A HIGH TEMPERATURE STUDY OF TRIPHILITE

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ABSTRACT Two samples of triphillite were studied at high temperature with a Guinier-Lenné camera. Triphillite 1 ($\text{Mn/Fe} + \text{Mn} \approx 0.22$) exhibits an ordered diffraction pattern up to 780°C under strictly reducing conditions (N_2 gas). Triphillite 2 ($\text{Mn/Fe} + \text{Mn} \approx 0.24$), upon oxidation, shows drastic changes in the value of the intensities of the 2.54 and $2.47 \text{ \AA}$ diffraction lines. These at 22°C exhibit values which are approximately the reverse than at 550°C . The strong disturbances affecting the $\text{M}(2)$ site as a consequence of the process of oxidation and of the temperature changes suggest that it is not unlikely that triphillites, representative of conditions of high entropy and rapid crystalization, could be disordered.

RESUMO Duas amostras de trifilita foram estudadas a altas temperaturas com uma câmara Guinier-Lenné. A trifilita 1 ($\text{Mn/Fe} + \text{Mn} \approx 0.22$) exibe um padrão de difração ordenado até 780°C , sob condições estritamente redutoras (gás N_2). A trifilita 2 ($\text{Mn/Fe} + \text{Mn} \approx 0.24$), uma vez oxidada, mostra mudanças drásticas no valor das intensidades das linhas de difração de $2.54 \text{ \AA}$ e $2.47 \text{ \AA}$, as quais, à temperatura de 22°C , exibem valores que são aproximadamente o inverso daqueles a 550°C . As fortes perturbações que afetam a posição $\text{M}(2)$, como consequência do processo de oxidação e das mudanças de temperatura, sugerem que é razoável supor que as trifilitas representativas de condições de entropia elevada e cristalização rápida possam exibir um retículo desordenado.

INTRODUCTION Progressive substitution of Fe^{+2} and Mn^{+2} in the formula $\text{Li Fe}_{1-x}^{+2} \text{Mn}_x^{+2} \text{PO}_4$ (1) results in a variety of phases constituting a solid solution whose end members are triphillite and lithiophilite (respectively LiFePO_4 and LiMnPO_4). Partial oxidation of (1) results in sicklerite ($\text{Li}_x \text{Fe}_{1-x}^{+3} \text{Mn}^{+2} \text{PO}_4$) which, upon removal of Li and exchange of Mn^{+2} to Mn^{+3} , converts to heterosite ($\text{Fe}_{1-x}^{+3} \text{Mn}_x^{+3} \text{PO}_4$). While this paragenesis is commonly accepted, no evidence has been reported regarding the thermal behavior of triphillites characterized by different cationic stoichiometries and degrees of oxidation. Such an information, aside from its academic interest, would prove particularly useful in the interpretation of the paragenesis of associations of the primary phosphates, particularly in relation to exolution phenomena. The point has been stressed by Moore (1972) in an introductory discussion of the problem.

Here we have focused our attention on two triphillites exhibiting slightly different $\text{Mn/Fe} + \text{Mn}$ ratios and studied them at different temperature, under reducing and slightly oxidizing conditions. Interpretation of the high temperature powder data was facilitated by a structural refinement of a sample of triphillite by Finger *et al.* (1970).

Triphillite 1 SINGLE CRYSTAL WORK Zero level photographs of a sample characterized by $\text{Mn/Fe} + \text{Mn} \approx 0.22$ exhibited a very sharp diffraction pattern lacking any evidence of streaking or diffuseness. Although the study was not carried out with strictly monochromated radiation, limitation which precludes a quantitative approach to a study of the crystal dynamics of the lattice, such a lack of planar and intraplanar disturbances suggests absence of structural defects. Furthermore it excludes significant contribution to scattering from thermal vibration of the atomic planes.

