

# Parkinsonite, $(\text{Pb}, \text{Mo}, \square)_8\text{O}_8\text{Cl}_2$ , a new mineral from Merehead Quarry, Somerset

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## Abstract

Parkinsonite, ideally  $(\text{Pb}, \text{Mo}, \square)_8\text{O}_8\text{Cl}_2$ , is a new mineral from the Merehead Quarry, Cranmore, Somerset, England. It occurs as compact clusters or patches of red to purplish red bladed crystals, which have an adamantine lustre and a perfect  $\{001\}$  cleavage and occupy fractures and cavities in carbonate vugs in veins of manganese and iron oxide and hydroxide minerals. Associated minerals are mendipite, diaboite, chloroxiphite, wulfenite, cerussite and hydrocerussite. Discrete crystals were not found; intergrown crystalline aggregates are the usual form of occurrence. The maximum grain size is about  $300 \times 100 \mu\text{m}$ , but most grains are appreciably smaller. Parkinsonite was synthesized using high purity chemicals. The measured density of the synthetic material is  $7.32 \text{ g/cm}^3$ ; the calculated density is  $7.39 \text{ g/cm}^3$ , the difference being due to minor impurity and slight porosity in the synthetic sample. Parkinsonite is translucent. Reflectance spectra were obtained in air and in oil. Refractive indices calculated from these (at 589 nm) are for  $R_o$ , 2.58, and  $R_e$ , 2.42, i.e. uniaxial negative.  $\text{VHN}_{50}$  is 113–133 from which the calculated Mohs hardness is 2–2.5.

X-ray studies show that parkinsonite is tetragonal with space group  $I4/mmm$ ,  $\bar{I}42m$ ,  $\bar{I}4m2$ ,  $I4/m\bar{m}$ , or  $I422$  and  $a$  3.9922(3),  $c$  22.514(2) Å. It has a cell volume of  $358.82(5) \text{ \AA}^3$  with  $Z = 1$ . The strongest six lines of the X-ray powder diffraction pattern are [ $d$  in Å ( $hkl$ )] 2.823, 2.813(100) (110,008); 5.63(85) (004); 2.251(33) (116, 0.0.10); 2.988(27) (105); 3.750(15) (006); 1.994(11) (200,118). Averaged electron microprobe analyses give the empirical formula  $\text{Pb}_{6.34}\text{Mo}_{0.89}\square_{0.77}\text{O}_{8.02}\text{Cl}_{1.98}$  on the basis of 10 atoms [O + Cl]. The name is for Reginald F. D. Parkinson, mineral collector of Somerset, UK, who first found the mineral.

KEYWORDS: parkinsonite, new mineral, lead molybdenum oxychloride, Merehead Quarry.

## Introduction

PARKINSONITE, is a new mineral, ideally  $(\text{Pb}, \text{Mo}, \square)_8\text{O}_8\text{Cl}_2$ , from the Merehead Quarry, Cranmore, Somerset, in the south west of England [lat.  $51^\circ 12' \text{N}$  long.  $2^\circ 26' \text{W}$ ]. It is named after Reginald F. D. Parkinson (1928-), mineral collector and dealer, who first found the mineral and who supplied a substantial collection of Merehead Quarry specimens to the Natural History Museum. The mineral and its name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. Type specimens are preserved at the Natural History Museum, Great Britain, as specimen BM 1987,478 and polished section E.1215, BM 1987,479.

## Occurrence

The characteristic suite of secondary lead minerals (mostly oxychlorides) associated with mineralized areas of the Mendip Hills, Somerset, was first described in detail by Spencer and Mountain (1923). At that time, the principal source was the small iron-ore mine at Higher Pitts, near Priddy. In the 1950s, when large-scale limestone production from the Carboniferous Limestone at Merehead Quarry started, veins, fissures and pockets rich in manganese and iron mineralization were encountered. These were associated with a secondary lead mineral assemblage. As quarrying has progressed, new exposures have been temporarily but repeatedly created (Symes and Embrey, 1977).

During the 1960s the mineral collector R. F. D. Parkinson passed to the Natural History Museum, minerals typical of the exposures in Merehead Quarry. Many of the specimens contain fine groups of cream and pinkish purple mendipite enclosing olive-green chloroxiphite within a matrix of cerussite, calcite and unidentified manganese oxides. Some of these mendipite specimens have their cleavage marked by small bright red crystalline patches; these proved to be the new mineral, parkinsonite.

Most specimens of parkinsonite were collected from loose blocks of manganese oxides believed to be derived from Vein 1 (see Symes and Embrey, 1977), but it was not until 1983 that specimens were collected (by Mr D. Lloyd) *in situ* from this vein. These specimens, associated with cerussite and mendipite, were from a manganese-rich pod which formed part of the floor of the second quarried level in the Black Rock Limestone formation. In this association, parkinsonite occurs as small patches (max 3mm) of brownish-red cleavage plates and crystalline aggregates in cerussite, hydrocerussite and mendipite. Less commonly, the mineral is associated with wulfenite or with a new and as yet unnamed boron-bearing lead oxychloride mineral.

