dioxide was slower. Concentrations of nitrogen dioxide dropped from 100 to 3 ppm after 24 hours, and autoclaving the soil reduced the uptake to 13 ppm after 24 hours. These results indicate that the major portion of sulfur dioxide and nitrogen dioxide is removed by some chemical reaction. However, a microbial contribution cannot be entirely excluded.

Uptake of carbon monoxide by soils was recently demonstrated by Inman *et al.* (*7*). They found that their soil samples reduced carbon monoxide concentrations from 120 ppm to near zero within 3 hours.

Extrapolating from our laboratory experiments, we calculated that 7×10^6 tons of ethylene may be removed from the air in the United States by means of microbial degradation. Since the rate of production (15×10^6 ton/year) exceeds uptake by soil by a factor of 2, other mechanisms of degradation are probably important. The uptake of sulfur dioxide and nitrogen dioxide was more rapid that that of ethylene. Our calculations yield values of 6×10^8 tons of nitrogen dioxide and 4×10^{10} tons of sulfur dioxide per year. These values are large enough to accommodate all the sulfur dioxide and nitrogen dioxide produced in the United States (sulfur dioxide = 32×10^6 tons, nitrogen dioxide = 33×10^6 tons) each year.

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References and Notes

1. "Environmental Quality: First Annual Report of the Council on Environmental Quality" (Government Printing Office, Washington, D.C., 1970).
2. P. A. Leighton, *Photochemistry of Air Pollution* (Academic Press, New York, 1961).
3. D. F. Adams, M. Corn, C. L. Harding, J. B. Pate, A. L. Plumley, F. P. Scaringelli, P. F. Urone, *Health Lab. Sci.* **7**, 4 (1970).
4. B. E. Saltzman, W. A. Cook, B. Dimitiades, E. L. Kothny, L. Levin, P. W. McDaniel, J. H. Smith, *ibid.* **6**, 106 (1969).
5. C. E. ZoBell, *Advan. Enzymol.* **10**, 443 (1950).
6. D. M. Anderson *et al.*, "Air Quality Criteria for Hydrocarbons," *Nat. Air Pollut. Contr. Admin. Publ. FS2,3000 AP 64* (1970).
7. R. E. Inman, R. B. Ingersoll, E. A. Levy, *Science* **172**, 1229 (1971).
8. L. S. Jaffe, *J. Air Pollut. Contr. Ass.* **18**, 534 (1968).
9. Q. R. Stahl, "Preliminary Air Pollution Survey of Ethylene," *Nat. Air Pollut. Contr. Admin. Pub. APTD 69-35* (1969).

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Eight-Membered Cyclosilicate Rings in Muirite

Abstract. *The determination of the crystal structure of muirite,* $Ba_{10}(Ca,Mn,Ti)_4Si_8O_{24}(Cl,OH,O)_{12} \cdot 4H_2O$, *revealed the presence of discrete cyclic silicate anions,* $(Si_8O_{24})^{16-}$, *formed by the condensation of eight silicate tetrahedra. This first reported occurrence of eight-membered rings is of particular interest, because rings with eight tetrahedra are reported to be energetically less stable than rings with six tetrahedra, which have been found in many minerals.*

Muirite has been found with many other barium-containing silicate minerals in metamorphic rocks in Fresno County, California. Its composition has been given as $Ba_{10}Ca_2MnTiSi_{10}O_{30}(OH,Cl)_{10}$. On the basis of the chemical analysis and the x-ray data supplied with the original description, it is not apparent to which group of silicates muirite belongs (*1*). Because of its tetragonal symmetry the formulation $Ba_5CaTiO_4(Si_4O_{12}) \cdot 3H_2O$, with four-membered silicate rings, has been proposed (*2*).

