Ellinaite, CaCr$_2$O$_4$, a new natural post-spinel oxide from Hatrurim Basin, Israel, and Juína kimberlite field, Brazil

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Abstract. Ellinaite, a natural analog of the post-spinel phase β-CaCr$_2$O$_4$, was discovered at the Hatrurim Basin, Hatrurim pyrometamorphic formation (the Mottled Zone), Israel, and in an inclusion within the super-deep diamond collected at the placer of the Sorriso River, Juína kimberlite field, Brazil. Ellinaite at the Hatrurim Basin is confined to a reduced rankinite–gehlenite paralava, where it occurs as subhedral grains up to 30 µm in association with gehlenite, rankinite and pyrrhotite or forms the rims overgrowing zoned chromite–magnesiochromite. The empirical formula of the Hatrurim sample is (Ca$_{0.960}$Fe$_{0.016}$Na$_{0.012}$Mg$_{0.003}$)$_{0.992}$(Cr$_{1.731}$V$_{0.183}$Ti$_{0.068}$Al$_{0.023}$Ti$_{4+}$$_{0.003}$)$_{2.008}$O$_4$. The mineral crystallizes in the orthorhombic system, space group $Pnma$, unit-cell parameters refined from X-ray single-crystal data: $a = 8.868(9)$, $b = 2.885(3)$, $c = 10.355(11)$ Å, $V = 264.9(5)$ Å$^3$ and $Z = 4$. The crystal structure of ellinaite from the Hatrurim Basin has been solved and refined to $R_1 = 0.0588$ based on 388 independent observed reflections. Ellinaite in the Juína diamond occurs within the micron-sized polyphase inclusion in association with ferropericlase, magnesioferrite, orthohombic MgCr$_2$O$_4$, unidentified iron carbide and graphite. Its empirical formula is Ca$_{1.07}$(Cr$_{1.71}$Fe$_{0.06}$V$_{0.06}$Ti$_{0.03}$Al$_{0.03}$Mg$_{0.02}$Mn$_{0.02}$)$_{1.93}$O$_4$. The unit-cell parameters obtained from HRTEM data are as follows: space group $Pnma$, $a = 9.017$, $b = 2.874$ Å, $c = 10.170$ Å, $V = 263.55$ Å$^3$, $Z = 4$. Ellinaite belongs to a group of natural tunnel-structured oxides of the general formula AB$_2$O$_4$, the so-called post-spinel minerals: marokite CaMn$_2$O$_4$, xieite FeCr$_2$O$_4$, harmunite CaFe$_2$O$_4$, wernerkrauseite CaFe$_3^{2+}$Mn$^{4+}$O$_6$, chenmingite FeCr$_2$O$_4$, maohokite MgFe$_2$O$_4$ and tschaunerite Fe(FeTi)O$_4$. The mineral from both occurrences seems to be crystallized under highly reduced conditions at high temperatures (>1000 °C), but under different pressure: near-surface (Hatrurim Basin) and lower mantle (Juína diamond).
1 Introduction

The double oxide CaCr$_2$O$_4$ is known as an important component of composite materials explored in metallurgy and as ceramic materials (Rög et al., 2007). The α- and β-polymorphs of CaCr$_2$O$_4$, corresponding to its high- and low-temperature forms, demonstrate the promising magnetic and magnetoelectric properties (Hill et al., 1956; Pausch and Müller Buschbaum, 1974; Hörkner and Müller Buschbaum, 1976; Degterov and Pelton, 1996; Lee and Nassaralla, 1997; Damay et al., 2010; Toth et al., 2011; Zhai et al., 2016, and references herein). The β-polymorph belongs to a series of double oxides having the parent structure of CaFe$_2$O$_4$ (CF), which, altogether with CaTi$_2$O$_4$ (CT) and CaMn$_2$O$_4$ (CM), are gathered under the group name of post-spinel phases (Hill et al., 1956; Bright et al., 1958; Hörkner and Müller Buschbaum, 1976; Irifune et al., 1991; Kirby et al., 1996; Damay et al., 2010; Xue et al., 2021). These oxides are regarded as structural models for the high-pressure (HP) oxyspinels stable at the conditions of Earth’s deep mantle (Chen et al., 2003a; Zhai et al., 2016, and references herein). Diverse synthetic compounds with post-spinel structure of the general formula AB$_2$O$_4$ are known, where A is Li, Na, Mg, Ca, Sr, Ba, La, and Eu and B is Ti, V, Cr, Mn, Fe, Ru, Rh, Al, Ga, In, Tl, Sc, Y and REE (Shizuya et al., 2007).

In nature, seven post-spinel minerals were described prior to 2019: marokite CaMn$_3$O$_4$ (Gaudefroy et al., 1963; Lepicard and Protas, 1966), xieite Cr$_2$O$_4$ (Chen et al., 2003a, b, 2008), harmunite FeCr$_2$O$_4$ (Galuskin et al., 2014), wernerkrauseite CaFe$_2$Mn$_4$O$_6$ (Galuskin et al., 2016), chenminite FeCr$_2$O$_4$ (Chen et al., 2003b; Ma et al., 2019), maohokite MgFeCr$_2$O$_4$ (Chen et al., 2019) and tschaunerite Fe$_2$+$\frac{1}{2}$Fe$^{3+}$Ti$_4$O$_{10}$O$_4$ (Ma and Prakapenka, 2018). Xieite, chenminite, maohokite and tschaunerite are considered to be HP polymorphs, whereas other minerals may be formed under low-pressure conditions. Xieite, a HP polymorph of chromite FeCr$_2$O$_4$, was found in the shock veins of the Suzhou Li6 meteorite, China (Chen et al., 2008), and maohokite, a HP polymorph of magnesioferrite, was reported in shocked gneiss from the Xiuyan crater in China (Chen et al., 2019). Chenminite and tschaunerite were observed as shock-induced phases in the Tissint and Shergottite martian meteorites (Ma et al., 2019; Ma and Prakapenka, 2018). Harmunite CaFe$_2$O$_4$ and wernerkrauseite CaFe$_2$Mn$_4$O$_6$ are more common of Ca-rich high-temperature low-pressure pyrometamorphic rocks (Chesnokov et al., 1991; Nigmatulina, 2006; Nigmatulina and Nigmatulina, 2009; Galuskin et al., 2014; Sharygin, 2015; Galuskin et al., 2016). The Ca–Cr oxide phase, chemically and structurally similar to synthetic $\beta$-CaCr$_2$O$_4$, and post-spinel (Mg,Mn)(Cr,Fe)$_2$O$_4$ were found as potentially new mineral species in a microinclusion in a diamond from Brazil (Kaminsky et al., 2015). Unfortunately, the HRTEM data obtained and very small sizes were insufficient to approve these phases as new minerals.

