The occurrence of tinsleyite in the archaeological site of Santana do Riacho, Brazil

GERALDO MAGELA DA COSTA^{1,*} AND RÚBIA RIBEIRO VIANA²

¹Chemistry Department, Universidade Federal de Ouro Preto, 35400, Ouro Preto, Minas Gerais, Brazil ²Geology Department, Universidade Federal de Ouro Preto, 35400, Ouro Preto, Minas Gerais, Brazil

ABSTRACT

A second occurrence of tinsleyite, KAl₂(PO₄)₂(OH)·2H₂O, is reported. The mineral exists as a thin layer in a quartzite wall partially covered by rock paintings, and was characterized by X-ray diffraction, thermal and chemical analysis, and by Mössbauer spectroscopy. The calculated cell parameters are a = 9.58(6), b = 9.53(4), c = 9.54(6) Å, $\beta = 103.2(4)^{\circ}$. Chemical analysis showed the presence of 3.9% Fe which probably replaces Al in the octahedral site. The Mössbauer spectra from room temperature down to 85 K show the existence of two Fe³⁺ doublets with $\Delta E_{Q1} \sim 0.57$ mm/s and $\Delta E_{Q2} \sim 1.0$ mm/s. At 77 K the spectrum drastically changes, suggesting that a structural transition might have occurred. The formation of tinsleyite might be due to the reaction of phosphate-rich water which runs along the fractures of the wall. The existence of tinsleyite in such a relatively large abundance indicates that this mineral might not be rare as previously thought.

INTRODUCTION

Tinsleyite, KAl₂(PO₄)₂(OH)·2H₂O, was first described by Dunn et al. (1984) from the Tip Top pegmatite in South Dakota. The cell parameters derived from powder X-ray diffraction data were given as a = 9.602(8), b = 9.532(6), c = 9.543(11)Å, $b = 103.16(6)^{\circ}$, and Z = 4. Recently, Dick (1999) characterized a synthetic tinsleyite obtained by the reaction of gibbsite with a potassium-phosphate solution. A structural analysis was made on a single-crystal specimen and the cell parameters were given as a = 9.499(2), b = 9.503(2), c = 9.535(2) Å, $\beta = 103.26(3)^{\circ}$ and Z = 4. According to this author, tinsleyite is isostructural with leucophosphite. Another closely related mineral is spheniscidite, [Fe₂(NH₄)(PO₄)₂(OH)·2H₂O], whose structure was first described by Cavellec et al. (1994), who also found that this mineral is isostructural with leucophosphite.

Tinsleyite, leucophosphite, and spheniscidite are monoclinic with space group $P2_1/n$ (Moore 1972; Cavellec et al. 1994; Dick 1999). However, Dunn et al. (1984) proposed for natural tinsleyite a different space group (Pn or P2/n) because of the presence of a weak reflection that could be indexed as (010). The basic structure consists of two octahedra sharing an edge containing the two OH groups, and two satellite octahedra sharing the same corner where the hydroxyl groups are located. One water molecule is bonded to the octahedra, whereas the other one is located in the cavities which run parallel to the *b* axis. The other cation (K^+ or NH_4^+) is also located in these tunnels. There are two non-equivalent octahedral Fe sites. In one site, Fe³⁺ is surrounded by two OH groups in a cis configuration; in the other site by one OH group and one water molecule. Thus, it can be anticipated that the Mössbauer spectrum

This second natural occurrence of tinsleyite was reported by da Costa et al. (1991), who described its presence as a pink layer in a quartzite wall. This material was found in an archaeological site named Santana do Riacho, located about 90 km north of the city of Belo Horizonte in the state of Minas Gerais. According to Karfunkel et al. (1991) the stratigraphy of the area is mainly composed of rocks from the Córrego dos Borges Formation (Espinhaço Supergroup) and from the Macaúbas and Bambuí Groups (São Francisco Supergroup). In this region there are important Mn and iron oxide deposits formed by lateritic alteration and supergenic concentration processes (Dossin 1983). These deposits were developed from the pelitic unit of the Macaúbas Group and a detailed study of these ores has shown that the main manganese oxides are psilomelane, criptomelane, and pirolusite. Both P and Al are present in concentration up to 2% and 14%, respectively (Dossin 1983).

