

A comparison of the structures and geometric stabilities of stilpnomelane and parsettensite: A distance least-squares (DLS) study

STEPHEN GUGGENHEIM

Department of Geological Sciences, University of Illinois at Chicago, Chicago, Illinois 60680, U.S.A.

R. A. EGGLETON

Department of Geology, Australian National University, Canberra, ACT 2601, Australia

ABSTRACT

Structural models for the islandlike modulated phyllosilicates, stilpnomelane and parsettensite, were examined by distance least-squares (DLS) calculations. Parsettensite occurs naturally only near the Mn end-member, whereas stilpnomelane may be both Mn and Fe²⁺ rich. Models for compositions between Fe²⁺ and Mn²⁺ end-member stilpnomelane demonstrated that the stilpnomelane structure is geometrically stable across the composition range. In principle, therefore, stilpnomelane may occur at Mn end-member compositions. DLS calculations indicated also that Fe²⁺- and Mn²⁺-rich stilpnomelane-cell edge lengths are geometrically controlled; *c* is fixed at approximately 17.835 Å ($d_{001} = 12.13$ Å). DLS-derived atomic coordinates are given for stilpnomelane.

Misfit in stilpnomelane between the tetrahedral and octahedral sheets is relieved by warping of the octahedral sheet and by adjustments to the double six-membered ring interisland connectors. These adjustments include an in-plane tetrahedral rotation and out-of-plane tilting. In Mg- or Fe³⁺-rich stilpnomelane, Si to Si distances within the interisland connectors are reduced and Si to Si repulsions increase. Thus, tetrahedral tilting in the interisland connectors increases, along with the magnitude of the d_{001} value. In contrast to parsettensite, however, only limited tilting of the tetrahedra in these connectors may occur, which accounts for the different d_{001} values in the two model structures.

In parsettensite, double four-membered ring interisland connectors do not allow for tetrahedral rotation, and, therefore, parsettensite requires the nearly perfect alignment of islands. Thus, parsettensite probably cannot have a composition with smaller octahedral cations (e.g., Fe²⁺).

INTRODUCTION

Stilpnomelane (Eggleton, 1972) and parsettensite (Eggleton and Guggenheim, 1994) are modulated layer silicates with continuous octahedral sheets coordinated by partial sheets of silicate tetrahedral rings. These rings form islands that are three tetrahedral rings wide, with islands connected by inverted tetrahedra. The two structures differ, however, by the topology of the island linkage. Parsettensite has partially tilted tetrahedra that form four-membered interisland connectors, thereby producing double four-membered rings to connect adjacent layers and $d_{001} = 12.6$ Å. In contrast, stilpnomelane has six-membered ring interisland connectors and, thus, double six-membered rings to connect adjacent layers, with a resulting $d_{001} = 12.1$ – 12.6 Å, depending on composition (see below). Figures depicting the geometry of the structures may be found in Eggleton (1972) and Eggleton and Guggenheim (1994).

The parsettensite structure is known to exist near Mn end-member compositions only (Eggleton and Guggenheim, 1994). Stilpnomelane, however, commonly occurs with Fe-rich compositions, although considerable Mg and

Mn substitutions are possible (Dunn et al., 1984, 1992). Where Mn is present, the amount of Mn substitution in stilpnomelane only approaches about half the possible octahedral sites. In addition, at least for the limited number of Mn-dominant stilpnomelane samples known, Mn is associated with a significant proportion of smaller cations, such as Mg and Zn. Guggenheim and Eggleton (1987, 1988), in a review of modulated phyllosilicate systematics, discussed the importance of misfit between the lateral dimensions of the octahedral and tetrahedral sheets in such structures. A major feature of such structures is a warping of the octahedral sheets, either wavelike or domelike, depending on the nature of the modulation. However, the relationships of the interisland connectors to misfit between the tetrahedral and octahedral sheets are not well understood.