This work covers all data obtained for a new mineral ellinaite, a natural analog of $\beta$-CaCr$_2$O$_4$, coming from two diverse localities: rankinite–gehlenite paralava at Hatrurim Basin, Hatrurim pyrometamorphic formation (Mottled Zone), Israel (holotype, Sharygin, 2019; Sharygin et al., 2019a), and a micron-sized inclusion in a diamond from the Sorriso River, Brazil (co-type; Kaminsky et al., 2015). The mineral was approved by the Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) as a new mineral species in December 2019, IMA 2019-091 (Sharygin et al., 2020). After the IMA registration, the same mineral has also been identified in varicolored spurrite marbles at Tulul Al Hammam, Daba-Siwaqa, Hatrurim pyrometamorphic formation, central Jordan (Galuskins et al., 2021a).

Ellinaite is named in honor of Ellina Vladimirovna Sokol (b. 1961) from IGM, Novosibirsk, Russia. Ellina (Ella) Sokol is a well-known Russian mineralogist and petrologist, who specialized in the studies of pyrometamorphic and combustion metamorphic rocks around the world, including the Hatrurim Formation (Mottled Zone) rocks, Israel–Jordan (Sokol et al., 2002, 2005, 2008, 2010, 2011, 2012, 2014a, b, 2015, 2017, 2019a, b, 2020; Khoury et al., 2016; Seryotkin et al., 2019; Sharygin et al., 2006, 2008, 2019b; Vapnik et al., 2007; Zateev et al., 2007, and many other works).

An individual grain of ellinaite from rankinite–gehlenite paralava, Hatrurim Basin, Israel (sample MP-2013-6, used for many studies), was deposited in the collections of the A.E. Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia, with the registration number 5439/1 (holotype). Another grain of ellinaite from this Hatrurim paralava (in polished thin section) is in the collections of the Central Siberian Geological Museum at V.S. Sobolev Institute of Geology and Mineralogy (IGM), Siberian Branch of the RAS, Novosibirsk, Russia (catalogue number VII-102/1, holotype). The co-type sample of ellinaite from Córigo Sorriso, Mato Grosso State, Brazil (TEM foil from diamond), is located in the scientific collection of F.V. Kaminsky (V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry, Moscow, Russia).

2 General data for ellinaite from Brazil

Natural ellinaite was first found in a polyphase inclusion within diamond #8-108 (foil #3601) (Kaminsky et al., 2015), collected from gravels of the Córigo Sorriso (Sorriso River, a right tributary of Rio Aripuanã), Juína kimberlite field, Mato Grosso State, Brazil (11°20' S, 59°12' W). It should be noted that the Juina kimberlite field is a well-known occurrence of the super-deep diamonds from both alluvial and primary kimberlite sources (Harte et al., 1999; Hutchison et al., 2001; Hayman et al., 2005; Kaminsky et al., 2001, 2007; Hayman et al., 2019).
Figure 1. (a) General view of diamond #8-108, Brazil. (b) Positions of TEM foils in the diamond. (c) Polyphase mineral inclusion with ellinaite, foil #3601, TEM image and elemental maps. Symbols: Eln – ellinaite; MgCr$_2$O$_4$ – orthorhombic MgCr$_2$O$_4$; MgFe$_2$O$_4$ – magnesioferrite; Iron carbide – Fe$_2$(C,N), Fe$_3$(C,N) or Fe$_7$(C,N)$_3$. Data were adapted from Kaminsky et al. (2015).

Unfortunately, no new data for ellinaite in the Brazilian diamond have been obtained since the IMA registration of this mineral (Sharygin et al., 2020). As a result, the text below and figures provided here for the Brazilian ellinaite represent a compilation of data adapted from Kaminsky et al. (2015).

Within the polyphase inclusion ellinaite is associated with ferropericlase (+magnesioferrite), orthorhombic MgCr$_2$O$_4$, iron carbide and graphite (Figs. 1 and S1 in the Supplement). It occurs as a 2 × 1 µm subhedral grain. The EDX TEM spectrum for ellinaite (Fig. S1) was obtained by applying the TIA™ software package and using the $k_{AB}$ factors from the software. The quantitative results were normalized to the total sum of 100%. The approximate uncertainties are ±3% for concentrations in the range 30 at%–50 at%, ±6%–12% for concentrations between 5 at%–25 at%, ±12%–25% for concentrations between 1 at%–5 at% and ±25%–100% for concentrations below 1 at%. The composition (in at%, without oxygen) is Ca = 35.72, Cr = 57.02, Fe = 1.93, Mg = 0.79, Mn = 0.69, Al = 0.80, Ti = 1.09 and V = 1.96. The empirical formula calculated on the basis of three cations and four oxygens is Ca$_{1.07}$(Cr$_{1.71}$Fe$^{3+}$_{0.06}V$_{0.06}$Ti$_{0.03}$Al$_{0.03}$Mg$_{0.02}$Mn$_{0.02}$)$_{1.93}$O$_4$.

The unit-cell parameters were calculated from HRTEM data (see Table 5 in Kaminsky et al., 2015) using high-resolution images and fast Fourier transform (FFT) software packages (Fig. S1) and gave the following results: orthorhombic symmetry, space group $Pnma$ (#62), $a = 9.017$ Å, $b = 2.874$ Å, $c = 10.170$ Å, $V = 263.55$ Å$^3$ and $Z = 4$.

3 Analytical methods for the Hatrurim Basin ellinaite

Double-polished sections (~50–100 µm in thickness) of the Hatrurim rankinite–gehlenite paralava (sample MP-2013-6, Fig. 2) were used for optical examination in transmitted and reflected light and for other studies.