A crystal of muirite (*3*) of approximately isometric shape (0.2 by 0.2 by 0.2 mm) was used for data collection on an automatic four-circle diffractometer with graphite crystal–monochromatized Ag$K\alpha$ radiation (wavelength $\lambda = 0.56083$ Å). From the usual processing and averaging (*4*) of 10,476 measured intensities 978 unique observed structure factors F_{obs} were obtained (maximum $\sin \theta / \lambda = 0.75$ Å^{-1}). No absorption correction was applied to the observed data (absorption coefficient $\mu = 53$ cm^{-1}; the maximum corrections would have been ± 8 percent on $F_{\text{obs}}{}^2$). The unit cell parameters (the figures in parentheses represent the standard deviations in units of the least significant digit) are $a = 14.030(10)$ Å and $c = 5.635(4)$ Å. Because no systematic absences of intensities have been observed, the space groups $P4/mmm$, $P4mm$, $P422$, $P\bar{4}m2$, and $P\bar{4}2m$ are possible (*1*). The structure was solved by Patterson methods in space group $P4/mmm$ and refined by full-matrix least-squares analysis to a discrepancy index R of 0.065 for all observed reflections. In the calculation the X-sites were assumed to be populated only by calcium atoms. The relatively low value of the isotropic temperature factor B (Table 1) for the X-sites reflects partial occupancy by Ti and Mn, as also evidenced by the chemical analysis (*1*). The occupancy factors of 0.5 for Ba(3) and O(2) (Table 1) are based on the Fourier maps and on the least-squares refinement. They may possibly be related to either a lower-symmetry space group for muirite ($P4mm$) or to the occurrence of a superstructure, since reflections on highly overexposed precession photographs indicate a doubling of the c cell constant. Because of the inconclusive evidence for either of these possibilities, we are reporting here the structure in space group $P4/mmm$ and are ignoring the superstructure reflections. Thus the statistical occupation of these two atomic sites either may reflect true disorder or may mean that we are describing an averaged structure. The fact that the temperature factors of most of the atoms (Table 1) in the structure are fairly high is another indication that some kind of disorder is present.

The eight-membered rings, $(Si_8O_{24})^{16-}$, of silicate tetrahedra, centered around the origin of the unit cell (Fig. 1), are the most striking and unusual feature of this crystal structure. The eight-membered rings are connected to neighboring rings both in the a and the c directions by the trigonal prismatic coordination polyhedra around the X-sites (populated by Ca, Mn, and Ti), thus forming a polyhedral three-dimensional framework of tetrahedra and trigonal prisms of composition $(Ca,Mn,Ti)_4Si_8O_{24}(OH,O)_4$. The spaces around this framework are filled with barium and chlorine atoms and H_2O molecules, so that the correct chemical and structural formula of muirite must be $Ba_{10}(Ca,Mn,Ti)_4Si_8O_{24}(Cl,OH,O)_{12} \cdot 4H_2O$ with one formula unit per unit cell. The assignment of particular atomic species to the different equipoints (Table 1) is based on the following: (i) the observed interatomic distances, (ii) the scattering factors giving the best agreement between observed and calculated structure factors, (iii) the multiplier refinement, and (iv) partly on the original chemical analysis (*1*).

The main differences between the original formulation (*1*) and the one arrived at here are that in this formulation: (i) there are only eight silicon atoms per unit cell, and the structure does not contain any space in which additional silicon atoms would fit; (ii) there is more chlorine per formula unit; and (iii) although most of the O(h4) atoms must be OH groups (in virtue of considerations of the bond strengths), some of them must be oxygen atoms, because the chemical formula would otherwise not be balanced.

Eight-membered rings have not been known up to now to occur in cyclosilicates. Electrostatic energy calculations (*5*) have shown that eight-membered rings should be energetically less stable than six-membered rings, which are found in many mineral crystal structures. However, they should be more stable than either three- or four-membered rings (*5*), which have been described previously in a number of minerals. The reason for this apparent paradox may be that three- and four-membered cyclosilicate rings pack more efficiently in the crystal structures than eight-membered rings. The presence of the large cations (barium) and large anions (chloride) in muirite may also be a stabilizing influence: these ions fill the large open spaces between the bulky eight-membered rings.

The average Si–O distance in the silicate tetrahedron is 1.629 Å, whereas the individual distances are as follows: Si–O(1), 1.658(9) Å; Si–O(2), 1.654(11) Å; and 2 × Si–O(3), 1.601(8) Å (2 × refers to the fact that two of the Si–O distances in the silicate tetrahedron are symmetrically equivalent). The deviations of the individual Si–O distances from the mean are significant. Moreover, their variation is consistent with the extended electrostatic valence rule (*6*), according to which

$$d(\text{Si–O})_{\text{calc}} = [d(\text{Si–O})_{\text{mean}} + 0.091\,\Delta p_{\text{O}}]$$