### Physical properties

Parkinsonite is red to purplish red (carmine, Ridgway, 1912) and translucent with a scarlet to grenadine-red streak and adamantine lustre, appearing pearly to resinous on bruised surfaces. It does not fluoresce either in short or long wave UV. It is sectile with a perfect {001} cleavage.

Small cleavage fragments (the largest 200µm across) were examined in transmitted light. Those

lying on the perfect cleavage face were brownish-red and in most cases produced a uniaxial negative interference figure, although one or two plates gave a confused figure that appeared to be biaxial with a small 2V. Some smaller fragments, the largest 25 µm, presumably lying parallel, or nearly parallel, to the optic axis were strongly dichroic with O = brownish-red and E = greenish-yellow and showed red and green interference colours (one of these smaller grains consisted of two segments showing straight extinction on rotation at about 13° apart and this divergence (or twinning) may explain the confused interference figure). Most of the grains lying on the perfect cleavage face and normal to the c-axis had an irregular outline, although some showed an additional cleavage direction along one edge; one grain was bounded in the same plane by six cleavage faces, four of them indistinct and two that were fair, adjacent and at right angles to each other. In addition, this grain had numerous straight growth lines on its upper surface; many were at right angles to each other and parallel to the fair cleavage directions. The cleavages of parkinsonite appear to be {001} perfect and possibly {100} fair and {350} indistinct.

Polished sections of the ore-bearing material were prepared using the techniques described in Stanley *et al.* (1991) with polishing finished by 0.25 µm diamond. Together with the associated minerals, parkinsonite takes a good polish. It has a VHN<sub>50</sub> of 122 with a range of 113–133 from 10 indentations. The Mohs hardness calculated from the VHN values is 2–2.5. The specific gravity could not be measured due to a lack of pure material and because of the size of the individual crystals. However, the mineral was synthesized and density of the synthesized product, determined

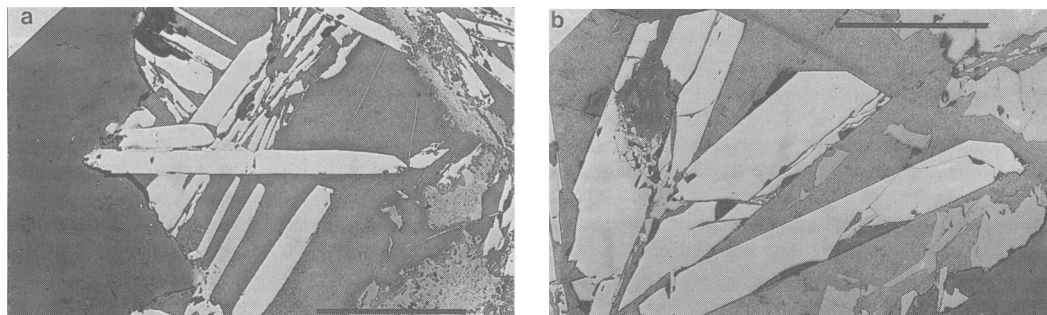


FIG. 1 Reflected light photomicrographs of parkinsonite. (a) Prismatic intergrown crystals of parkinsonite in cerussite with paralaurionite at the margin. Scale bar is 250µm. (b) Prismatic crystals of parkinsonite projecting into cerussite and illustrating {001} cleavage and irregular fracture. Associated mineral is wulfenite. Scale bar is 250µm.

on a Berman balance by immersion in ethylene dibromide, is  $7.32 \text{ g/cm}^3$ . This is in good agreement with the calculated density of  $7.39 \text{ g/cm}^3$ , the difference being due to minor impurity and the slight porosity of the synthetic product. Reflected light photomicrographs of parkinsonite are given in Fig. 1.

In reflected light, parkinsonite is grey with moderate bireflectance and weak pleochroism from pale grey to pale bluish grey. It displays weak to moderate anisotropy, but the rotation tints (if any) are masked by the internal reflections. The latter, deep red to orange red, are abundant and the usual precautions were taken to ensure accurate reflectance measurements, which were obtained in air and in oil using the procedures summarized in Criddle *et al.*, (1983), with a SiC standard (Zeiss no 472). Pleochroism is absent. The data are given in Table 1 and Fig. 2. Only two

grains were measurable: the identity of dispersion and similarity of reflectance for one vibration direction ( $R_{\max}$ ) of these grains suggested that the mineral is optically near-uniaxial. Refractive indices (calculated using the Koenigsberger equations) at 589 nm are (for  $R_o$  and  $R_e$  respectively) 2.58(1) and 2.42; i.e. confirming the transmitted light observation that the mineral is uniaxial negative.

