and Nigmatulina 2009). Furthermore, $CaFe_2O_4$ also named "aciculite," was described from a burned damp of the Chelyabinsk coal basin by Chesnokov et al. (1998). The origin of this phase is considered as anthropogenic; therefore it was not approved by the CNMNC of the IMA as a valid mineral species.

Synthetic calcium ferrite, CaFe₂O₄ is a well-known material widely used as a pigment, catalyzer, thermally stable material, conductor, solid electrolyte, ceramic material, etc. (Candeia et al. 2004; Kharton et al. 2008). Its crystal structure was first reported by Hill et al. (1956) and then by Decker and Kasper (1957).

Many isotypic compounds have been reported and "calciumferrite type" became the common term used for structural description. For instance, Shizuya et al. (2007) has summarized related compounds having the CaFe₂O₄ structure type, based on the AB₂O₄ chemical formula (A = Li, Na, Mg, Ca, Sr, Ba, La, and Eu; B = Ti, V, Cr, Mn, Fe, Ru, Rh, Al, Ga, In, Tl, Sc, Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Yb, and Lu). In Nature only two phases possessing this structure type are known: xieite FeCr₂O₄ [*Bbmm*, a = 9.462(6), b = 9.562(9), c = 2.916(1) Å] = high-pressure polymorph of chromite (Chen et al. 2008), and

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marokite CaMn₂O₄ [*Pmab* or *P*21*ab*, a = 9.71(2), b = 10.03(2), c = 3.162(5) Å] = low-pressure phase (Gaudefroy et al. 1963; Lepicard and Protas 1966).

The CaFe₂O₄ (CF) structure type, including the two slightly distorted modifications CaTi₂O₄ (CT) and CaMn₂O₄ (CM) became interesting for the geoscience community when they were proposed as high-pressure form of spinels (Irifune et al. 1991; Kirby et al. 1996). At the *P*,*T*-conditions of the mantle transition zone the spinel structure is no longer stable and it is expected to transform to the calcium-ferrite type. Thus this structure type is considered as "potential geochemical reservoir in the mantle for alkaline and other large cations" (Merlini et al. 2010).

In the present paper we report results on the properties and mineral association of harmunite from the Hatrurim Complex. In addition, we use the opportunity to provide better quality structure data obtained from single-crystal X-ray analysis than the original data reported by Hill et al. (1956).

GEOLOGAL SETTING

The Jabel Harmun is one of several pyrometamorphic complexes of the Hatrurim Formation located in the Judean Desert in the vicinity of the Jerusalem-Jericho highway (Fig. 1; Khesin et al. 2010a, 2010b; Sokol et al. 2010, 2011, 2012; Seryotkin et al. 2012; Novikov et al. 2013). Hilly landscape of the Hatrurim Formation is characterized by the differently colored outcrops of rocks (Fig. 2), consisting of high- and ultrahigh-temperature calcium-silicate, -aluminate, and -ferrite minerals embedded in a low-temperature hydrated calcium silicate matrix (Fig. 3). Formation of paralava suggests that the pyrometamorphic process was locally intense causing partial or bulk melting of the rocks. The rock complexes do not preserve any sedimentary features and are extremely brecciated, showing numerous genetically different types of breccias.

The origin of pyrometamorphic rocks of the Hatrurim Formation found on the territory of Israel, Palestinian Autonomy, and Jordan remains disputable (Matthews and Gross 1980; Sokol et al. 2010, 2012; Geller et al. 2012; Kolodny et al. 2013; Vapnik and Novikov 2013). Most researchers adopt the point of view that fires causing pyrometamorphism were induced by combustion of bituminous chalk containing carbon Corg. content up to 15 wt% in the Negev (Minster et al. 1997) and up to 22 wt% in the Nabi Musa (Picard 1931) of the Ghareb Formation (Maastrichtian) (Gur et al. 1995; Burg et al. 1991, 1999). According to this model, combustion occurred in the time space from 16 Ma to 200 Ka (Gur et al. 1995; Porat et al. 1991). Such a model encounters numerous problems (Novikov et al. 2013). For example, geological observations indicate that the stratigraphic position of the Hatrurim Formation is different than that of the Ghareb Formation, e.g., pyrometamorphic complexes of the Hatrurim Formation may occur above, below, and/or in the same horizon as the Ghareb Formation (Vapnik and Novikov 2013; Novikov et al. 2013). The term "Hatrurim Formation" has stratigraphic implication and has been erroneously applied in the past to those pyrometamorphic rocks. Therefore, we prefer to use the term "Hatrurim Complex."

Recently, the origin of the Hatrurim Complex was connected to neotectonic activity in the vicinity of the Dead Sea Transform Fault. Anomalously high pressures were noted within the deep sedimentary layers and led to hydrothermal flows of hydrocarbon gas and fluidized matter. Such process is described as mud volcanism (Kopf 2002). The spontaneous combustion of hydrocarbons near the surface is a known phenomenon related to modern mud volcanoes (Kovalevskiy 1940; Shnyukov et al. 1978; Fishman et al. 2012).

The major features supporting at least partial influence of the mud volcanism for the Hatrurim Complex genesis are: (1) the existence of feeder channels and clastic dikes, rich in quartz sand and filled by breccias, composed of fragments of sedimentary and pyrometamorphic rocks (Vapnik and Sokol 2006; Vapnik and Novikov 2013); and (2) the existence of several outcrops of the Hatrurim Formation on the slopes of modern wadies (Vapnik and Novikov 2013).

