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# Crystal structures of the humite minerals: V. Magnesian manganhumite

CARL A. FRANCIS[1] AND PAUL H. RIBBE

*Department of Geological Sciences*
*Virginia Polytechnic Institute and State University*
*Blacksburg, Virginia 24061*

## Abstract

The crystal structure of type manganhumite from the Brattfors mine, Nordmark, Sweden [$(Mn_{0.68}Mg_{0.30}Fe_{0.01}Ca_{0.01})_7(SiO_4)_3(OH)_2$, *Pbnm*, $a = 4.815(1)$, $b = 10.580(2)$, $c = 21.448(5)$A] has been refined by conventional least-squares methods to $R = 0.051$ ($R_w = 0.081$), using 1562 structure factors with $F_{obs} > 2\sigma(F_{obs})$. Mean Si–O distances for the isolated tetrahedra are $\langle Si(1)–O\rangle = 1.628$A and $\langle Si(2)–O\rangle = 1.632$A. The apical Si–O distances of 1.600 and 1.604A are the shortest yet observed in humite-group minerals. Site refinement yielded Mg/(Mg+Mn) ratios of 0.30 in the $M(1)O_6$ octahedron (mean $M$–O distance = 2.170A), 0.0 in the $M(2)O_6$ and $M(2)O_5OH$ octahedra ($\langle M–O\rangle$ = 2.222 and 2.206A), and 0.75 in the $M(3)O_4(OH)_2$ octahedron ($\langle M–O\rangle = 2.117$A). The correlation coefficient of Mg/(Mg+Mn) occupancy and mean octahedral bond length is $r = 0.986$, and as expected, octahedral sizes correspond almost exactly to the weighted radii of the larger Mn and smaller Mg cations ($r = 0.989$).

## Introduction

The humite minerals are a homologous series of magnesium orthosilicates based on hexagonal closest-packed arrays of anions and structurally related to forsterite. Microprobe analyses of fifty-five humite samples (Jones *et al.*, 1969) led to the establishment of the general formula:

$$n[M_2SiO_4] \cdot M_{1-x}Ti_x(OH,F)_{2-2x}O_{2x}$$

where $M$ is Mg,Fe,Mn,Ca,Zn in decreasing order of abundance, $0 \leq x \leq 1$, and $n = 1$ for norbergite, 2 for chondrodite, 3 for humite, and 4 for clinohumite (see Table 1). Manganese end-members of three of the four homologues are well-known, and unpublished microprobe analyses by C. Richardson (private communication, 1976) indicate extensive, if not complete, solid solution between Mg and Mn end-members.

Ordering of the small concentrations of Fe normally present in Mg humites was initially detected by Ribbe and Gibbs (1969, 1971) in a humite with composition $Mg_{6.6}Fe_{0.4}Si_3O_{12}F(OH)$. Mg/Fe ordering has been observed in all subsequent refinements of humite group minerals, including several titanian humites (Robinson *et al.*, 1973; Kocman and Rucklidge, 1973). Ribbe and Gibbs (1971) concluded that distortion and ligancy rather than size of the octahedral sites govern the ordering of Fe in Mg humites, Fe preferring those octahedra with no (F,OH) ligands, *i.e.*, $M(1)O_6$ and $M(2)O_6$.

The recent discovery of Mn humites containing considerable Mg provides an opportunity for further investigation of cation ordering in humites. This paper reports the results of a site occupancy refinement of magnesian manganhumite.

## Experimental procedures

Crystals of manganhumite from the type specimen from Brattfors Mine, Nordmark, Sweden, were generously donated by Professor P. B. Moore, University of Chicago, and upon completion of this study will be deposited in the Mineralogical Museum of Harvard University. Moore (1978) reports their composition to be $(Mn_{0.68}Mg_{0.30}Fe_{0.01}Ca_{0.01})_7(SiO_4)_3(OH)_2$.

Manganhumite is orthorhombic and was refined in the nonstandard space group *Pbnm* to conform with

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[1] Present address: Mineralogical Museum, Harvard University, 24 Oxford Street, Cambridge, Massachusetts 02138.