### Synthesis

The synthetic parkinsonite used in this work was prepared as part of a wider study of lead oxychlorides. A series of seven mixtures of  $\text{PbO}$ ,  $\text{MoO}_3$  and  $\text{PbCl}_2$  (BDH Analar) were prepared, covering the composition range  $\text{Pb}_{7.5}\text{Mo}_{0.5}\text{O}_8\text{Cl}_2$  to  $\text{Pb}_{4.5}\text{Mo}_{1.5}\text{O}_8\text{Cl}_2$ . 10 g of each mixture were heated with swirling in a covered platinum crucible

TABLE 1. Reflectance data for two grains of parkinsonite.

$\lambda$ nm	Grain 1				Grain 2			
	$R_o$	$R'_e$	${}^{im}R_o$	${}^{im}R'_e$	$R_o$	$R'_e$	${}^{im}R_o$	${}^{im}R'_e$
400	22.6	21.8	8.92	8.40	22.4	22.2	8.79	8.68
420	22.4	21.2	8.79	7.87	22.25	21.9	8.68	8.45
440	22.3	20.5	8.73	7.43	22.1	21.6	8.57	8.22
460	22.15	19.9	8.63	7.05	21.9	21.2	8.45	8.00
<b>470</b>	<b>22.0</b>	<b>19.6</b>	<b>8.56</b>	<b>6.88</b>	<b>21.8</b>	<b>21.05</b>	<b>8.37</b>	<b>7.63</b>
480	21.9	19.35	8.50	6.71	21.7	20.9	8.28	7.26
500	21.6	18.9	8.25	6.40	21.4	20.6	8.05	7.29
520	21.2	18.5	7.99	6.13	20.95	20.1	7.74	7.19
540	20.6	18.1	7.62	5.89	20.4	19.6	7.42	6.90
<b>546</b>	<b>20.5</b>	<b>18.0</b>	<b>7.51</b>	<b>5.82</b>	<b>20.3</b>	<b>19.5</b>	<b>7.32</b>	<b>6.82</b>
560	20.2	17.75	7.26	5.66	20.0	19.2	7.10	6.62
580	19.8	17.5	7.00	5.51	19.6	18.9	6.84	6.41
<b>589</b>	<b>19.6</b>	<b>17.4</b>	<b>6.89</b>	<b>5.46</b>	<b>19.45</b>	<b>18.75</b>	<b>6.75</b>	<b>6.34</b>
600	19.4	17.25	6.79	5.41	19.3	18.6	6.66	6.27
620	19.1	17.1	6.60	5.30	19.0	18.4	6.53	6.16
640	18.9	17.0	6.50	5.22	18.8	18.2	6.44	6.08
<b>650</b>	<b>18.8</b>	<b>16.95</b>	<b>6.45</b>	<b>5.20</b>	<b>18.7</b>	<b>18.15</b>	<b>6.39</b>	<b>6.04</b>
660	18.7	16.9	6.40	5.18	18.6	18.1	6.35	6.01
680	18.6	16.7	6.32	5.13	18.5	18.0	6.27	5.94
700	18.5	16.7	6.25	5.10	18.4	17.8	6.20	5.89
Colour values (Illuminant C)								
$x$	0.298	0.297	0.288	0.286	0.298	0.298	0.288	0.285
$y$	0.307	0.302	0.299	0.290	0.307	0.306	0.299	0.296
$Y^{\%}$	20.3	17.9	7.39	5.78	20.1	19.4	7.22	6.75
$\lambda_d$	481	476	481	476	481	479	480	478
$P_e^{\%}$	3.0	3.0	5.5	5.7	2.9	2.9	5.3	5.3

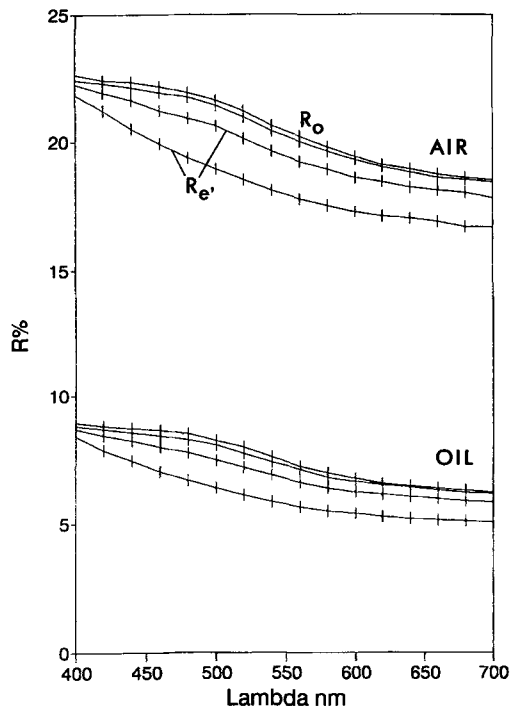


Fig. 2 Reflectance spectra for parkinsonite in air and oil.

to dull red heat until total melting and assimilation of the solid was achieved. They were removed from the heat, swirled till solid, and the outside of the crucible was cooled rapidly by partial immersion in cold water, after which the intact solid mass was easily removed. As the  $\text{PbCl}_2$  and  $\text{MoO}_3$  content of the starting mixtures increased, complete assimilation of solid by the melt took longer and more fumes of  $\text{PbCl}_2$  were evolved. The colour of the solid product also varied progressively with composition from orange-brown to deep lake-red.