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POWDER WORK Experiments have been carried out at 25°, 100°, 220°, 340°, 550°, 650°, 780°, 850° and 900 °C* with a Guinier-Lenné camera connected to a system capable of erogating N₂ gas at different pressure. The hot N₂ coming from the X-ray chamber was collected into a container via a line sealed to the gas outlet. This system was devised in order to prevent oxidation of Fe⁺² and Mn⁺². Prior to the commencement of each run, N₂ gas was flushed into the specimen-chamber for about 2 hrs. and then allowed to flow in the system for the entire duration of each experiment. The samples were mounted on a platinum grid, the diffraction lines of which were used to check the temperature readings obtained from a recorder potentiometer operated in continuous mode. This was possible since the coefficients of thermal expansion of Pt are quite accurately known (Campbell, 1968).

Upon heating, the relative intensities of the diffracta uniformly decrease in agreement with theoretical considerations. No other change is noticed up to 780 °C, temperature at which two weak diffraction lines ($d = 4.11$ and $2.71 \text{ \AA}$, respectively) appear. Further temperature increments result in a better resolution of the "new" diffracta at the expenses of the basic pattern which is very little evidenced (Fig. 1). Three additional independent runs were carried out with fresh material in order to test the reproducibility of the results and try to improve the quality of the diffraction pattern in the temperature range 780°-900 °C. While reproducibility of the results was obtained in all instances, the relative intensities of the diffracta at a temperature above 800 °C were consistently too weak for any meaningful study. After slow cooling of the specimen to room temperature under a constant flow of N₂ gas, a microscopic examination was carried out. This did not show any trace of oxidation of the sample.

Figura 1 — Triphillite 1. Notice the stability of the sample to the phononic disturbance and the two extra diffraction lines at $d = 4.11$ and $2.71 \text{ \AA}$. These are indicated by arrows

*Estimated accuracy of temperature readings for the powder work reported in this paper: $\pm 8 \text{ }^{\circ}\text{C}$

Triphillite 2 SINGLE CRYSTAL WORK Upon examination with the precession camera (hkO and Okl levels), a sample of triphillite characterized by $Mn/Fe + Mn = 0.24$ did not exhibit significant changes in the diffraction pattern at 22 and 550 °C*, aside from the expected decrease in the value of the relative intensities. No immediate evidence of temperature — induced diffuseness that could be related either to disorder or to strong contributions of thermal diffuse scattering was recorded. These observations might be considered in terms of the results of a three-dimensional refinement of a sample of triphillite by Finger *et al.* (1970). According to these authors the structure is well ordered at room temperature and isotypic with monticellite (Table I).

Table I — Atomic parameters of triphillite

*Atom	x	y	z	
M(1)	0	0	0	
M(2)	0.989	0.277	0.25	**a = 4.7031 (3) Å
Si	0.427	0.094	0.25	b = 10.3586 (9) Å
O(1)	0.766	0.092	0.25	c = 6.0285 (6) Å
O(2)	0.220	0.448	0.25	
O(3)	0.278	0.163	0.034	

*The values of the atomic coordinates are from Birle *et al.* (1968)

**The cell originally given by Finger *et al.* (1970) has been transformed from Pmnb according to an orientation compatible with Pbnm

It is, however, stressed that lack of use of monochromated radiation and the short wavelength used (Zr filtered Mok α) precluded a constructive study of the crystal dynamics of the lattice.

POWDER WORK Being the sample characterized by an almost total statistical distribution of the Fe^{+2} over Fe^{+3} **, it was decided to carry out a high temperature study under slightly oxidizing conditions. The Guinier-Lenné camera was flushed with N_2 gas for 2 hrs. prior to commencement of the high temperature cycle. No other N_2 gas was flushed into the system for the entire duration of all the subsequent high temperature runs. These were carried out with exposure times of 12 hrs. at each experimental temperature (22°, 100°, 183°, 247°, 326°, 390°, 440°, 483°, 550 °C). Since, among the other ones, a drastic change in the relative intensities of the 2.54 and 2.47 Å diffraction lines was recorded at 550 °C (Fig. 2), the sample was let to stabilize at this temperature prior to beginning a cooling cycle. This was carried out by lowering the experimental temperature sequentially through the same values used in the high temperature cycle. In all instances a stabilization time of 2 hours elapsed prior to exposure of the sample to X-rays (12 hours). Fig. 3 shows that the most interesting feature of the diffraction pattern is a gradual change in the values of the relative intensities of the 2.47 and 2.54 Å diffraction lines. These, at room temperature, exhibit values approximately opposite to the ones recorded at 550 °C.