The oldest human remains were dated to 13500 B.C., but the age of the paintings could not be determined. Hundreds of rock paintings were painted on a quartzite wall, which is about 80 m long and 15 m high and was used as a natural shelter (Prous and Malta 1991). The pigments were identified as iron oxihydroxides, mainly hematite and goethite. The pink layer is present both in the upper part of the wall and near and over some paintings. Sometimes it is also present below the paintings, suggesting that the formation begun a long time ago and is still occurring today (da Costa et al. 1991). Consequently, the original layer of paintings can be masked by the pink color, with serious implications for the conservation of the entire archaeological site. Hence the goal of this work is to characterize the mineralogy of the pink layer and to understand its formation.

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might show the signals corresponding to Fe in these two nonequivalent octahedral sites. A schematic arrangement of this structure is shown in Figure 1.

^{*} E-mail: magela@iceb.ufop.br



FIGURE 1. Perspective view of the octahedral arrangement in leucophosphite.

EXPERIMENTAL METHODS

The pink material was carefully scraped off a small quartzite block, which was loosely fixed to the wall. In spite of the care taken, part of the rock (mainly quartz and probably small amounts of muscovite) is present in the sample studied (about 200 mg in total).

Chemical analysis was performed by atomic absorption spectroscopy (AAS) for Fe and K and by inductively coupled plasma mass spectrometry (ICP-MS) for P and Al. The pink material could easily be dissolved in warm 1 *M* HCl and a whitegray residue remained after the treatment.

A powder X-ray diffraction pattern was obtained with a Rigaku Geigerflex diffractometer with $CuK\alpha$ radiation and graphite monochromator. Quartz was used as an internal standard and peak positions were determined by fitting the numerical profiles with a Pearson VII function. Cell parameters were determined using the eleven strongest reflections.

Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed on about 10 mg of the sample in a Du Pont SDT2960 module. The temperature ranged from 25 to 1000 °C, using a constant flow of nitrogen (100 mL/min) and a heating rate of 10 °C/min.

Mössbauer spectra were collected between room tempera-

ture and 77 K with a time-mode spectrometer with constantacceleration drive and triangular reference signal. Velocity calibration was achieved from the spectrum of α -Fe foil. Center shifts quoted hereafter are relative to metallic iron.

RESULTS AND DISCUSSION

The powder diffractogram is shown in Figure 2. Almost all the strongest lines can be assigned to tinsleyite and quartz. A small peak centered at 16.5° 20 could not be identified. The calculated cell parameters are a = 9.58(6), b = 9.53(4), c =9.54(6) Å, $\beta = 103.2(4)^{\circ}$, and Z = 4. These values are similar to those reported by Dunn et al. (1984) for a natural tinsleyite, but differ from those of the synthetic sample (Dick 1999). Considering the similarity of the structure and composition of tinslevite and leucophosphite, it is very likely that a solid solution might exist between these two end-members. The fact that some Fe was found in the tinsleyite reported by Dunn et al. (1984) and in the present sample is evidence for a possible isomorphic substitution. The clear correlation between cell parameters and the amount of Fe present in the structure of leucophosphite and tinsleyite (Fig. 3) might be used to check the Fe³⁺ content when a chemical analysis is obtained from impure material. The data in Figure 3 were taken from our results and from Dick and Zeiske (1997), Dick (1999), Simmons (1964), and Dunn et al. (1984).

The results of the chemical analysis, the molecular proportions of oxides of the present sample, along with the theoretical values and those reported by Dunn et al. (1984) are shown in Table 1. The molar proportions of $(Al_2O_3 + Fe_2O_3)$ and P_2O_5 are close to the theoretical values, and a composition with approximately 0.25 Fe atoms per formula unit (apfu) can be determined. The high value of K₂O suggests that another phase was partially dissolved by HCl.

The thermal behavior of the analyzed sample is shown in Figure 4. According to Dick (1999), one water molecule in tinsleyite is linked by hydrogen bonding and released at 68 °C,



FIGURE 2. X-ray diffraction pattern of the studied sample. Arrows point to the main observed peaks of tinsleyite and Q is the main peak of quartz.