Jabel Harmun pyrometamorphic complex is composed of spurrite- and larnite-bearing rocks, and overlies the phosphorite, carbonate, and chert layers of the Mishash Formation (Campanian). Jabel Harmun rocks grades laterally into bituminous and non-bituminous chalk of the Ghareb Formation (Maastrichtian) (Soudry 1973). Bituminous series show the maximum thickness of 40 m and overlain by 10-30 m of non-bituminous chalk. The maximal thickness of the Jabel Harmun complex is 90-100 m (Novikov et al. 2013). The rocks of the Jabel Harmun complex are also located as isolated foci within non-bituminous chalk of the Ghareb Formation (Fig. 2). High-temperature rocks are commonly altered and hosted by low-temperature hydrothermal hydrated calcium silicate rocks, often enriched in secondary carbonates. It seems that larnite-bearing rocks are most intensely subjected to low-temperature alteration, resulting in the formation of larnite nodules or pseudo-conglomerates (the local term; Gross 1977), occasionally included in the low-temperature hydrothermal matrix (Fig. 3) and/or form loose deposits. A few outcrops of gehlenite-bearing rock were also found. In several cases such rock shows amygdular texture, suggesting at least partial melting of the original rocks.

METHODS OF INVESTIGATIONS

Crystal morphology and chemical composition of harmunite and associated minerals were examined using optical microscopes, analytical electron scanning microscope (Philips XL30 ESEM/EDAX, Faculty of Earth Sciences, University of Silesia) and electron probe microanalyzer (CAMECA SX100, Institute of Geochemistry, Mineralogy and Petrology, University of Warsaw). Electron probe microanalyses of harmunite were performed at 15 kV and 20 nA using the following lines and standards: $CaK\alpha$, $SiK\alpha$ = wollastonite; $AIK\alpha$ = orthoclase; $CrK\alpha$ = Cr_2O_3 ; $FeK\alpha$ = hematite; $MnK\alpha$ = rhodochrosite; $TiK\alpha$ = rutile; $MgK\alpha$ = diopside; $NaK\alpha$ = albite.

The Raman spectra of harmunite were recorded using a WITec confocal CRM alpha 300 Raman microscope (Jagiellonian Centre for Experimental Therapeutics, Cracow) equipped with an air-cooled solid-state laser operating at 488 nm and a CCD detector which was cooled to -82 °C. The laser was coupled to the microscope via a single mode optical fiber with a diameter of 50 µm. An Olympus MPLAN (1006/0.90NA) objective was used. The scattered radiation was focused onto a multi-mode fiber (50 µm diameter) and monochromator. The power of the laser at the sample position was 44 mW for measurement. One hundred and fifty scans with integration times of 0.3-0.5 s and a resolution of 3 cm⁻¹ were collected and averaged. The monochromator of the spectrometer was calibrated using the Raman scattering line produced by a silicon plate (520.7 cm⁻¹).

Single-crystal X-ray study of harmunite was carried out using a Bruker APEX II SMART diffractometer, MoK α , $\lambda = 0.71073$ Å (Institute of Geological Sciences, University of Bern). Diffraction data were collected with ω scans at different φ settings (φ - ω scan) (Bruker 1999). Data were processed using SAINT (Bruker 2011). An empirical absorption correction using SADABS (Bruker 2011) was applied. The harmunite structure was refined using neutral atom scattering factors with the program SHELX97 (Sheldrick 2008) to $R_1 = 2.6\%$.



Highway Jerusalem-Jericho

FIGURE 1. Schematic geological map of the Judean Desert and eastern part of the Judean mountains (modified after Sneh et al. 1998). The Hatrurim Complex: (a) Nabi Musa; (b) Jabel Harmun; (c) Hyrcania; (d) Ma'ale Adummim.

X-ray powder diffraction data were collected using an X'Pert PRO 3040/60 diffractometer (CuK α , $\lambda = 1.540598$ Å), Theta-Theta geometry (Faculty of Earth Sciences, University of Silesia). PANalytical HighScore+ software, using the ICDD PDF 4+ database version 2011, was used for interpretation and Rietveld refinement. Structural parameters of synthetic CaFe₂O₄ (PDF 04-007-8642; Decker and Kasper

1957) were used as starting structural model of harmunite.

Reflectance data of harmunite measured using a Zeiss 521 VIS microscope for standard wavelengths are as following (max/min %): 470 nm 21.60/20.10, 546 nm 20.65/19.20, 589 nm 19.30/18.45, 650 nm 18.70/17.75 (Standard Zeiss SiC reflectance standard, number 472, 20% Refl.).



FIGURE 2. The eastern view of the Jabel Harmun. The rocks of the Hatrurim Complex overlay and occur inside of the non-bituminous chalk belonging to the Ghareb Formation.



FIGURE 3. Larnite-bearing nodules (pseudo-conglomerate) included into low-temperature matrix composed of hydrated calcium silicates.

