

## The relationship of destinezite to the acid sulfate alteration at the El Laco magnetite deposit, Chile

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### ABSTRACT

Destinezite, ideally  $\text{Fe}_2^+(\text{PO}_4)(\text{SO}_4)(\text{OH}) \cdot 6(\text{H}_2\text{O})$ , is found as nodular lumps in hematite-rich epiclastic sediments accumulated in small crater lakes on the slopes of El Laco volcano. These lumps are almost entirely dominated by fine-grained destinezite replacing earlier lipscombite, and associated with gray hematite. The crystal structure of destinezite has been re-examined to test for possible differences with respect to the earthy and poorly crystalline destinezite that forms by weathering in cave soils and mine waste dumps. The structural refinements confirm that the differences are minor. The El Laco destinezite was refined in space group  $P\bar{1}$  with  $a = 9.5828(2)$ ,  $b = 9.7440(3)$ ,  $c = 7.3302(3)$  Å, and  $\alpha = 98.796(3)^\circ$ ,  $\beta = 107.985(3)^\circ$ ,  $\gamma = 63.898(2)^\circ$ ,  $V = 584.50(4)$  Å<sup>3</sup>, and  $Z = 1$ . We measured by calorimetry the enthalpy and derived the entropy and the Gibbs free energy of formation of destinezite ( $-4051.7 \pm 4.3$ ,  $-1518.5 \pm 20.0$ , and  $-3598.9 \pm 7.1$  kJ/mol, respectively). This has allowed us to estimate the equilibrium constant in the temperature range 0–300 °C ( $\log K = -27.97 \pm 1.1$ ). We can predict that destinezite coexists with hematite over the range of conditions that typically encompass the steam-heated hydrothermal environments recognized at El Laco. The presence of destinezite along with hematite and the occurrence of alunite, jarosite, and variscite in the system provide evidence of intense hydrothermal alteration during the extrusion of Fe-rich melts at El Laco volcano. The mineral assemblage and the available geochemical data suggest that destinezite formed in hydrothermal conditions by “maturation” of an immiscible Fe–P-rich melt. An unknown Fe–P–O phase produced by this melt was first replaced by lipscombite and later, owing to intense sulfidation, by destinezite. This replacement took place in the vadose zone above the paleowater table by relatively cool (<150 °C) groundwaters acidified by oxidation of magmatic SO<sub>2</sub> to aqueous sulfate in a steam-heated system. Our model precludes other modes of formation, such as devitrification of hypothetical Fe–P–S–O-rich melts ejected from the volcano and supergene crystallization.

**Keywords:** Destinezite, acid-sulfate alteration, magnetite–apatite deposit, El Laco volcano, Chile