

*A numerical system of classification for chlorites
and septechlorites*

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Summary. Only two, or at most three, variables can be considered on a two-dimensional composition diagram; six variables must be fixed to completely define a variety of the chlorite or septechlorite groups. The positions of tetrahedral coordination may be described by a single variable and positions of sixfold coordination require three independent variables for complete definition. The number of OH⁻ ions is probably very near the theoretical value of eight, however, it may vary somewhat from this value, and, in so doing, influences the ratio of trivalent and bivalent cations in octahedral coordination.

The normal 14 Å chlorites and 7 Å septechlorites have traditionally been associated together and, although they represent two distinct structural groups, are considered together for classification purposes, since they share many identical variety compositions; a sixth variable denotes structural type, as determined by X-ray powder diffraction or D.T.A.

Each chlorite or septechlorite variety can be described by a numerical notation (chlorite number) consisting of six units and, by dividing the chlorite numbers into units according to accepted nomenclature, each possible chlorite composition can be assigned a variety name, and all variety names can be assigned to a definite composition range.

CHLORITES represent one of the complex silicate mineral groups that offer a challenge to the investigator who strives to subdivide these large mineralogical units into logical and significant mineral varieties. G. Tschermak (1891), J. OrceI (1926, 1927), A. N. Winchell (1926, 1928, 1936), and B. W. Nelson and R. Roy (1958) have divided the ferrous-magnesium chlorites, in accordance with some systematic and logical procedure. A review of the chlorite nomenclature has been presented by H. M. Hey (1954) in which the common iron-magnesium chlorites are subdivided with special emphasis on original definitions. More recently Foster (1962), in an extensive work, has again imposed new limits on the ferrous-magnesium chlorite varieties.

Pauling (1930) declared the normal chlorite structure to consist of alternating sheets of mica-like and brucite-like layers and concluded that the magnesium analogue of kaolinite could not exist. Gruner (1944), however, proposed a 7 Å 'kaolinite' structure for antigorite,

amesite, cronstedtite, and some chamosites, and Roy and several of his co-workers synthesized numerous chlorite varieties and demonstrated the fact that the 14 Å and 7 Å chlorite structures are polymorphous forms of the same compounds. Nelson and Roy (1958) proposed a 'septe-' prefix to denote the 7 Å 'kaolinite' structure and proposed, further, that the septechlorites be considered as part of the broadly defined chlorite group.

Classification procedures of all workers cited above have several factors in common. Each investigator subdivided a 'square', two-dimensional diagram into a number of smaller areas with a chlorite variety name for each pigeon-hole. Across the bottom of the diagram, aluminium ions replace silicon ions in a magnesium chlorite and, vertically, ferrous iron replaces magnesium. Such a two-dimensional diagram has the obvious advantage of being an easily understood, pictorial representation of a portion of the possible chlorite varieties, but it also has the obvious disadvantage of being a representation of only a portion of the possible chlorite varieties; it is inadequate for the classification of chlorites containing ferric iron, chromium, manganese, or nickel, and each investigator has attempted, almost as an afterthought, to inject one or more of these elements into his classification by some arbitrary rule foreign to his basic classification. Although these elements are present in more or less minor amounts in most chlorites, they are present in very appreciable amounts in many chlorite varieties, and their presence in even minor amounts reflects genetic significance.

Winchell (1926) postulated some improbable chromium and nickel end-member molecules and constructed diagrams that allowed the consideration of either chromium or nickel but excluded ferrous iron, ferric iron, and magnesium. In spite of the fact that some chlorites may analyse 25 % or more Fe_2O_3 , Winchell believed that ferric iron was due only to oxidation of ferrous iron, and that chlorites containing it should be given the same name as chlorite varieties containing only ferrous iron.

Nelson and Roy (1958) recognized the need to consider ferric iron and added a third dimension to their diagram making it a cube but did not subdivide the ferric chlorites or incorporate chromium, manganese, and nickel chlorites. Hey (1954) also recognized the need to consider ferric iron and proposed that chlorite analyses containing more than 4 % Fe_2O_3 be referred to another, similar diagram with new pigeon-holes and separate variety names. This procedure fails to distinguish between chlorites containing 5 % Fe_2O_3 and those containing

25 % Fe_2O_3 , and again does not incorporate chromium, manganese, or nickel.