OCCURENCE AND PARAGENESIS

The occurrence of harmunite is restricted to pebbles of a pseudo-conglomerate collected on the southern slope of the Jabel Harmun. Srebrodolskite Ca₂Fe₂O₅, magnesioferrite MgFe₂O₄, and harmunite form together black porous aggregates in the central part of these pebbles (Fig. 4). Besides larnite β -Ca₂SiO₄, fluorellestadite $Ca_5(SiO_4)_{1,5}(SO_4)_{1,5}F$, ye'elimite $Ca_4Al_6(SO_4)O_{12}$, fluormayenite Ca₁₂Al₁₄O₃₂F₂ (IMA2013-019; Galuskin et al. 2013b), gehlenite Ca₂Al₂SiO₇, and ternesite Ca₅(SiO₄)SO₄ are the main associated minerals. Minor and accessory minerals are magnesioferrite, minerals of the srebrodolskite-brownmillerite series Ca₂Fe³⁺₂O₅-Ca₂Fe³⁺AlO₅, Si-bearing perovskite, and barite. Vorlanite CaUO₄ (Galuskin et al. 2011), recently discovered nabimusaite KCa₁₂(SiO₄)₄(SO₄)₂O₂F (Galuskin et al. 2013c), shulamitite Ca₃TiFeAlO₈ (Sharygin et al. 2013), and vapnikite Ca₃UO₆ (IMA2013-082; Galuskin et al. 2013a), and the potentially new mineral CaCu₂S₂, are rarely noted. Ternesite was discovered from xenoliths in volcanites of Eifel, Germany (Irran et al. 1997), the Jabel Harmun locality is the second natural finding. Ternesite from the Jabel Harmun locality is characterized by high-phosphorus content (up to 6 wt% P_2O_5) and forms poikiloblasts up to 5 mm in size in the dark-brown parts of the pebble (Fig. 4a). Less frequently it forms light-green spherules 3–4 mm in diameter irregularly distributed in larnite rocks.

Light colored aggregates of hydrated Ca, K, and Na sulfates (Fig. 4b) became obvious around black ore minerals after the sample was rinsed with water. We were able to identify the following sulfates: calciolangbeinite $K_2Ca_2(SO_4)_3$, aphthitalite K₃Na(SO₄)₂, and thenardite Na₂SO₄. Thenardite forms decomposition structures in aphthitalite and occurs on fresh surfaces within porous aggregates of ore minerals (Figs. 5a and 6). Calciolangbeinite has a composition according to the ideal crystal-chemical formula K₂Ca₂(SO₄)₃. This is in contrast to holotype calciolangbeinite, which has a significant Mg content, recently discovered in the Yadovitaya fumarole, Tolbachik volcano, Kamchatka Oblast', Far-Eastern Region, Russia (Pekov et al. 2012). Calciolangbeinite with inclusions of relatively large crystals (up to 100 µm) of magnesioferrite and fluorellestadite sometimes fill short cracks about 1 mm in thickness, in larnite rocks. Aphthitalite with relics of thenardite occurs as amoeboidal aggregates in calciolangbeinite (Fig. 6). Even if aphthitalite is partially dissolved, it may be assumed that calciolangbeinite and aphthitalite (+thenardite) formed as a result of simultaneous crystallization from a sulfate-bearing liquid phase or decomposition of a complex sulfate solid solution. Barite and fluorellestadite are noted at the boundary of Ca-K and Na-K sulfates (Fig. 6).

At the margins of ore aggregates magnesioferrite with admixture of srebrodolskite is predominant (Fig. 5a), whereas at the central part of the aggregates harmunite and srebrodolskite are prevail (Fig. 4c). In porous ore aggregates, partially filled by Ca-, K-, and Na-sulfates, well-formed crystals of fluorellestadite (Fig. 5b), larnite, native copper and umangite Cu₃Se₂ (Figs. 5a and 5c), and also native silver (Fig. 5c) are observed.







HARMUNITE: PHYSICAL PROPERTIES, CHEMICAL COMPOSITION, AND RAMAN SPECTRA

Aggregates of harmunite, srebrodolskite, and magnesioferrite have skeletal structure (Figs. 4c–4f and 5a). Parallel aggregates of prismatic orthorhombic harmunite crystals reach 2–3 mm in size. Twinning of harmunite is not observed. Harmunite crystals are bounded by faces of the {100}, {110}, {210}, {011}, {001}, and {010} forms, but also occur as rounded fragments (Fig. 4c). Rounded crystals were also recognized for srebrodolskite and magnesioferrite. This phenomenon, known as antiskeletal growth (Punin and Franke 2004), is well displayed on octahedral crystals of magnesioferrite with minor {001} and {110} faces (Fig. 5b).

Macroscopically harmunite is black. In reflected light it is light gray with internal red reflections (Figs. 4e, 4f, and 7). Reflectance intensity of harmunite decreases with wavelength

◄ FIGURE 5. (a) General view of the rim of a black aggregation containing harmunite, sample not rinsed by water; skeletal crystals of magnesioferrite and srebrodolskite are cemented by calciolangbeinite, less frequent by aphthitalite and thenardite; (b) octahedral crystal of magnesioferrite with rounded faces and tops (anti-skeletal growth); (c) twinned crystal of native copper, umangite, and native silver. Backscattered electron (BSE) image.

100 μm FIGURE 6. Periphery of ferrite aggregation filled by calciolangbeinite

with aphtitalite exsolution. Magnified fluorellestadite crystal is shown in inset.