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Table 1. Nomenclature of humite group minerals $n[M_2SiO_4]\cdot M(OH,F)_2$ with references to modern crystal structure refinements

| Homologue | Mg end-member | Mn end-member |
|---|---|---|
| $\underline{n}$ = 1 | Norbergite<br>(Gibbs and Ribbe, 1969) | MAN* |
| $\underline{n}$ = 2 | Chondrodite<br>(Gibbs et al., 1970) | Alleghanyite<br>(Rentzeperis, 1970) |
| $\underline{n}$ = 3 | Humite<br>(Ribbe and Gibbs, 1971) | Manganhumite<br>(This study) |
| $\underline{n}$ = 4 | Clinohumite<br>(Robinson et al., 1973) | Sonolite<br>(Kato, in preparation) |

*Manganese Analog of Norbergite (MAN), synthesized by CAF: $\underline{a}$=4.869(2), $\underline{b}$=10.796(2), $\underline{c}$=9.179(2) A.

previous studies (Taylor and West, 1928; Ribbe and Gibbs, 1971) and the recommendations of Jones (1969). Unit cell dimensions, $a = 4.815(1)$, $b = 10.580(2)$, $c = 21.448(5)$A, were determined by least-squares refinement (program of Appleman and Evans, 1973) of 22 powder X-ray lines (16–60°$2\theta$) recorded with monochromatized Cu$K\alpha$ radiation ($\lambda = 1.5418$A) on a Philips Norelco powder diffractometer using $BaF_2$ ($a = 6.198$A) as an internal standard.

A cubic fragment 0.2 mm on an edge was mounted with $b$ nearly parallel to the phi axis of a Picker FACS-1 four-circle diffractometer. Intensity data were collected in two octants ($2\theta \leq 70°$) using Nb-filtered Mo$K\alpha_1$ radiation ($\lambda = 0.70926$A) and a $2\theta$ scan rate of 1°/minute. Background measurements were made for 20 seconds on either side of dispersion-corrected scan ranges (1.2°$2\theta$ base width).

Symmetrically related standard diffractions monitored after every 50 data showed a maximum variability of ±5 percent. No interpolation of the data was made, but an "ignorance factor" of 0.025 was incorporated in the calculation of the weighting function (Finger and Prince, 1975, p. 5). The data were corrected for background, Lorentz, polarization and absorption effects ($\mu_{MoK\alpha} = 63.1$ cm$^{-1}$) and then averaged to yield a set of 1800 unique structure factors using the programs DATALIB and DATASORT from the World List of Crystallographic Computer Programs (3rd ed. and supplements).

## Refinement

A full-matrix least-squares refinement was carried out using the program RFINE4 (Finger and Prince, 1975), and atomic scattering factors for neutral atoms taken from Volume 4 of the International Tables for Crystallography (1974, p. 99, 149). The refinement was initiated using the positional parameters of humite (Ribbe and Gibbs, 1971) and assuming that all octahedral sites were completely occupied by Mn. Reasonable isotropic temperature factors were assigned, and after two cycles of refining the scale factor and several more cycles of refining both the scale factor and the positional parameters, the conventional $R$ factor dropped to 0.22. At this stage, diffractions of the type $h + k = 2n + 1$ showed good agreement between $F_{obs}$ and $F_{calc}$, while diffractions of the type $h+k = 2n$ showed poor agreement. This systematic discrepancy was attributed to Mn/Mg ordering, and when Mg was assigned to the four non-equivalent octahedral sites on the basis of average $M$–O bond distances, the $R$ factor improved sufficiently to release the temperature factors. Using the temperature factors, atomic coordinates, and scale factor generated in this manner, site refinement followed.

Being the chief substituent, Mg was selected as the independent variable and, subject to the restriction that the total magnesium content must equal 2.1 atoms, was first distributed randomly over all four octahedral sites. The trace levels of Fe and Ca were ignored throughout the site refinement. The concentrations of Mg in M(2)$_5$ and M(2)$_6$ dropped to slightly negative values, so these sites were subsequently considered to be fully occupied by Mn. The site occupancies then converged to the values 0.304(6) Mg in M(1) and 0.746(6) Mg in M(3), irrespective of the site chosen as the dependent variable.

