

Carlosturanite: HRTEM evidence of a polysomatic series including serpentine

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Abstract

Carlosturanite, ideally $M_{21}[T_{12}O_{28}(OH)_4](OH)_{30} \cdot H_2O$, is a water and magnesium-rich, silicon-poor serpentine-like asbestiform mineral. TEM techniques revealed the fiber texture, which consists of randomly rotated fibers approximately 1000Å in cross section intermixed with smaller chrysotile fibers. TEM also permitted the unit cell to be found and a plausible structural model to be proposed.

The model is based on the ideal structure of serpentine, from which carlosturanite differs by the presence of infinite rows of vacancies in tetrahedral sites. As a result, carlosturanite is a chain silicate, characterized by the presence of triple chains. These chains are related to the four-repeat single crankshaft chains of haradaite and could be formed by linking three haradaite chains. This model explains the physical and chemical properties of the mineral.

Starting from the carlosturanite arrangement, a comprehensive discussion of the possible carlosturanite-like phases is given and the family name inophites is proposed. Inophites belong to a polysomatic series, S_nX , resulting from combination of serpentine S modules, with composition $M_3T_2O_5(OH)_4$, and of X modules, with composition $M_6T_2O_3(OH)_{14} \cdot H_2O$. Evidence of the existence of the S_4X , S_6X and S_7X structures as fault lamellae within carlosturanite, S_5X , is given.

Introduction

Carlosturanite is a new metamorphic rock-forming silicate (Compagnoni et al., 1985), closely related to the serpentine minerals. With X-ray diffraction methods, only the powder pattern and the existence of a 9.4Å fiber axis could be ascertained, an X-ray based structural determination being prevented by the fibrous habit of the mineral. However, transmission electron microscopy (TEM) techniques (electron diffraction, lattice imaging, TEM/EDS microanalysis) have allowed us to elucidate the crystal chemistry of carlosturanite and its relationships with structurally related phases and paragenetic minerals. The aim of this paper is to describe a structural model for carlosturanite that has been derived by analogy with serpentine and that is consistent with the observed physical and chemical properties of carlosturanite.

Experimental

The electron microscopy investigation used a Philips 400T instrument, operating at 120 kV and equipped with a

hairpin filament, according to standard procedures (e.g. Mellini, 1982a). TEM/EDS analytical data were gathered by an EDAX 707A multichannel analyzer and off-line processed by the ratio method (Champness et al., 1981), using experimentally determined K_{XSi} values (Mellini and Menichini, unpublished). Both ion-milled petrographic thin sections and ground fibers from the holotype specimens were studied.

Image simulation was performed with the SHRLI set of programs (O'Keefe and Buseck, 1979), starting from the structure model we propose.

The unit cell

Grinding of the fiber bundles produces elongated lath-shaped fragments. Due to the presence of a good {001} cleavage, preferred orientation of the fibers on the support film is obtained, and, with a few degrees of tilt, $hk0$ electron diffraction patterns with mm symmetry are obtained (Fig. 1a). These patterns can be indexed on the basis of $a = 36.7$, $b = 9.4\text{Å}$, with systematic extinctions for reflections having