TABLE 1. Reflectance data (%) for harmunite

mean 13

| | () | | |
|------------------------------------|-----------|------------------------------------|-----------|
| R _{max} /R _{min} | λ (nm) | R _{max} /R _{min} | λ (nm) |
| 22.20/20.10 | 400 | 20.05/18.95 | 560 |
| 22.90/19.90 | 420 | 19.70/18.65 | 580 |
| 22.30/20.10 | 440 | 19.30/18.45 | 589 (COM) |
| 22.00/20.25 | 460 | 19.30/18.35 | 600 |
| 21.60/20.10 | 470 (COM) | 19.00/18.00 | 620 |
| 21.40/20.00 | 480 | 18.80/17.80 | 640 |
| 21.30/19.70 | 500 | 18.70/17.75 | 650 (COM) |
| 21.20/19.55 | 520 | 18.30/17.50 | 660 |
| 20.80/19.25 | 540 | 18.30/17.35 | 680 |
| 20.65/19.20 | 546 (COM) | 18.10/17.15 | 700 |

s.d.

from ~22% (400 nm) to ~18% (700 nm) (Table 1). The measured microhardness is VHN₅₀ = 655 kg mm⁻² (mean of 10 measurements), range 540–700 kg mm⁻²; equivalent to a Mohs hardness of ~5½. It was not possible to measure the density of harmunite due to the high porosity of its aggregates. The calculated density is 4.404 g/cm³ using the empirical formula (Table 2, analysis 1).

Harmunite was also found in pebbles of greenish larnite rock (pseudo-conglomerate) collected a few tens of meters away from the original locality of harmunite. Here it forms exsolution-like structures in magnesioferrite (Fig. 8). The composition of this rock is approximately the same as for the holotype specimen containing harmunite. However, the main difference is the absence of ternesite and fluorellestadite, instead of which fluorapatite with high-Si and -S contents appears. The rock riches in spinel, brownmillerite-srebrodolskite, and shulamitite (up to 15% of the total volume). Spinel composition varies from ferrian spinel to magnesioferrite.

Composition of holotype harmunite is close to the composition of the end-member CaFe₂O₄ (Table 2). Increased impurities of Mn, Cr, and Al are characteristic for harmunite of exsolutionlike structures in magnesioferrite. Impurity of manganese in holotype harmunite is below the detection limit of EPMA (Table 2).

The Raman spectrum of holotype harmunite (Fig. 9) corresponds to the spectrum of synthetic ferrite CaFe₂O₄, for which 42 Raman modes are active (Kolev et al. 2003). The main Raman bands of harmunite are follows (cm⁻¹): 1228 [combination first-order phonons A_g (648) + A_g (585)]; 648 (A_g); 585 (A_g); 519 (B_{2g}); 453 and 435 (A_g); 379 and 364 ($A_g/B_{1g}/B_{3g}$); 298 (A_g); 270 (A_g); 206 (A_g); 182 (A_g/B_{2g}); 117 (A_g). The Raman spectrum of

3

mean 2

range

4

mean 9

5

mean 5

 TABLE 2.
 Composition of holotype harmunite (1), harmunite exsolutions in magnesioferrite (2), harmunite with maximum Cr content (3) and associated minerals: magnesioferrite (4) and srebrodolskite (5) from the Jabel Harmun

mean 11

range

2

s.d.

| В | 1.993 | | | 1.998 | | | 1.999 | 2.000 | 1.990 |
|---|-------|------|-------------|--------|------|-------------|-------|-------|-------|
| Si | | | | | | | | | 0.033 |
| AI | 0.015 | | | 0.03 | | | 0.035 | 0.134 | 0.035 |
| Mg | 0.003 | | | 0.003 | | | 0.004 | | 0.002 |
| Fe ²⁺ | | | | | | | | | 0.023 |
| Cr ³⁺ | 0.011 | | | 0.014 | | | 0.036 | 0.014 | 0.003 |
| Ti ⁴⁺ | 0.004 | | | 0.003 | | | 0.001 | | 0.002 |
| Fe ³⁺ | 1.957 | | | 1.947 | | | 1.924 | 1.852 | 1.892 |
| Α | 1.013 | | | 1.002 | | | 1.001 | 1.000 | 2.011 |
| Zn | | | | | | | | 0.012 | |
| Со | | | | | | | | 0.003 | |
| Ni ²⁺ | | | | | | | | 0.024 | |
| Na | | | | 0.002 | | | 0.003 | | |
| Mg | | | | | | | | 0.797 | |
| Fe ²⁺ | | | | | | | | 0.116 | |
| Mn ²⁺ | | | | 0.014 | | | 0.01 | 0.002 | |
| Ca | 1.013 | | | 0.986 | | | 0.988 | 0.046 | 2.011 |
| Total | 99.04 | | | 100.74 | | | 99.59 | 99.51 | 99.05 |
| Na₂O | n.d. | | | 0.03 | 0.02 | 0.00-0.07 | 0.04 | n.d. | n.d. |
| CoO | n.d. | | | n.m. | | | n.m. | 0.11 | n.d. |
| ZnO | n.d | | | n.d | | | n.d | 0.56 | n.d. |
| NiŌ | n.d | | | n.d | | | n.d | 0.86 | n.d. |
| MgO | 0.06 | 0.02 | 0.04-0.09 | 0.06 | 0.03 | 0.03-0.15 | 0.08 | 15.82 | 0.02 |
| CaO | 26.15 | 0.14 | 25.80-26.31 | 25.92 | 0.29 | 25.31-26.42 | 25.71 | 1.26 | 41.42 |
| MnO | n.d. | | | 0.48 | 0.14 | 0.14-0.62 | 0.34 | 0.08 | n.d. |
| Al ₂ O ₃ | 0.36 | 0.07 | 0.26-0.45 | 0.71 | 0.16 | 0.50-1.00 | 0.83 | 3.36 | 0.65 |
| Cr ₂ O ₃ | 0.38 | 0.09 | 0.20-0.52 | 0.51 | 0.16 | 0.11-0.75 | 1.25 | 0.53 | 0.09 |
| FeO ^a | | | | | | | | 4.14 | 0.59 |
| Fe ₂ O ₃ ^a | 71.94 | 0.35 | 71.36-72.56 | 72.9 | 0.5 | 71.75-73.49 | 71.32 | 72.08 | 55.48 |
| TiO | 0.15 | 0.08 | 0.07-0.31 | 0.13 | 0.2 | 0.02-0.75 | 0.02 | n.d. | 0.07 |
| SiO | | | | | | | | | 0.72 |