Data for which $F_{obs} < 2\sigma(F_{obs})$ were considered unobserved. The 238 data rejected from the refinement by this criterion are indicated in the structure factor table (Table 2)[2] by asterisks. In the final cycles

Table 3. Positional parameters, isotropic temperature factors and r.m.s. equivalents, $\mu$, for manganhumite

| Atom | x/a | y/b | z/c | B(A$^2$) | <u>(A) |
|---|---|---|---|---|---|
| M(1) | 0.0015(1)* | 0.3797(1) | 0.1758(1) | 0.90(2) | 0.107(1) |
| M(2)$_6$ | .5141(2) | .1583(1) | .25 | .63(2) | .089(1) |
| M(2)$_5$ | .0085(1) | .0974(1) | .1091(1) | .93(2) | .109(1) |
| M(3) | .4907(2) | .8657(1) | .0270(1) | .84(3) | .103(2) |
| Si(1) | .0750(4) | .9699(1) | .25 | .63(2) | .089(1) |
| Si(2) | .5753(3) | .2844(1) | .1043(1) | .57(2) | .085(1) |
| O(2.3) | .7150(6) | .2178(2) | .1659(1) | .84(4) | .103(2) |
| O(1.3) | .2168(6) | .0381(2) | .1896(1) | .86(4) | .104(2) |
| O(2.4) | .7197(6) | .2130(2) | .0447(1) | .75(4) | .098(3) |
| O(2.1) | .2432(7) | .2850(3) | .1029(1) | .89(4) | .106(2) |
| O(1.2) | .2785(8) | .3293(3) | .25 | .80(5) | .101(3) |
| O(1.1) | .7421(9) | .9680(4) | .25 | .97(6) | .111(3) |
| O(2.2) | .7778(6) | .9252(2) | .1031(1) | .72(4) | .096(3) |
| OH | .2631(6) | .0306(2) | .0333(1) | .87(4) | .105(2) |

*Numbers in parentheses are estimated standard deviations and refer to to the last decimal place.

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[2] To receive a copy of Table 2, order Document AM-78-086 from the Business Office, Mineralogical Society of America, Suite 1000 Lower Level, 1909 K Street, N.W., Washington, D.C. 20006. Please remit $1.00 in advance for the microfiche.

of refinement, corrections for anomalous dispersion and extinction were included without significantly altering the results. The final unweighted $R$ factor is 0.051 ($R_w = 0.081$) for the observed data; $R = 0.058$ and $R_w = 0.082$ for all 1800 data. Atomic coordinates and isotropic temperature factors and their r.m.s. equivalents are listed in Table 3. Interatomic distances and angles are reported in Table 4. The atomic designations follow those used by Ribbe and Gibbs (1971).

Table 4. Si–O, $M$–O and O–O distances (in angstroms) and O–Si–O and O–$M$–O angles (in degrees) in manganhumite