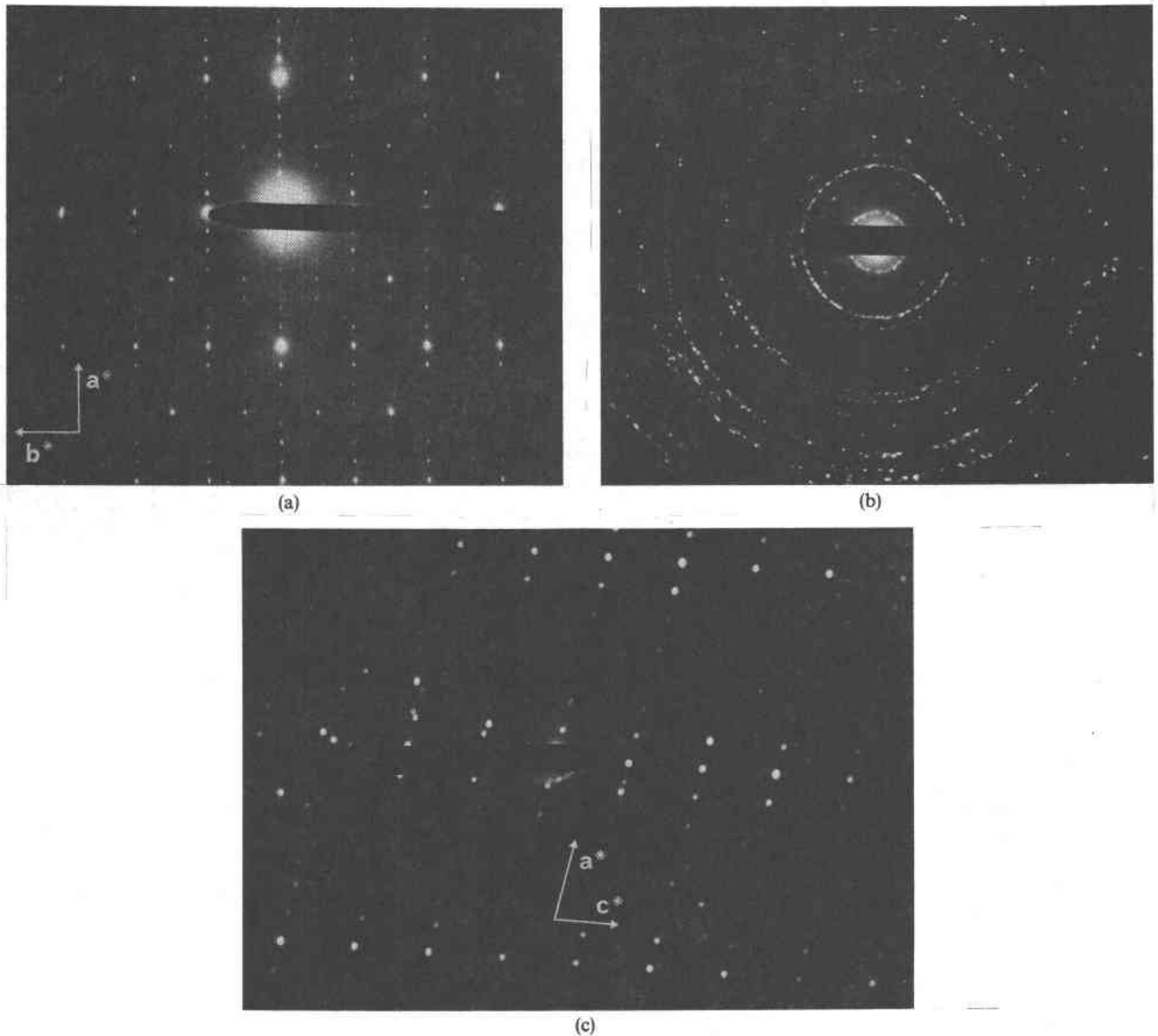


Fig. 1. (a) [001] electron diffraction pattern of carlosturanite; (b) [010] electron diffraction pattern from a fiber bundle, showing spotty diffraction rings; (c) [010] electron diffraction pattern from a single fiber.

$h + k = 2n + 1$. The short 9.4\AA translation is parallel to the fiber axis, in keeping with the X-ray results (Compagnoni et al., 1985).

The [010] view usually produces spotty ring diffraction patterns, which can be interpreted as due to rotational disorder around [010] of single crystalline fibers (Fig. 1b). Nevertheless, in some cases single-fiber patterns as in Figure 1c were obtained. These patterns possess no symmetry higher than the inversion center and give lattice parameters $a' = a/2$ (because of extinctions) = 18.4 , $c = 7.3\text{\AA}$ and $\beta = 101^\circ$. Carlosturanite therefore is monoclinic, $a = 36.7$, $b = 9.4$, $c = 7.3\text{\AA}$, $\beta = 101^\circ$, space group $C2/m$, Cm , or $C2$. Possible dynamical diffraction effects that could produce forbidden reflections $h0l$ for $l = 2n + 1$, and would

mask c glide planes, seem to be excluded. In fact, such reflections occur within the indexed X-ray powder pattern (Compagnoni et al., 1985), and odd rows appear as strong as even ones in the electron diffraction patterns.

A sinusoidal trend in the intensity of diffracted spots along a^* (Fig. 1a, c) can be easily recognized, with maxima occurring for $h = 14n$ and for $h = 14n + 7$ where k is even and odd respectively. These intensity features suggest the presence of a C -centered subunit cell with $a'' = 36.7/7 = 5.2$, $b = 9.4$, $c = 7.3\text{\AA}$, $\beta = 101^\circ$, which is characteristic of the serpentine minerals, and a modulation of the serpentine structure. For comparison, lizardite 1T has $a = 5.332$, $b = 9.235$, $c = 7.233\text{\AA}$ in the C centered orthorhombic setting (Mellini, 1982b).

The structure model

The close relationships between carlosturanite and 1:1 layer silicates, already suggested by the X-ray rotation photographs and powder patterns, also are supported by HRTEM images. For instance, Figure 2 shows a pair of randomly-rotated carlosturanite fibers as seen along [010] and connected one to the other by a narrow region where curved-layer serpentine is present. The (001) lattice fringes of the serpentine are smoothly connected with coherent interfaces to the (001) lattice fringes of carlosturanite in the two fibers, with no faults or dislocations visible at the contact between serpentine and carlosturanite. In this view, the 1:1 tetrahedral/octahedral layers of serpentine are seen edge on, and the coherency suggests that similar, although not identical, layers are also present in carlosturanite. In Figure 2, these layers are stacked one upon the other in the *c* direction. The occurrence of a 9.4 Å fiber axis in carlosturanite leads us to assume a similar value in the coherent, intermixed serpentine.

Any model for carlosturanite should be consistent with (1) a ratio of octahedral to tetrahedral cations of 1.75 and a water content of 17 wt.%, both higher than in serpentine where they are 1.5 and 13 respectively; (2) the observed unit cell; (3) a serpentine-like structure (*Cm* symmetry). Furthermore, the model must eventually accord with other

properties, such as the fibrous habit and the thermal behavior. Within these boundary conditions, two types of models can be tested: those formed by addition of M cations and those formed by removal of T cations relative to serpentine. The most likely model belongs to the latter type and is shown in Figure 3. It is obtained by preserving the octahedral sheet of serpentine but introducing ordered tetrahedral vacancies and substituting hydroxyl anions or water molecules for oxygen atoms in positions now bonded to only one or no silicon atom. One-seventh of the $[\text{Si}_2\text{O}_7]^{6-}$ groups arranged along [010] rows are replaced by $[(\text{OH})_6\text{H}_2\text{O}]^{6-}$ groups having tetrahedral arrangements of hydrogen-bonded water molecules and hydroxyl anions. A similar mechanism operates, for instance, in hydrogarnets and sheet silicates such as zeophyllite (Merlino, 1972).