Notes: 1–4 = calculated on 3 cations and 40, 5 = calculated on 4 cations and 50. s.d. = standard deviation, n.d. = not detected, n.m. = not measured. ^a FeO/Fe₂O₃ calculated on charge balance.



► FIGURE 7. (a) BSE image of parallel intergrowth of harmunite, polished sample; (b, c) reflected light: (b) light-gray color of harmunite under reflected light, (c) red reflections of harmunite in crossed polars.





FIGURE 8. (a) Replacement of harmunite after magnesioferrite. (b) Thin exolution-like structure of harmunite in magnesioferrite. High-contrast BSE image, silicates are black.

harmunite from exsolutions in magnesioferrite is very similar to that of one of holotype harmunite. The main difference is a strong band at 344 cm⁻¹ ($A_g/B_{1g}/B_{3g}$) on the spectrum of harmunite from exsolutions in magnesioferrite reported for zz Raman scattering configurations of synthetic CaFe₂O₄ (Kolev et al. 2003).

 TABLE 3.
 X-ray powder diffraction data for harmunite

| 1/ | ABLE 3. X-ray powder diffraction data for harmunite | | | | | | | | |
|----|---|---|---------------|------------------|-------------------|------------|--------------------------|------------------|--|
| | | | Observ | /ed | Calculated | | Decker and Kasper (1957) | | |
| 'n | k | 1 | $d_{\rm obs}$ | I _{rel} | d_{calc} | I_{calc} | $d_{\rm obs}$ | I _{rel} | |
|) | 0 | 2 | 5.3393 | 2 | 5.3465 | 3 | | | |
| 1 | 0 | 2 | 4.6203 | 5 | 4.6249 | 8 | | | |
| 2 | 0 | 0 | 4.6090 | 13 | 4.6090 | 21 | 4.617 | 20 | |
| 2 | 0 | 2 | 3.4889 | 6 | 3.4909 | 10 | 3.498 | 5 | |
| 3 | 0 | 1 | 2.9529 | 2 | 2.9532 | 2 | | | |
|) | 1 | 1 | 2.9007 | 4 | 2.9045 | 7 | | | |
| 1 | 1 | 1 | 2.7669 | 3 | 2.7703 | 4 | | | |
|) | 0 | 4 | 2.6697 | 52 | 2.6733 | 51 | 2.676 | 100 | |
| 3 | 0 | 2 | 2.6632 | 100 | 2.6641 | 100 | | | |
| 1 | 0 | 4 | 2.5643 | 2 | 2.5675 | 2 | | | |
| 1 | 1 | 2 | 2.5244 | 60 | 2.5275 | 73 | 2.531 | 65 | |
| 2 | 1 | 0 | 2.5225 | 35 | 2.5249 | 35 | | | |
| 3 | 0 | 3 | 2.3260 | 1 | 2.3273 | 1 | | | |
| 2 | 0 | 4 | 2.3101 | 1 | 2.3124 | 1 | | | |
|) | 1 | 3 | 2.3002 | 4 | 2.3033 | 4 | | | |
| 2 | 1 | 2 | 2.2808 | 3 | 2.2831 | 3 | | | |
| 1 | 0 | 1 | 2.2527 | 3 | 2.2528 | 3 | | | |
| 1 | 1 | 3 | 2.2318 | 34 | 2.2346 | 31 | 2.240 | 20 | |
| 1 | 0 | 2 | 2.1159 | 10 | 2.1163 | 10 | 2.115 | 25 | |
| 3 | 1 | 1 | 2.1093 | 17 | 2.1108 | 17 | | | |
| I | 0 | 5 | 2.0806 | 3 | 2.0833 | 2 | | | |
| 2 | 1 | 3 | 2.0581 | 3 | 2.0603 | 3 | | | |
| 3 | 1 | 2 | 1.9957 | 4 | 1.9972 | 3 | | | |
| I | 1 | 4 | 1.9531 | 13 | 1.9556 | 12 | 1.961 | 15 | |
| 3 | 1 | 3 | 1.8414 | 8 | 1.8430 | 8 | | | |
| 2 | 1 | 4 | 1.8335 | 40 | 1.8356 | 41 | 1.837 | 40 | |
| 1 | 1 | 0 | 1.8307 | 27 | 1.8316 | 27 | | | |
| 1 | 1 | 1 | 1.8044 | 13 | 1.8053 | 12 | 1.808 | 15 | |
| 1 | 0 | 6 | 1.7475 | 2 | 1.7498 | 2 | | | |
| 5 | 0 | 2 | 1.7427 | 3 | 1.7449 | 4 | | | |
|) | 1 | 5 | 1.7426 | 4 | 1.7429 | 3 | 1.745 | 10 | |
| 1 | 1 | 2 | 1.7317 | 3 | 1.7327 | 3 | | | |
| 2 | 0 | 6 | 1.6603 | 14 | 1.6622 | 13 | 1.664 | 20 | |
| 2 | 1 | 5 | 1.6300 | 1 | 1.6319 | 1 | | | |
| 1 | 1 | 3 | 1.6280 | 2 | 1.6291 | 2 | | | |
| 3 | 0 | 6 | 1.5401 | 16 | 1.5416 | 14 | 1.545 | 20 | |
| 5 | 0 | 0 | 1.5364 | 12 | 1.5363 | 12 | 1.539 | 20 | |
| 5 | 0 | 4 | 1.5170 | 2 | 1.5177 | 2 | | | |
| l | 1 | 6 | 1.5118 | 18 | 1.5138 | 17 | | | |
| 1 | 1 | 4 | 1.5098 | 19 | 1.5110 | 25 | 1.512 | 25 | |
| 5 | 1 | 2 | 1.5086 | 17 | 1.5093 | 17 | | | |
|) | 2 | 0 | 1.5070 | 19 | 1.5090 | 22 | | | |
| 2 | 1 | 6 | 1.4543 | 11 | 1.4560 | 10 | 1.458 | 15 | |
| 2 | 2 | 0 | 1.4324 | 1 | 1.4341 | 1 | | | |
| 1 | 0 | 6 | 1.4086 | 2 | 1.4098 | 2 | 1.411 | 8 | |
| 2 | 2 | 2 | 1.3835 | 1 | 1.3851 | 1 | | | |
| 3 | 1 | б | 1.3714 | 2 | 1.3729 | 2 | 1.374 | 8 | |
| 1 | 1 | 7 | 1.3465 | 2 | 1.3483 | 2 | | | |
|) | 0 | 8 | 1.3348 | 2 | 1.3366 | 2 | | | |
| 5 | 0 | 4 | 1.3316 | 11 | 1.3320 | 10 | 1.335 | 20 | |