Foster (1962) imposed new limits on established iron-magnesium chlorite varieties, took no account of chlorites rich in manganese, chromium, or nickel, and ignored the presence of ferric iron, making only the provision that one may apply the designation 'ferrian' to those chlorites containing 'considerable Fe_2O_3 '.

This writer agrees with the nomenclature of Hey (1954) where the chlorite composition and structural type will allow (i.e. normal 14 Å chlorites containing only 'minor' amounts of ferric iron, chromium, manganese, and nickel), but prefers to include the septechlorites of Nelson and Roy (1958) as part of the broad chlorite group. This necessarily reintroduces the names amesite and antigorite, which have traditionally been associated with the chlorites.

Chlorite variables. The basic framework for both 14 Å and 7 Å structural types is simply a close pack arrangement of anions with four positions of tetrahedral coordination and six positions of octahedral coordination available for cation emplacement in the standard eighteen anion unit. Although eighteen anions do not represent a complete unit cell, they do form a convenient working unit that has been adopted by most investigators.

To define completely any given chlorite, it becomes necessary to consider the kinds of cations in tetrahedral coordination and their relative abundance, the kinds of cations in octahedral coordination and their relative abundance, the relative number of O^- and OH^- anions, and the structural type.

Cations in tetrahedral coordination

Bivalent anions of 1.40 Å radius supply an opening to accommodate a quadrivalent cation of radius 0.32 Å in tetrahedral coordination. Silicon ions (0.40 Å) most nearly fit the tetrahedral cavity, but, as in many silicate structures, aluminium ions (0.49 Å) often proxy for silicon. It is assumed that all positions of tetrahedral coordination are occupied by some cation, that Si^{4+} ions occupy only positions of tetrahedral coordination, and that only silicon and aluminium ions occur in tetrahedral coordination, except in the mineral cronstedtite, the composition of which demands Fe^{3+} in tetrahedral coordination.

The Y number. Only one variable is necessary to describe the kinds of cations in tetrahedral coordination and their relative abundance; Y is the number of Al^{3+} ions (or Fe^{3+}) in every four available tetra-

hedral positions. The Y of any common silicate never exceeds 2.00 and Nelson and Roy (1953) have shown that for the magnesium chlorites Y may assume any value from zero to two. Limits of Y are probably more restricted when cations other than Mg^{2+} and Al^{3+} appear in octahedral coordination.

Cations in octahedral coordination

Each position of octahedral coordination should represent an opening of radius 0.58 Å and require a charge of plus two, assuming tetrahedral positions to be filled by quadrivalent cations. For each trivalent cation in tetrahedral coordination, however, one trivalent cation should exist in octahedral coordination to establish electrostatic equilibrium. Trivalent cations in the 'brucite' layer matched by trivalent cations in tetrahedral sites in the 'mica' layer are responsible for the electrostatic attraction which holds these layers together. Chlorites with Y near zero and all octahedral sites filled with bivalent cations have a soapy feel like talc, since only residual forces hold the layers together. Chlorite layers with Y near two are held together by comparatively strong electrostatic forces, and consequently display properties more like brittle mica.

It is assumed that the ions Mg^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Al^{3+} , Fe^{3+} , and Cr^{3+} may appear as major chlorite constituents in positions of octahedral coordination. Other elements may appear in chlorite analyses, but not as major constituents. Although small amounts of titanium are often present, the replacement of many bivalent ions by quadrivalent titanium should produce local areas of high electropositivity and electronegativity and lead to structural instability.

Alkalis and especially CaO are commonly reported in chlorites, but they find no place in the chlorite structure and must be present as cation exchange or mineral impurities. For chlorites, Grimm (1953, p. 129) proposes a maximum limit of 40 meq CaO/100 g (i.e. 2.24 % CaO) as exchangeable cations located either between layers or on broken edges. Since no expansion in the [001] unit-cell dimension is noted for chlorites high in CaO, location on broken edges seems most probable. One may also note that magnesium may appear as base exchange in some chlorites.