A starting mixture consisting of 75.5 wt.%  $\text{PbO}$ , 7.4 wt.%  $\text{MoO}_3$ , and 17.1 wt.%  $\text{PbCl}_2$  gave rise to a product with composition  $\text{Pb}_{6.55}\text{Mo}_{0.83}\text{O}_{8.08}\text{Cl}_{1.92}$  and it was this that was used in this study.

#### Chemical composition

Electron probe microanalysis was used to determine the chemistry of parkinsonite. The analyses were obtained on a Cambridge Instruments Microscan IX instrument operated at 20kV, with a beam current of  $2.50 \times 10^{-8}$  amps on the Faraday cage.

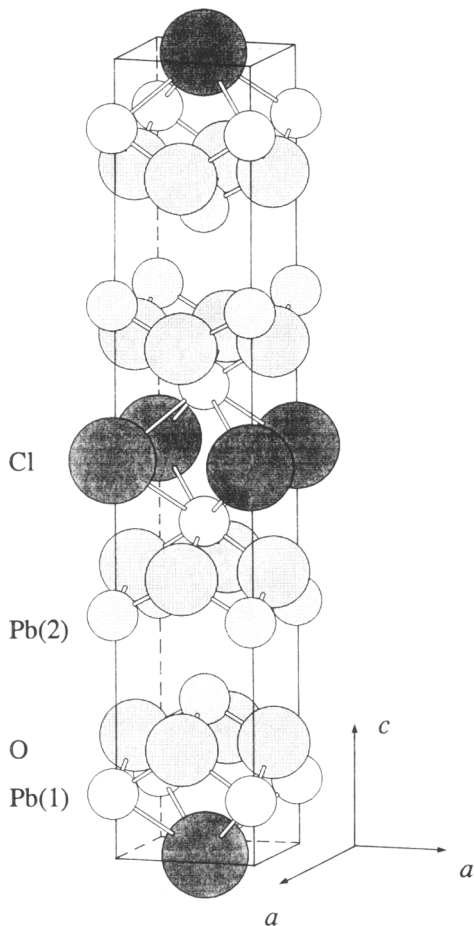


Fig. 3 The  $I4/mmm$  model structure proposed for parkinsonite; topologically this is identical to the structure of  $\text{Pb-Mo-oxbromide}$  determined by Aurivillius (1982).

The electron microprobe analyses for natural and synthetic parkinsonite are given in Table 2. The empirical formulae derived from these are  $\text{Pb}_{6.34}\text{Mo}_{0.89}\square_{0.77}\text{O}_{8.02}\text{Cl}_{1.98}$  for natural parkinsonite, and  $\text{Pb}_{6.55}\text{Mo}_{0.83}\square_{0.62}\text{O}_{8.08}\text{Cl}_{1.92}$  for the synthetic, on the basis of 10 atoms [O + Cl].

#### X-ray powder diffraction study

Parkinsonite proved to be difficult to characterize, partly due to the paucity of material but also because of difficulties in indexing the X-ray powder data. It was found that the Debye-

TABLE 2. Electron microprobe data for parkinsonite and synthetic parkinsonite.

wt. %	PbO	MoO <sub>3</sub>	Cl	less O=Cl	Total
1	88.4	8.0	4.4	1.0	100.8
2	88.2-88.9	7.7-8.3	4.3-4.5		
3	89.0	7.3	4.1	0.9	99.5

1. Parkinsonite, average of six analyses
2. Parkinsonite, range of six analyses
3. Synthetic parkinsonite, average of three analyses

Cambridge Instruments Mark 9 operated at 20 kV with a beam current of  $2.50 \times 10^{-8}$  A on the Faraday cage.