A distance least-squares (DLS) investigation was made to establish geometric constraints on the stilpnomelane structure with Fe vs. Mn octahedral occupancy as the important variable. This study was made (1) to determine why parsettensite has a d_{001} value of near 12.6 Å, whereas a Mn-rich stilpnomelane has a value near 12.1 Å, and (2) to establish the role, if any, of the interisland connectors

in relieving misfit between the tetrahedral and octahedral components. An investigation of the extent of cation substitutions in stilpnomelane is potentially more revealing petrologically than an alternate investigation regarding the extent of cation substitutions in parsettensite because stilpnomelane is a rock-forming mineral. In addition, however, data given below suggest that it may not be possible to predict accurately an appropriate set of cell parameters for a hypothetical Fe-rich parsettensite, which is a requirement for a successful DLS investigation of this type.

The DLS approach (Meier and Villiger, 1969) uses interatomic distances in a least-squares refinement. Atomic positional positions are adjusted so that the calculated distances match, as best as possible, the distances used as input. Because the distances may be given weights equal to interatomic forces, the modeling approach may be considered an analogy to a force model. The distances used for input are generally established by using interatomic distances from similar materials. In this study on parsettensite and stilpnomelane, the only parameters derived experimentally are those based on cell parameters and space group and, of course, the topology (polyhedral linkages) of the structure as derived in the structure determinations (Eggleton, 1972; Eggleton and Guggenheim, 1994). Thus, because the models utilize such limited observed data, the procedure confirms only that the linkages are dimensionally reasonable. However, even if the linkages are plausible, the technique cannot determine the correctness of the structure without ancillary techniques.

EXPERIMENTAL METHODS

Both the stilpnomelane and the parsettensite structures have interatomic distances at the Mn end-member in common. DLS input parameters for parsettensite included Mn-O distances (2.230 Å at 0.5 weight), T-O distances (1.625 Å at 1.0), O-O distances about the Mn sites (3.280 Å at 0.07), O-O distances about the T sites (2.655 Å at 0.07), and T-T distances (3.100 Å at 0.3). Because of differences in Al occupancy, the input for stilpnomelane was identical, except for T-O distances of 1.633 Å (wt = 1.0) and O-O distances about the tetrahedra of 2.665 Å (wt = 0.07). No attempt was made to model the positions of exchangeable cations for either structure. These cations do not represent an integral part of the structure, and first coordination spheres are difficult to locate. The DLS program (DLS-76) of Baerlocher et al. (1978) was used in the analysis, along with bond distances from Shannon (1976) and weights primarily from Baur (1977).

Parsettensite

DLS modeling was done in space group $C2/m$ using $a = 39.1$, $b = 22.84$, $c = 17.95$ Å and $\beta = 135.6^\circ$ (Eggleton and Guggenheim, 1994). Because of the expected misfit between the tetrahedral and octahedral sheets, a small domed shape (± 0.2 Å) was imparted to the apical O plane associated with the Mn sheet, with the dome crest at the center of the islands. There were 98 independent

atoms, 267 variables, and 414 distances. Besides parameters held invariant by special positions, all z coordinates of the apical O atoms and O atoms at $z = 0.5$ were fixed for five cycles of refinement, after which only space group invariant coordinates and O z coordinates at $z = 0.5$ were fixed. This model, using the above input distances, assumes complete Al vs. Si disorder. Refinement converged in six additional cycles ($R = 0.006$), and atom positions are given in Table 3 of Eggleton and Guggenheim (1994).

Additional DLS models were made to determine ^{14}Al ordering, with Al being concentrated either in the island regions or in the interisland (double four-membered ring) connectors. The latter model would not converge; Al-rich tetrahedra expanded to unreasonable sizes (T-O distances of 1.82 Å). This result, therefore, suggests that this model is topologically impossible. The model, involving Al-rich tetrahedra within the islands, could not be distinguished by DLS refinement from the original model, with complete Si vs. Al disorder.

Stilpnomelane

Starting atomic coordinates were derived from figures in Eggleton (1972), which resulted in 168 independent atoms, 494 variables, and 767 observations (distances) in $P\bar{1}$ symmetry. The M1 site was held fixed, as were the six apical O z coordinates ($z = 0.00$) for the interisland tetrahedral connectors. Similar to parsettensite, a dome-like shape was imparted to the apical O plane. Unlike in parsettensite, where only one composition is known, cell parameters from many stilpnomelane compositions may be used to extrapolate to a hypothetical Mn end-member composition based on Eggleton and Chappell (1978) and the ideal cell geometry (Eggleton, 1972).