| | | | | | |
|---|---|---|---|---|---|
| [SiO$_4$] tetrahedra | | | | | |
| Si(1)-O(1,1)$^{A}$ | 1.604* | | Si(2)-O(2,1)$^{A}$ | 1.600* | |
| O(1,2) | 1.645 | | O(2,2) | 1.648 | |
| O(1,3)[2] | 1.633 | | O(2,3) | 1.640 | |
| Mean | 1.628 | | O(2,4) | 1.640 | |
| | | | Mean | 1.632 | |
| O···O distances* | | Angles at Si(1)** | O···O distances* | | Angles at Si(2)** |
| (1,3)-(1,2)[2] | 2.559$^{t}$ | 102.7 | (2,3)-(2,2) | 2.574$^{t}$ | 103.0 |
| (1,3)-(1,3) | 2.591 | 105.0 | (2,4)-(2,2) | 2.570$^{t}$ | 102.8 |
| (1,2)-(1,1) | 2.735 | 114.7 | (2,3)-(2,4) | 2.599$^{t}$ | 104.8 |
| (1,3)-(1,1)[2] | 2.731 | 115.1 | (2,1)-(2,2) | 2.742 | 115.2 |
| Mean | 2.651 | 109.2 | (2,4)-(2,1) | 2.721 | 114.2 |
| | | | (2,3)-(2,1) | 2.737 | 115.3 |
| | | | Mean | 2.657 | 109.2 |
| [$M$(O,OH)$_6$] octahedra | | | | | |
| M(1)-O(2,2) | 2.114 | | M(2)$_5$-O(1,3)$^{A}$ | 2.093 | |
| O(1,2) | 2.144 | | O(2,2)$^{A}$ | 2.136 | |
| O(1,1) | 2.186 | | O(2,3) | 2.258 | |
| O(2,1) | 2.191 | | O(2,1) | 2.286 | |
| O(1,3) | 2.175 | | O(2,4) | 2.309 | |
| O(2,3) | 2.209 | | OH | 2.155 | |
| Mean | 2.170 | | Mean | 2.206 | |
| O···O distances* | | Angles at M(1)** | O···O distances* | | Angles at M(2)$_5$** |
| (2,3)-(2,2) | 2.574$^{t}$ | 73.0 | (2,3)-(2,4) | 2.599$^{t}$ | 69.4 |
| (1,3)-(1,2) | 2.559$^{t}$ | 72.7 | (2,4)-(2,1) | 2.915$^{o}$ | 78.7 |
| (1,3)-(1,1) | 2.937$^{o}$ | 84.7 | (2,3)-(2,1) | 2.967$^{o}$ | 81.5 |
| (1,2)-(1,1) | 2.905$^{o}$ | 84.3 | (1,3)-(2,2) | 3.055 | 92.5 |
| (2,1)-(2,2) | 2.915$^{o}$ | 85.2 | (2,3)-(1,3) | 3.102 | 91.4 |
| (2,3)-(2,1) | 2.967$^{o}$ | 84.8 | (1,3)-(2,1) | 3.206 | 94.0 |
| (2,1)-(1,2) | 3.193 | 94.9 | (2,4)-(2,2) | 3.301 | 95.8 |
| (1,1)-(2,2) | 3.186 | 95.6 | (2,3)-(2,2) | 3.386 | 100.7 |
| (2,3)-(1,1) | 3.200 | 93.8 | OH-(2,2) | 2.968 | 88.4 |
| (1,3)-(2,1) | 3.263 | 96.7 | OH-(2,1) | 3.077 | 87.7 |
| (2,3)-(1,2) | 3.465 | 105.5 | OH-(2,4) | 3.192 | 93.8 |
| (1,3)-(2,2) | 3.487 | 108.8 | OH-(1,3) | 3.359 | 104.5 |
| Mean | 3.054 | 90.0 | Mean | 3.094 | 89.9 |
| M(2)$_6$-O(1,2)$^{A}$ | 2.134 | | M(3)-O(2,4)$^{A}$ | 2.021 | |
| O(2,3)$^{A}$[2] | 2.141 | | O(2,1) | 2.155 | |
| O(1,1) | 2.292 | | O(2,4)' | 2.167 | |
| O(1,3)[2] | 2.311 | | O(2,2) | 2.229 | |
| Mean | 2.222 | | OH | 2.063 | |
| | | | OH' | 2.069 | |
| | | | Mean | 2.117 | |
| O···O distances* | | Angles at M(2)$_6$** | O···O distances* | | Angles at M(3)** |
| (1,3)-(1,3)' | 2.591$^{t}$ | 68.2 | (2,4)-(2,2) | 2.570$^{t}$ | 71.5 |
| (1,3)-(1,1)[2] | 2.937$^{o}$ | 79.3 | (2,4)-(2,1) | 2.915$^{o}$ | 84.8 |
| (2,3)-(1,2)[2] | 3.010 | 89.5 | (2,1)-(2,2) | 2.915$^{o}$ | 83.3 |
| (1,3)-(2,3)[2] | 3.101 | 88.2 | OH-OH' | 2.980$^{o}$ | 84.1 |
| (2,3)-(1,1)[2] | 3.208 | 92.4 | OH-(2,4) | 2.935 | 91.7 |
| (1,3)-(1,2)[2] | 3.352 | 97.8 | OH-(2,1) | 2.994 | 90.4 |
| (2,3)-(2,3)' | 3.608 | 114.8 | OH'-(2,2) | 2.991 | 87.3 |
| Mean | 3.118 | 89.8 | OH'-(2,4)' | 3.070 | 97.8 |
| | | | OH'-(2,2) | 3.102 | 92.5 |
| | | | OH'-(2,4) | 3.191 | 97.5 |
| | | | (2,1)-(2,4)' | 3.166 | 98.6 |
| | | | (2,4)-(2,4)' | 3.175 | 98.6 |
| | | | Mean | 3.000 | 89.8 |