Standards: mendipite, pure Mo

Scherrer data (Table 3) were subject to absorption effects, and it was necessary therefore to attempt to obtain a diffractometer pattern for the small amount of natural material available and also for the synthetic specimen. These data are given in Tables 4 and 5 respectively. The effects of absorption on the diffraction pattern are demonstrated by comparing Tables 3 and 4. Unlike the Debye-Scherrer (transmission) film data, absorption by the diffractometer sample can be regarded as constant at all angles and, for this sample, (linear absorption coefficient =  $1569 \text{ cm}^{-1}$ ) diffractometer peak positions are essentially unaffected by the absorption. The refined unit cell parameters from the diffractometer data (Table 4) are  $a$  3.9922(3),  $c$  22.514(2) Å,  $V$  358.82(5) Å<sup>3</sup>. Single crystal Weissenberg and precession photographs of the natural parkinsonite sample show Laue symmetry  $I4/mmm$ . The only systematic absences are for  $h+k+l = 2n+1$ ,

TABLE 3. Debye-Scherrer powder X-ray diffraction data for parkinsonite:  $\text{Pb}_{6.34}\text{Mo}_{0.89}\text{O}_8\text{Cl}_2$ 

$a = 3.988(1)$ $c = 22.34(1)$ Å							
$I4/mmm, I42m, \bar{I}4m2, I4mm$ or $I422$							
$I_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$	$I_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$
18	5.58	5.587	004	24	1.243	1.242	0.0.18
23	3.910	3.925	101	8	1.197	1.194	316
8	3.720	3.724	006	15	1.153	1.149	318
32	3.507	3.515	103	15	1.144	1.144	2.0.16
100	2.983	2.975	105	<1	1.127	1.128	1.0.19
78	2.816	2.819	110	9	1.099	1.098	3.1.10
<1	2.706	2.733	112	14	1.074	1.073	325
20	2.494	2.492	107	15	1.058	1.058	2.1.17
21	2.244	2.248	116			1.045	327
75	1.989	1.984	118	8	1.045	1.044	3.1.12
12	1.872	1.877	204	6	0.9965	0.9967	400
23	1.756	1.757	206	<1	0.9742	0.9747	2.0.20
17	1.735	1.734	213	17	0.9473	0.9451	415
51	1.658	1.656	215			0.9364	332
15	1.627	1.623	208	12	0.9364	0.9359	3.1.16
33	1.586	1.579	1.0.13	15	0.9323	0.9316	2.2.18
18	1.560	1.557	217	14	0.8896	0.8887	422
9	1.492	1.488	2.0.10	6	0.8662	0.8662	3.3.10
18	1.410	1.410	220	9	0.8576	0.8595	0.0.26
9	1.368	1.367	224	8	0.8503	0.8493	428
6	1.309	1.308	303	9	0.8449	0.8454	4.0.14
17	1.277	1.274	305	15	0.8277	0.8280	4.2.10
24	1.263	1.260	310				
<1	1.253	1.253	312				
		1.252	1.1.16				

Debye-Scherrer film data,  $\text{CuK}\alpha$  radiation. Line positions and intensities not corrected for the effects of absorption. Unit cell refined from 44 indexed reflections through least-squares cycles.

TABLE 4. Powder X-ray diffraction data for parkinsonite:  $\text{Pb}_{6.34}\text{Mo}_{0.89}\text{Cl}_2$ 

$a = 3.9922(3) \text{ c} = 22.514(2) \text{ \AA}$   
 $I4/mmm, I42m, I\bar{4}m2, I4mm$  or  $I422$

$I_{\text{obs}}$	$I_{\text{obs}}^*$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$
4		11.27	11.257	002
85		5.63	5.628	004
4	17	3.931	3.931	101
15		3.750	3.752	006
8	29	3.528	3.525	103
27	100	2.988	2.987	105
100		{2.823	2.823	110
		{2.813	2.814	008
6	22	2.505	2.505	107
33		2.251	{2.256	116
			{2.251	0.0.10
11	41	1.994	{1.996	200
			{1.993	118
2	7	1.880	1.881	204
11		1.876	1.876	0.0.12
3	11	1.7598	1.7602	1.1.10
2	7	1.7367	1.7369	213
6	22	1.6598	1.6597	215
2	7	1.6284	1.6282	208
4		1.6086	1.6082	0.0.14
5	19	1.5885	1.5888	1.0.13
2	7	1.5619	{1.5626	1.1.12
			{1.5610	217
<1	3	1.4948	1.4936	2.0.10
2	7	1.4113	1.4115	220
2		1.4077	1.4071	0.0.16
1	5	1.2766	1.2762	305
2	7	1.2625	1.2625	310
7		1.2504	1.2508	0.0.18
2	8	1.2430	1.2431	2.1.13
1	5	1.1517	1.1519	318
<1	3	1.0752	1.0752	325
<1	3	1.0600	1.0599	2.0.18

TABLE 5. Powder X-ray diffraction data for synthetic parkinsonite:  $\text{Pb}_{6.55}\text{Mo}_{0.82}\text{O}_8\text{Cl}_2$ 

$a = 3.9874(5) \text{ c} = 22.535(3) \text{ \AA}$   
 $I4/mmm, I42m, I\bar{4}m2, I4mm$  or  $I422$