A final microscopic examination of the sample revealed the presence of a red patina which was interpreted as a product of oxidation. This observation clarifies the uneven

*This study was carried out with a serpentine gas heater using N_2 gas, according to a technique briefly outlined elsewhere (Deganello, 1972)

**This analysis was kindly carried out by Prof. S. Hafner using techniques of Mössbauer spectroscopy

Figura 2 — Triphilitite 2. Heating cycle. Notice the uneven temperature dependence of the relative intensities of the diffraction lines upon oxidation and increasing temperature. Arrows indicate position of the 2.54 and 2.47 Å diffraction lines, respectively

Figura 3 — Triphilitite 3. Cooling cycle. Notice the intensity change affecting the 2.54 and 2.47 Å diffraction lines. These are indicated by arrows

thermal behavior of the relative intensities of the diffraction pattern recorded during the preliminary heating cycle (Fig. 2).

DISCUSSION OF RESULTS Triphilitite 1 is remarkably stable to phononic disturbances. Although powder patterns are much too insensitive for tackling the problem of order-disorder in a structural array, it is evident (Fig. 1) that neither a process of long range order nor any evidence of an incoming phase transition is recorded up to 780 °C. The

appearance of the two extra diffraction lines in the temperature range 800°-900 °C cannot be satisfactorily accounted for in this context. Their persistency up to 900 °C, concomitantly to the gradual disappearance of the basic diffraction pattern, might indicate that triphillite is disordering. It would appear more realistic, however, to ascribe such a behavior to the loss of structural regularity expected in proximity of the melting point of the sample (≈ 950 °C).

Particularly interesting is the process of oxidation of triphillite 2. As expected on the basis of its chemical formula and substantiated by the regular temperature dependence of the intensity of the 222 diffractum, whose contribution to scattering is limited to the M(1) site, oxidation is preferentially affecting M(2). The increase in intensity of 112 ($d \approx 2.47$ Å) at the expenses of the unresolved doublet 131, 102 ($d = 2.54$ Å) suggests that adjustments in the atomic coordinates are taking place in a manner much more drastic than the one expectable from a simple expansion of an unoxidized reticle. This, in fact, has to adjust itself not only to the increased frequency of the atomic vibration but, also, to the overall charge unbalance caused by the oxidation process. Consequently it would be most interesting to see how the value of the fractional $\frac{z}{c}$ coordinate of O(3) is affected, being this the only coordinated anion free of symmetry constraints along this direction. As shown in Fig. 2 the shift in intensity between 131, 102, and 112 is not an abrupt one but takes place as a function of the experimental temperature. In particular, the approximately equivalent intensity of the two diffracts at 326 °C indicates that at this temperature sufficient activation energy has been reached to start promoting significant changes in M(2). However, the reversibility of the process of the reported intensity shift excludes that major changes are affecting the structural framework and that breakage of the sp^3 configuration of the P-O bonds occurs in the temperature range studied (22°-550 °C). Such bonds are responsible for the packing of the serrated chains of the oxygen octahedra along c and, consequently, any change tending to lower the value of their orbital hybridization is keen to favor structural instability.

In conclusion it would not appear too surprising if triphillites, which are frozen representatives of conditions of high entropy and rapid crystallization histories, could be disordered. Additional insight into the subtle interrelationship between cationic stoichiometries, temperature and degree of oxidation will undoubtedly be given by a study of the kinetics of oxidation.

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