Compositional variability and crystal structural features of guanacoite

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ABSTRACT

Guanacoite with high Mg content from the type locality (El Guanaco mine, Chile) was investigated to elucidate the crystal-chemical characteristics of this arsenate mineral. In this study, WDS X-ray intensity maps revealed that guanacoite single crystals from the investigated specimen show distinct and characteristic compositional zoning, which varies cyclically along [100], which is in the direction of the elongation of the prismatic crystals (Witzke et al. 2006); the boundaries separating different compositional regions lie perpendicular to the prism faces. The crystal structure of a selected fragment \([a = 5.459(2), b = 16.808(9), c = 6.917(3) \text{ Å}], \beta = 100.44(1)°, V = 624.1(5) \text{ Å}^3, P_2_1/c, \text{ and } Z = 2\), was solved using direct methods and refined to an \(R\) index of 3.09% for 1385 observed \([I > 4\sigma(I)]\) reflections measured at 103 K using Mo\(\alpha\) X-radiation. The chemical formula based on the refinement is \((\text{Cu}_0.85\text{Mg}_0.15)_2\text{Mg}_2\text{Mg}_0.83\text{Cu}_0.17\text{(OH)}_4\text{(H}_2\text{O})_4\text{(AsO}_4)_2\). The structure model obtained is in good agreement with the previous structure determination, although the occupancies of the three \(M\) sites (\(M = \text{Mg or Cu}\)) are distinctly different, i.e., the sites are considerably richer in Mg, especially \(M1\) and \(M3\). These structural results suggest that guanacoite’s chemical formula should be enlarged from the \(Cu\)-rich composition \((\text{Cu}_2\text{Mg}_2\text{(Mg,Cu)}\text{(OH)}_4\text{(H}_2\text{O})_4\text{(AsO}_4)_2\) to \((\text{Cu,Mg})_2\text{Mg}_2\text{Mg}_0.83\text{Cu}_0.17\text{(OH)}_4\text{(H}_2\text{O})_4\text{(AsO}_4)_2\) to include the \(Mg\)-rich members (\(Mg\) up to 3.395 apfu). It appears that the chemical variability of guanacoite is mainly due to Mg-Cu substitution on the \(M1\) and \(M2\) sites.

Keywords: Guanacoite, copper magnesium arsenate hydrate, crystal structure, chemical analysis, Jahn-Teller distortion

INTRODUCTION

Guanacoite, a new secondary hydrated Cu-Mg arsenate, was recently discovered in a mine dump at the El Guanaco mine, 93 km east of Taltal, 230 km southeast of Antofagasta, in northern Chile (Witzke et al. 2006). Kolitsch et al. (2000) introduced the unknown Cu-Mg arsenate mineral for the first time; subsequently, the mineral name guanacoite was approved by the IMA Commission on New Minerals and Mineral Names (no. 2003-021). Recently, its description, including chemical composition, optics, morphology, crystal structure, and vibrational spectroscopy, has been documented in detail by Witzke et al. (2006) who also report a further occurrence of guanacoite at Taghouni, Bou Azer district, Morocco, and provide results from quantitative chemical analyses and a crystal-structure refinement of this material. Guanacoite from the El Guanaco mine occurs as blue to pale blue, prismatic to needle-like crystals elongated along [100], usually as a subparallel intergrowth or radiating sprays, and is accompanied by copper arsenate minerals, arbarite Cu\(_2\)Mg(AsO\(_4\))(OH), conichalcite CaCu(AsO\(_4\))(OH), and olivenite Cu\(_2\)AsO\(_4\)(OH). At the type locality, the component metals are derived from weathering of enargite Cu\(_2\)AsS\(_4\) and an apparently dolomitic country rock (Witzke et al. 2006). The ideal chemical formula of guanacoite has been expressed as \(\text{Cu}_2\text{Mg}_2\text{(Mg}_0.83\text{Cu}_0.17\text{(OH)}_4\text{(H}_2\text{O})_4\text{(AsO}_4)_2\) according to single-crystal structure refinement analysis (Witzke et al. 2006); the empirical formula derived from the chemical analysis of the type material is slightly richer in Mg, Cu\(_2\text{Mg}_2\text{(OH)}_4\text{(H}_2\text{O})_4\text{(AsO}_4)_2\) to include the Mg-rich members (Mg up to 3.395 apfu).

This paper presents the crystal-chemical characteristics of a new guanacoite sample from the type locality, which has a considerably higher Mg content, significantly exceeding the small range reported previously for the guanacoite type material (Witzke et al. 2006). The chemical compositions inferred from the Mg-rich guanacoite are apparently beyond the range of the recently reported chemical formula of guanacoite. The finding suggests that it may be appropriate to define the Mg-rich guanacoite as separate species.

EXPERIMENTAL METHODS

The sample used in this study is from the type locality, the El Guanaco mine, Chile (Kolitsch et al. 2000; Witzke et al. 2006), commercially available from Dakota Matrix Minerals (South Dakota, U.S.A.). The guanacoite is associated with arbarite, quartz, and enargite, as mentioned previously (Witzke et al. 2006). The sample’s chemical composition was determined using an electron microprobe (EMP) equipped with a fully automated X-ray wave-dispersive spectrometer (JXA8621 Superprobe; JEOL). The electron beam diameter was 10 µm with acceleration voltage of 20 kV and beam current of 10 nA. Raw data were corrected using the conventional ZAF program. Cuprite (Cu\(_2\)O), MgO (MgK\(_\alpha\)), and Ga\(_2\)O\(_3\) (AsK\(_\alpha\)) were used as standards. Other elements that were sought (e.g., Pb, Ca, Na, Bi, Fe, Mn, Sn, Zn, Sh, Co, Ni, P, V, and S) were below the detection limits. The paucity of pure uncontaminated material prevented quantitative determination of \(\text{H}_2\text{O}\) using classical methods. However, its presence was confirmed using infrared spectroscopic analysis; \(\text{H}_2\text{O}\) was calculated by stoichiometry. In the present study,