

The Crystal Structure of $\text{Sr}_{9.402}\text{Na}_{0.209}(\text{PO}_4)_6\text{B}_{0.996}\text{O}_2$ – a Deviant Apatite

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The structure of flux-grown crystals with composition $\text{Sr}_{9.402}\text{Na}_{0.209}(\text{PO}_4)_6\text{B}_{0.996}\text{O}_2$ is trigonal, apatitic in character but with space group $P\bar{3}$. The lattice parameters are $a = 9.734$ (4) and $c = 7.279$ (2) Å with $Z = 1$. The structure was refined by full-matrix least-squares methods, using 960 reflexions, to a final R value of 0.065. Ninefold and sixfold coordinated cations alternate in columns parallel to the c axis. The former cations are Sr and the latter are either Sr, Na or a vacancy randomly distributed. The PO_4 groups rotate in order to stabilize these sites and as a result destroy the mirror plane in the $P6_3/m$ space group characteristic of the apatite structure. Simultaneously, this rotation constricts and expands the available volume near alternate centres of symmetry on the threefold axis through the origin. A linear O–B–O group is found at the site of the larger void. The six remaining Sr ions per cell lie in general positions and are coordinated to seven oxygen atoms. The average PO bond length in the PO_4 groups is 1.535 Å and the B–O bond length is 1.253 (10) Å.

Introduction

Apatite, both natural and synthetic, has been the object of a considerable volume of research. This results from the fact that apatite is the major industrial source of phosphates, that a carbonate–calcium apatite is the major crystalline component of bones and teeth and that apatite, as a catalyst, is thought to have contributed to the conversion of amino acids to polypeptides in the early evolution of life on earth (Neuman & Neuman, 1973). In addition, recently silicoapatites have been proposed as laser host (Hopkins, Roland, Steinbruegge & Partlow, 1971).

Mackie, Elliot & Young (1972) have studied a monoclinic hydroxyapatite counterpart of chloroapatite mineral reported by Hounslow & Chao (1970). Compounds with an apatitic structure, but lower symmetry, are important because they cast doubt upon the identification of the apatite structure, with space group $P6_3/m$, solely from powder patterns. In addition there is continuing activity in quest of a non-centrosymmetric apatite supportive of piezo-electricity and the bioelectric effect reported for bones (Bassett, Pawluk & Becker, 1964), although Shamos & Lavine (1967) suggested that these effects arise from the collagen in bone.

The structural site occupied by minor constituents in apatite is of major importance. The nature of the CO_3^{2-} sites in bones and teeth is uncertain (McConnell, 1973). Mn^{2+} is known not to be uniformly distributed in synthetic fluoapatite from the results of electron paramagnetic resonance (Warren, 1970) and luminescence experiments (Ryan, Ohlman, Murphy, Mazelsky, Wagner & Warren, 1970).

Experiments

Crystals of the present compound were grown in a Pt crucible from a mixture of $(\text{NH}_4)_2\text{HPO}_4$, SrCO_3 and

$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ in the molar ratios of 2:3:6 heated to 1450°C and then cooled to room temperature. The product, washed with hot water, contained clear, colourless crystals in a matrix of powdered $\text{Sr}_3(\text{PO}_4)_2$. A summary of the chemical analysis of the crystals, hand selected from an excess of powdered $\text{Sr}_3\text{P}_2\text{O}_8$, is shown in Table 1. Neutron activation analysis indicated that the Sr to Na molar ratio was 46 ± 5 to 1. Both sodium and boron have been detected by nuclear quadrupole resonance. Unfortunately, the line broadening in both cases was too large to show quadrupolar splitting and crystals large enough for a single-crystal study have not been obtained. An infrared spectrum of a crystal ground in nujol revealed a pair of weak peaks at 2040 (15) and 1940 (10) cm^{-1} attributed to the ^{10}B –O and ^{11}B –O stretch modes respectively.

Accurate parameters were determined by least-squares methods, fifteen reflexions being used. 2θ values were measured with a Syntex $P\bar{1}$ automatic diffractometer. Graphite monochromatized Mo $K\alpha$ radiation, $\lambda(\alpha_1) = 0.70926$ Å, was used.