The value for d_{001} for stilpnomelane varies from 12.6 to about 12.15 Å for compositions where the octahedral cation radius (r_o) is between about 0.66 and 0.70 Å, but it remains nearly constant (about 12.13 Å) for compositions between values for r_o of 0.71–0.76 Å. Thus d_{001} for Mn end-member stilpnomelane is expected to be similar upon extrapolation (12.13 Å), resulting in $c = 17.835$ Å. The a dimension varies linearly from r_o values of 0.65–0.76 Å (linear equation: $a = 18.6345 + 4.5738r$, $R = 0.97$). Therefore, the derived Mn end-member cell parameters are $a = b = 22.43$ Å, $c = 17.835$ Å, $\alpha = 125.125^\circ$, $\beta = 96.015^\circ$, $\gamma = 120.0^\circ$.

DLS calculations were made also for an Fe^{2+} end-member stilpnomelane and intermediate compositions at $(\text{Fe}_{0.3}\text{Mn}_{0.7})$, $(\text{Fe}_{0.5}\text{Mn}_{0.5})$, and $(\text{Fe}_{0.7}\text{Mn}_{0.3})$. Cell dimensions for an Fe^{2+} end-member stilpnomelane are $a = b = 22.20$ Å, $c = 17.835$ Å, $\alpha = 125.03^\circ$, $\beta = 95.98^\circ$, and $\gamma = 120.0^\circ$. The Fe-O distance was assigned at 2.180 Å, and O-O distances around the M sites were given values of 3.07 Å. Bond distances for intermediate compositions were assumed to be linear between the two end-members. The refinements converged within 18 cycles to an R value of 0.01. Because the atomic coordinates for stilpnomelane have not been published previously, they are listed for Fe end-member stilpnomelane in Table 1. Estimated