Identification of ellinaite and related minerals in the Hatrurim rankinite–gehlenite paralavas was based on energy-dispersive spectra (EDS), back-scattered electron (BSE) images and elemental mapping (EDS system), using a TESCAN MIRA 3MLU scanning electron microscope equipped with an INCA Energy 450 XMax 80 microanalysis system (Oxford Instruments Ltd., Abingdon, UK) at the IGM, Novosibirsk, Russia. EDS analyses of minerals were operated at an accelerating voltage of 20 kV and a probe current of 1 nA in high-vacuum mode and at an accumulation time of 20–40 s. Synthetic compounds, pure metals and
Mineralogy and Geoecology, Miass, Russia. Measurements were done in the air using a ×40 objective with numerical aperture of 0.65: photometric diaphragm – 0.3 mm, size of analyzing area – 0.007 mm, diffraction grating – 600 grooves per millimeter, spectral interval – 6 nm, voltage for PEI – 450 V and standard – elemental silicon. Measurements were provided for the 400–700 nm range.

Single-crystal data were collected by means of a Bruker Kappa APEX DUO CCD diffractometer using MoKα radiation. The crystal structure of ellinaite has been solved by the dual space method and refined to \( R_1 = 0.059 \) using the SHELX-2014 set of programs (Scheldrick, 2015) via the Olex2 v.1.2.8 graphical user interface (Dolomanov et al., 2009). Further details of data collection and structure refinement can be retrieved from the CIF attached to the Supplement.

The Raman spectra for ellinaite were recorded on a LabRAM HR 800 mm (HRIBA Scientific Ltd.) spectrometer equipped with a 1024 pixel LN/CCD detector and coupled to an Olympus BX40 confocal microscope (×100 objective) at the IGM. A semiconductor laser emitting at 514.5 nm with a nominal output power of 50 mW was used for excitation. In each case, 20 spectra were recorded for 20 s each at a hole diameter of 200 µm and a resolution of 0.5 cm\(^{-1}\) and then integrated. Most spectra were recorded between 100 and 1400 cm\(^{-1}\). The monochromator was calibrated using the 520.7 cm\(^{-1}\) Raman line of elemental Si.

Electron backscatter diffraction (EBSD) studies were provided for one grain of ellinaite. The sample containing ellinaite and intended for EBSD studies was subjected to polishing by BuehlerMasterMet2 non-crystallizing colloidal silica suspension (0.02 µm). EBSD measurements were carried out by means of a FE-SEM ZEISS SIGMA VP scanning electron microscope equipped with an HKL Technology Nordlys HKL EBSD, operated at 20 kV and 1.4 nA in focused beam mode with a 70° tilted stage at the NANOtech Center, Ural Federal University, Ekaterinburg, Russia. Structural identification of ellinaite was performed by matching its EBSD patterns with the reference structural models using the program FLAMENCO. The structural data for synthetic \( \beta\)-CaCr\(_2\)O\(_4\) (Damay et al., 2010) and \( \alpha\)-CaCr\(_2\)O\(_4\) (Pausch and Müller Buschbaum, 1974) were used for the Kikuchi pattern simulation and comparison.

4 General information for ellinaite-bearing paralava at Hatrurim Basin, Israel

Ellinaite was observed in one of the rankinite-gehlenite paralavas, which were first found in 2011 in the southern part of the Hatrurim Basin, the largest combustion metamorphism complex of the Hatrurim Formation (also known as the “Mottled Zone”) within Israel (Gross, 1977; Burg et al., 1992; Vapnik et al., 2007). The paralava with ellinaite (sample MP-2013-6) was found as a boulder in the dry Zohav wadi (nahal Zohav), near the Arad – Dead Sea...
The rock is moderately to highly weathered and brecciated (31°09′47″N, 35°17′57″E). Similar paralavas with abundant phosphides are also known in the midstream of the Halamish wadi (nahal Halamish, neighboring nahal Zohav) in the Hatrurim Basin (Britvin et al., 2015, 2017, 2019a–d, 2020a–c). The following metal-phosphide assemblages with Cr–V-rich pyrrhotite are most common in the Zohav paralava: kamacite, steadite (Fe–P eutectics, mainly kamacite + schreibersite Fe3P) + kamacite, barringerite Fe2P + steadite, schreibersite + barringerite, barringerite + murskoite and murskoite + transjordanite. Other phosphide phases, cohenite, graphite, copper, Mo-rich phases, unidentified phosphates and daubreelite sometimes occur in such assemblages. The formation of paralava and metal-phosphide mineralization appears to be unrelated in that the metal-phosphide assemblage was probably formed in the solidified paralava from reduced gases (Britvin et al., 2015, 2017, 2019a–d). In addition to the metal phosphide and sulfide association, the new Fe-Ni-rich phosphates were found in the carbonate–gypsum–Ca–hydrsilicate matrix as alteration products of phosphides (phosphocyclite-(Fe) Fe7P2O12 (IMA 2020-087), phosphocyclite-(Ni) Ni2P2O12 (IMA 2020-088), beershevaite CaFe3+(PO4)3O (IMA 2020-095a), lisanite CaNi5+2P2O7 (IMA 2021-014), shasuite CaNi3+(PO4)2 (IMA 2021-20), nabateite Fe2+(P2O7) (IMA 2021-26) and samraite Ni2+(P2O7) (IMA 2021-29)) in the Halamish rocks (Britvin et al., 2021a).
Morphology and optical and physical properties of ellinaite from Hatrurim Basin

Ellinaite is a very rare mineral in the Hatrurim Basin, and only two grains were observed in a dark unaltered part of the rankinite–gehlenite paralava (Fig. 2). It forms subhedral opaque grains in association with gehlenite, rankinite and pyrrhotite (size – 30 × 20 µm, ellinaite-1 grain, Figs. 3a, 4 and S2) or is intergrown with chrome–magnesiochromite (size – 10 × 10 µm, ellinaite-2 grain, Figs. 3b and S3). In reflected light and in BSE images this phase resembles perovskite and chromite, which are more abundant in the studied paralava. Mineral relations indicate that ellinaite crystallized after gehlenite, rankinite and chromite, but before pyrrhotite (Fig. 3).