$I_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$hkl$
1	11.27	11.267	002
20	5.64	5.634	004
11	3.925	3.926	101
4	3.757	3.756	006
25	3.522	3.522	103
100	2.986	2.986	105
74	2.817	{2.819	110
		{2.817	008
8	2.504	2.505	107
13	{2.256	2.255	116
		2.252	2.254
34	1.992	{1.993	118
		{1.993	200
4	1.879	{1.880	204
		{1.878	0.0.12
12	1.7607	1.7610	1.1.10
3	1.7330	1.7350	213
19	1.6577	1.6581	215
5	1.6284	1.6273	208
<1	1.6098	1.6096	0.0.14
15	1.5903	1.5897	1.0.13
5	1.5624	{1.5630	1.1.12
		{1.5599	217
2	1.4938	1.4932	2.0.10
4	1.4092	{1.4097	220
		{1.4084	0.0.16
2	1.2747	1.2748	305
6	1.2605	1.2607	310
<1	1.2498	1.2519	0.0.18
5	1.2437	1.2430	2.1.13
2	1.1510	1.1509	318
2	1.0740	1.0740	325
2	1.0606	1.0602	2.0.18

Diffraction data,  $\text{CuK}\alpha$  radiation. Unit cell refined from 30 indexed reflections through least-squares cycles. Silicon external standard. Very small sample, acetone-mounted on single-crystal-silicon substrate. Because of the  $\{00l\}$  cleavage, all  $00l$  reflections have enhanced intensities due to preferred orientation in the diffractometer sample mount. Therefore, integrated intensities relative to the 105 reflection for non- $00l$  reflections are also listed  $I_{\text{obs}}^*$

Diffraction data,  $\text{CuK}\alpha$  radiation. Unit cell refined from 27 indexed reflections through least-squares cycles. Silicon external standard.

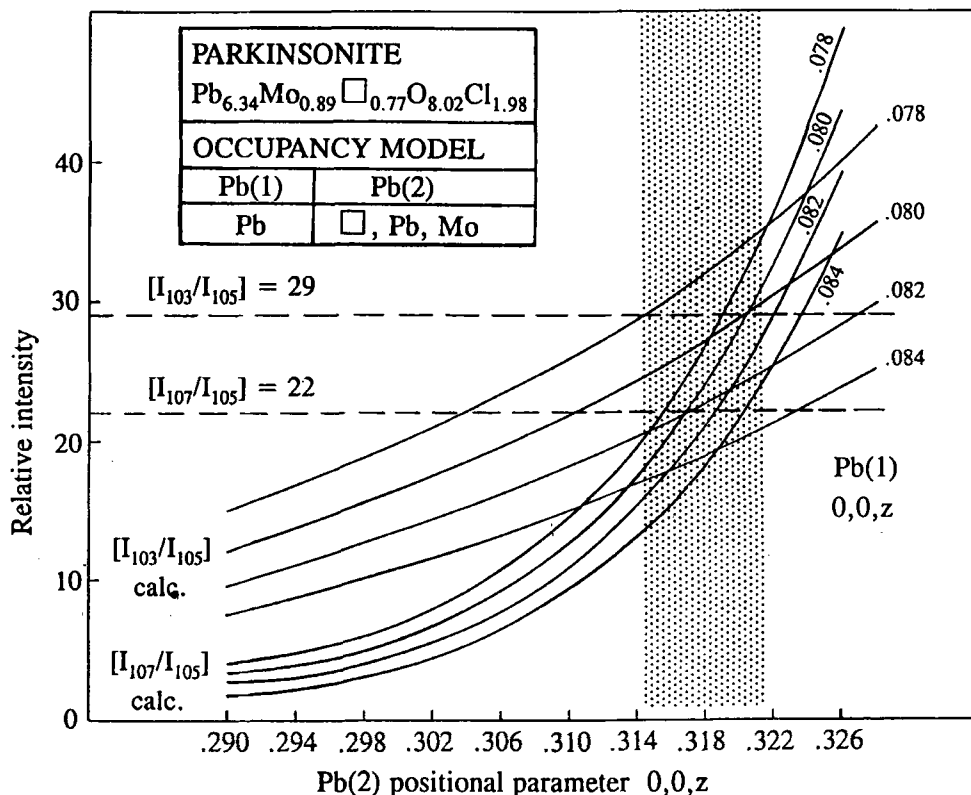


FIG. 4 Calculated intensities of 103 and 107 reflections (relative to 105) and their dependence on the Pb positional parameters in the model structure for parkinsonite constructed with Mo and vacancies on the Pb(2) sites. Observed intensities for parkinsonite are shown by horizontal dotted lines. See text for details.

thus possible space groups are  $I4/mmm$ ,  $I\bar{4}2m$ ,  $I\bar{4}m2$ ,  $I4/m$  or  $I422$ .