Starting from a sevenfold serpentine unit cell ($a = 5.2 \times 7 \text{ \AA}$), with a content



substitution of twelve hydroxyl anions and two water molecules for oxygen atoms and elimination of four T atoms (namely substitution of sixteen hydrogens for four T atoms) leads to

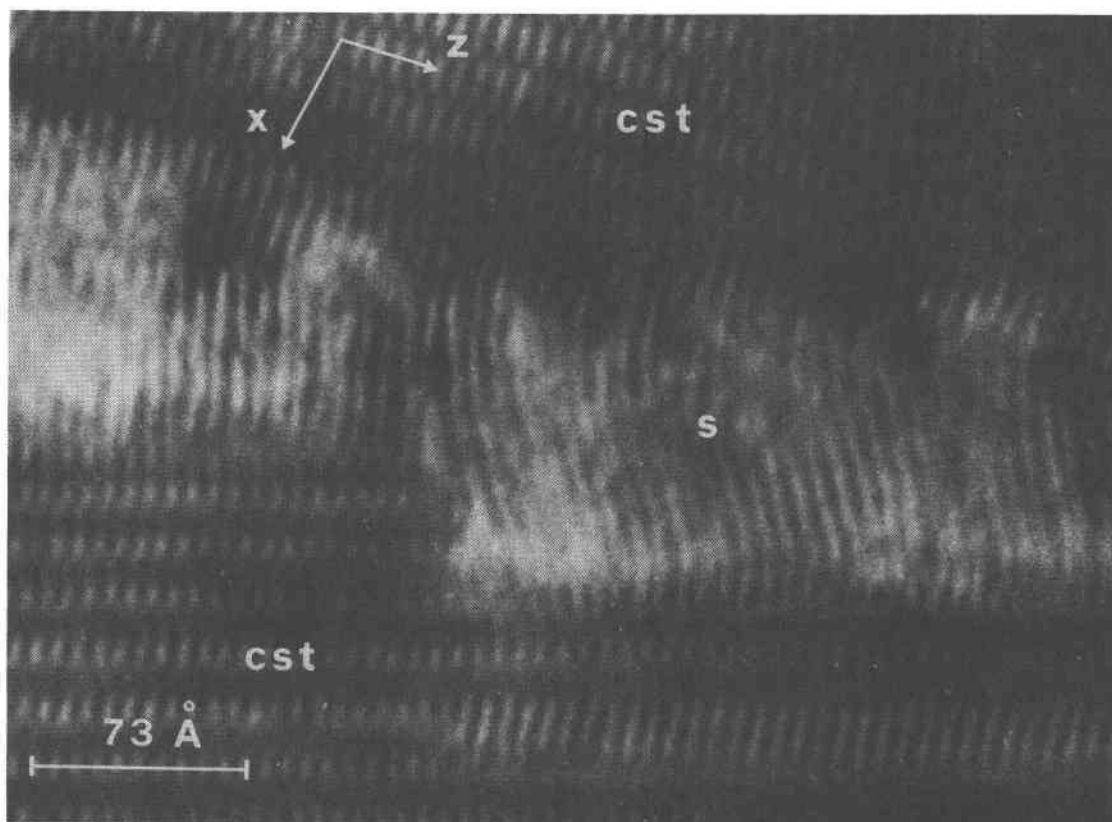
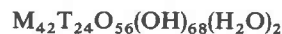


Fig. 2. Curved layer serpentine (s) coherently connects adjacent carlosturanite (cst) fibers.

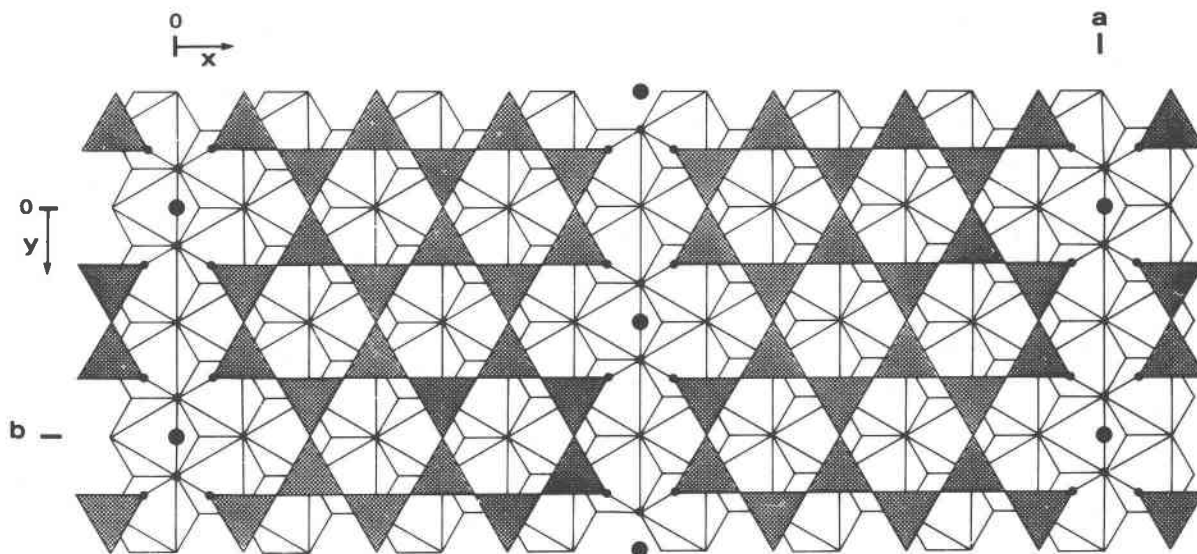


Fig. 3. Structure model for carlosturanite. Small filled circles are hydroxyl anions, large filled circles water molecules.

or



for carlosturanite, with brackets enclosing the silicate strip composition. This ideal formula compares well with the empirical formula $(Mg, Fe, Ti, Mn, Cr, \square)_{21} [(Si, Al)_{12} O_{28}(OH)_4](OH)_{30} \cdot H_2O$, $Z = 2$, given by Compagnoni et al. (1985). The fibrous habit of carlosturanite is evidently the result of the infinite silicate chains along the fiber direction. More evidence that supports this structural model, such as calculated density, thermal behavior, water loss during heating, and formation conditions can be found in the companion paper by Compagnoni et al. (1985). Also the intensity distributions they reported for X-ray patterns are strongly supportive of a serpentine-like structure.