TABLE 1. Derived atomic coordinates for stilpnomelane

Atom	x	y	z	Atom	x	y	z
Fe1	0.3038	0.3533	0.5300	O16	0.4199	0.0228	0.4077
Fe2	0.2171	0.4317	0.5217	O17	0.4963	0.4307	0.4015
Fe3	0.1335	0.2639	0.5223	O18	0.4945	0.6794	0.3978
Fe4	0.3803	0.5102	0.5144	O19	0.5024	0.9361	0.4048
Fe5	0.0476	0.3439	0.5155	O20	0.5013	0.1847	0.4037
Fe6	0.2153	0.1784	0.5180	O21	0.5791	0.3430	0.3951
Fe7	0.4618	0.4217	0.5073	O22	0.5732	0.5889	0.3879
Fe8	0.2964	0.5921	0.5125	O23	0.5821	0.8500	0.4016
Fe9	0.1295	0.5084	0.5124	O24	0.5854	0.1016	0.4045
Fe10	0.9679	0.1768	0.5164	O25	0.6673	0.2635	0.3991
Fe11	0.0452	0.0893	0.5095	O26	0.6583	0.5019	0.3836
Fe12	0.3828	0.2617	0.5153	O27	0.6624	0.7626	0.3932
Fe13	0.5416	0.3321	0.4984	O28	0.6708	0.0213	0.4071
Fe14	0.2087	0.6698	0.5035	O29	0.7459	0.4235	0.3895
Fe15	0.9637	0.4212	0.5068	O30	0.7440	0.6735	0.3817
Fe16	0.8772	0.2541	0.5061	O31	0.7507	0.9349	0.4005
Fe17	0.7931	0.0841	0.5036	O32	0.7529	0.1840	0.4038
Fe18	0.8732	-0.0021	0.4972	O33	0.8387	0.3502	0.4038
Fe19	0.2947	0.0882	0.5075	O34	0.8292	0.5908	0.3864
Fe20	0.3747	0.0009	0.5004	O35	0.8333	0.8500	0.3950
Fe21	0.4616	0.1711	0.5043	O36	0.8447	0.1116	0.4178
Fe22	0.3752	0.7519	0.5028	O37	0.9233	0.2738	0.4125
Fe23	0.2905	0.8323	0.4992	O38	0.9119	0.5086	0.3899
Fe24	0.5420	0.0832	0.5004	O39	0.9098	0.7599	0.3850
Si1	0.2804	0.2733	0.2901	O40	0.9231	0.0261	0.4108
Si2	0.1991	0.3526	0.2869	O41	0.0052	0.4375	0.4087
Si3	0.0380	0.2717	0.2876	O42	0.0000	0.6807	0.3947
Si4	0.9582	0.1107	0.2882	O43	0.0057	0.9416	0.4064
Si5	0.0390	0.0298	0.2872	O44	0.0109	0.1986	0.4221
Si6	0.2029	0.1141	0.2933	O45	0.0931	0.3635	0.4215
Si7	0.4320	0.3383	0.2681	O46	0.0843	0.5998	0.4013
Si8	0.2744	0.5075	0.2772	O47	0.0845	0.8529	0.3994
Si9	0.9534	0.3451	0.2751	O48	0.0933	0.1160	0.4211
Si10	0.7952	0.0274	0.2841	O49	0.2221	0.1652	0.2497
Si11	0.9530	0.8591	0.2728	O50	0.2224	0.2847	0.2468
Si12	0.2797	0.0268	0.2821	O51	0.1010	0.2826	0.2454
Si13	0.5059	0.4910	0.2552	O52	0.9801	0.1631	0.2461
Si14	0.4306	0.5798	0.2648	O53	0.9825	0.0437	0.2459
Si15	0.1940	0.5873	0.2722	O54	0.1041	0.0438	0.2484
Si16	0.0307	0.5022	0.2684	O55	0.3366	0.2757	0.2378
Si17	0.7899	0.2606	0.2703	O56	0.2184	0.4012	0.2405
Si18	0.7090	0.0993	0.2710	O57	0.9791	0.2800	0.2396
Si19	0.7066	0.8552	0.2678	O58	0.8596	0.0402	0.2444
Si20	0.7872	0.7728	0.2623	O59	0.9794	0.9180	0.2382
Si21	0.0312	0.7741	0.2664	O60	0.2246	0.0444	0.2462
Si22	0.1950	0.8583	0.2716	O61	0.4506	0.2656	0.2240
Si23	0.4366	0.0994	0.2712	O62	0.4472	0.3860	0.2210
Si24	0.5120	0.2557	0.2630	O63	0.4505	0.5083	0.2190
Si25	0.8615	0.5596	0.1301	O64	0.3340	0.5130	0.2299
Si26	0.7219	0.5600	0.1311	O65	0.2133	0.5158	0.2339
Si27	0.5821	0.4205	0.1315	O66	0.0955	0.5187	0.2293
Si28	0.5819	0.2803	0.1309	O67	0.9789	0.3957	0.2311
Si29	0.7212	0.2791	0.1311	O68	0.8550	0.2722	0.2316
Si30	0.8603	0.4191	0.1303	O69	0.7323	0.1525	0.2297
Si31	0.5280	0.8945	0.1308	O70	0.7398	0.0396	0.2371
Si32	0.3877	0.8937	0.1302	O71	0.7369	0.9153	0.2348
Si33	0.2476	0.7543	0.1305	O72	0.7298	0.7871	0.2239
Si34	0.2460	0.6138	0.1309	O73	0.8542	0.7927	0.2268
Si35	0.3865	0.6149	0.1313	O74	0.9784	0.7933	0.2288
Si36	0.5268	0.7543	0.1313	O75	0.0964	0.7883	0.2280
O1	0.1801	0.2865	0.4307	O76	0.2166	0.9163	0.2361
O2	0.1723	0.5253	0.4153	O77	0.3399	0.0380	0.2357
O3	0.1683	0.7695	0.4023	O78	0.4575	0.1496	0.2265
O4	0.1737	0.0295	0.4142	O79	0.5613	0.2572	0.2012
O5	0.2562	0.4452	0.4209	O80	0.5576	0.4843	0.1969
O6	0.2511	0.6855	0.4055	O81	0.4368	0.6137	0.2033
O7	0.2526	0.9391	0.4045	O82	0.2105	0.6185	0.2080
O8	0.2607	0.2036	0.4273	O83	0.9605	0.4907	0.2054
O9	0.3383	0.3627	0.4241	O84	0.7324	0.2618	0.2071
O10	0.3346	0.6048	0.4107	O85	0.6077	0.0133	0.2058
O11	0.3349	0.8538	0.4056	O86	0.6055	0.7811	0.2033
O12	0.3393	0.1123	0.4156	O87	0.7300	0.6563	0.2005
O13	0.4188	0.2730	0.4115	O88	0.9616	0.6575	0.2044
O14	0.4149	0.5193	0.4087	O89	0.2115	0.7845	0.2070
O15	0.4160	0.7686	0.4046	O90	0.4405	0.0130	0.2062