Aurivillius (1982) investigated a number of non-stoichiometric mixed lead oxyhalides that have many properties in common with parkinsonite. He produced tetragonal crystals ( $a = 4.015$ ,  $c = 22.92$  Å) from a starting composition  $7\text{PbO}\cdot\text{MoO}_3\cdot\text{PbBr}_2$ , and their measured density gave approximately 0.9 of the formula unit per unit cell. Aurivillius refined the structure of this Pb-Mo-oxybromide in space group  $I4/mmm$  with  $8\text{Pb}(\text{Mo})$  fully occupying two 4-fold special positions,  $00z$ ; with  $z(1) = 0.085$  and  $z(2) = 0.307$  (see Fig. 3). However, since no information is given by Aurivillius about the composition(s) of any crystallized phase(s), or about the composition of the Pb-Mo-oxybromide itself, the role of cation-site vacancies in the structure cannot be properly assessed.

By using the Aurivillius Pb-Mo-oxybromide  $I4/mmm$  structure as a model structure for parkinsonite,

we have attempted to establish the location of the site vacancies in parkinsonite from a comparison of observed and calculated powder diffraction intensities. In order to do this, the positions of the two metal sites, Pb(1) and Pb(2), first need to be determined for the oxychloride (parkinsonite) rather than the oxybromide. The  $c$  cell parameter for the oxybromide (22.92 Å) is slightly greater than in parkinsonite (22.51 Å), as might be expected for the larger halogen (Br) occupying the special position  $001/2$ . For topologically identical structures determined by Aurivillius, the Pb(1)-Br distances in Pb-Mo-oxybromide and in Pb-W-oxybromide are 3.45 Å and 3.44 Å respectively, and in Pb-P-oxychloride the Pb(1)-Cl distance is 3.36 Å. If this latter value is appropriate for Pb(1)-Cl in parkinsonite, then the Pb(1) atomic coordinate ( $0\ 0\ z$ ) in parkinsonite must have a  $z$  value smaller than 0.085 (the value in the oxybromide) and is probably in the range  $0.085 > z > 0.078$ .

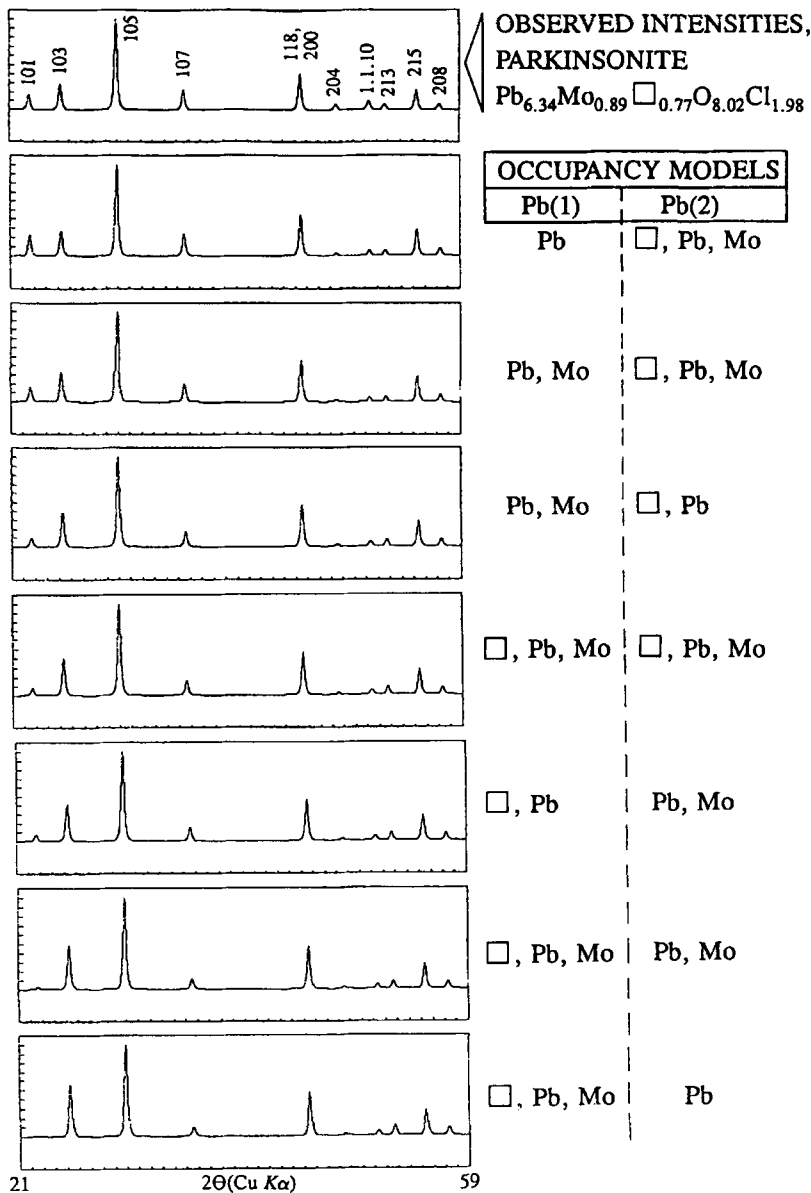


FIG. 5 Observed powder diffraction intensities for parkinsonite compared with those calculated for different possible cation occupancy/vacancy models. The pattern at the top is a representation of the non-00/ reflections of parkinsonite convoluted from observed intensities (00/ reflections have been omitted because they have enhanced intensities due to preferred orientation effects). Clearly the 'best-fit' models are those with all vacancies assigned to Pb(2) sites.