Crystal data

$\text{Sr}_{9.402}\text{Na}_{0.209}(\text{PO}_4)_6\text{B}_{0.996}\text{O}_2$, F.W. 1441.31.
 $a = 9.734$ (4) Å, $c = 7.279$ (2) Å at 21°C.
 Space group $P\bar{3}$, $D_c = 4.006$, $Z = 1$.

All reflexions in a hemisphere with $2\theta \leq 60^\circ$ were measured from a crystal ground into a sphere of diameter 0.25 mm. Peaks were scanned at a rate between 2 and 24° per min in 2θ , depending upon the peak intensity, and backgrounds were measured one degree in 2θ removed from each side of the peak. Reflexions whose intensity measure was less than zero were not considered further. The data set consisted of 960 symmetry-independent reflexions which were corrected for Lorentz, polarization and absorption effects. No systematic extinctions were apparent and in particular 00 l reflexions with l odd were present signalling the

Table 1. *Chemical analysis of Sr_{9+y/2}Na_x(PO₄)₆B_{x+y}O₂*

	SrO	Na ₂ O	CaO	P ₂ O ₅	B ₂ O ₃
Found*	65.90	0.46	0.12	31.08	2.44 %
Sr _{9.402} Na _{0.209} (PO ₄) ₆ B _{0.996} O ₂	67.59	0.46	—	29.54	2.40 %
Sr _{9.25} Na _{0.75} (PO ₄) ₆ B _{0.92} O ₂	66.56	1.64	—	29.57	2.22 %

* Analyst was J. Muysson, Department of Geology, McMaster University.

loss of the 6₃ axis characteristic of the apatite space group. The data showed the point group to be no higher than $\bar{3}$ and thus a solution for the structure was attempted in space group $P\bar{3}$.

Atomic scattering curves for Sr²⁺, Na⁺, P, O, and B were obtained from *International Tables for X-ray Crystallography* (1959) and corrected for dispersion. Refinement utilized a full-matrix least-squares program written for the CDC 6400 computer by Stephens (1967). The trial model was based upon the positional parameters for strontium hydroxyapatite (Sudarsanan & Young, 1972) but with space group $P\bar{3}$ and without the OH group. The temperature parameters suggested that the M cation sites should be deficient in Sr and when the population parameter was varied the site was only two thirds filled with Sr. The occupancy of this site was set to equal amounts of Sr and Na when it was found that the O(5) site, corresponding to one of the OH sites in strontium hydroxyapatite, was fully occupied. The *R* value showed a slight decrease upon insertion of the Na ion into the refinement. At this stage the composition corresponded to Sr₉Na(PO₄)₆O₂ but the model was deficient of three positive charges per unit cell. A difference synthesis revealed a substantial peak at 00 $\frac{1}{2}$ and this was assigned as B³⁺.

The refinement was continued by varying the population parameters of all sites and only those of M and B were found to have varied significantly. Then the ratio of Sr and Na in site M was varied under the restriction that the Sr and Na account for 10 cations per cell and that the cell be neutral. The composition found, Sr_{9.152(7)}Na_{0.848}(PO₄)₆B_{0.960}O₂, was not consistent with the chemical analysis. Therefore, models with less than 10 cations per unit cell, arising solely from less than two cations at the M site were tried. At convergence the composition obtained was

Sr_{9.402(7)}Na_{0.209}(PO₄)₆B_{0.996}O₂. The final *R* and $\omega R = \{\sum\omega(F_o^2 - F_c^2)/\sum\omega F_o^2\}^{1/2}$ with $\omega = [3.24 - 0.044F_o +$

$0.00067F_o^2 + 83.5\sigma^2(F)/F^2]^{-1}$ were the same for both trial compositions. The atomic positional parameters are in Table 2 and the thermal parameters are in Table 3.* Save for a 30% increase in the thermal parameters for the atoms in site M the two compositions yield the same solution.

