Natural cubic perovskite, Ca(Ti,Si,Cr)O$_3$–$\delta$, a versatile potential host for rock-forming and less-common elements up to Earth’s mantle pressure

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**Abstract**

Perovskite, CaTiO$_3$, originally described as a cubic mineral, is known to have a distorted (orthorhombic) crystal structure. We herein report on the discovery of natural cubic perovskite. This was identified in gehlenite-bearing rocks occurring in a pyrometamorphic complex of the Hatrurim Formation (the Mottled Zone), in the vicinity of the Dead Sea, Negev Desert, Israel. The mineral is associated with native α-(Fe,Ni) metal, schreibersite (Fe,P), and Si-rich fluorapatite. The crystals of this perovskite reach 50 μm in size and contain many micrometer-sized inclusions of melilitic glass. The mineral contains significant amounts of Si substituting for Ti (up to 9.6 wt% SiO$_2$), corresponding to 21 mol% of the davemaoite component (cubic perovskite-type CaSiO$_3$), in addition to up to 6.6 wt% Cr$_2$O$_3$. Incorporation of trivalent elements results in the occurrence of oxygen vacancies in the crystal structure; this is the first example of natural oxygen-vacant ABO$_3$ perovskite with the chemical formula Ca(Ti,Si,Cr)$_{1-x}$O$_{3-\delta}$ (δ ~0.1). Stabilization of cubic symmetry (space group $Pm\overline{3}m$) is achieved via the mechanism not reported so far for CaTiO$_3$, namely displacement of an O atom from its ideal structural position (site splitting). The mineral is stable at atmospheric pressure to 1250 ± 50 °C; above this temperature, its crystals fuse with the embedded melilitic glass, yielding a mixture of titanite and anorthite upon melt solidification. The mineral is stable upon compression to at least 50 GPa. The a lattice parameter exhibits continuous contraction from 3.808(1) Å at atmospheric pressure to 3.551(6) Å at 50 GPa. The second-order truncation of the Birch-Murnaghan equation of state gives the initial volume $V_0$ equal to 55.5(2) Å$^3$ and room temperature isothermal bulk modulus $K_0$ of 153(11) GPa. The discovery of oxygen-deficient single perovskite suggests previously unaccounted ways for incorporation of almost any element into the perovskite framework up to pressures corresponding to those of the Earth’s mantle.

**Keywords:** Cubic perovskite, site splitting, disordered oxygen vacancies, davemaoite, mantle, high pressure, pyrometamorphism, Dead Sea Transform

**Introduction**

The perovskite structure is an aristotype for a diversity of minerals and advanced materials (Mitchell 2002; Mitchell et al. 2017). Perovskite-structured silicates, bridgmanite (MgSiO$_3$), and davemaoite (CaSiO$_3$) are considered the major phases constituting the Earth’s mantle (Tschauener et al. 2014, 2020; Nestola et al. 2018). Archetypal perovskite, originally described as cubic CaTiO$_3$ (Rose 1839), has a distorted, orthorhombic framework that is determined by its composition and Goldschmidt’s tolerance factor (Barth 1925; Goldschmidt 1926). Synthetic CaTiO$_3$ undergoes consecutive phase transitions to tetragonal and then to cubic modifications above 1100 °C (Redfern 1996; Ali and Yashima 2005). These transformations are reversible and non-quenchable, thus, CaTiO$_3$ returns to an orthorhombic form upon cooling to room temperature. It was demonstrated in synthetic systems that substitution of Ti by Fe$^{3+}$ results in obtaining quenched cubic perovskite (Becerro et al. 1999; McCammon et al. 2000). However, natural perovskite is practically devoid of Fe. The high-pressure behavior of synthetic CaTiO$_3$ was studied in detail as a predictive model for the evolution of silicate perovskites under conditions of the Earth’s mantle (Ross and Angel 1999; Guennou et al. 2010). It was found that orthorhombic CaTiO$_3$ does not undergo phase transitions up to 60 GPa. Therefore, cubic perovskite was not considered as a phase that can exist in nature.

In the course of ongoing research of phosphide assemblages occurring in the pyrometamorphic rocks of the Hatrurim Forma-