The color of ellinaite is black, and the color of the powdered mineral is black. It is brittle and has submetallic luster. Its hardness is ≈ 4.5–5 (Mohs), which is close to neighboring chrome (Fig. 3b). No cleavage and parting were observed; fracture is uneven. Microhardness and density were not measured directly because of the small grain size of ellinaite. Density calculated from unit-cell
dimensions and results of electron-microprobe analyses is 5.217 g cm⁻³. Ellinaite is weakly distinguishable optically from the black chromite–magnesiochromite in reflected light and in BSE images (Figs. 3b and S3). Under reflected light it is gray with a blue tint and shows weak red-brown internal reflections. Bireflectance and pleochroism are not observed; anisotropy is weak. The reflectance data for the mineral in air are given in Table 1. Reflectance percentages for the four \( R_{\text{max}} \) and \( R_{\text{min}} \) COM (Commission on Ore Mineralogy) wavelengths are 15.63, 15.35 (470 nm); 14.73, 14.59 (546 nm); 14.55, 14.42 (589 nm); and 14.54, 14.48 (650 nm).

6 Chemical composition of the holotype specimen (Hatrurim Basin)

The empirical formula of ellinaite calculated on the basis of four oxygens is \((\text{Ca}_9\text{Cr}_2\text{Al}_2\text{Ti}_4\text{O}_{12})\). Ellinaite is weakly distinguishable optically from the black chromite–magnesiochromite in reflected light and in BSE images (Figs. 3b and S3). Under reflected light it is gray with a blue tint and shows weak red-brown internal reflections. Bireflectance and pleochroism are not observed; anisotropy is weak. The reflectance data for the mineral in air are given in Table 1. Reflectance percentages for the four \( R_{\text{max}} \) and \( R_{\text{min}} \) COM (Commission on Ore Mineralogy) wavelengths are 15.63, 15.35 (470 nm); 14.73, 14.59 (546 nm); 14.55, 14.42 (589 nm); and 14.54, 14.48 (650 nm).

| \( \lambda \) (nm) | \( R_{\text{max}} \) | \( R_{\text{min}} \) | \( \lambda \) (nm) | \( R_{\text{max}} \) | \( R_{\text{min}} \) |
|-------------------|----------------|----------------|-------------------|----------------|----------------|
| 400               | 17.19          | 16.85          | 560               | 14.63          | 14.51          |
| 420               | 16.55          | 16.25          | 580               | 14.56          | 14.45          |
| 440               | 16.26          | 16.00          | 589               | 14.55          | 14.42          |
| 460               | 15.82          | 15.56          | 600               | 14.51          | 14.41          |
| 470               | 15.63          | 15.35          | 620               | 14.54          | 14.42          |
| 480               | 15.45          | 15.17          | 640               | 14.57          | 14.43          |
| 500               | 15.12          | 14.94          | 650               | 14.54          | 14.48          |
| 520               | 14.89          | 14.76          | 660               | 14.69          | 14.52          |
| 540               | 14.75          | 14.62          | 680               | 14.80          | 14.59          |
| 546               | 14.73          | 14.59          | 700               | 14.95          | 14.70          |

The ellinaite-1 grain was used for measurements. Bold – interpolated values.

![Figure 5](https://doi.org/10.5194/ejm-33-727-2021)

**Figure 5.** Chemical variations (in wt %) of TiO₂ and V₂O₅ versus Cr₂O₃ in ellinaite from the Hatrurim Basin. Ellinaite-1 grain: blue squares – WDS data; red circles – EDS data. Green circles = EDS data for the ellinaite-2 grain. For the database for the Hatrurim Basin ellinaite, see Tables S3 and S4.

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**Table 2.** Chemical composition (in wt %) for ellinaite from rankinite–gehlenite paralava (sample MP-2013-6), Hatrurim Basin, in comparison with ellinaite from the Daba-Siwaqa spurrite marble and the Brazilian diamond and ideal composition CaCr$_2$O$_4$.

|             | Ellinaite-1 | Ellinaite-2 | Ellinaite Daba-Siwaqa, Jordan | Ideal CaCr$_2$O$_4$ |
|-------------|-------------|-------------|-----------------------------|-------------------|
| **Locality** | Hatrurim Basin, Israel | Hatrurim Basin, Israel | Daba-Siwaqa, Jordan | Sorriso River, Brazil |
| n           | = 38        | = 10        | = 10                        | = 1               |
| TiO$_2$     | 0.14 0.19 0.00 0.53 | 0.12 0.14 0.00 0.47 | 1.27 1.17               |                  |
| Ti$_2$O$_3$ | 2.75 0.71 1.47 4.23 | 0.91 0.23 0.42 1.12 |                |                  |
| Cr$_2$O$_3$ | 62.50 0.82 60.64 63.97 | 67.64 0.49 66.43 68.07 | 65.44 63.27          | 73.05            |
| V$_2$O$_3$  | 7.17 0.44 6.55 8.11 | 4.59 0.39 4.19 5.49 | 2.19                  |                  |
| Al$_2$O$_3$ | 0.62 0.10 0.40 0.89 | 0.35 0.07 0.26 0.47 | 1.71 0.74             |                  |
| Fe$_2$O$_3$ |                | 1.43 2.33    |                          |                  |
| FeO         | 0.56 0.12 0.37 0.88 | 0.59 0.22 0.30 0.85 |                |                  |
| MnO         | 0.01 0.01 0.00 0.04 | 0.01 0.03 0.00 0.09 | 0.69                |                  |
| MgO         | 0.00 0.01 0.00 0.03 | 0.23 0.18 0.00 0.50 | 0.62 0.39           |                  |
| CaO         | 26.13 0.17 25.87 26.51 | 25.65 0.44 25.08 26.23 | 27.95               | 29.21            |
| SrO         | 0.54        |                |                          |                  |
| Na$_2$O     | 0.17 0.05 0.07 0.31 | 0.21 0.03 0.00 0.25 |                |                  |
| Sum         | 100.04      | 100.30       | 98.96                     | 100.00            |

**Formula based on three cations and four oxygens**

|        | Ellinaite-1 | Ellinaite-2 | Ellinaite Daba-Siwaqa, Jordan | Ideal CaCr$_2$O$_4$ |
|--------|-------------|-------------|-----------------------------|-------------------|
| Ti$^{4+}$ | 0.004       | 0.003       | 0.033                       | 0.030             |
| Ti$^{3+}$ | 0.079       | 0.026       |                             |                  |
| Cr      | 1.702       | 1.841       | 1.785                       | 1.710             |
| V$^{3+}$ | 0.198       | 0.127       |                             | 0.060             |
| Al      | 0.025       | 0.014       | 0.070                       | 0.030             |
| Fe$^{3+}$ | 0.026       | 0.037       | 0.037                       | 0.060             |
| Sum     | 2.008       | 2.011       | 1.924                       | 1.890             |
| Fe$^{2+}$ | 0.016       | 0.017       | 1.033                       | 1.070             |
| Mn      | 0.000       | 0.000       | 0.011                       | 1.110             |
| Mg      | 0.000       | 0.012       | 0.032                       | 0.020             |
| Ca      | 0.964       | 0.946       | 0.946                       | 1.000             |
| Sr      | 0.011       | 0.014       |                             | 1.110             |
| Na      | 0.011       | 0.014       |                             | 1.110             |
| Sum     | 0.992       | 0.989       |                             | 1.000             |