TABLE 1.—Continued

Atom	x	y	z	Atom	x	y	z
O91	0.8454	0.4906	0.1493	O100	0.2782	0.7082	0.1495
O92	0.8134	0.5970	0.1667	O101	0.3249	0.6255	0.1671
O93	0.6728	0.4951	0.1548	O102	0.4546	0.7107	0.1531
O94	0.5846	0.3685	0.1677	O103	0.8241	0.4906	0.0000
O95	0.6718	0.3164	0.1519	O104	0.6683	0.4881	0.0000
O96	0.8124	0.3669	0.1665	O105	0.5125	0.3321	0.0000
O97	0.5555	0.8551	0.1674	O106	0.5102	0.1776	0.0000
O98	0.4544	0.8839	0.1501	O107	0.6673	0.1761	0.0000
O99	0.3266	0.8546	0.1665	O108	0.8230	0.3314	0.0000

standard deviations are not included because they have no physical meaning.

RESULTS

Stilpnomelane

The DLS calculations indicate that solid solution in stilpnomelane between Fe and Mn end-members is plausible on the basis of geometric connectivity. Comparisons between Fe²⁺ and Mn²⁺ end-members as derived by DLS indicate that both the islands and the interisland connectors adjust to compensate for the variation in octahedral cation size. Misfit is relieved between the tetrahedral and octahedral sheets in both Fe and Mn structures by the warping of the octahedral sheet (maximum variation in Δz for Fe cations of 0.28 vs. 0.32 Å for Mn) to form a dome and out-of-plane tilting of the attached tetrahedral sheets, with the Mn structure having greater curvature. In order to achieve interlayer connectivity, three island boundaries must meet at a six-membered silicate ring.

The tetrahedral rotation angle, α , involves an in-plane rotation of adjacent tetrahedra in opposite directions around the silicate ring. For ideal phyllosilicates, tetrahedral rotation is usually considered a measure of misfit between the octahedral sheet and the attached tetrahedral sheet, with a larger α value indicating greater misfit. For these phyllosilicates, the tetrahedral sheet is laterally larger than the octahedral sheet, and thus inplane rotation reduces a tetrahedral sheet that is too large. In the case of stilpnomelane, however, the tetrahedral sheet is laterally smaller than the octahedral sheet. Thus, the rotation angle is not a useful parameter for describing the silicate rings within the islands, since they are fully extended, but α can be used to describe the silicate rings that serve as interisland connectors.

The α values for the interisland connectors are 11° for the Mn end-member and 13.5° for Fe, which represent approximately a 1% change in lateral length for an idealized single tetrahedral ring. This result suggests that island boundary positions as they relate to island neighbors, in plan view, are only slightly affected by differences in the Mn and Fe²⁺ sizes. Thus, because the interisland connectors in stilpnomelane do not link directly to the octahedral sheets, α is determined for the most part by the remaining space available between island boundaries.