Table 2. *Positional parameters for Sr_{9.402}Na_{0.209}(PO₄)₆B_{0.996}O₂ with standard errors in parentheses*

	Site	<i>x</i>	<i>y</i>	<i>z</i>
M*	2(<i>d</i>)	$\frac{1}{3}$	$\frac{2}{3}$	0.0067 (2)
Sr(1)	2(<i>d</i>)	$\frac{1}{3}$	$\frac{2}{3}$	0.5098 (2)
Sr(2)	6(<i>g</i>)	0.25482 (8)	0.98189 (8)	0.23949 (9)
P	6(<i>g</i>)	0.3942 (2)	0.3642 (2)	0.2529 (2)
O(1)	6(<i>g</i>)	0.3315 (6)	0.4817 (6)	0.2563 (7)
O(2)	6(<i>g</i>)	0.5756 (6)	0.4540 (6)	0.2303 (8)
O(3)	6(<i>g</i>)	0.3154 (8)	0.2474 (6)	0.0936 (8)
O(4)	6(<i>g</i>)	-0.3555 (6)	-0.2666 (6)	0.5712 (6)
O(5)	2(<i>c</i>)	0	0	0.3278 (13)
B ⁺	2(<i>c</i>)	0	0	$\frac{1}{2}$

* The average composition of each of the two M sites per cell is 0.701 Sr, 0.104 Na and 0.195 vacancy. The average unit cell contains 0.996 B.

Additional crystals were prepared at 1400°C with the molar ratio of Sr₃(PO₄)₂ to Na₂B₄O₇ of one to three. Neutron activation analysis indicated that these had a molar ratio of Sr to Na of 11.3 ± 1.1 to 1. The composition found for a limited data set (644 reflexions) was Sr_{9.25}Na_{0.75}(PO₄)₆B_{0.92}O₂ with unit-cell parameters *a* = 9.752 (15) and *c* = 7.280 (3) Å. This structure, except for the composition, is essentially the same as that for the title compound.

* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30640 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Thermal parameters (× 10³) in Sr_{9.402}Na_{0.209}(PO₄)₆B_{0.996}O₂ with standard errors in parentheses*

The thermal factor used is of the form $\exp \{-2\pi^2[U_{11}h^2b_1^2 + \dots + 2U_{12}hkb_1b_2 + \dots]\}$.

	<i>U</i> ₁₁ (Å ²)	<i>U</i> ₂₂ (Å ²)	<i>U</i> ₃₃ (Å ²)	<i>U</i> ₁₂ (Å ²)	<i>U</i> ₁₃ (Å ²)	<i>U</i> ₂₃ (Å ²)
M	21.8 (8)	<i>U</i> ₁₁	13.6 (7)	$\frac{1}{2}U_{11}$	—	—
Sr(1)	14.5 (5)	<i>U</i> ₁₁	16.7 (5)	$\frac{1}{2}U_{11}$	—	—
Sr(2)	18.1 (3)	14.9 (3)	13.3 (3)	7.8 (3)	-0.3 (3)	1.0 (2)
P	12.4 (8)	11.0 (8)	10.2 (7)	7.1 (6)	-0.4 (6)	-1.3 (6)
O(1)	13.7 (24)	14.3 (24)	13.1 (23)	7.4 (20)	2.7 (20)	4.4 (20)
O(2)	8.8 (23)	16.5 (26)	28.7 (30)	5.4 (21)	2.5 (21)	3.7 (22)
O(3)	56.5 (4)	82.8 (24)	14.3 (24)	12.7 (27)	-15.9 (27)	-7.3 (20)
O(4)	20.4 (26)	21.7 (26)	41.0 (20)	10.9 (22)	5.4 (18)	4.6 (18)
O(5)	17 (4)	<i>U</i> ₁₁	22.0 (5)	$\frac{1}{2}U_{11}$	—	—
B	7 (8)	<i>U</i> ₁₁	38.0 (14)	$\frac{1}{2}U_{11}$	—	—

Description of the structure

Strontium hydroxyapatite contains columns of trigonal prisms which share faces about Sr(1). In the present compound cation sites are occupied alternately by M and Sr(1) ions. Adjacent columns are joined by phosphate groups with each of the six oxygen atoms of the trigonal prism about a cation contributed by a separate phosphate group (Fig. 1). In the former compound these oxygen atoms, O(1) and O(2), lie in a mirror plane. The remaining two oxygen atoms, O(3) and O(4), are symmetry-related and cap the rectangular faces of two successive trigonal prisms in the same column. The mirror plane is destroyed in the present compound by the rotation of the phosphate group. This shortens one of the cation O(3) (2.798 Å) interactions and lengthens the other (3.172 Å), relative to Sr apatite, with the sodium ion presumably stabilizing the distortion caused by the latter arrangement.