| Crystal | uala |
|--|--|
| Unit-cell dimensions (Å) | <i>a</i> = 9.2183(3) |
| | b = 3.01750(10) |
| | c = 10.6934(4) |
| | $\alpha = \beta = \gamma = 90^{\circ}$ |
| Volume (ų) | 297.450(18) |
| Space group | Pnma |
| Ζ | 4 |
| Chemical formula | CaFe ₂ O ₄ |
| Intensity mea | surement |
| Crystal shape | prismatic |
| Crystal size (mm) | 0.05 	imes 0.01 	imes 0.01 |
| Diffractometer | APEX II SMART |
| X-ray radiation | Mo <i>K</i> α λ = 0.71073 Å |
| X-ray power | 50 kV, 30 mA |
| Monochromator | graphite |
| Temperature | 296 K |
| Time per frame | 30 s |
| Max. 0 | 32.31 |
| Index ranges | -13 ≤ <i>h</i> ≤ 13 |
| | $-4 \le k \le 14$ |
| | −15 ≤ <i>l</i> ≤ 16 |
| No. of measured reflections | 6067 |
| No. of unique reflections | 623 |
| No. of observed reflections $[l > 2\sigma(l)]$ | 483 |
| Refinement of t | he structure |
| No. of parameters used in refinement | 44 |
| R _{int} | 0.0629 |
| R _σ | 0.0317 |
| $R1, l > 2\sigma(l)$ | 0.0262 |
| R1, all data | 0.0423 |
| wR2 (on F ²) | 0.0546 |
| GooF | 1.030 |
| $\Delta \rho_{min} (-e/Å^3)$ | -0.82 close to O3 |
| $\Delta \rho_{max}$ (e/Å ³) | 0.82 close to O2 |

Data collection and structure refinement details for harmunite



FIGURE 9. Raman spectra of harmunite. (**A**) Grain on Figure 7a; (**B**) exsolution-like lamellae in magnesioferrite in Figure 8.

TABLE 5. Final atom coordinates and anisotropic displacement parameters (Å²) for harmunite

| INDEE DI | i intar aconn e | oorannates a | na ambotropie | anspiacement | parameters () | () for marina | litte | | | |
|----------|-----------------|--------------|---------------|---------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Atom | Х | У | Ζ | $U_{\rm iso}$ | U ₁₁ | U ₂₂ | U ₃₃ | U ₂₃ | U ₁₃ | U ₁₂ |
| Ca1 | 0.75664(9) | -0.2500 | 0.34592(7) | 0.00828(18) | 0.0086(4) | 0.0073(4) | 0.0090(3) | 0 | -0.0004(3) | 0 |
| Fe1 | 0.56673(6) | 0.2500 | 0.61181(5) | 0.00735(15) | 0.0080(3) | 0.0070(3) | 0.0070(2) | 0 | -0.0002(2) | 0 |
| Fe2 | 0.08148(6) | -0.7500 | 0.39465(5) | 0.00754(16) | 0.0080(3) | 0.0068(3) | 0.0079(3) | 0 | 0.0004(2) | 0 |
| 01 | 0.5813(3) | 0.2500 | 0.4271(2) | 0.0078(6) | 0.0093(14) | 0.0077(14) | 0.0064(11) | 0 | -0.0018(10) | 0 |
| 02 | 0.8815(3) | -0.7500 | 0.4767(2) | 0.0078(6) | 0.0089(13) | 0.0063(13) | 0.0083(12) | 0 | 0.0013(10) | 0 |
| O3 | 0.7063(3) | -0.2500 | 0.6635(2) | 0.0079(5) | 0.0059(12) | 0.0084(14) | 0.0093(12) | 0 | 0.0015(10) | 0 |
| 04 | 0.4757(3) | 0.2500 | 0.7827(2) | 0.0073(5) | 0.0086(13) | 0.0076(13) | 0.0058(11) | 0 | 0.0019(9) | 0 |