Interisland connectors are tilted out of plane, however, with greater tilt for the Fe end-member than for the Mn end-member (Mn: $\sim 7^\circ$, Fe: $\sim 13^\circ$). This result may indicate that the c cell edge is incorrect for the following reasons: (1) the tilt involves primarily the z coordinate of the ^{29}Si and O atoms, (2) atomic coordinates were constrained to fit within a fixed cell, and (3) the c edge length was extrapolated from samples that were compositionally quite Fe rich. In order to test the validity of the c edge length, the Mn end-member c edge length was arbitrarily increased in size by 1 and by 4% to determine if the interisland tetrahedral rings would be affected. Interestingly, unreasonable distortions in the interisland tetrahedral sites occur, with bond distances varying from 1.615 to 1.641 Å for the 1% increase in c and 1.633–1.652 Å for the 4% increase. In both cases, however, the tetrahedra within the connector rings did not increase their tilt. This result indicates that the derived c edge length for Mn end-member stilpnomelane is reasonable, that the length is geometrically controlled, and that the observed tetrahedral tilts from the analysis are a requirement for the geometric connectivity of the islands. Clearly, however, there is a geometric limit to the amount of tetrahedral tilting within the connector rings, which cannot be compensated by a change in cell dimensions. In addition, the result argues against a similar DLS treatment for a hypothetical Fe end-member analysis for parsettensite, unless cell-parameter data for more Fe-rich samples become available.

Application of DLS analysis of stilpnomelane to parsettensite

A fundamental difference between the stilpnomelane and parsettensite structures is that six-membered ring connectors serve to join three adjacent island boundaries in stilpnomelane, but four-membered ring connectors link only two adjacent islands in parsettensite. Because the results from the DLS analysis of stilpnomelane solid solutions suggest that misfit is relieved by adjustments to the islands and (to a lesser degree) the island connectors, and because the geometry of the connectors in parsettensite differs from that in stilpnomelane, it is difficult to assess in detail how the two geometries may relieve misfit between the tetrahedral and octahedral sheets. For example, in parsettensite, warping of the octahedral sheet ($\Delta z = 0.24$ Å) is less than in stilpnomelane (Fe: 0.28 Å, Mn: 0.32 Å), but the significance of these differences cannot be easily evaluated.

Although the stilpnomelane d_{001} value is about 12.13 Å at Mn end-member compositions, this spacing is considerably less than that of parsettensite ($d_{001} = 12.6$ Å). The parsettensite model, as indicated by Fourier analysis (Eggleton and Guggenheim, 1994) and the DLS analysis, has considerable tetrahedral tilting associated with the four-membered ring interisland connector, which is clearly not a requirement in the six-membered ring tetrahedral connectors in stilpnomelane. The higher tetrahedral tilt in parsettensite may reduce Si-Si repulsion by placing the

shared O atom of the four-membered ring more directly between the Si atoms than they would be if the bases of the tetrahedra were, as in the six-membered rings in stilpnomelane, parallel to (001). Thus, the difference in the d_{001} values between a Mn-rich stilpnomelane and parsettensite is the ability of the four-membered ring connectors in parsettensite to tilt so that a tetrahedral edge can be vertical; island curvature is not the major factor.

In stilpnomelane, the interisland connectors have the ability to reduce their lateral dimensions by tetrahedral rotation. In contrast, parsettensite connectors, which are four-membered rings, cannot accomplish such reductions. Thus, parsettensite requires the nearly perfect alignment of islands, since connections are made by rigid four-membered rings. For islands that are too small, neighboring islands are imperfectly aligned, and parsettensite cannot exist.

In Mg- or Fe³⁺-rich stilpnomelane with relatively small lateral dimensions of the islands, the six-membered ring connectors can pull the tetrahedra of neighboring islands closer to maintain registry. However, the interisland connectors approach a ditrigonal configuration with the reduction in size of the lateral axes. As tetrahedral rotation increases within the interisland connectors, Si to Si distances are reduced and Si-Si repulsions would increase, thereby causing tilting of tetrahedra and an increase in the d_{001} value.

The question of the possible coexistence of Mn-rich stilpnomelane and parsettensite remains. Perhaps, because the Mn-Si ratios differ for parsettensite and stilpnomelane, the apparent lack of parsettensite and Mn-rich stilpnomelane intergrowths, which are not yet known to exist, may simply be a result of bulk chemistry. Nothing is known about the stability relations of either Mn-rich stilpnomelane or parsettensite, and experimental studies are needed for a better understanding of their phase relations.

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