where $d(\text{Si–O})_{\text{calc}}$ is the calculated Si–O distance within the tetrahedron (in angstroms), and Δp_{O} is the difference between the bond strength of the individual oxygen atom and the mean bond strength of all oxygen atoms within the tetrahedron. Since O(1), O(2), and O(3) have Pauling bond strengths of 2.13, 2.31, and 1.71 valence units, respectively, the values calculated for the Si–O(1), Si–O(2), and Si–O(3) distances are 1.644, 1.661, and 1.606 Å, respectively, in reasonable agreement with the observed values. The angles Si–O(1)–Si and Si–O(2)–Si are, respectively, 121(1)° and 154(1)°. The angle of 121° is one of the smallest ever observed for a bridging oxygen atom in a condensed silicate. According to simple *d-p* π-bonding theory (*7*), this value would mean that the Si–O(1) distance should be considerably longer than the Si–O(2) distance. Since that is not the case, this model of *d-p* π-bonding does not seem to apply to this silicate.

Table 1. Positional and thermal parameters for muirite (C.N. = coordination number; estimated standard deviations in units of the least significant digit are given in parentheses).

Atom	Equipoint	C.N.	Refined coordinates *x*	*y*	*z*	*B* (Å^2)
Ba(1)	4n	10	0.5000	0.1656 (1)	0.0000	1.15 (3)
Ba(2)	1a	16	.0000	.0000	.0000	3.3 (1)
0.5 × Ba(3)	2h	8	.5000	.5000	.2447 (8)	1.78 (7)
Ba(4)	4k	11	.2671 (1)	.2671	.5000	1.14 (3)
X (= Ca,Mn,Ti)	4m	6	.3635 (3)	.0000	.5000	0.5 (1)
Si	8p	4	.2654 (3)	.1030 (3)	.0000	0.97 (6)
O(1)	4l	3	.2074 (11)	.0000	.0000	1.7 (3)
0.5 × O(2)	8r	4	.1801 (9)	.1801	.0643 (31)	1.3 (3)
O(3)	16u	4	.3289 (5)	.1141 (5)	.2345 (14)	1.9 (2)
O(h4) (= OH, O)	4i	4	.5000	.0000	.2619 (38)	3.7 (4)
O(w5) (= H_2O)	4k	3	.0977 (11)	.0977	.5000	4.7 (5)
Cl(1)	4o	5	.5000	.2777 (4)	.5000	1.6 (1)
Cl(2)	4j	5	.3525 (3)	.3525 (3)	.0000	1.5 (1)

The trigonally prismatic six-coordination around the X-sites is the second unusual feature of the muirite structure [4 × X–O(3), 2.244(8) Å; and 2 × X–O-(h4), 2.338(13) Å]. In predominantly ionic compounds, such as muirite, the six-coordinated cations tend to have an octahedral environment. Trigonally prismatic coordinations usually are found in compounds with covalent bonding character such as MoS_2, WC, and AlB_2. None of the three kinds of atoms that are populating the X-sites (Ca, Mn, or Ti) appears to have been known to occur in such coordination.

The coordination polyhedra around the Ba(1) atom [4 × Ba(1)–O(3), 2.834(8) Å; 2 × Ba(1)–O(h4), 2.753(12) Å; 2 × Ba(1)–Cl(1), 3.226(3) Å; and 2 × Ba(1)–Cl(2), 3.340(3) Å] and the Ba(4) atom [2 × Ba(4)–O(2), 3.001(15) Å; 4 × Ba(4)–O(3), 2.756(8) Å; 1 × Ba(4)–O(w5), 3.362(12) Å; 2 × Ba(4)–Cl(1), 3.271(6) Å; and 2 × Ba(4)–Cl(2), 3.288(2) Å] are typical for this cation, both with regard to coordination numbers and interatomic distances. The other two barium atoms are coordinated atypically. The Ba(2) atom is surrounded by 16 oxygen