According to this model, carlosturanite is not a layer silicate but a multiple-chain (strip) silicate, unless we extend the classification of Zoltai (1960) to include the tetrahedral arrangements of hydrogen-bonded oxygens among the tetrahedrally coordinated cations. The silicate strip consists of triple chains that result from connection of four-repeat single-crankshaft chains (Fig. 3), like those present in haradaite (Takéuchi and Joswig, 1967). Therefore, carlosturanite is quite distinct from other silicate structures, not only because of the presence of a continuous octahedral sheet, but also because of the different kind of chain. In particular, it is different from triple-chain pyriboles like jimthompsonite (Veblen et al., 1977; Veblen and Burnham, 1978), which are based on the two-repeat single chain of pyroxene, fragments of which run in carlosturanite at 30° from the $[010]$ haradaite chain. Still larger differences occur between carlosturanite and $Ba_2Si_3O_8$ (Katscher and Liebau, 1965), where alternating apical oxygens of the two-repeat triple chain point towards opposite directions.

Carlosturanite reveals a new way in which misfit relief is achieved in serpentine-like structures (Wicks and Whittaker, 1975), by separating the tetrahedral sheet into strips while retaining a continuous octahedral sheet. In this way, flat tetrahedral–octahedral layers are obtained instead of the curved layers that occur in chrysotile and parachrysotile (Wicks and Whittaker, 1975). Moreover, extensive substitution of hydrogens for silicon atoms leads surely to a higher number of hydrogen bonds within the crystal. This higher number probably results in a higher density of inter-layer hydrogen bonds, thus leading to further stabilization of the flat layer structure (Mellini, 1982b) and to the extremely small 7.15\AA d_{001} spacing. The b value is virtually equal to that of brucite, suggesting complete relaxation of the octahedral sheet. Closer comparison with serpentine cell data is, however, prevented by the major structural and chemical modifications that occur in carlosturanite, namely interruption of the tetrahedral sheet and extensive hydration.

As a further test, the structure model was checked by comparing observed and computed HRTEM lattice images (Fig. 4). General consistency was found, but an exhaustive one-to-one comparison for different imaging conditions was not possible due to the asbestiform nature of the mineral. In fact, only an average orientation for a whole diffracting fiber bundle could be achieved, with individual fibers misaligned up to a few degrees. Furthermore, carlosturanite suffers from beam damage, and search for fresh areas may also lead to loss of the average orientation. As a consequence, not only do defocus and thickness variations affect the image contrast, but also systematic misalignment should be taken into account. The best fit with calculated images usually occurs for specimen thicknesses greater than 200\AA , and this is probably due to separation of the thinnest single fibers during ion milling.

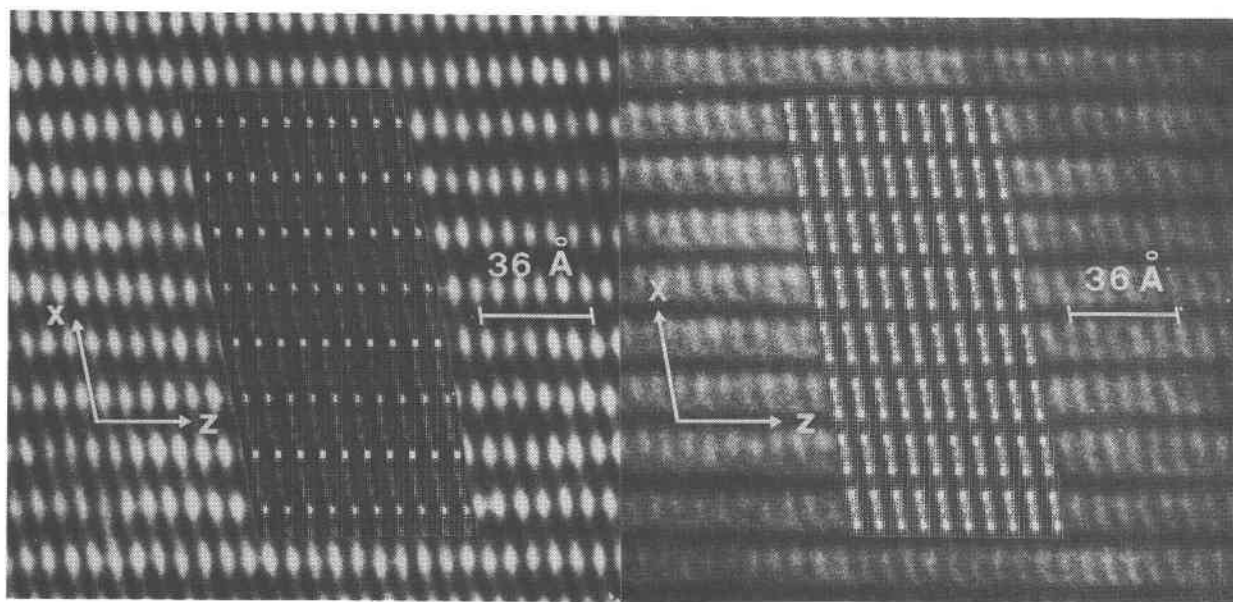


Fig. 4. Comparison between observed and calculated lattice images; (a) thickness 190 Å; defocus -1200 Å; (b) thickness 380 Å, defocus -800 Å.