In the strontium hydroxyapatite six of these columns, related by the 6_3 axis, surround the origin and contain OH collinear with this axis. Such groups, if ordered, would lead to short oxygen–oxygen interactions because of the mirror plane. It has been suggested either that columns have all the O–H dipoles similarly ordered with random arrangement between columns or that vacancies within a column allow reversals in the dipoles without introducing these short separations (Elliot, Mackie & Young, 1973). Thus, since the mirror plane results from the disorder it is not an element of symmetry of a unit cell, but only of the space-averaged unit cell. In the borate compound the $0,0,\frac{1}{4}-z$ and $0,0,\frac{1}{4}+z$ sites are not equivalent and the O–B–O groups are accommodated at those centres of symmetry which have had their ‘free volume’ enlarged by the rotation of the phosphate groups.

These structures are based upon columns of phosphate groups forming hexagonal rods, with OH or O–B–O groups at the centre, fitted so as to leave gaps with triangular cross sections (Fig. 2). The Sr(2) is

bonded to seven oxygen atoms arising from five phosphate groups and one BO_2 group. Four of these phosphate groups lie in the surface of the rod and Sr(2) shares an O–O edge with only one of these PO_4 groups. The columns are linked through Sr(2)–O bonds involving O(2), and by the bonding of the M and Sr cations.

The cationic bond lengths are compared with those of Sr and Ca hydroxyapatite in Table 4. The nine oxygen atoms about Sr(1) lie within a narrower spherical shell than the comparable interactions in the hydroxyapatites. Sr(2) is bonded to seven oxygen atoms with a Sr–O(5) bond length of 2.652 Å, compared with the Sr–O(H) bond length of 2.498 Å in strontium hydroxyapatite. Since O(3) caps the trigonal prism about the M site, it was not unexpected that this oxygen atom would show enhanced thermal disorder in the *ab* plane. This disorder reflects the two positions occupied by this oxygen atom, which depend upon whether M is Sr, Na or vacant.

The phosphate group is slightly irregular with a mean P–O bond length of 1.535 Å (Table 5). The BO_2 group is linear with BO bond lengths of 1.253 (10) Å. Each oxygen atom in this unit is tetrahedrally surrounded by three Sr(2) ions in addition to the boron. The oxygen is displaced towards the plane of these Sr ions creating an Sr–O–B angle of 104.0 (2)°. The O–B–O groups have been reported in the gas phase (Herzberg, 1966) and as part of the B_2O_3 molecule which is considered to have C_{2v} symmetry in the gas (White, Walsh & Mann, 1958). The band at 2041 cm^{-1} assigned to B–O stretch in the B_2O_3 vapour is near the value found for this compound.

Discussion

The analytical results are in qualitative agreement with the composition determined by the X-ray refinement. A high value for the P_2O_5 might have arisen from contamination by $\text{Sr}_3(\text{PO}_4)_2$, but the amount needed should

Table 4. *Cationic environments in apatitic structures with standard errors in parentheses*

The M(1), Sr(1) and Sr(2) are either all Sr in Sr hydroxyapatite or all Ca in Ca hydroxyapatite. In the present compound the average composition of site M is 70% Sr and 10% Na and the B site is 0.4% vacant. O(3) and O(4) are related by the mirror planes in the hydroxyapatites.