For Hatrurim Basin, SiO$_2$, NiO and SrO are below detection limits (<0.005 wt %). Formula based on three cations and four oxygens. TiO$_2$ and Ti$_2$O$_3$ is calculated by charge balance. Ellinaite-1 – WDS + EDS data; Ellinaite-2 – EDS data. The database for the Hatrurim Basin ellinaite is given in Tables S3 and S4. Composition of ellinaite in the Brazilian diamond (Kaminsky et al., 2015) are recalculated in wt % of oxides. Data for ellinaite at Tulul Al Hammam, Daba-Siwaqa, Jordan, are quoted from Galuskina et al. (2021a).

$2Cr^{3+} \leftrightarrow V^{3+} + Ti^{3+}$. Unfortunately, we have no possibility to check the valence state of Ti and other elements due to the small amount of ellinaite present.

Ellinaite from the Hatrurim Basin paralava essentially differs in composition from the same mineral in the Brazilian diamond, Ca$_{1.07}$(Cr$_{1.71}$Fe$^{3+}_{0.06}$V$_{0.06}$Ti$^{4+}_{0.03}$Al$^{3+}_{0.03}$Mg$_{0.02}$Mn$^{2+}_{0.02}$)$_{1.93}$O$_4$ (Kaminsky et al., 2015), and in the Jordanian spurrite marble, (Ca$_{1.03}$Mg$_{0.03}$Sr$^{2+}_{0.01}$)$_{1.076}$(Cr$_{1.785}$Fe$^{3+}_{0.037}$Ti$^{4+}_{0.033}$Al$_{0.070}$)$_{1.924}$O$_4$ (Galuskina et al., 2021a). The Hatrurim ellinaite has higher concentrations of Ti (dominantly Ti$^{3+}$) and V and a lower amount of Fe (dominantly Fe$^{2+}$) compared with the other two occurrences. The Brazilian and Jordanian ellinaites are characterized by a high concentration of Fe$^{3+}$ and low content of total Ti$^{4+}$. In the Brazilian sample the valence state of Fe (as Fe$^{3+}$) in ellinaite is anomalous considering the presence of associated Fe carbide and ferropericlase in the diamond-hosted inclusion (Kaminsky et al., 2015). In the Jordanian case we do not see any contradictions since Fe-oxide minerals (brownmillerite, srebrodolskite, hematite) and garnet-supergroup minerals (mainly andradite and priscillagrewite-(Y)) in spurrite marble are dominated by Fe$^{3+}$ (Galuskina et al., 2021a, b).
7 Structural data for ellinaite from Hatrurim Basin

7.1 Raman spectroscopy

The Raman spectra for the Hatrurim ellinaite show the complete band set common to synthetic $\beta$-CaCr$_2$O$_4$ (Zhai et al., 2016). However, in addition to the strong 596 cm$^{-1}$ band, the Hatrurim phase indicates the strong and broad band at 690 cm$^{-1}$ with respect to the synthetic compound (Fig. 6). This seems to be related to crystallographic orientation of the natural sample. The appearance and disappearance of some bands and their shifting and intensity change in the dependency on orientation have been shown for the Raman spectra of synthetic CaFe$_2$O$_4$ (Kolev et al., 2003). The vibration modes of the Raman spectrum of ellinaite may be interpreted by analogy with the Raman spectra of harmunite and wernerkrauseite and related synthetic compounds (Kolev et al., 2003; Galuskina et al., 2014; Galuskin et al., 2016; Zhai et al., 2016). Observed Raman bands are (cm$^{-1}$): $\sim$1300 (combination first-order phonons $A_g$ in the 680–700 range); 689, 598 and 556 ($A_g$ – stretching modes); 470 and 441 ($B_{2g}$ and $A_g$ – tilting and bending modes); 387, 337 and 324 ($A_g$, $B_{1g}$ and $B_{2g}$ – rotating modes); 243 and 204 ($A_g$); 140 ($A_g$ and $B_{2g}$); and 123 and 107 ($A_g$) (Ca-related vibrations). In general, Raman spectra of ellinaite from Hatrurim Basin are similar to those of ellinaite from Jordan (Galuskina et al., 2021a).

7.2 EBSD study

Before single-crystal X-ray study, we attempted to obtain the EBSD data for ellinaite. Two structural patterns of synthetic CaCr$_2$O$_4$ were used for EBSD comparison studies: $\alpha$-CaCr$_2$O$_4$ (Toth et al., 2011) and $\beta$-CaCr$_2$O$_4$ (Damay et al., 2010). We determined a good diffraction pattern, but, unfortunately, it was not indexed in both comparison structural models. This appears to have been due to unsuccessful orientation of the ellinaite crystal, although the data obtained indicated an orthorhombic symmetry. The forced Kikuchi pattern using the $\beta$-CaCr$_2$O$_4$ model (Damay et al., 2010) outlined strong mean angular deviation for some diffraction lines (Fig. S4).

7.3 X-ray data for ellinaite

Single-crystal X-ray studies for the Hatrurim ellinaite indicate that ellinaite is related to the orthorhombic crystal system: space group $Pnma$ (No.62), $a = 8.868(9)$ Å, $b = 2.885(3)$ Å, $c = 10.355(11)$ Å, $V = 264.9(5)$ Å$^3$ and $Z = 4$. X-ray powder diffraction data could not be obtained because of scarcity of material. Powder diffraction pattern calculated on the basis of single-crystal structural data and chemical composition is given in Table 3. Data were calculated using the STOE WinXPOW v.2.02 software (Stoe & Cie, 2006).