The Σ number. Unlike tetrahedral sites, empty positions of octahedral coordination may exist in the chlorite structure, and the Σ number is here defined as the number of octahedral sites in an eighteen anion unit (with six available octahedral positions) that are filled by any cation

or combination of cations. Any bivalent ion can fill all six octahedral positions but, if trivalent ions occupy these positions, only two-thirds of the octahedral sites need be filled. Tschermak, Winchell, Nelson and Roy, Hey, and other writers have assumed a Σ number of six. A notable exception is Pauling (1930) who states, using m instead of Σ : 'This structure leads to the general chemical formula $X_m Y_4 O_{10} (OH)_8$ with $4 \leq m \leq 6$. Actually m is equal to 6 in a great majority of the chlorites.'

Although the theoretical limits of the Σ number are 4.00 and 6.00, the value does, indeed, tend to be near six and cannot be less than $(4 + \frac{1}{3}Y)$, since a trivalent ion in tetrahedral coordination demands a trivalent ion in octahedral coordination to balance it. Y numbers near zero are suggestive of a deficiency of Al^{3+} ions, and a large concentration of Al^{3+} ions in octahedral coordination is not then to be expected, but large trivalent ions like Fe^{3+} and Cr^{3+} , which do not fit well into tetrahedral coordination, may well show distinct preference for octahedral sites, and low aluminum chlorites having high concentration of ferric iron or chromium might be expected to have Σ numbers less than about 5.00. The writer has observed that low Σ numbers often accompany high ferric iron content.

The R^{3+} and R^{2+} numbers. To describe completely the positions of octahedral coordination, we must know the number of available positions that are filled (i.e. Σ), the relative abundance of trivalent and bivalent ions in octahedral sites, the relative abundance of the several trivalent ions (Al^{3+} , Cr^{3+} , Fe^{3+}) in octahedral coordination, and the relative abundance of the several bivalent ions (Mg^{2+} , Fe^{2+} , Mn^{2+} , Ni^{2+}). The second of these is not an independent variable, being a function of Y and Σ .

The R^{3+} number is here defined as a number, taken from fig. 1, that represents the relative abundance of the three possible trivalent ions Al^{3+} , Fe^{3+} , and Cr^{3+} in octahedral coordination.

The R^{2+} number is similarly defined as a number, taken from fig. 2, that represents the relative abundance of the four possible bivalent ions Mg^{2+} , Fe^{2+} , Mn^{2+} , and Ni^{2+} in octahedral coordination. Four independent variables strictly require a three-dimensional diagram for complete representation (fig. 2A), but since no known chlorite variety contains appreciable amounts of both nickel and manganese, a plane representation of two faces of the tetrahedron will suffice (fig. 2B).

Although the limits of Y and Σ have been well established, the limits to which the various cations can enter into positions of octahedral coordination in a chlorite structure have yet to be established.

Anyone who has ever attempted to construct models of the layered silicate structures knows that close-packed anion layers fit together perfectly but, when cation spheres are introduced into appropriate positions of tetrahedral and octahedral coordination, the anion spheres are forced apart, since the cations are usually too large for the available

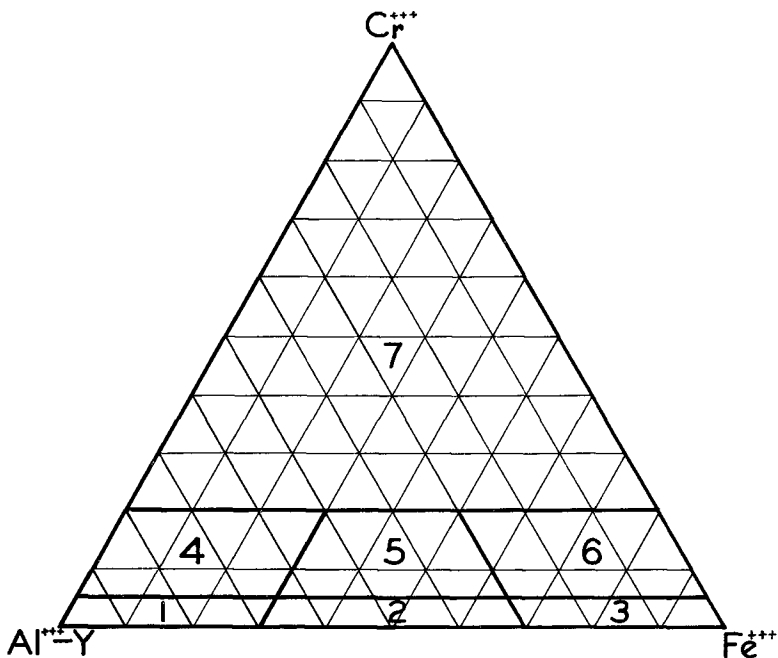


FIG. 1. Triangular coordinate diagram used to find the R^{3+} number by plotting the relative percentages of trivalent ions in octahedral coordination. (For chlorites having a Y number between 0.0 and 0.5, this number is of no significance, since only minor amounts of trivalent ions are present.)