* *Estimated standard errors are 0.003 A for Si-O and M-O, less than 0.006 A for O···O distances. [2] indicates multiplicity.*

** *The estimated standard error in all bond angles is 0.1°.*

t *Edge shared between tetrahedron and octahedron.*

o *Edge shared between two octahedra.*

A = *apical bond after the convention of Ribbe and Gibbs (1971).*

## Results and conclusions

Manganhumite is confirmed to be isotypic with humite, and because of its close similarity to humite, the reader is referred to Ribbe and Gibbs (1971) for structure diagrams and detailed discussion of the stereochemistry. We note, however, that the apical Si–O bond distances of 1.600 and 1.604A in manganhumite (Table 4) are the shortest yet observed in humite-group minerals.

The cations in manganhumite are ordered (Table 5), the magnesium being concentrated in the M(1)O$_6$ and M(3)O$_4$(OH)$_2$ octahedra, each of which are "interior" sites in the serrated chain of edge-sharing octahedra (Ribbe and Gibbs, 1971, Fig. 1). These sites, being constrained by the sharing of polyhedral edges bounding opposite faces of the octahedra, are smaller than the M(2) sites at the "elbows" of the chains (see Table 5 for details). The correlation coefficient of Mg/(Mg + Mn) occupancy and mean octahedral bond length is $r = 0.986$, and as expected, octahedral sizes correspond very closely to the weighted radii of the larger Mn$^{2+}$ and smaller Mg$^{2+}$ cations, $r = 0.989$ (see Fig. 1). The correlation of octahedral site occupancy with size rather than ligancy or octahedral distortion, as expressed quantitatively by octahedral angle variance (Robinson *et al.*, 1971), can be rationalized by the fact that Mn$^{2+}$ with its high spin $d^5$ electronic configuration has no crystal field stabilization energy (Burns, 1970), whereas Fe$^{2+}$ ($d^6$) does. Although Fe is larger than Mg, it prefers the M(2)O$_6$ and M(1)O$_6$ octahedra in the Mg humite (Ribbe and Gibbs, 1971), whereas in manganhumite Mn prefers M(2)O$_6$, M(2)O$_5$(OH), and, to a lesser extent, the smaller M(1)O$_6$ octahedron. The results for manganhumite are consistent with observed cation distribution in (Mn$_{1.30}$Mg$_{0.35}$Zn$_{0.23}$Fe$_{0.12}$)SiO$_4$ studied by Brown (1970) and (Mg$_{1.06}$Mn$_{0.94}$)SiO$_4$ studied by Ghose and Weidner (1974).

Table 5. Octahedral ligancy and shared edges, octahedral angle variance, $\sigma_\theta^2$, mean bond lengths, and Mg/(Mg + Mn) ratios for manganhumite

| Site | Ligancy | No. of edges shared with Octahedra | No. of edges shared with Tetrahedra | ($\sigma_\theta^2$)* | Mean M-(O,OH) | Mg/(Mg+Mn) |
|---|---|---|---|---|---|---|
| M(1) | O$_6$ | 4 | 2 | 128 | 2.170A | 0.304(6) |
| M(2)$_6$ | O$_6$ | 2 | 1 | 97 | 2.222 | 0.0 |
| M(2)$_5$ | O$_5$(OH) | 2 | 1 | 94 | 2.206 | 0.0 |
| M(3) | O$_4$(OH)$_2$ | 3 | 1 | 66 | 2.117 | 0.746(6) |

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* $\sigma_\theta^2 = \sum_{i=1}^{12}(\theta_i-90°)^2/11$. See Robinson et al. (1971)