7.4 Crystal structure of ellinaite

The crystal structure of ellinaite has been solved by the dual space method and refined to $R_1 = 0.059$ using the SHELX-2014 set of programs (Scheldrick, 2015) via Olex2 v.1.2.8 graphical user interface (Dolomanov et al., 2009). The data collection and structure refinement details are summarized in Table 4. Fractional atomic coordinates, displacement parameters and selected bond lengths for the crystal structure of ellinaite are given in Tables 5 and 6.

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Table 3. Calculated X-ray powder diffraction pattern (d in angstroms) for ellinaite from the Hatrurim Basin.

| I_{calc} | d_{calc} | hkl | I_{calc} | d_{calc} | hkl |
|----------|----------|-----|----------|----------|-----|
| 3        | 5.1774   | 002 | 2        | 1.6940   | 106 |
| 6        | 4.4712   | 102 | 6        | 1.6824   | 015 |
| 23       | 4.4341   | 200 | 3        | 1.6779   | 502 |
| 15       | 3.6678   | 202 | 4        | 1.6646   | 412 |
| 2        | 3.2666   | 103 | 15       | 1.6083   | 206 |
| 4        | 2.8425   | 301 | 3        | 1.5664   | 413 |
| 9        | 2.7791   | 011 | 10       | 1.4904   | 306 |
| 2        | 2.7237   | 203 | 9        | 1.4780   | 600 |
| 6        | 2.6519   | 111 | 1        | 1.4632   | 601 |
| 54       | 2.5887   | 004 | 1        | 1.4631   | 504 |
| 100      | 2.5761   | 302 | 1        | 1.4621   | 315 |
| 4        | 2.4850   | 104 | 14       | 1.4608   | 116 |
| 69       | 2.4241   | 112 | 1        | 1.4591   | 107 |
| 32       | 2.4181   | 210 | 20       | 1.4543   | 414 |
| 1        | 2.2452   | 303 | 12       | 1.4504   | 512 |
| 1        | 2.2356   | 204 | 17       | 1.4425   | 020 |
| 6        | 2.2135   | 013 | 1        | 1.4212   | 602 |
| 3        | 1.9099   | 212 | 9        | 1.4047   | 216 |
| 3        | 1.6769   | 401 | 1        | 1.4032   | 207 |
| 34       | 2.1476   | 113 | 1        | 1.3717   | 220 |
| 11       | 2.0380   | 402 | 3        | 1.3618   | 406 |
| 16       | 2.0248   | 311 | 1        | 1.3587   | 603 |
| 3        | 2.0167   | 105 | 1        | 1.3259   | 222 |
| 2        | 1.9805   | 213 | 2        | 1.3241   | 316 |
| 5        | 1.9178   | 312 | 1        | 1.3154   | 610 |
| 15       | 1.8828   | 114 | 1        | 1.3020   | 117 |
| 2        | 1.8764   | 205 | 1        | 1.2944   | 008 |
| 9        | 1.7718   | 313 | 6        | 1.2835   | 604 |
| 35       | 1.7671   | 214 | 3        | 1.2808   | 108 |
| 22       | 1.7579   | 410 | 1        | 1.2749   | 612 |
| 1        | 1.7482   | 501 | 1        | 1.2619   | 217 |
| 14       | 1.7331   | 411 | 6        | 1.2600   | 024 |
| 1        | 1.7258   | 006 | 13       | 1.2575   | 322 |
| 1        | 1.6961   | 305 |          |          |     |

The ellinaite-1 grain was used. The nine strongest lines are in bold. Data were calculated using the STOE WinXPOW v.2.02 software (Stoe & Cie, 2006).

In general, the crystal structure of ellinaite may be represented as a framework built up of two types of the distorted $[\text{Cr}^{3+}\text{O}_6]$ octahedra (Cr1 and Cr2), sharing common edges and corners and containing the system of channels (tunnels) propagated along the b axis. The channels are occupied by calcium ions (Fig. 7). The framework is composed of two types of the distorted $[\text{Cr}^{3+}\text{O}_6]$ octahedra (Cr1 and Cr2), which form double chains, connected by common oxygen corners. The distorted octahedra $[\text{Cr}^{3+}\text{O}_6]$ in the chains have different average distances: Cr1–O = 1.950(3) Å and Cr2–O = 1.962(9) Å (Table 6). Owing to the specific connection of the chains, each tunnel has a cross section of a distorted trigonal prism (Fig. 7).

8 Discussion and final remarks

Ellinaite is related to multiple oxides with the general formula $\text{AB}_2\text{O}_4$. However, ellinaite does not belong to the spinel subgroup of the spinel supergroup (Biagioni and Pasero, 2014; Bosi et al., 2019) because it has a tunnel structure (post-spinel structure). Currently, minerals with this structure are regarded as belonging to the hypothetical marokite subgroup, which now includes eight minerals: marokite CaMn$_2^{3+}$O$_4$ (Gaudefroy et al., 1963; Lepicard and Protas, 1966), xieite FeCr$_{2}^{3+}$O$_4$ (Chen et al., 2003a, b, 2008), harmunite CaFe$_2^{3+}$O$_4$ (Galuskina et al., 2014), wernerkausite CaFe$_2^{3+}$Mn$^{4+}$O$_6$ (Galuskin et al., 2016), chenmingite FeCr$_3^{3+}$O$_4$ (Chen et al., 2003b; Ma et al., 2018), maohokite MgFe$_2^{3+}$O$_4$ (Chen et al., 2019), tschaunerite Fe$_2^{3+}$Fe$_{2}^{4+}$Ti$_{2}^{4+}$O$_4$ (Ma and Prakapenka, 2018) and ellinaite CaCr$_2^{3+}$O$_4$ (this work). Comparative crystallographic data for these minerals are given in Table 7. Moreover, the orthorhombic MgCr$_2$O$_4$ phase ($a = 9.467$ Å, $b = 2.905$ Å, $c = 9.550$ Å), which is associated with ellinaite in the Brazilian diamond-hosted inclusion (Kaminsky et al., 2015), appears to be related to the marokite supergroup. This phase may be considered a Mg analog of chenmingite FeCr$_2$O$_4$ observed as a shock-induced phase in the Tissint martian
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Table 5. Fractional atomic coordinates and displacement parameters ($\tilde{A}^2$) for ellinaite (Hatrurim Basin).