cavity, and the octahedral and tetrahedral layers no longer 'fit' perfectly together. This phenomenon must be related to strain in the actual chlorite structure. For the antigorite composition $\text{Mg}_6\text{Si}_4\text{O}_{10}(\text{OH})_8$, $Y = 0$, anions of the octahedral layer are 'pushed apart' more than those of the tetrahedral layer and, for the amesite composition $\text{Mg}_4\text{Al}_2\text{Si}_2\text{Al}_2\text{O}_{10}(\text{OH})_8$, $Y = 2$, the reverse is true, and the tetrahedral layers are 'too large' for the octahedral layers. At some intermediate value of Y , maximum structural stability should exist.

When Fe^{2+} or Mn^{2+} substitute for Mg^{2+} , the result is expansion of the octahedral layer, and the composition of maximum stability should

occur at a larger Y . This leads to the conclusion that the ferrous and manganese analogues of the low Y magnesium chlorites are less stable and may not exist. Bivalent nickel, having an ionic radius closer to that of the Mg^{2+} ion, is more likely to form an analogue of antigorite,

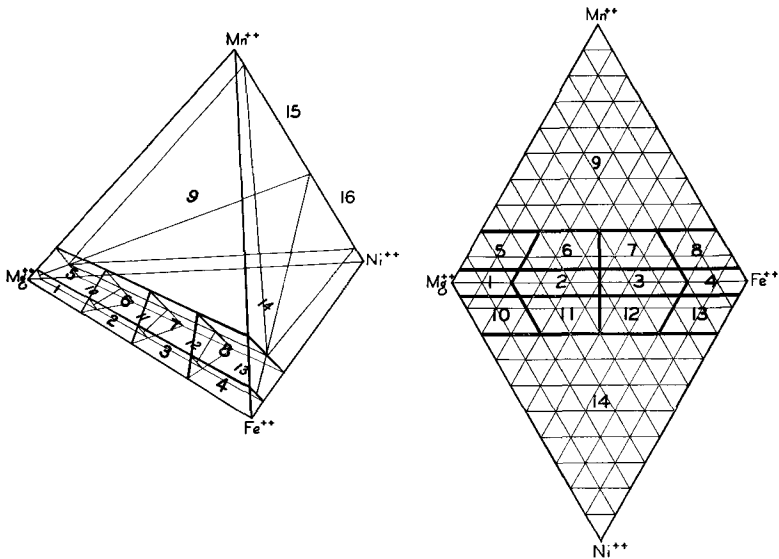


FIG. 2. Tetrahedral and triangular coordinate diagrams used to find the R^{2+} number by plotting the relative percentages of bivalent ions in octahedral coordination.

and, indeed, Roy and Roy (1954) have reported the synthesis of the 7 Å compound.

Substitution of Fe^{3+} or Cr^{3+} ions for Mg^{2+} in the octahedral layers, accompanied by substitution of Al^{3+} for Si^{4+} in the tetrahedral layers, results in contraction of the octahedral and expansion of the tetrahedral layers. Therefore, ferric or chromium chlorites should be most stable at lower Y numbers, and the ferric and chromium analogues of pennine might be expected in nature. Since trivalent ions in octahedral coordination do not greatly exceed Y , and, since Fe^{3+} and Cr^{3+} chlorites should be most stable for low Y numbers, the Fe_2O_3 or Cr_2O_3 content of chlorites will be small compared to the possible MgO , FeO , MnO , or NiO content. This does not imply, however, that the genetic significance of ferric iron or chromium is correspondingly less important.