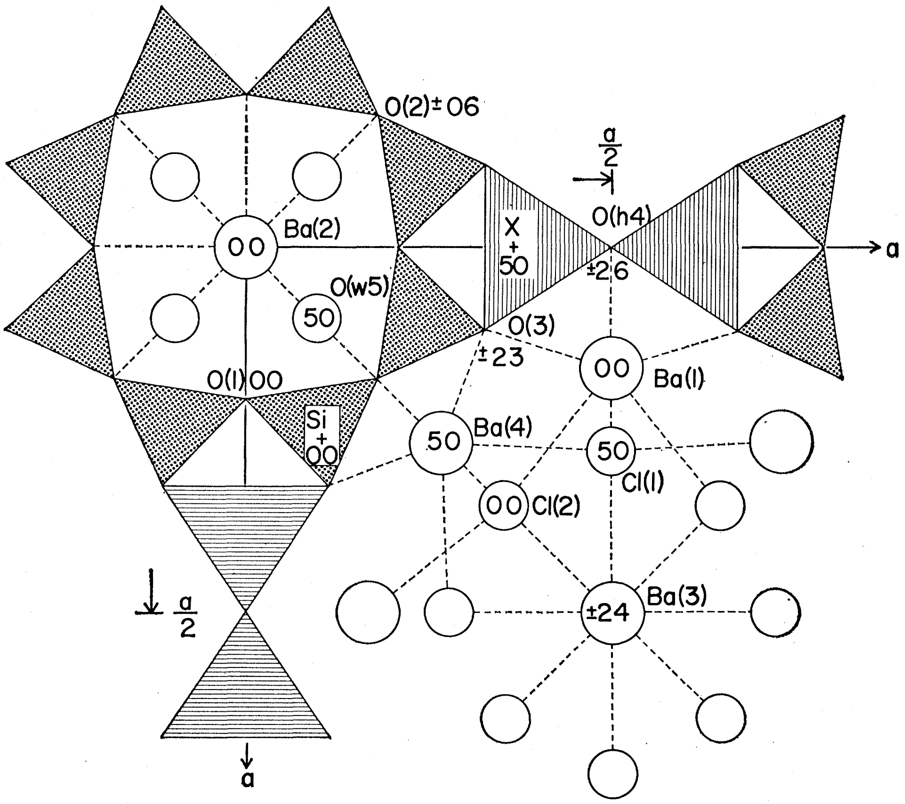

Fig. 1. Crystal structure of muirite viewed parallel to the [001] direction. The coordinations around silicon and X are shown as polyhedra. The bonds to the barium atoms are indicated by broken lines. The heights of the atoms are indicated in $z \times 100$.

atoms at an average distance of 3.335 Å [4 × Ba(2)–O(1), 2.910(16) Å; 4 × Ba(2)–O(2), 3.592(9) Å; and 8 × Ba(2)–O(w5), 3.419(7) Å]. Eight chlorine atoms form square antiprisms around Ba(3) which share with each other a square face [4 × Ba(3)–Cl(1), 3.435(5) Å; and 4 × Ba(3)–Cl(2), 3.235(3) Å]. This brings the Ba(3) atoms to within 2.76 Å of each other. However, the Ba(3) atoms have an occupancy factor of 0.5, which means that statistically only every other Ba(3)-site is occupied, and therefore the Ba(3) atoms actually do not have to be in this close contact.

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References and Notes

1. J. T. Alfors, M. C. Stinson, R. A. Matthews, A. Pabst, *Amer. Mineral.* **50**, 314 (1965).
2. H. Strunz, *Mineralogische Tabellen* (Akademische Verlagsgesellschaft, Leipzig, ed. 5, 1970), p. 404.
3. We thank the staff of the Field Museum of Natural History and Dr. E. Olsen for the loan of a specimen from the type locality (Esquire No. 7 mine, Big Creek, Fresno County, California, No. M18578).
4. For details of experimental and computational procedures, see: W. H. Baur and A. A. Khan, *Acta Crystallogr.* **B26**, 1594 (1970); A. A. Khan, W. H. Baur, W. C. Forbes, *ibid.*, in press.
5. T. Zoltai and M. J. Buerger, *Z. Kristallogr.* **114**, 1 (1960).
6. W. H. Baur, *Trans. Amer. Crystallogr. Ass.* **6**, 129 (1970); *Amer. Mineral.*, in press.
7. D. W. J. Cruickshank, *J. Chem. Soc. (London)* **1961**, 5486 (1961); G. E. Brown, G. V. Gibbs, P. H. Ribbe, *Amer. Mineral.* **54**, 1044 (1969).
8. We thank the Computer Center and the Research Board of the University of Illinois at Chicago and the National Science Foundation (grant GA-314) for support of this work.

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Early Silurian Spore Tetrads from New York: Earliest New World Evidence for Vascular Plants?