Fiber texture and intergrowth phenomena

Several intergrowth phenomena affect carlosturanite. Among them, intergrowth with diopside is the largest-scale phenomenon, evident in both the electron and optical microscopes. Bundles of [010] carlosturanite fibers run parallel to [001] fibrous diopside. The chemical composition of this pyroxene, estimated by TEM/EDS analysis, corresponds to a nearly stoichiometric diopside with minor iron substitution. Electron-opaque inclusions of chromian magnetite were also detected. The only crystallographic relationship between carlosturanite and diopside is due to the parallel orientation of their fiber axes, while individual fibers are randomly rotated around their fiber axes. TEM/EDS analyses on several carlosturanite fibers show variable chemical compositions from fiber to fiber, particularly as regards titanium. Within the individual fibers, homogeneous, reproducible compositions are observed.

When examined along the fiber axis (Fig. 5), carlosturanite is seen to consist of randomly-rotated parallel fibers, approximately polygonal in cross section, with sizes ranging from 200 to 2000 Å. The sections tend to be elongated parallel to [100], but the actual shape is conditioned by the adjacent interlocking fibers. Smaller fibers of chrysotile, previously seen in X-ray rotation photographs, run parallel to carlosturanite, and TEM/EDS analyses reveal high iron content, but no titanium, manganese or chromium. As previously shown in Figure 2, serpentine occurs not only as fully rolled fibers but also as partially-rolled layers connecting adjacent carlosturanite fibers.

Apart from interstitial rolled or partially-rolled serpentine, some other mechanisms can bond the carlosturanite fibers together. They can be directly connected (Fig. 6a),

with no evidence of intermixed phases. The lack of coherency at the interface can be marked by sharp white dots (Fig. 6b), which could result from local structure deformations, from tunnels at the interface, or from preferential beam damage at the interface. Apparently empty areas separate adjacent fibers, but they could be due either to partially-developed, low-contrast chrysotile or to separation that has arisen during specimen preparation. Finally, {100} twins are common, exhibiting a characteristic 22° twin angle (Fig. 6c); the twin plane alternatively can be interpreted as a fault in the stacking sequence.

Related structures and chain multiplicity faults

Carlosturanite can be considered as a member of a family of substitutional chain-silicate derivative structures, the parent phase of which is the layer silicate serpentine. It is also evident that the mechanism that produces the carlosturanite structure from the serpentine structure also could produce other structures with different chain multiplicity. Depending on the proportion of tetrahedral vacancies, they are expected to have variable water contents, ranging from 13 wt.% (no vacancy, i.e. serpentine itself) to higher values. They may actually occur as well-developed phases, perhaps identified as ill-defined, water-rich and silicon-poor serpentine-like minerals, or they may occur only as fault structures within carlosturanite.

These possible structures define a polysomatic series, as all of them can be regarded as composed of two chemically distinct modules (Thompson, 1978), respectively indicated by *S* and *X* in Figure 7a. The *S* slab is a (100) section of the serpentine structure, with $\frac{1}{2}a_s$ thickness (where a_s is the fundamental serpentine *a* translation). The (100) *X* slab has