FIGURE 3. Correlation between the iron content and the unit-cell parameters of tinsleyite and leucophosphite. The data for Fe = 0.25 are for the present sample, and the solid line connects the data for the synthetic materials.

whereas the other molecule is bonded to the Al ions and released at 198 °C. Cavellec et al. (1994) proposed that in spheniscidite one water molecule is bonded to Fe³⁺ ions, whereas the tunnels are occupied by the NH₄₊ cations and by water molecules. Moore (1972) suggested that water molecules in the tunnel are tightly held, and therefore would require a relative high temperature to be removed. In the present case it can be observed that the decomposition occurs in three endothermic steps, at 114 °C (7.5 wt%), at 198 °C (3.9 wt%), and at 393 °C (3.0 wt%). A splitting in the TGA signal close to 100 °C, better seen in the derivative curve (Fig. 3), suggests loss of moisture together with a weakly bonded water molecule. The loss at 198 °C is in agreement with the result of Dick (1999), whereas the third decomposition at 393 °C remains unclear.

Mössbauer spectra of the present sample recorded at room temperature and at 77 K are shown in Figure 5. At room tem-

 TABLE 1.
 Chemical analysis and theoretical molecular proportions of oxides in tinsleyite

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Oxide	wt%	Theoretical value	Dunn et al. (1984)	This work	
Al ₂ O ₃	17.4	0.30	0.261	0.171	
P_2O_5	28.4	0.30	0.297	0.200	
K₂O	16.4	0.15	0.132	0.174	
Fe ₂ O ₃	3.9	-	0.033	0.024	
Mn ₂ O ₃	n.d.	-	0.007	n.d.	

Notes: n.d. = not determined. The values in the last column are not normalized to pure tinsleyite.



FIGURE 4. Thermogravimetric curve (solid line) of the analyzed sample. The different steps are better resolved using the derivative (dotted line) of the thermogravimetric curve.

perature, the spectrum consists of a broad, slightly asymmetric doublet, which was fitted using two symmetric Fe^{3+} doublets. The derived hyperfine parameters are listed in Table 2. From 293 K down to 85 K the overall shape of the spectrum remains the same, but at 77 K the spectrum drastically changes, being composed of a broad central envelope with no visible magnetic splitting. Again the spectrum could be decomposed into two quite broad doublets, but surprisingly one of them has a



FIGURE 5. Mössbauer spectra recorded at 77 K (top) and at room temperature (bottom) for tinsleyite. Crosses represent the experimental data, and full lines represent the fitted subspectra and their sum.

 TABLE 2. Mössbauer parameters derived from the spectra of tinsleyite

T (K)	ΔE_{Q1}	δ1	Г	ΔE_{Q2}	δ2	Γ2			
293	0.57	0.37	0.34	0.88	0.39	0.58			
200	0.54	0.43	0.48	1.10	0.38	0.54			
85	0.52	0.48	0.49	1.14	0.41	0.52			
77	0.17	0.46	0.69	0.99	0.44	0.69			
<i>Notes:</i> The quadrupole splittings (ΔE_{Q}), isomer shifts (δ), and line widths									

 (Γ) are given in mm/s.

very small quadrupole splitting ($\Delta E_{\rm Q}$, see Table 2). This small value of $\Delta E_{\rm Q}$ points to a quasi-cubic lattice, and the difference in the temperature dependence of two quadrupole splittings could be explained by different changes in bond lengths. Thus, it seems that a structural transition occurs in the temperature interval between 77 K and 85 K. Finally, the strong overlap of the two broad sub-spectra at all temperatures does not allow a reliable estimation of the site occupation because some of the iterated results depends on the initial values of the adjustable parameters (da Costa et al. 1994).

A question that emerges is related to the formation of tinsleyite in the region of Santana do Riacho. During the rainy season it is observed that water percolates through the fractures of the quartzite wall. On the top of the shelter there is relatively dense vegetation and not far behind a small stream runs year round. Simmons (1964) proposed a mechanism for the formation of leucophosphite that involves the reaction of iron oxides or serpentine with phosphate-rich water that passed over bat guano or bird dung. In the present case, meteoric water might leach and carry the necessary P to react with Al and Fe to form thin layers of tinsleyite. If this is the case, it will be extremely difficult to protect the rock paintings from this natural degradation.

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