Abstract. *Several taxa of abundant cutinized trilete spores from earliest Silurian shale in New York predate by almost an entire period vascular land plant megafossils. Paleoecological evidence suggests that these spores may represent vascular land or semiaquatic plants but a bryophytic origin cannot be precluded on the basis of spore characters. An algal origin is considered unlikely.*

Extracted samples of the Medina Group (Lower and Middle Llandovery, basal Silurian) of western New York have yielded abundant spore tetrads that may provide some of the earliest evidence for the presence of vascular land plants. This record, to our knowledge, is preceded only by the recent discovery of rare triradiate spores, tracheids, plant tissues, and cuticle fragments from the Middle Ordovician (Llanvirnian Sarka Formation) of the Bohemian Massif (*1*). If the Bohemian remains can be authenticated, they will provide the earliest evidence of vascular plants (*2*).

Sandstone and shale of the Medina Group are exposed in a section along the Niagara River, about 11 km to the north of Niagara Falls at the Robert Moses Power Plant site. In this region, the Medina Group overlies the Late Ordovician Queenston Formation. The basal unit of the Medina is the Whirlpool Sandstone ("White Medina"); above it (in ascending order) are the Power Glen Formation ("Gray Medina") and the Grimsby Formation ("Red Medina"). The uppermost Medina Group unit is the Thorold Sandstone, above which is the Neahga Shale.

Berry and Boucot (*3*) review the available evidence for correlation of these Silurian units. Neither the Medina units nor the Queenston or Thorold formations of this area have yielded zonable invertebrate megafossils (*3*). All are considered to be largely nonmarine, estuarine, or very nearshore marine on the basis of their physical characteristics, their lithofacies relationships with richly fossiliferous, zonable, wholly marine units occurring to the west on the northern rim of the Michigan Basin, or the extreme rarity and restriction to certain limited horizons of marine invertebrate megafossils. Microfossil evidence (discussed below) and the presence of infrequent marine invertebrates (*4*) suggest that the shales of the Medina Group were indeed deposited in a marine environment, although possibly near shore in a situation unsuited for the presence of abundant marine shelly invertebrate megafossils.

Shale from the Whirlpool, Power Glen, and Grimsby of the Medina Group, as well as from the Queenston and Neahga, were extracted for plant spores and other organic microfossils, by using several of the chemical and other methods described in detail by Gray (*5*) (Table 1). No organic microfossils of any type were recovered from three extracted samples of the Queenston; marine organic microfossils including scolecodonts, acritarchs, and chitinozoans were, however, recovered from the Neahga [see also (*6*)].

The three Medina Group samples provided spore tetrads (*6*) and other organic microfossils in a hash of organic material, much of which appears to be highly carbonized. Other organic objects suggestive of plant origin, such as cuticular tissues of the type common in abundantly sporiferous Late Silurian samples from Gotland (*7*), were not found in any of the samples. The Gotland samples, however, have spore tetrads reminiscent of the simple tetrahedral type described herein, in addition to single spores with triradiate laesurae.

The Medinan spore tetrads are most often dark brown, or even opaque, and quite brittle. They are arranged in the conventional tetrahedral tetrad configuration (Fig. 1) common to the development of most modern pollen and to some spores of both vascular and nonvascular plants, which indicates that the precursor spore mother cell underwent meiotic division. The individual spores are arranged in two planes and appear to be at the apices of a pyramidal tetrahedron. Where individual spores have broken away from the tetrad, a generally distinct, clearly marked triradiate scar is present, with the simple rays extending to the equator of the spore. The tetrads range in size from approximately 18 to 50 μm, most being in excess of 20 μm, and have a smooth, faintly scabrate, or microspinous surface (Figs. 1 and 2). Some few appear to be reticulate (Fig. 1). A denser marginal coloration on some of the spores suggests real differences in wall thickness or even the possibility of an equatorial thickening. These morphologic variations appear to indicate a greater diversity of spore taxa than have been previously recorded from the Llandovery. Some clusters of spore tetrads may have come directly from sporangia without breaking up into individual tetrad units, although such clusters may also indicate clumping of the type that is known to occur among the pollen of certain modern plants (*8*).

Spore tetrads are common to abundant as compared with other organic microfossils in both the Whirlpool and Power Glen formations; in the Grimsby, however, spore tetrads are rare compared with other microfossils (Table 1). The other recognizable organic micro-