| Site* | $x/a$ | $y/b$ | $z/c$ | $U_{iso}$ | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{13}$ |
|-------|-------|-------|-------|-----------|----------|----------|----------|----------|
| Ca1 (4c) | 0.2589(2) | 3/4 | 0.34162(17) | 0.0222(7) | 0.0220(10) | 0.0315(11) | 0.0133(11) | −0.0007(6) |
| Cr1 (4c) | 0.41706(16) | 3/4 | 0.60142(13) | 0.0160(6) | 0.0181(9) | 0.0209(9) | 0.0091(9) | −0.0002(4) |
| Cr2 (4c) | 0.56064(17) | 1/4 | 0.88744(13) | 0.0163(6) | 0.0196(9) | 0.0200(9) | 0.0094(9) | 0.0001(4) |
| O1 (4c) | 0.4729(6) | 1/4 | 0.7152(5) | 0.0160(12) | 0.021(3) | 0.020(3) | 0.006(2) | 0.0002(2) |
| O2 (4c) | 0.5828(6) | 1/4 | 0.0733(6) | 0.0179(13) | 0.018(3) | 0.027(3) | 0.010(3) | 0.001(2) |
| O3 (4c) | 0.7043(7) | 3/4 | 0.8416(5) | 0.0173(3) | 0.021(3) | 0.012(3) | 0.001(2) |
| O4 (4c) | 0.3837(6) | 1/4 | 0.4759(5) | 0.0170(12) | 0.020(3) | 0.021(3) | 0.010(3) | 0.004(2) |

* Site multiplicities and Wyckoff symbols are given in parentheses. $U^{11}$ and $U^{22}$ are equal to zero by default.

Table 6. Selected bond lengths ($\tilde{A}$) for ellinaite (Hatrurim Basin).

| Bond | Length | Bond | Length | Bond | Length |
|------|--------|------|--------|------|--------|
| Ca1–O1 | 1.927(4) | Cr1–O1 | 2.450(6) | Cr1–O3 | 1.964(4) |
| Ca1–O1 | 1.977(7) | Cr1–O2 | 2.438(6) | Cr1–O4 | 1.940(6) |
| Cr1–O2 | 1.964(4) | Cr2–O1 | 2.301(5) | Cr2–O3 | 1.982(4) |
| Cr1–O3 | 1.927(4) | Cr2–O2 | 2.405(5) | Cr2–O3 | 1.982(4) |
| Cr1–O4 | 1.964(4) | Cr2–O3 | 2.289(5) | Cr2–O4 | 1.946(6) |

Figure 7. The crystal structure of ellinaite. A framework composed of edge- and corner-sharing [CrO$_6$] octahedra (green) contains the system of channels propagated along the $b$ axis. The channels are occupied by calcium ions (blue spheres).

Initially high content of Cr in the sedimentary protolith (100–480 ppm Cr) was favorable to high abundance of Cr in the Hatrurim Basin pyrometamorphic rocks (100–800 ppm Cr) and then the appearance of Cr-rich minerals in them (Geller et al., 2012; Seryotkin et al., 2019; Sokol et al., 2019a). In the rankinite–gehlenite paralava this is fixed in the presence of Cr-dominant oxides (chromite – 62.2 wt %–64.3 wt % Cr$_2$O$_3$, magnesiochromite – 61.3 wt %–62.3 wt % Cr$_2$O$_3$, ellinaite – 60.6 wt %–68.6 wt % Cr$_2$O$_3$, magnetite – up to 3.0 wt % Cr$_2$O$_3$) and Cr-containing oxides (Si-rich perovskite – 1.6 wt %–2.8 wt % Cr$_2$O$_3$, magnesiochromite – 61.3 wt %–62.3 wt % Cr$_2$O$_3$) and sulfides (pyrrhotite – 0.0 wt %–2.4 wt % Cr, Ba–Cr sulfide – 21.7 wt %–26.7 wt % Cr) (Tables 1 and S2). Like ellinaite, chromite, magnesiochromite and perovskite are also enriched in V$_2$O$_5$ and fluorapatite in the paralava are virtually free in these oxides (Table S2). In contrast to the above minerals Ca silicates and fluorapatite are free in the paralava (Table S2). It should also be mentioned that varicolored spurrite marbles at Tulul Al Hammam, central Jordan (third occurrence of ellinaite), are also characterized by high concentrations of Cr (40–1880 ppm Cr; Sokol et al., 2020), and in addition to ellinaite these rocks contain mccoonellite CuCrO$_2$, zinkochromite and magnesiochromite (Galuskina et al., 2021a, b). In general, all types of pyrometamorphic rocks of the Hatrurim Formation (Israel–Jordan) have a remarkably high concentration of Cr (40–1880 ppm Cr; Sokol et al., 2020), and in addition to ellinaite these rocks contain mccoonellite CuCrO$_2$, zinkochromite and magnesiochromite (Galuskina et al., 2021a, b). In general, all types of pyrometamorphic rocks of the Hatrurim Formation (Israel–Jordan) have a remarkably high concentration of Cr (Gross, 1977; Sharygin et al., 2008; Sokol et al., 2011, 2014a, b, 2019a, 2020; Geller et al., 2012; Seryotkin et al., 2019; Galuskina et al., 2021a, b).

The overview of ellinaite from the three localities assumes different PT–X–$f$O$_2$ conditions for the mineral and its host rocks. The structural data for ellinaite strongly indicate the $\beta$-CaCr$_2$O$_4$ modification and no evidence of the precursor $\alpha$-CaCr$_2$O$_4$. According to the phase diagram CaO-Cr$_2$O$_3$ (Degterov and Pelton, 1996; Shabanova et al., 2019),

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the phase transition between $\alpha$-CaCr$_2$O$_4$ and $\beta$-CaCr$_2$O$_4$ (ellinaite) is near 1600°C (Fig. S5). The mineralogy of the diamond-hosted inclusion with ellinaite from Brazil (Fig. 1) indicates lower-mantle crystallization conditions and low $f_O_2$ due to the presence of iron carbide and/or carbonitride (Kaminsky et al., 2015). Ellinaite-containing rocks of the Hatrurim Formation are characterized by near-surface pressure conditions and different $T$–$f_O_2$ (this work; Galuskina et al., 2021a, b). Mineral relations in the Hatrurim Basin rankinite–gehlenite paralava indicate that gehlenite, rankinite and larnite are the earliest phases crystallizing from Ca-rich silicate paralava melt (Fig. 3). Other minerals occupy interstitial spaces between the above phases and were clearly formed after them. Ellinaite crystallized after chromitite but before pyrrhotite. According to experimental and calculated data for the system CaO–SiO$_2$–Al$_2$O$_3$ (Mao et al., 2006; Haccuría et al., 2015), gehlenite+rankinite+larnite is the liquidus association (peritectic) at 1317–1343°C, and rankinite occupies a very narrow field at temperatures near 1308°C. The formation of pyrrhotite as the latest phase was probably near 1000°C according to Kosyakov et al. (1996). Silicate-melt inclusions in schorlomite–rankinite–melilitie paralava from the Hatrurim Basin indicate that rankinite crystallized at $T > 1160°C$ (Sharygin et al., 2006).

