

Crystal structure refinement of palygorskite from neutron powder diffraction

ROBERTO GIUSTETTO* and GIACOMO CHIARI

Dip. di Scienze Mineralogiche e Petrologiche, Università di Torino, Via Valperga Caluso 35, I-10125 Torino, Italy
Corresponding author, e-mail: roberto.giustetto@unito.it

Abstract: Palygorskite is a Mg-rich fibrous clay, present in nature as a mixture of two intricately intertwined polymorphs – monoclinic ($C2/m$) and orthorhombic ($Pbmn$) – characterized by the presence of channels along Z -axis, filled by weakly bound zeolitic water. A neutron powder diffraction study was carried out by full Rietveld refinement on a deuterated sample, measured at ISIS on the HRPD beam-line. The positions of oxygen and deuterium atoms of the zeolitic water were located *ab initio* through cyclically repeated Difference Fourier maps, and their atomic coordinates and occupancy factors were refined. The frameworks of both monoclinic and orthorhombic palygorskite do not differ significantly from the models reported in the literature, although they are more distorted. The arrangement of the zeolitic water molecules is highly disordered and different in the two polymorphs. Given the coexistence of several deuterium sets, two different H-bonding schemes are proposed for each polymorph. Further H-bonding alternatives could be derived by considering the location of oxygen atoms in partially occupied symmetry related sites. The links between the zeolitic water and the clay framework appear to be weaker in orthorhombic than in monoclinic palygorskite, as shown by the lower number and different strength of H-bonds. The detailed knowledge of the zeolitic water arrangement may help in better understanding the structural features and production techniques of palygorskite-based compounds of great interest, such as the Maya Blue pigment.

Key-words: palygorskite structure, neutron powder refinement, zeolitic water, clay mineral.

1. Introduction

Palygorskite is a Mg-rich dioctahedral clay, with fibrous morphology. Usually it is a mixture of two polymorphs: a monoclinic one (space group $C2/m$, MP hereafter) and an orthorhombic one (space group $Pbmn$, OP hereafter), both with ideal composition $(Mg, Al)_4 (Si)_8 (O, OH, H_2O)_{26} \cdot nH_2O$.

In the structure of both polymorphs of palygorskite (Fig. 1) discontinuous octahedral layers, forming ribbons elongated in the Z -axis direction, are alternated to continuous tetrahedral ones, in which a regular change in the orientation of the SiO_4 tetrahedra apexes occurs every two chains. These shifts allow for the interruption of the octahedral layer in the b direction, thus neutralizing the dimensional mismatch between tetrahedral and octahedral sheets due to the presence of the smaller Mg among the Al atoms. The missing octahedral chain generates zeolitic-like channels along Z , usually occupied by weakly bound, non structural water (*zeolitic water*). Mg and Al cations complete their co-ordination with tightly bound water molecules (*structural water*). The axis of the fibre coincides with the channel elongation.

De Lapparent (1938) used the name attapulgitite to describe a fibrous clay, found near Attapulgis (Georgia, U.S.A.), which was later identified as palygorskite. The

name palygorskite was first used by Kukovsky & Ostrovskaya (1961), to identify a mineral discovered in 1860 in a mine near Palygorsk (ex U.S.S.R.), and was therefore officially accepted by IMA in 1985.¹

The structure of palygorskite was first proposed by Bradley (1940) and later reviewed by Preisinger (1963), although uncertainties remained about the correct space group and cell dimensions. Zvyagin *et al.* (1963), using electron diffraction techniques, proposed for palygorskite a monoclinic model with space group $P2/a$ which was later discarded. Drits & Aleksandrova (1966) showed that palygorskite contains 4 octahedral cations per crystal chemical formula and should be considered as dioctahedral. In terms of the dioctahedral structure of the mineral, Drits & Sokolova (1971) confirmed the model of Bradley (1940) because positions and intensities of all observed reflections were treated in the unique monoclinic unit cell.

Christ *et al.* (1969) analysed several palygorskite sam-

¹ In spite of this, the name attapulgitite is still often inappropriately used. Just as an example, in the Dictionary of Descriptive Terminology (Roberts & Etherington, 2002), a much consulted online tool, the entry “attapulgitite” is present but not “palygorskite”. Furthermore, a simple search by name in the Internet lists 5370 hits for attapulgitite and only 1670 for palygorskite. This is probably due to the numerous applications of the mineral, ranging from molecular sieves to material science, from medical use to paints, fertilizers, mud for well drilling in the oil industry, to cat litter. Most of the users and sellers are not scientists and keep using the old name in spite of the international regulation.