FIGURE 10. (a) Crystal structure and (b) Ca-O bonds in the channels of $CaFe_2O_4$ (4 octahedra are omitted for better visual representation).

TABLE 6. Selected interatomic distances (Å) and bond-valence sums (v.u.) for harmunite

| Atom1 | Atom2 | Distance (Å)/bvs (v.u.) |
|-------|------------------|-------------------------|
| Ca1 | O2 | 2.358(2) ×2 |
| | O1 | 2.375(2) ×2 |
| | O3 | 2.489(2) ×2 |
| | O4 | 2.545(3) |
| | O4 | 2.558(3) |
| | average | 2.4438 |
| | bvs ^a | 2.259(5) |
| Fe1 | 01 | 1.980(3) |
| | O4 | 2.011(3) |
| | O3 | 2.0583(19) ×2 |
| | 01 | 2.0767(18) ×2 |
| | average | 2.0435 |
| | bvs ^a | 2.795(6) |
| Fe2 | O4 | 1.9969(17) ×2 |
| | O2 | 2.042(3) |
| | O3 | 2.053(3) |
| | O2 | 2.0699(18) ×2 |
| | average | 2.03798 |
| | bvs ^a | 2.832(6) |
| | 1 (2 1 | |

^a bvs = bond-valence sums (Brown and Altermatt 1985).

TABLE 4.

| | 2 4 9 1 4 9 | 2 4 9 1 4 9 | | |
|---|---|---------------------------------|------|-------------------------------------|
| Compounds with calcium ferrite structure | bvs of Ca ²⁺ /Mg ²⁺ | bvs of (3+) cation in octahedra | GII | References for structural data |
| CaFe ₂ O ₄ harmunite | 2.259(5) | 2.832(6)/2.795(6) | 0.15 | this paper |
| CaMn ₂ O ₄ marokite | 2.263(10) | 2.886(14) | 0.16 | Lepicard and Protas (1966) |
| FeCr ₂ O ₄ (meteorite) | structural data not available | | | Chen et al. (2008) |
| | Synthetic compounds | (conditions of synthesis) | | |
| CaSc ₂ O ₄ (2110 °C) | 1.879(28) | 2.895(48)/2.870(46) | 0.12 | Horyń and Lukaszewicz (1966) |
| CaTi ₂ O ₄ (1000 °C) | 2.271(4) | 2.903(5)/1.989(2) | 0.13 | Rogge et al. (1998) |
| CaV ₂ O ₄ (1200 °C) | 2.225(16) | 2.735(21)/2.758(20) | 0.19 | Niazi et al. (2009) |
| CaGa ₂ O ₄ (700 °C/4 GPa) | 2.363(10) | 2.792(13)/2.827(12) | 0.19 | Lazic et al. (2005) |
| β-CaCr ₂ O ₄ (1300 °C) | 2.371 | 2.769/2.847 | 0.19 | Hörkner and Müller-Buschbaum (1976) |
| CaRh ₂ O ₄ (1500 °C/6 GPa) | 2.308(4) | 3.252(6)/3.114(6) | 0.21 | Yamaura et al. (2005) |
| CaYb ₂ O ₄ (2300 °C) | 1.661 | 2.678/2.942 | 0.24 | Müller-Buschbaum and |
| | | | | von Schenk (1970) |
| CaAl ₂ O ₄ (1100 °C/10 GPa) | 2.595(6) | 2.520(7)/2.557(7) | 0.36 | Lazic et al. (2006) |
| CaCo ₂ O ₄ (1500 °C/6 GPa) | 2.793(16) | 2.535(14)/2.728(16) | 0.37 | Shizuya et al. (2007) |
| MgAl ₂ O ₄ (2200 °C/27 GPa) | 1.833(11) | 2.690(19)/2.822(18) | 0.21 | Kojitani et al. (2007) |
| CaTi ₂ O ₄ (1000 °C) | 2.271(4) | 2.903(5)/1.989(2) | 0.13 | Rogge et al. (1998) |
| CaTi ₂ O ₄ (80 GPa) (CT) | 3.742(249)/3.734(329) | 4.341(390)/4.316(397) | 1.29 | Yamanaka et al. (2005) |
| MgFe ₂ O ₄ (37.3 GPa) (CM) | 4.587(710) | 3.233(537) | 1.29 | Andrault and Bolfan Casanova (2001) |

TABLE 7. Bond-valence sums (bvs) and global instability index (GII) calculated for diverse compounds with calcium-ferrite structure type and two slightly distorted modifications CaTi₂O₄-type (CT) and CaMn₂O₄-type (CM)

CRYSTALLOGRAPHY

X-ray powder-diffraction data (in Å for CuK α) are listed in Table 3. (A CIF file is on deposit¹.) Unit-cell parameters refined from the powder data are: *Pnma*, *a* = 9.2179(2), *b* = 3.0180(9), *c* = 10.6929(2) Å, *V* = 297.47(1) Å³, *Z* = 4.

