The modular structure of dovyrenite, Ca₆Zr[Si₂O₇]₂(OH)₄: Alternate stacking of tobermorite and rosenbuschite-like units

Milen Kadiyski, Thomas Armbruster, Evgeny V. Galuskin, Nikolay N. Pertsev, Aleksander E. Zadov, Irina O. Galuskina, Roman Wrzalik, Piotr Dzierzanowski, and Evgeny V. Kislov

ABSTRACT

The average structure, space group \( Pnnm \) [subcell: \( A = 5.666(16), B = 18.844(5), C = 3.728(11) \) Å, \( V = 398.0(2) \) Å\(^3\), \( Z = 1 \)], of the new mineral dovyrenite \( Ca_6Zr[Si_2O_7](OH)_4 \) has been refined from single-crystal X-ray data to \( R = 7.97\% \). The modular structure of dovyrenite is build by alternate stacking of Ca-polyhedral layers characteristic of the tobermorite structure and octahedral layers with attached disilicate groups known from the rosenbuschite group of minerals. No indications of ordered polytypes were detected for the potential OD-structure. Either the small crystal size producing only weak diffraction intensities did not allow detecting diffuse diffraction features (or “super-structure” reflections) or the structure is build by disordered stacks of OD layers. Nevertheless, the resolved average structure allowed unraveling the possible order patterns within the rosenbuschite-like octahedral layers. The key for understanding the polytypic character of this structure is the short periodicity of the tobermorite-like Ca polyhedral layer of only 3.73 Å along \( c \), whereas the periodicity of the attached rosenbuschite-like octahedral layer is doubled. In dovyrenite Ca occurs in sixfold-, sevenfold-, and eightfold-coordination. The octahedral Ca site is only half occupied and may reveal additional vacancies, which must be charge balanced by disordered OH-groups replacing O. A corresponding modular structure with the same subunits but different composition and without octahedral vacancies exists for rinkite \((Ti,Nb,Al,Zr)(Na,Ca)_{3}(Ca,Ce)_{4}[Si_{2}O_{7}]_{2}(O,F)_{4}\), which has hitherto been considered as heterophyllosilicate.

Keywords: Dovyrenite, zirconosilicates, single-crystal X-ray diffraction, structure solution, modular structure, tobermorite, rinkite, heterophyllosilicate

INTRODUCTION

Ferraris et al. (2004) begin their book on crystallography of modular materials citing a phrase by Galileo Galilei: “Nature does not act by means of many things when it can do so by means of few.” This is also particularly true for the crystal structure of the new mineral dovyrenite \( Ca_6Zr[Si_2O_7](OH)_4 \), assembled of two well-known modules characteristic of the polyhedral Ca-sheet in tobermorite group minerals and the octahedral layer with attached disilicate moieties of the rosenbuschite group. Minerals of the rosenbuschite group are disilicates with attached disilicate moieties of the rosenbuschite group. The key for understanding the polytypic character of this structure is the short periodicity of the tobermorite-like Ca polyhedral layer of only 3.73 Å along \( c \), whereas the periodicity of the attached rosenbuschite-like octahedral layer is doubled. In dovyrenite Ca occurs in sixfold-, sevenfold-, and eightfold-coordination. The octahedral Ca site is only half occupied and may reveal additional vacancies, which must be charge balanced by disordered OH-groups replacing O. A corresponding modular structure with the same subunits but different composition and without octahedral vacancies exists for rinkite \((Ti,Nb,Al,Zr)(Na,Ca)_{3}(Ca,Ce)_{4}[Si_{2}O_{7}]_{2}(O,F)_{4}\), which has hitherto been considered as heterophyllosilicate.

Keywords: Dovyrenite, zirconosilicates, single-crystal X-ray diffraction, structure solution, modular structure, tobermorite, rinkite, heterophyllosilicate


A remarkable coincidence is the similarity of the subcell dimensions and symmetry between riversideite \( Ca_{10}[Si_{6}O_{18}(OH)_{18}] \times nH_2O \) (tobermorite 9 Å) and doveryrenite. In standard space-group setting \( Pnnm \) doveryrenite has \( A = 5.67, B = 18.84, C = 3.73 \) Å, whereas riversideite has \( A = 5.58, B = 18.70, C = 3.66 \) Å (Taylor 1959; Ferraris et al. 2004), although the true structures and chemical compositions show important differences. The definition and description of dovyrenite as a new mineral will be published elsewhere (Galuskin et al. 2007). This manuscript deals with the analysis and interpretation of the modular structure of the new mineral (accepted by CNMMN IMA 2007-002).

OCURRENCE

The new mineral dovyrenite was discovered in altered skarn-dolomite xenoliths in the Dovyren (Yoko-Dovyren) subvolcanic layered gabbro-peridotite massif of Proterozoic Age (~700 Ma)