The presence of Cr-rich pyrrhotite, wüstite, native iron, cohenite and phosphides (Table S1) in the Hatrurim rankinite–gehlenite paralava indicates highly reduced conditions. Thus, local melting of the calcareous sedimentary protolith, and crystallization of resultant rankinite–gehlenite paralava under reduced conditions with the formation of holotype ellinaite, is suggested to have occurred between 1000–1343°C.

With respect to the ellinaite-bearing marbles in the Tulul Al Hammam area of Jordan, the presence of spurrite and calcite implies maximum metamorphic temperatures for these rocks of $<950°C$ (Sokol et al., 2005); Khoury et al. (2016) and Sokol et al. (2020) have subsequently determined values of 800–850°C. On the other hand, Galuskina et al. (2021a, b) consider a value of $\sim 1000°C$ as the maximum temperature for the ellinaite-bearing marbles and suggest the possibility that these rocks may be retrograde products of earlier pyrometamorphic crystallization with the formation of high-temperature Ca silicates and lime. The crystallization of the Tulul Al Hammam spurrite marbles with ellinaite occurred under oxidized conditions as evidenced by the presence of Fe-rich minerals (brownmillerite, srebrodolskite, hematite, andradite and priscillagrewite-(Y)), in which iron is largely present as Fe$^{3+}$ (Galuskina et al., 2021a, b).

The compositional and structural data of ellinaite from three known localities show that it is stable under a wide range of PT–$X$–$f_O_2$ conditions, i.e., from the Earth’s surface to the lower mantle. Limited solid solutions in ellinaite such as CaCr$_2$O$_4$ (ellinaite) ↔ CaFe$_2$O$_4$ (harmunite), CaCr$_2$O$_4$ ↔ CaV$_2$O$_4$ and CaCr$_2$O$_4$ ↔ CaTiO$_3$ involving reduced and oxidized elements reflect variable redox environments, in which ellinaite formed.

Table 7. Comparative crystallographic data for ellinaite and related post-spinel minerals.

| Mineral       | Formula     | Structure type | Space group | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å$^3$) | Z | Reference                                                                 |
|---------------|-------------|----------------|-------------|---------|---------|---------|-------------|----|---------------------------------------------------------------------------|
| Ellinaite     | CaCr$_2$O$_4$ | CF             | Pnma        | 8.868   | 2.885   | 10.355  | 264.9       | 4  | Holotype, Hatrurim Basin, Israel (this work)                               |
|               | CaCr$_2$O$_4$ | CF             | Pnma        | 9.017   | 2.874   | 10.17   | 263.55      | 4  | Co-type, Córigo Sorriso, Brazil (Kaminsky et al., 2015)                    |
|               | CaCr$_2$O$_4$ | CF             | Pnma        | 9.0875  | 2.9698  | 10.6270 | 286.80      | 4  | Daba-Siwaqa, Jordan (Galuskina et al., 2021a)                              |
| Marokite      | CaMn$_2$O$_4$ | CM             | Phcma $^*$  | 7.91    | 3.162   | 10.03   | 307.76      | 4  | Gaudefroy et al. (1963); Lepicard and Protas (1966)                        |
| Xieite        | FeCr$_2$O$_4$ | CT             | Cmcm $^*$   | 9.462   | 2.916   | 9.562   | 263.8       | 4  | Chen et al. (2003a, b, 2008)                                               |
| Harmunite     | CaFe$_2$O$_4$ | CF             | Pnma        | 9.2183  | 3.0175  | 10.6934 | 297.45      | 4  | Galuskina et al. (2014)                                                    |
| Wernerkrausei | CaFe$_2$Mn$_3$O$_6$ | CF     | Pnma        | 9.0548  | 2.8718  | 10.9908 | 285.8       | 4  | Galuskin et al. (2016)                                                    |
| Maothokite    | MgFe$_2$O$_4$ | CF             | Pnma        | 8.907   | 9.937   | 2.981   | 263.85      | 4  | Chen et al. (2019)                                                        |
| Chenningite   | FeCr$_2$O$_4$ | CF             | Pnma        | 9.715   | 2.87    | 9.49    | 264.6       | 4  | Chen et al. (2003b); Ma et al. (2019)                                      |
| Tschauerite   | Fe$^{2+}$(Fe$^{3+}$Ti$^{4+}$)O$_4$ | CT       | Cmcm $^*$   | 9.216   | 2.71    | 9.103   | 227.35      | 4  | Ma and Prakapenka (2018)                                                   |

Tunnel structures: CF – CaFe$_2$O$_4$; CT – CaTi$_2$O$_4$; CM – CaMn$_2$O$_4$. $^*$ Transformed to standard setting.
Data availability. Crystallographic data for ellinaite (CIF) are available in the Supplement. This part also additionally contains four tables (Tables S1 to S4) and five figures (Figs. S1 to S5).

Supplement. The supplement related to this article is available online at: https://doi.org/10.5194/ejm-33-727-2021-supplement.

Author contributions. VVS provided Raman spectroscopy and SEM and microprobe analysis for the Hatrurim ellinaite and wrote the paper, with help from all coauthors. SNB performed single-crystal X-ray studies and refinement of the crystal structure for the Hatrurim ellinaite. FVK and RW conducted HRTEM and interpreted the results for the Brazilian ellinaite. ENN provided microscope analyses and their complete processing for the Hatrurim ellinaite. GAY helped with EBSD study of the Hatrurim ellinaite. KAN identified optical properties of ellinaite. MNM provided fieldwork and collected phosphide-containing rocks at Hatrurim Basin, Israel.

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