Britvin, S.N., et al., 2020, Cyclophosphates, a new class of native phosphorus compounds, and some insights into prebiotic phosphorylation on early Earth: Geology, v. 49, https://doi.org/10.1130/G48203.1

Cyclophosphates, a new class of native phosphorus compounds, and some insights into prebiotic phosphorylation on early Earth

Sergey N. Britvin, Michail N. Murashko, Yevgeny Vapnik, Natalia S. Vlasenko, Maria G. Krzhizhanovskaya, Oleg S. Vereshchagin, Vladimir N. Bocharov, and Maksim S. Lozhkin

Supplementary materials

Topographic coordinates of locality (WGS84 coordinate system):

Locality of the collected specimens: 31° 12' 53" N; 35° 14' 44" E

Materials and Methods:

Scanning electron microscopy (SEM) and electron microprobe analysis (EMPA). Chemical composition of the minerals was studied using a Hitachi S-3400N scanning electron microscope (SEM) which was equipped with an Oxford Instruments AzTec Energy X-Max 20 energy dispersive (EDX) detector. Electron microprobe analyses of cyclophosphates (Supplementary Table 1) were carried out by means of an INCA WAVE 500 wavelength-dispersive (WDX) spectrometer attached to a Hitachi S-3400N SEM. The analytical conditions were: 20 kV accelerating voltage, 15 nA beam current, 20 s peak counting time; 10 s background counting time. The following standards were used: chlorapatite (P-*K* series), trevorite (Fe-*K*, Ni-*K*), diopside $CaMgSi_2O_6$ (Mg-*K*, Ca-*K*), $MnCO_3$ (Mn-*K*), and V_2O_3 (V-*K*). No other elements with the atomic number greater than 4 were detected.

Electron backscatter diffraction (EBSD). Prior to EBSD study, polished sections containing cyclophosphates were treated using reactive ion etching (RIE) with Ar^+ ions, by means of an Oxford Instruments IonFab-300 ion beam etching system operated at 500 V acceleration voltage and 2.4 mA cm^{-2} flow current. EBSD measurements were carried out by means of a Hitachi S-3400N scanning electron microscope equipped with an Oxford Instruments Nordlys-HKL EBSD detector, operated at 25 kV and 1.5 nA in a focused beam mode, using a 70° tilted stage. Structural identification of studied cyclotetraphosphates (Supplementary Fig. 2) was carried out by matching the obtained EBSD patterns with the reference structure of $Ni_2P_4O_{12}$ (Nord, 1983).

Raman spectroscopy. Raman spectrum of $(Ni,Fe)_2P_4O_{12}$ (Fig. 3) was obtained by means of a Horiba Jobin-Yvon LabRam HR800 spectrometer equipped with Ar-ion laser (λ = 514 nm) and Olympus BX41 microscope using a 50× confocal objective. The spectrum was recorded with a resolution of 2 cm^{-1} and acquisition time 30 s with 20 scans. The spectrometer was calibrated against 520.7 cm^{-1} line of a silicon standard.

