

## Two new members of the rhodesite mero-plesiotype series close to delhayelite and hydrodelhayelite: synthesis and crystal structure

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**Abstract:** Two new members of the mero-plesiotype rhodesite series ( $\text{KCa}_2\text{Na}[\text{Si}_8\text{O}_{19}]\cdot 5\text{H}_2\text{O}$ , abbreviated as TR03;  $a$  6.5850,  $b$  23.776,  $c$  7.0250 Å;  $Pn2_1m$ ; and  $\text{KNa}_3\text{Sr}[\text{Si}_8\text{O}_{19}]\cdot 4.3\text{H}_2\text{O}$ , TR04;  $a$  6.5699,  $b$  23.7225,  $c$  7.0225 Å,  $\beta$  91.81°;  $P2_1/m$ ) have been hydrothermally synthesized in Teflon-lined autoclaves at 200–230 °C and structurally characterized using X-ray diffraction single-crystal data (Bruker-AXS Smart Apex diffractometer equipped with a CCD area detector,  $\text{MoK}\alpha$  radiation). The crystal structures were solved by direct methods and refined to  $R = 0.090$  [TR03; 2634 reflections with  $I_o > 2\sigma(I_o)$ ; {010} twinning by merohedry] and  $R = 0.062$  [TR04; 4535 reflections with  $I_o > 2\sigma(I_o)$ ]. Both structures are based on a rhodesite-type porous heteropolyhedral framework, where two types of channels (effective width about 3.5 Å in the widest channel) cross the double silicate layer. They show specific “octahedral”  $O$  layers that are discussed with particular reference to delhayelite and hydrodelhayelite. TR03 can be considered a Na-bearing hydrodelhayelite; this extra cation resides in the  $O$  layer and connects two edge-sharing rows of Ca-octahedra that, instead, are isolated in hydrodelhayelite. A further increase of the number of cations pfu leads to a fully occupied  $O$  layer, as found in delhayelite and TR04. The  $\text{H}_2\text{O}$  molecules are hosted both in the channels and in the  $O$  layer; bond lengths and Raman spectra show that they are loosely hydrogen bonded. The structural features that support the wide range of chemical compositions found in the rhodesite series are discussed.

**Key-words:** hydrothermal synthesis, crystal structure, rhodesite series, delhayelite, hydrodelhayelite, twinning by merohedry, layered microporous silicate.

### 1. Introduction

Minerals and synthetic phases belonging to the rhodesite ( $\text{KCa}_2[\text{Si}_8\text{O}_{18}(\text{OH})]\cdot 6\text{H}_2\text{O}$ ,  $a$  23.416,  $b$  6.555,  $c$  7.050 Å,  $Pm\bar{m}$ ; Hesse *et al.*, 1992) mero-plesiotype series (Ferraris & Gula, 2005) are well-known modular (Ferraris *et al.*, 2008) microporous silicate phases based on a heteropolyhedral framework (Ferraris & Merlino, 2005). The crystal structures of this series (Table 1) are based on a double silicate layer that is formed via corner sharing of two apophyllite-like tetrahedral sheets (Fig. 1). The layer is crossed by eight-membered channels along two different directions that have an effective width (McCusker *et al.*, 2003) of about 3 Å (Fig. 2). The silicate module alternates with different types of “octahedral” ( $O$ ) layer (Fig. 3). According to the categorization proposed by Makovicky (1997), the rhodesite series is merotypic because the common silicate module alternates with a variable  $O$  layer; at the same time, the series is plesiotypic because the ratio between the number of up- and down-pointing

tetrahedra in the apophyllite-like sheets may vary between members of the series and, also, Al can substitute Si (Fig. 1; Ferraris & Gula, 2005).

The rhodesite-type microporous structure shows at the same time layered and heteropolyhedral-framework features. The former aspect allows synthesizing chemically different compounds while keeping constant a module of the structure. Contrary to the porous materials whose framework is based only on tetrahedra (*e.g.*, zeolites), which can be occupied by a limited number of cations, the heteropolyhedral frameworks allow a wider chemical variability, because the higher coordination polyhedra (*e.g.*, octahedra) can host a large variety of cations. The heteropolyhedral porous structures are well represented in the mineral realm (Ferraris & Merlino, 2005) and often were the incentive for the synthesis of new compounds suitable for technological applications [*e.g.*, ion exchange and luminescence due to the presence of rare earth elements (REE) in the framework]. Several synthetic members of the rhodesite series have been described (Rocha & Lin, 2005;