	Present compound	$\text{Sr}_{10}(\text{PO}_4)_6(\text{OH})_2^*$	$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2^\dagger$
M(1)–O(1) (3 ×)	2.552 (6) Å	2.561 (3) Å	2.405 (1) Å
Sr(1)–O(1) (3 ×)	2.572 (6)	2.561 (3)	2.405 (1)
M(1)–O(2) (3 ×)	2.486 (7)	2.565 (3)	2.454 (1)
Sr(1)–O(2) (3 ×)	2.605 (7)	2.565 (3)	2.454 (1)
M(1)–O(3) (3 ×)	3.172 (8)	2.901 (4)	2.802 (1)
Sr(1)–O(4) (3 ×)	2.798 (7)	2.901 (4)	2.802 (1)
Sr(2)–O(1)	2.693 (6)	2.757 (5)	2.710 (1)
–O(3)	2.575 (6)	2.661 (3)	2.511 (1)
–O(3')	2.467 (6)	2.512 (3)	2.345 (2)
–O(4)	2.797 (6)	2.512 (3)	2.345 (2)
–O(4')	2.529 (5)	2.661 (3)	2.511 (1)
–O(2)	2.456 (5)	2.476 (4)	2.357 (1)
–O(5)	2.652 (2)	2.498 (2)	2.389 (1)

* Sudarsanan & Young (1972). † Sundarsanan & Young (1969).

Table 5. Bond lengths and angles about the phosphate group in $\text{Sr}_{9.402}\text{Na}_{0.209}(\text{PO}_4)_6\text{B}_{0.996}\text{O}_2$ with standard errors in parentheses

P-O(1)	1.543 (7) Å	O(2)-P-O(3)	110.3 (4)°
P-O(2)	1.538 (5)	-O(4)	107.5 (3)
P-O(3)	1.534 (5)	O(3)-P-O(4)	107.3 (3)
P-O(4)	1.525 (5)		
O(1)-P-O(2)	110.4 (3)°	Sr(2)-O(5)-B	104.0 (2)°
-O(3)	109.0 (4)	Sr(2)-O(5)-Sr (2)'	114.3 (2)
-O(4)	112.4 (3)	B-O(5)-B	180.0
B-O (5)	1.253 (10) Å		

have been detected in a Debye-Scherrer pattern. The amounts of Na and B, in particular, agree satisfactorily.

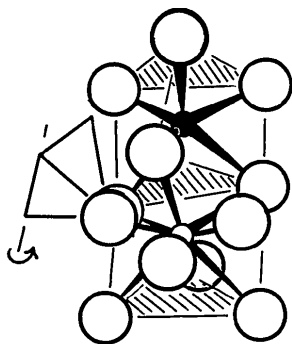


Fig. 1. The environment of the Sr(1) and M sites is shown. The open circles are oxygen atoms. One of the six phosphate tetrahedra about a cation is shown and it is rotated about the indicated axis from its position in strontium hydroxyapatite. The small filled circle is the M site and the small open circle is the Sr(1) site.

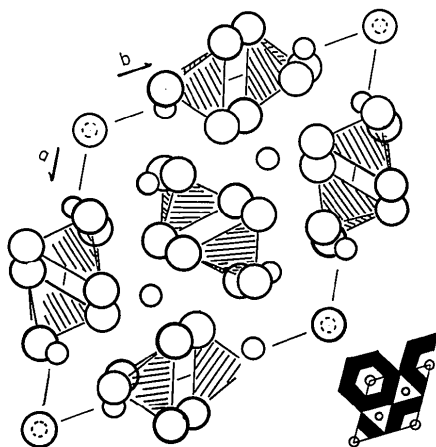


Fig. 2. The structure of $\text{Sr}_{9.402}\text{Na}_{0.209}(\text{PO}_4)_6\text{B}_{0.996}\text{O}_2$ projected down the c axis. The large circles are oxygen atoms and the dashed ones are the boron atoms. The phosphate tetrahedra are outlined. The cations are indicated by the smaller circles. The insert shows the hexagonal rod arrangement.

All possible models for the distribution of Na and B have not been tested. The most general chemical formula, assuming no B substitution for P is $\text{Sr}_{9+y}\text{Na}_x(\text{PO}_4)_6\text{B}_{x+2y}\text{O}_2$ with $x+y$ and $x+2y \leq 1$. A more complex formula would result if B substitutes into the tetrahedrally coordinated P site. However, the deviation of the average P-O bond length, 1.535 Å, from the grand mean P-O bond length, 1.537 Å, (Baur, 1973), although hardly significant, suggests one B out of every 26 tetrahedral sites. This is assuming a B-O bond length for tetrahedrally coordinated B of 1.475 Å and the validity of Vegard's law.