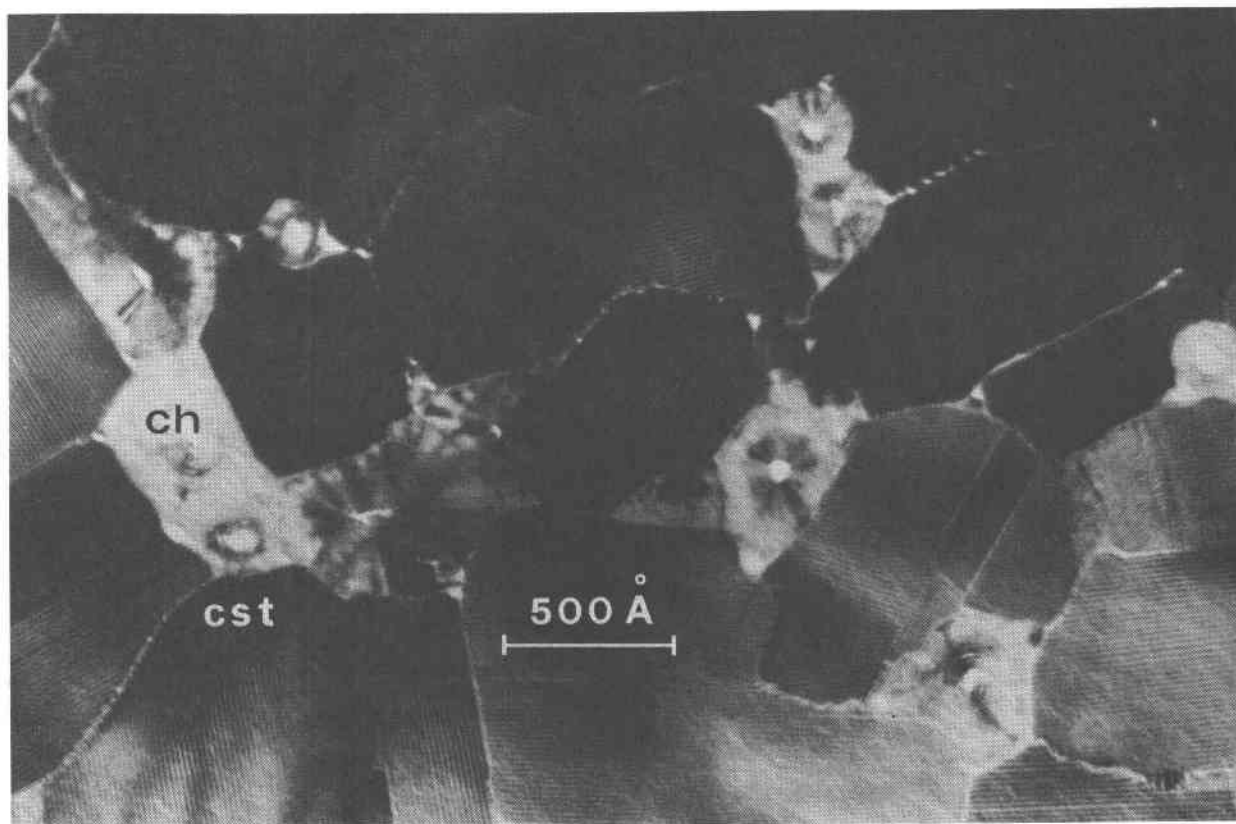


Fig. 5. Intergrowth between carlosturanite (cst) and chrysotile (ch), as seen along the fiber axis.

a_s thickness and, when regularly repeated, would produce a hypothetical hydro-sorosilicate. This hypothetical structure can be derived from serpentine by substitution of four hydrogen atoms for one silicon atom, as previously discussed. According to this choice of building modules, carlosturanite is the S₅X structure. Other structures, as S₄X shown in Figure 7b, can be easily sketched. The full series would be X, SX, ..., S₅X (carlostranite itself), ..., S (serpentine). The different polysomes in the series would be structurally and chemically intermediate between the hypothetical group silicate X and the layer silicate serpentine S.

The ideal chemical formula of the generic S_nX polysome, obtained based on the chemical composition of the S slab, M₃T₂O₅(OH)₄, and of the X slab, M₆T₂O₃(OH)₁₄ · H₂O, is simply



Polysomes with an even number of S slabs (Fig. 7b) have primitive unit cells, Z = 1, and their a parameter is given by ((n + 2)/2)a_s. Polysomes with an odd number of S slabs, as carlosturanite, have C-centered cells, Z = 2, and a = (n + 2)a_s. Further structures might be produced by relative b/3 shift between adjacent silicate chains.

The S_nX polysomes, apart from the end members S and X, are four-repeat chain silicates, and the silicate strip contains (n + 1)/2 haradaite chains. Whereas the silicate strip

simply consists of a number of haradaite chains in odd-n polysomes, additional lateral Si₂O₇ groups (haradaite "half-chains") are required to describe the silicate strip in even-n polysomes (see the chains in Fig. 7b). The different polysomes could be identified either by HRTEM or X-ray powder diffraction. In fact, the primitive even-n S_nX structures will produce lattice fringes in HRTEM images or diffraction peaks in the powder patterns according to their d₁₀₀ periods, and the odd-n C-centered structures according to their d₂₀₀ periods. Either spacing can be calculated by the relationship (n/2 + 1)d₁₀₀, and one-to-one correspondence occurs between this d value and the present polysome.

Several types of faults are observed to affect the a periodicity of carlosturanite and can be interpreted as chain multiplicity faults. Usually, they are isolated lamellae, continuous along (010) and scattered throughout the carlosturanite matrix. Neither wide domains of phases different from carlosturanite or superstructures consisting of different alternating periodicities (i.e., the analog, in this system, of the pyribole chesterite, Veblen and Burnham, 1978) have been observed. A highly disordered case is illustrated in Figure 8, and several more examples can be found in the previous figures. A survey of several fibers shows that only three periodicities different from 18Å occur in the lattice images. These are the 16Å periodicity of the S₄X polysome,