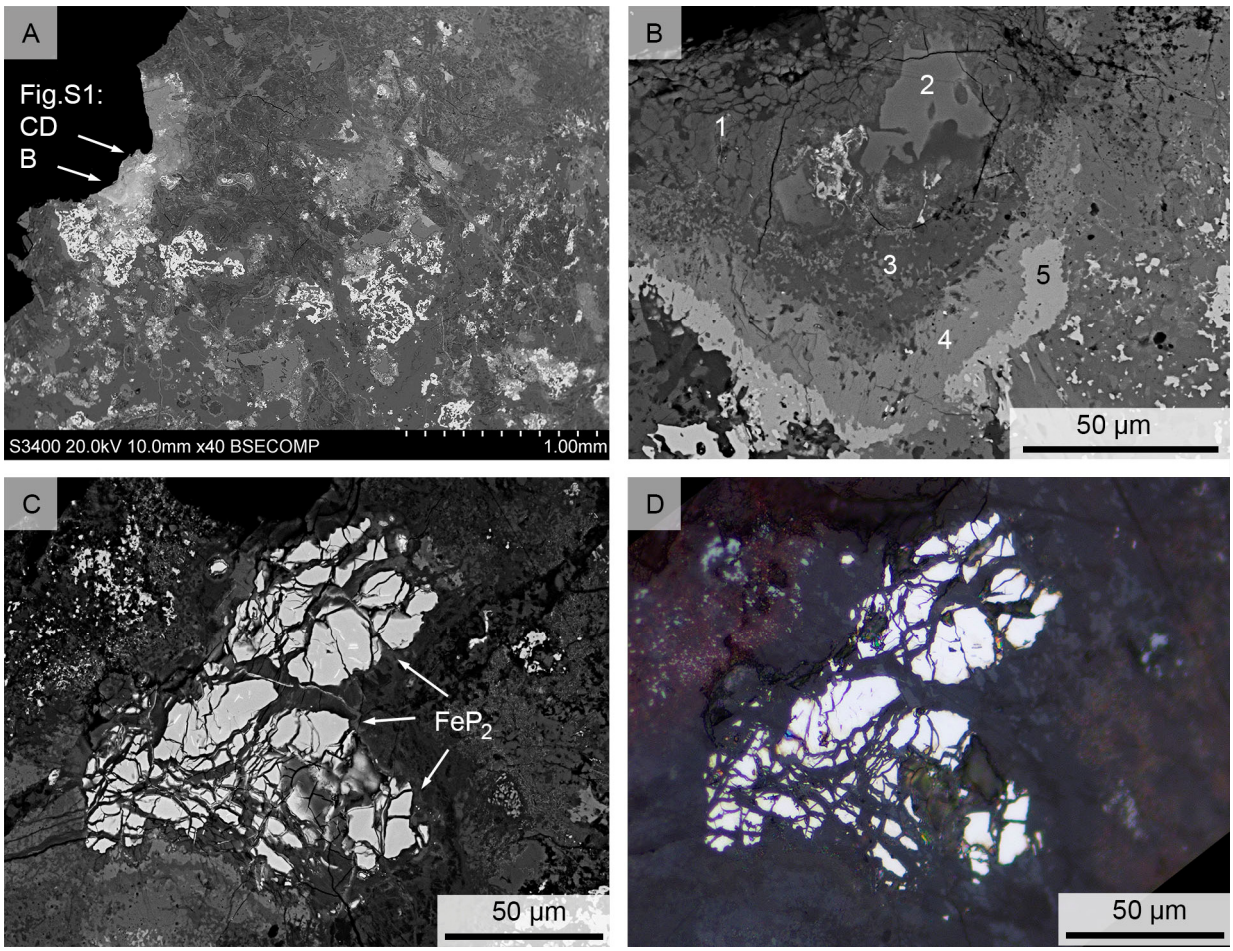

Figure S1. Cyclophosphate and associated minerals in the metamorphic rock of the Hatrurim Basin, Israel (supplement to Fig. 2). (A) General view of a polished section containing cyclophosphate. The fields corresponding to (B) and (C,D) are marked by arrows. SEM BSE image. **(B)** Cyclophosphate and associated phosphate minerals. SEM BSE image of the area shown in Fig. 2B. Phosphate phases numbering: **1**, $(Ni,Fe)_2P_4O_{12}$; **2**, $(Ca,Ni)_3(PO_4)_2$; **3**, $K(Fe,V)P_2O_7$; **4**, $NaCa(Fe,Ni)_3(PO_4)_3$; **5**, $FeNi(PO_4)O$. **(C)** SEM BSE image of partially decomposed grain of zuktamrurite, FeP_2, situated in the nearest vicinity to cyclophosphate. **(D)** The same area as in (c) captured in the reflected light.