A cell containing both some Na at the M site and B ions on the threefold axis explains the structural difference between strontium hydroxyapatite and the present structure. Further, a highly charged species is needed to stabilize the short separation between the pair of O(5) atoms generated by a centre of symmetry.

The bond-valence (strength) sums about O(5), using the parameter of Brown & Shannon (1973), yield a value of 2.1 v.u. rather than 2 as expected. The contribution of the three Sr(2), computed from $S = (2.143/R)^{7.0}$, yields a value of 0.674 while the boron obtained from $S = (1.375/R)^{3.9}$, is 1.436.

The present compound is the first example of a BO_2 group reported in a crystalline phase. Chemically similar B-O bond lengths for comparison are not available. Donnay & Donnay (1973) have compared a variety of empirically predicted B-O bond lengths with one another and with the experimentally determined values. The B-O bond length at a bond order of 1.5 predicted by the procedures of Donnay & Allmann (1970) and Brown & Shannon (1973) are shorter than the value found here, while that obtained by an extrapolation of the bond-order-bond-length curve suggested by Zachariasen (1963), 1.26 Å, agrees with the present value.

It is clear that the $\text{M}_3(\text{PO}_4)_2\text{-NaBO}_2$ system bears further investigation. In fact a calcium analogue with a composition, as determined by structure analysis, nearly the same as the present compound has an apatitic structure with space group $P\bar{1}$. Here all the cation sites contain both Na and Ca but in unequal proportions with deviations supportive of the same mechanism for the lowering of the crystal symmetry as in the Sr salt.

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Crystal Structure of Hemimellitic Acid Dihydrate (1,2,3-Benzenetricarboxylic Acid Dihydrate)

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Hemimellitic acid dihydrate crystallizes in space group $P\bar{1}$ with $Z=2$. The structure was solved by special application of the Σ_2 method. Full-matrix least-squares refinement converged at an R of 0.039 based on 2121 F_o ($R_w=0.035$). The molecular structure is strongly influenced by the three vicinal carboxyl groups. The central group is twisted 87.2° out of the best plane through the slightly boat-shaped benzene ring. The other two groups are twisted 4.1 and 9.6° out of this plane. This arrangement causes bond lengths and valency angles to be closely similar in pairs across the ring diagonal passing through the central carboxyl group. The water molecules are hydrogen bonded in closed loops around centres of symmetry. The acid molecules form stacks with a as the stack axis. Carboxyl groups in adjacent molecules are hydrogen bonded to each other both *via* a system of bonds involving the water molecules and within each layer of a stack directly as dimers. These results are discussed in relation to previous infrared spectroscopic studies of the compound.

Introduction

Free radicals are produced in crystalline hemimellitic acid dihydrate upon γ -irradiation, and the formation of radicals has been studied by e.s.r. spectroscopy (Zaugg, 1970). The X-ray analysis of this compound was initiated in order to provide crystallographic data to aid the interpretation of the spectroscopic results.

All 12 benzenecarboxylic acids including four that also exist as hydrates have been examined in the solid state by infrared spectroscopy (González-Sánchez, 1958). To our knowledge the following members have also been studied by X-ray diffraction methods: ben-

zoic (Sim, Robertson & Goodwin, 1955), phthalic (1,2-) (Nowacki & Jaggi, 1957), isophthalic (1,3-) (Alcala & Martínez-Carrera, 1972), terephthalic (1,4-; two forms) (Bailey & Brown, 1967), trimesic (1,3,5-) (Duchamp & Marsh, 1969), pyromellitic dihydrate (1,2,4,5-. $2\text{H}_2\text{O}$) (Takusagawa, Hirotsu & Shimada, 1971) and mellitic (1,2,3,4,5,6-) (Darlow, 1961). All these structure analyses were based on photographic data and for some of them the precision is further limited by a low degree of overdetermination. The dihydrate of hemimellitic acid (1,2,3-. $2\text{H}_2\text{O}$) forms crystals of good quality. By using diffractometer-collected data we expected to obtain more precise parameters for this type of molecule. Of particular interest in the present case are conformational and intermolecular effects of three vicinal carboxyl groups and a comparison of the results with those obtained from the infrared spectra.

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