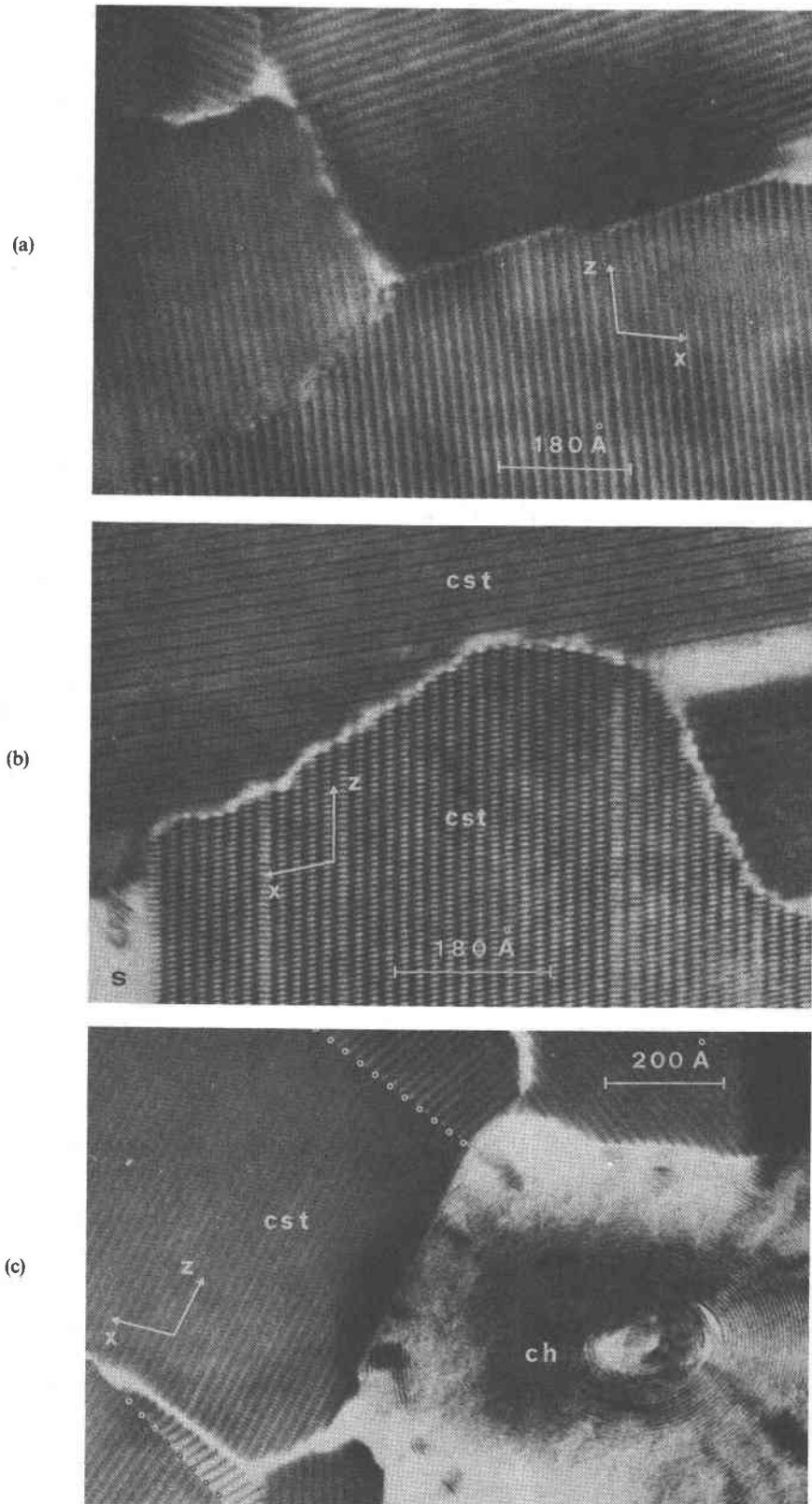


Fig. 6. (a) Direct connection between carlosturanite fibers; (b) incoherent interface between carlosturanite fibers; serpentine (s) occurs on the left; (c) {100} twin planes (marked by circles) in carlosturanite. A fully rolled chrysotile fiber is also evident.

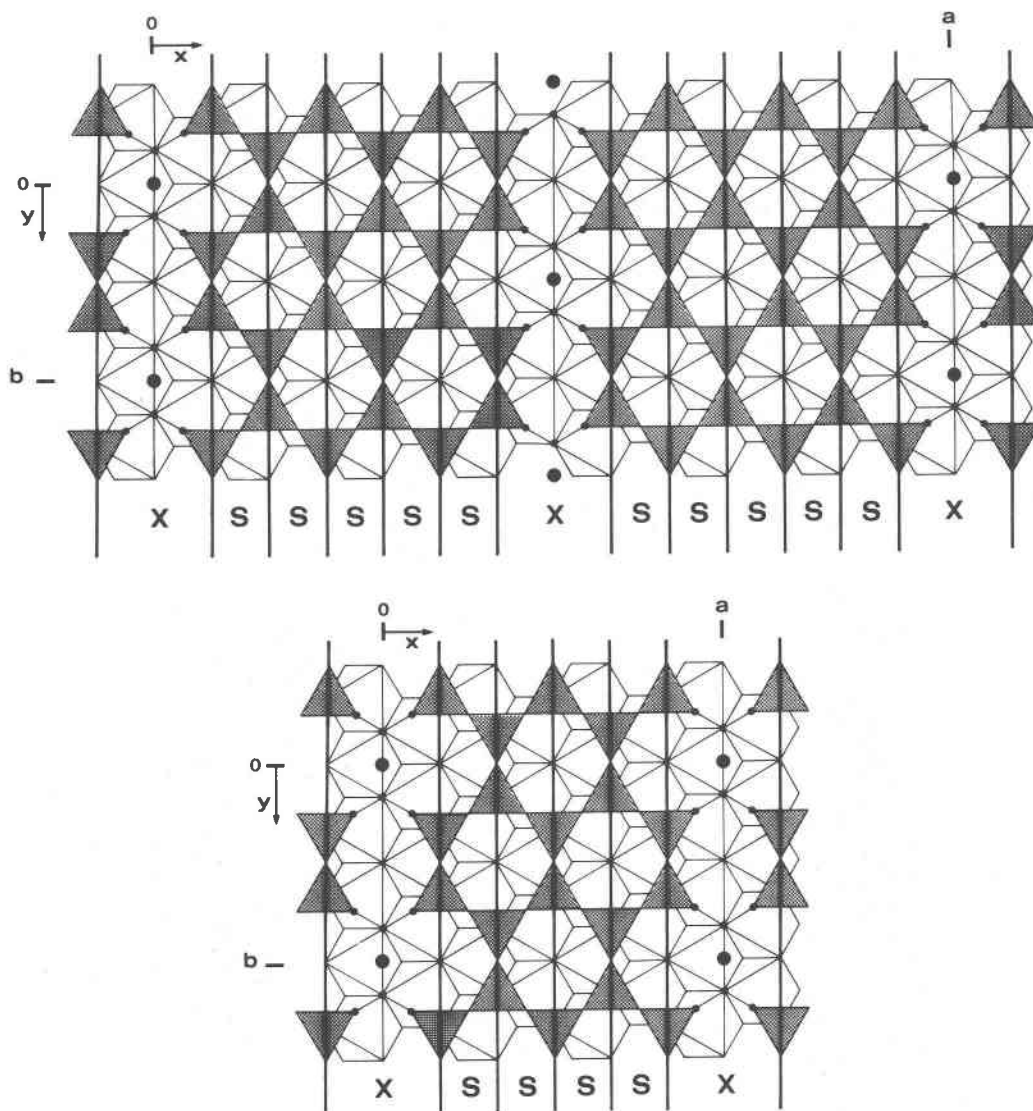


Fig. 7. (a) S and X slabs in carlosturanite; (b) model for the hypothetical S_4X structure. Small and large filled circles are hydroxyl anions and water molecules, respectively.