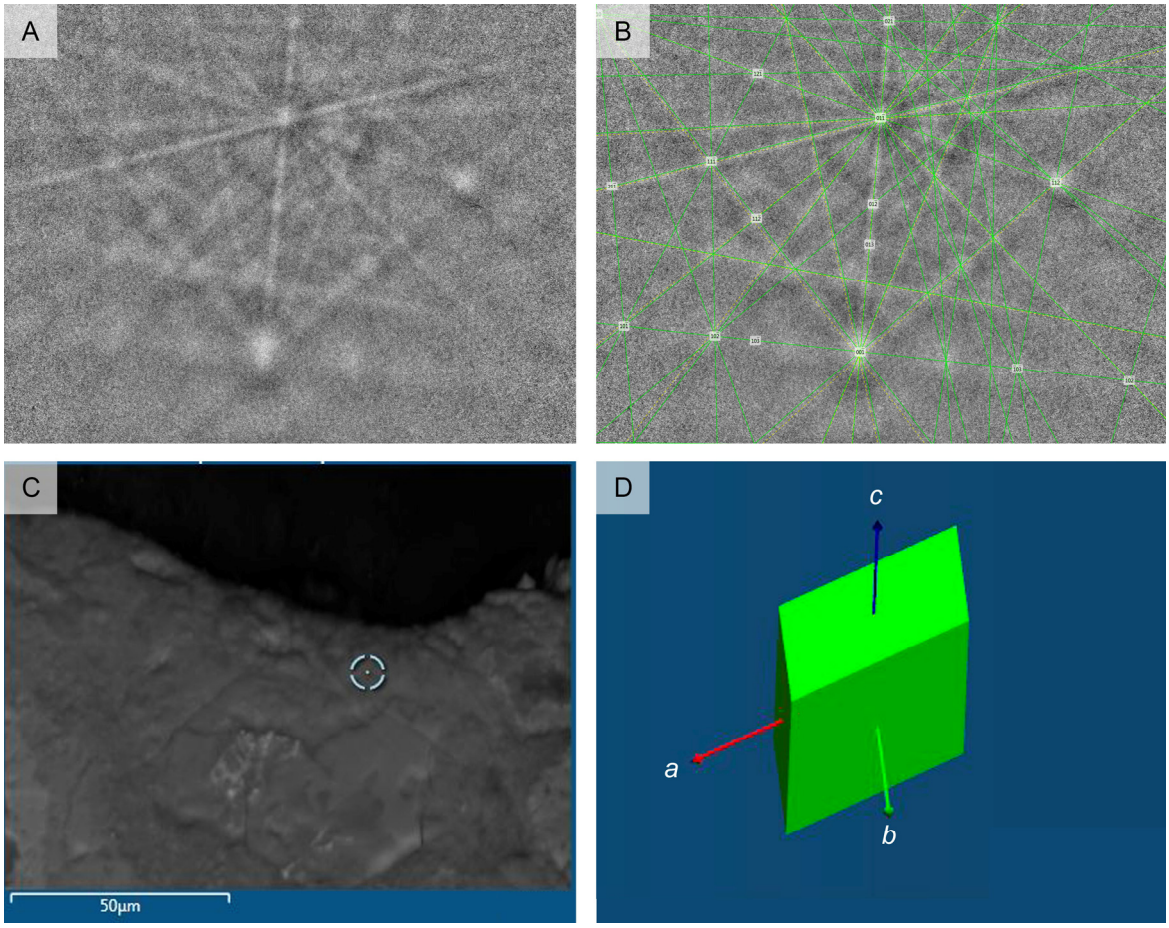

Figure S2. Electron backscatter diffraction of $(Ni,Fe)_2P_4O_{12}$. (A) An example of as-recorded electron backscatter pattern (EBSP). (B) The same EBSP indexed using the input data of synthetic $Ni_2P_4O_{12}$ (Nord, 1983). Parameters of EBSP matching: 2×2 binning, 12 bands, mean angular deviation (MAD) 0.58°. (C) The point of a given EBSP take-off. (D) Crystallographic orientation of recorded $(Ni,Fe)_2P_4O_{12}$ domain.

Table S1. Chemical composition of Ni- and Fe-richest members of $Ni_2P_4O_{12}$ – $Fe_2P_4O_{12}$ series

	Max. Ni content	Max. Fe content
	Wt. %	
FeO	13.51	23.83
NiO	17.69	8.82
MgO	0.26	0.40
CaO	2.30	0.45
MnO	0.00	0.14
V_2O_3	0.13	0.12
P_2O_5	66.72	66.94
Total	100.61	100.70
	Atoms per $M_2P_4O_{12}$ formula unit	
Fe	0.80	1.41
Ni	1.01	0.50
Mg	0.03	0.04
Ca	0.17	0.03
Mn	0.00	0.01
V	0.01	0.01
ΣM	2.02	2.00
P	3.99	4.00