Water content

The H number. The H number is here defined as the number of OH⁻ ions per eighteen anions in the basic chlorite framework. In the generally accepted chlorite structures (7 Å and 14 Å) there are eight OH⁻ and ten O²⁻ ions in the eighteen anion working unit, and most investigators have assumed this theoretical ratio. Although it is difficult to deny the ability of the 'dimensionless' H⁺ ions to enter the chlorite structure, very few O²⁻ ions can become OH⁻ ions, since the bonding power of an OH⁻ ion would be completely used up in its tie to a Si⁴⁺ and it could not form other bonds necessary to hold the structure together. The loss of H⁺ ions is yet more difficult to deny, and Winchell (1926) apparently accepted this process in proposing the oxidation of ferrous to ferric iron within the chlorite structure. The fact that ferrous iron can be artificially oxidized to the ferric state has been demonstrated by this writer (Phillips, 1963) and others; however, ferric iron in chlorites cannot all be due to this oxidation, since most Fe³⁺ can be shown to be necessary for original electrostatic equilibrium and since natural chlorites high in Fe₂O₃ are not unusually low in H₂O+. Analytical procedures for determining H₂O+ are probably much less sound than those for any other oxide, but although the H₂O+ value may be somewhat inaccurate, this is not justification for casting doubt on the validity of other values in an analysis.

This writer, therefore, concludes, with others, that the H number should be very near to 8.00 and may not be a variable at all. Complete definition of a chlorite variety, however, may call for an H value, since it affects the ratio of trivalent and bivalent ions in octahedral coordination.

Structural type

The logical definition of a mineral group like the amphiboles, feldspars, or chlorites is based on a uniform structural pattern. Since Gruner (1944) proposed a 7 Å structure for antigorite, amesite, and other compositions previously considered as belonging to normal chlorites, most workers have excluded these 7 Å minerals from the chlorite group. The writer supports the septechlorite designation proposed by Nelson and Roy (1953), because it separates these mineral varieties as a coherent mineral group defined by a specific structural pattern, and yet the traditional association with the chlorites is preserved in the group name. Since Nelson and Roy (1953) have demonstrated the fact that many

common chlorite compositions may exist as either normal 14 Å chlorites or as 7 Å septechlorites, the two mineral groups cannot be distinguished from composition alone. Only one additional variable, the structural type, need be considered in order to classify both normal chlorites and septechlorites by a single system. The structural variable may assume only two possible 'values', either normal 14 Å chlorite or 7 Å septechlorite.

Observation of the 001 spacing on an X-ray powder pattern is generally sufficient to fix the structural variable. The writer has also proposed differential thermal analysis as a method of distinguishing the two chlorite structural types (Phillips, 1963).

Chlorite numbers and names

Although a numerical designation will probably never replace variety names, a number designation is here proposed, which can be much more descriptive of chlorite varieties than their unsystematic and nondescriptive variety names. A chlorite number composed of Y , R^{3+} , R^{2+} , Σ , and H plus the appropriate structural designation will serve to fix the composition and structure of any chlorite or septechlorite within the allowed limits of the R^{3+} and R^{2+} numbers. For practical use in assigning chlorite variety names, the writer proposes an abbreviated chlorite number composed only of Y , R^{3+} , R^{2+} , and the structural designation.

A name is of value only in so far as it identifies, and, in this sense, chlorite variety names are of varying degrees of value. The magnesium-ferrous-iron chlorites, and especially the antigorite-amesite series, represent an important section of the chlorite group in which variety names have been repeatedly redefined. All other chlorite varieties are essentially without definition except for the ferric-iron chlorites of Hey (1954) and the definition of individual varieties from specific localities.

The Y divisions are adopted from the work of Hey (1954) with the reintroduction of the traditional amesite and antigorite at the two ends of the series, and these divisions are carried throughout the entire group. The writer is aware that the antigorite-amesite series is apparently not continuous for the normal 14 Å chlorites, and magnesium chlorites with Y numbers from about 0.08 to 0.00 are rare or do not exist. Septechlorites do exist throughout this range, however (Nelson and Roy, 1953), and so the series is represented by continuous values of Y from 2.00 to 0.00. Since the antigorite composition exists only as a 7 Å