the 21\AA periodicity of the S_6X polysome, and the 24\AA half periodicity of the S_7X polysome. Among them, S_6X and S_7X are common, whereas S_4X is rare. Fortuitously, all of these periodicities are imaged in Figure 8. It is interesting to observe that the chemical compositions of these other structures cluster around the chemical composition of S_5X , carlosturanite, and that faulting usually leads to the less hydrated structures (S_6X and S_7X) that are the ones nearest in composition to carlosturanite.

The occurrence of chain multiplicity faults in carlosturanite recalls once more their analogous occurrence within the biopyribole polysomatic series (Veblen and Buseck, 1979).

Conclusions

Although not corroborated by a classical structure determination, the model proposed for carlosturanite seems

highly plausible. In fact, it explains the observed properties of the mineral and predicts defect structures that are found in our specimens.

The analogy with pyriboles is striking, even if the two types of structures are different. The multiple silicate chains of pyriboles are derived by condensation of pyroxene chains. For carlosturanite-like structures, however, the structure models may be derived conveniently by introducing rows of T vacancies in a tetrahedral layer of a serpentine structure. The resulting structures have been described in this paper as an S_nX polysomatic series; with the exception of the end member X , that is a hypothetical hydrosilicate, they are hybrids between serpentine (ophite in ancient literature) and inosilicates. The family name inophites, for these structures, has been proposed and approved by the I.M.A. Commission on New Minerals and Mineral Names.

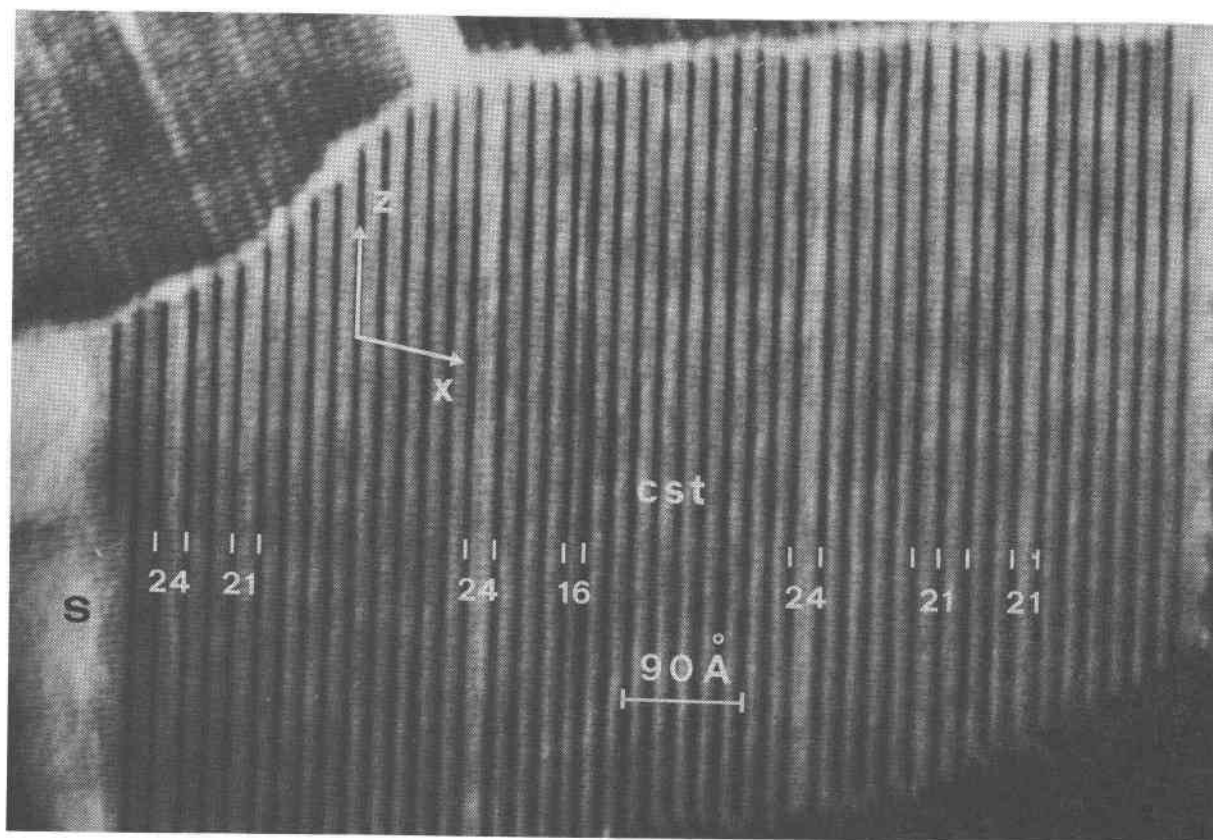


Fig. 8. Chain multiplicity faults in carlosturanite. Numbers represent the faulted periods. Serpentine (s) is present on the left.

Acknowledgments

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