In the  $I4/mmm$  model structure the halogen is on the special position  $00\frac{1}{2}$  and, apart from the Pb coordinates, the only other variable parameter is that of the oxygen at special position  $\frac{1}{2}0z$ . However, oxygen will

only contribute to the scattered amplitude for  $hkl$  with  $h = 2n$ . Therefore, in principle, an estimate of Pb(1) and Pb(2) atomic coordinates can be made from the observed intensities such as 103 and 107 (see Fig. 4); for these reflections,



only Pb and Cl contribute to the scattered amplitude. For the experimentally observed intensities and for the expected range of the Pb(1) coordinate (0.078-0.085), it turns out that 107 is quite sensitive to the Pb(2) positional parameter. A satisfactory solution is found with  $z(1) \approx 0.08$  and  $z(2) \approx 0.318$  (see Fig. 4) for an occupancy model which places all the vacancies and Mo in Pb(2).

Using these Pb coordinates, together with the oxygen coordinate determined by Aurivillius for the oxybromide, powder diffraction intensities for parkinsonite have been calculated for different possible cation occupancy/vacancy models, and the results are shown in Fig. 5. Reduced scattering powers appropriate to each partial occupancy model have been incorporated in the calculated structure factor amplitudes. A further reduction in structure factor amplitude has also been made using the anisotropic temperature factors found for the oxybromide by Aurivillius (1982). The calculated powder diffraction intensities incorporate multiplicity, arc length, Lorentz and polarization factors. Because of the perfect {001} cleavage of parkinsonite, 00 $l$  reflections have enhanced intensities due to preferred orientation in the diffractometer mount, so only the non-00 $l$  reflections are compared in Fig. 5. As expected, the  $h0l$  ( $l = 2n + 1$ ) reflections are sensitive to the different partial occupancy schemes involving reduced scattering on the Pb sites. The intensities of the other reflections shown in Fig. 5 are well-replicated by any of the models; this indicates that the atomic positions in the model structure provide a close description of the parkinsonite structure. It is clear that the vacancies occur only on Pb(2) sites; any of the models with vacancies on Pb(1) give poorer fits. Pb scattering cannot be distinguished from Mo scattering with certainty, however, the model with Pb(1) fully occupied by Pb and with Mo only on Pb(2) gives the best fit. Since the vacancies appear to occur exclusively on Pb(2), it is reasonable to expect that Mo<sup>6+</sup> (replacing Pb<sup>2+</sup>) will also be partitioned into Pb(2) sites in close association with the vacancies in order to maintain local charge balance.

The Pb coordinates estimated for parkinsonite define the thickness of the Pb(2)-O-Pb(1)-Cl-Pb(1)-O-Pb(2) layer structure (see Fig. 3). It is apparent from our results that the oxychloride 'sandwich' layer is slightly thinner than that of the oxybromide investigated by Aurivillius (1982). Factors that may be responsible for this include the smaller halogen ion in parkinsonite and the possibility of a higher proportion of smaller cations (Mo and 'vacancies') substituting for Pb in parkinsonite.

## Discussion

In addition to the Merehead Quarry locality, parkinsonite has been found at Wesley mine, Didsbury, near Bristol (Alabaster, 1989), where it is again a constituent of a lead oxychloride assemblage associated with manganese oxide veins in the Carboniferous Limestone.

The close association of parkinsonite with wulfenite on some specimens might indicate a common supply of molybdenum into the mineralizing solutions responsible for the lead oxychloride assemblages in this area. Molybdenum could have been released during the weathering and erosion of shales, possibly those associated with the Coal Measures (Din *et al.*, 1986). That the reactions to form the oxychloride assemblage took place at low temperature has been suggested by Symes and Embrey (1977) and the work of Humphreys *et al.* (1980) has shown that mendipite occupies a large stability field and should readily form from cold, aqueous, mineralizing solutions containing variable amounts of lead and chloride ions over a broad pH range. The intimate association of parkinsonite with mendipite and other oxychloride minerals indicates that it could also be formed by similar cold, aqueous solutions, whenever molybdenum came into the system.

## Acknowledgements

Many people have worked on the attempt to characterize this mineral in the time since its first discovery, and we particularly wish to thank Eva Fejer and Peter Embrey (formerly Natural History Museum), Paul Keller (Stuttgart), and Joe Finney and Robert Hamilton (USA). The authors thank Foster Yeoman PLC for permission to study mineralization in Merehead Quarry.

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[Manuscript received: 16th July 1993  
revised 21 September 1993]