TABLE I. Chlorite variety names and corresponding chlorite numbers*

	Y	$R^{3+}\dagger$	$R^{2+}\ddagger$	Structure*
Amesite	2.0-1.8	1	1	14 Å
Corundophilite	1.8-1.5	1	1	14 Å
Sheridanite	1.5-1.2	1	1	14 Å
Clinochlore	1.2-0.9	1	1	14 Å
Pennine	0.9-0.5	1	1	14 Å
Antigorite§	0.5-0.0	1, 2, 3, 4	1	7 Å*
Corundophilite	1.8-1.5	1	2	14 Å
Ripidolite (Prochlorite)	1.5-1.2	1	2	14 Å
Pycnochlorite	1.2-0.9	1	2	14 Å
Diabantite	0.9-0.5	1, 2, 3, 4	1	14 Å
	0.5-0.0		2	14 Å
Pseudothuringite... ..	1.8-1.5	1	3	14 Å
Aphrosiderite	1.5-1.2	1	3	14 Å
Brunsvigite	1.2-0.9	1	3	14 Å
Diabantite	0.9-0.5	1	3	14 Å
Pseudothuringite... ..	1.8-1.5	1	4	14 Å
Daphnite	1.5-1.2 1.2-0.9 0.9-0.5	1	4	14 Å
		1	4	14 Å
		1	4	14 Å
		1	4	14 Å
Klementite	1.8-1.5 1.5-1.2	2	1, 2	14 Å
		2	1, 2	14 Å
Chamosite... ..	1.2-0.9	2	1, 2	14 Å
Delessite	0.9-0.5	2	1, 2	14 Å
Thuringite	1.8-1.5 1.5-1.2	2	3, 4	14 Å
		2	3, 4	14 Å
Chamosite... ..	1.2-0.9	2	3, 4	14 Å
Strigovite	0.9-0.5	2	3, 4	14 Å
Cronstedtite§	1.5-1.2	3	3, 4	14 Å
Rhodophyllite	1.8-1.5 1.5-1.2	7	1	14 Å
		7	1	14 Å
Kochubeite	1.2-0.9	7	1	14 Å
Kämmererite	0.9-0.5	7	1	14 Å
Pennantite	1.2-0.9	1	9	14 Å
Gonyerite	1.2-0.9	3	9	14 Å
Nepouite	1.2-0.9	1	14	14 Å

* Variety names are for the normal 14 Å chlorite structural type; the 7 Å septe-chlorites bear the same names with a septe- prefix.

† If the R^{3+} number is 4, 5, or 6, the prefix chromian should be applied to the variety name used when R^{3+} is 1, 2, or 3.

‡ If the R^{2+} number is 5, 6, 7, or 8, the prefix manganoan should be applied to the variety name used when R^{2+} is 1, 2, 3, or 4 respectively; similarly nickeloan when R^{2+} is 10, 11, 12, or 13.

§ The name 'antigorite' is appropriate for the 7 Å septechlorite structure, since the 14 Å equivalent apparently does not exist. The same may well be true for cronstedtite.

|| Y numbers near zero indicate (neglecting the Σ number) negligible amounts of trivalent ions, and the R^{3+} number is then unimportant to the variety name.

structural type, 'antigorite' and 'septantigorite' are synonymous. This may also be true for cronstedtite and other chlorite varieties.

The fourfold division between Mg^{2+} and Fe^{2+} (fig. 3) was also proposed by Hey (1954), while the remaining divisions are those of the writer.

A threefold division is sufficient to distinguish Fe^{3+} -rich varieties, Al^{3+} -rich varieties, and varieties that contain approximately equal amounts. For the more unusual ions Cr^{3+} , Mn^{2+} , and Ni^{2+} , a threefold division is made according as these elements are present in negligible amounts, in appreciable amounts, or as major constituents.

For more detailed work, more limited ranges and subdivisions could be imposed, but the divisions here proposed far exceed the available variety names and adjoining divisions are frequently assigned the same variety name. In overworked sections of the magnesium-ferrous-iron chlorites, however, some variety names must be discarded.

Even with the writer's divisions, many chlorite numbers are possible to which no variety name has been assigned. Many of these chlorite numbers probably represent compositions that have no representative in nature (e.g. 0.0-1-4-14 Å), but other varieties should exist (e.g. 1.0-2-9-14 Å). It is to be expected that new, unusual chlorite and septtechlorite varieties will be continuously discovered, and such varieties could readily be assigned to a range of chlorite numbers and incorporated into the scheme.

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