The crystal structure of harmunite [*Pnma*; a = 9.2183(3), b = 3.0175(1), c = 10.6934(4) Å; V = 297.45(2) Å³] was refined from X-ray single-crystal data to R1 = 0.0262. Details of data collection and structure refinement are given in Table 4, final atomic coordinates are summarized in Table 5. Selected bond lengths are listed in Table 6. The structure corresponds to that of synthetic CaFe₂O₄ (Decker and Kasper 1957; Yamanaka et al. 2008; Merlini et al. 2010). The structure of CaFe₂O₄ consists of two symmetrically independent FeO₆ octahedra connected over common edges, forming double rutile-type $\frac{1}{\alpha}$ [Fe₂O₆] chains. Four such double chains are further linked by common oxygen corners creating a tunnel-structure with large trigonal prismatic cavities along [001] (Fig. 10). These cavities are occupied by Ca-cations. Ca atoms have six shorter bonds (trigonal prism) and two longer bonds to oxygen atoms (Table 6; Fig. 10).

DISCUSSION

After marokite CaMn₂O₄ (Gaudefroy et al. 1963), harmunite CaFe₂O₄ is the second "calcium ferrite" structure type mineral forming at low pressure. Analysis of the bond-valence sums (bvs) (Brown and Altermatt 1985) in harmunite and marokite shows that Ca-atoms are squeezed into structural tunnels. Typical signs for this compression are the overbonding of the Ca-atom with bvs(Ca) = 2.259 v.u. for harmunite and bvs(Ca) = 2.263 v.u. for marokite (Table 7) as well as underbonding of the two octahedral sites [bvs(Fe1) = 2.795(6) and bvs(Fe2) = 2.832(6) v.u. in harmunite and bvs(Mn) = 2.886(14) for both octahedra in marokite]. This tendency is also observed for the high-pressure phases of CaAl₂O₄ (Lazic et al. 2006) and CaGa₂O₄ (Lazic et al. 2005), showing even more pronounced bond-sums deviations, as expected from high-pressure structures. A few similar examples

are listed in Table 7. For all compounds, the global instability index (GII) was calculated (Salinas-Sánchez et al. 1992) at different P and T conditions. The GII gives a numerical value for overall structure stability, comparing the calculated bondvalence sums with ideal values. According to Brown (2002), a GII larger than 0.20 v.u., indicates a structure so strained to be unstable, the usual case for structures synthesized under extreme conditions (Table 7).

The rarity of Ca-ferrites in nature can be explained by their high-formation temperature. Data on the synthesis and stability of synthetic CaFe₂O₄ and Ca₂Fe₂O₅, and also the known conditions of cement clinker production, suggest that crystallization of these ferrites begins above 700 °C (Candeia et al. 2004; Žáček et al. 2005). CaFe₂O₄ and Ca₂Fe₂O₅ are stable at atmospheric pressure up to 1216 and 1449 °C, respectively (Forsbers et al. 2002).

The size of harmunite, srebrodolskite, and magnesioferrite crystals in ore aggregates and in rare cracks filled by K-, Ca-, and Na-sulfates is two orders of magnitude greater than the size of srebrodolskite-brownmillerite and magnesioferrite grains in larnite rock formed as a result of solid-phase reactions. It may be assumed that a small amount of sulfate melt, filling small pores in larnite rock, formed as a result of protolith clinkerization. Appearance of intergranular sulfate melts is well known in industrial production of clinker with high-gypsum content (Taylor 1997). Growth of relatively large ferrite crystals took place with the participation of sulfate melt, which later solidified as calciolangbeinite and aphthitalite (Fig. 6). The angular form of ore aggregates containing harmunite (Fig. 4b) suggests primary fragments of sedimentary rock enriched in iron. As a result of pyrometamorphic processes the original Fe minerals were replaced by aggregates of srebrodolskite and harmunite. The protolith was also a source of Mg leading to magnesioferrite enrichment in the marginal zone of these aggregates and occurrence of individual magnesioferrite crystals in the core. The melting point of calciolangbeinite is just above 1000 °C (Taylor 1997). However, we are unable to reconstruct the detailed composition of this sulfate melt (probably, sulfate-chloride with cations like Na, K, Ca, Fe, Ba). Thus the melt temperature could have been significantly lower. It may be assumed that locally elevated Fe inside an ore aggregate leads to the reaction of sulfates with early srebrodolskite: $Fe_2(SO_4)_3 + Ca_2Fe_2O_5 = 2CaFe_2O_4 + 3SO_3$. This

¹ Deposit item AM-14-506, CIF. Deposit items are stored on the MSA web site and available via the *American Mineralogist* Table of Contents. Find the article in the table of contents at GSW (ammin.geoscienceworld.org) or MSA (www.minsocam. org), and then click on the deposit link.

sulfate melt was probably the sulfur source for the subsequent formation of relatively large poikiloblasts such as ternesite and fluorellestadite.

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