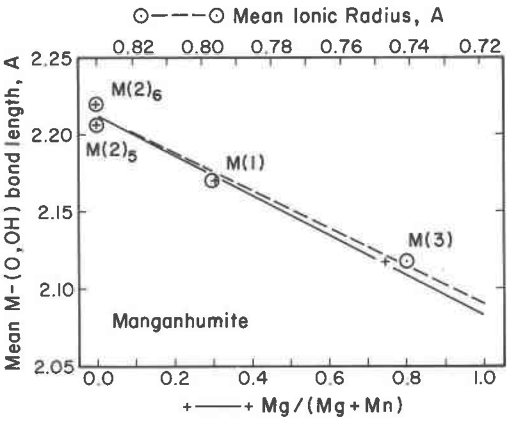

Fig. 1. Plot of mean $M$–(O, OH) bond distances as a function of content of the octahedral site. Lower abscissa: Mg/(Mg + Mn) indicated by + and the solid line. Upper abscissa: mean cation radius determined from site occupancy, using $r_{Mg}$ = 0.72A and $r_{Mn}$ = 0.83A (Shannon, 1976), indicated by circles and the dashed line.

Further discussion of Mg/Mn order in olivines and the Mn-analogues of the humite minerals is deferred pending the completion of other refinements now in progress.

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## References

Appleman, D. E. and H. T. Evans (1973) Job 9214: Indexing and least squares refinement of powder diffraction data. *Natl. Tech. Inf. Serv., U.S. Dep. Commerce, Springfield, Virginia, PB-216 188.*

Brown, G. E., Jr. (1970) *Crystal Chemistry of the Olivines.* Ph.D. Thesis, Virginia Polytechnic Institute and State University, Blacksburg, Virginia.

Burns, R. G. (1970) *Mineralogical Applications of Crystal Field Theory.* Cambridge University Press, Cambridge, England.

Finger, L. W. and E. Prince (1975) A system of Fortran IV computer programs for crystal structure computations. *U.S. Natl. Bur. Stand. Tech. Note 854.*

Ghose, S. and J. R. Weidner (1974) Site preference of transition metal ions in olivine (abstr.). *Geol. Soc. Am. Abstracts with Programs, 6,* 751.

Gibbs, G. V. and P. H. Ribbe (1969) The crystal structures of the humite minerals: I. Norbergite. *Am. Mineral., 54,* 376–390.

———, ——— and C. P. Anderson (1970) The crystal structures of the humite minerals: II. Chondrodite. *Am. Mineral., 55,* 1182–1194.

*International Tables for X-ray Crystallography,* Vol. IV (1974) Kynoch Press, Birmingham, England.

Jones, N. W. (1969) Crystallographic nomenclature and twinning in the humite minerals. *Am. Mineral., 54,* 309–313.

———, P. H. Ribbe and G. V. Gibbs (1969) Crystal chemistry of the humite minerals. *Am. Mineral., 54,* 391–411.

Kocman, V. and J. Rucklidge (1973) The crystal structure of a titaniferous clinohumite. *Can. Mineral., 12,* 39–45.

Moore, P. B. (1978) Manganhumite, a new species. *Mineral. Mag., 42,* 133–136.

Rentzeperis, P. J. (1970) The crystal structure of alleghanyite, $Mn_5[(OH)_2|(SiO_4)_2]$. *Z. Kristallogr., 132,* 1–18.

Ribbe, P. H. and G. V. Gibbs (1969) Mg/Fe ordering in humite, $Mg_{6.6}Fe_{0.4}Si_3O_{12}F(OH)$ (abstr.). *Geol. Soc. Am. Abstracts with Programs, 1,* 188.

——— and ——— (1971) Crystal structures of the humite minerals: III. Mg/Fe ordering in humite and its relation to other ferromagnesian silicates. *Am. Mineral., 56,* 1155–1173.

Robinson, K., G. V. Gibbs and P. H. Ribbe (1971) Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science, 172,* 567–570.

———, ——— and ——— (1973) The crystal structures of the humite minerals. IV. Clinohumite and titanoclinohumite. *Am. Mineral., 58,* 43–49.

Shannon, R. D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr., A32,* 751–767.

Taylor, W. H. and J. West (1928) The crystal structure of the chondrodite series. *Proc. R. Soc. London, A117,* 517–532.

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