AM-81-252

American Mineralogist, Volume 66, pages 376-384, 1981

The crystal structure of bartonite, a potassium iron sulfide, and its relationship to pentlandite and djerfisherite

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Abstract

The structure of a bartonite crystal from Coyote Peak, Humboldt County, California, has been solved and refined in anisotropic mode to a conventional $R = 0.068$ for 504 observed reflections. The tetragonal unit cell [space group $I4/mmm$, $a = 10.424(1)$, $c = 20.626(1)$Å] contains 2 formula units, which were found by site-occupancy refinement to be $(K,Na)_{5.68}(Fe,Cu,Ni)_{20.27}S_{26}(S,Cl)_{0.93}$. The structure is closely related to those of the cubic minerals pentlandite and djerfisherite. All three minerals have cubic close-packed sulfur layers, which with eight Fe atoms in edge-shared FeS_4 tetrahedra form Fe_8S_{14} cube clusters. Substitutions of K for S in the close-packed layers, the stacking sequence of the cube clusters, and variations in the kinds of atoms and vacancies occupying octahedral and tetrahedral sites explain the structural differences among the three minerals. Average bond distances in bartonite are: Fe–S, 2.289Å; Fe–Fe, 2.724Å; and K–S, 3.369Å.

Introduction

Bartonite was discovered at Coyote Peak, Humboldt County, California, and a complete mineralogical description is given in the accompanying paper by Czamanaske *et al.* (1981). From their study and the present one, bartonite is assigned the idealized chemical formula $K_{6-x}Fe_{24-y}S_{26}(S,Cl)_{1-z}$ with 2 formula units in the tetragonal cell of $I4/mmm$: $a = 10.424(1)$, $c = 20.626(1)$Å. A preliminary description of the crystal structure was given by Clark *et al.* (1979).

Bartonite has a close relationship to pentlandite ($Fm3m$, $a = 10.04$Å) and djerfisherite ($Pm3m$, $a = 10.36$Å), with a shift to tetragonal symmetry and doubled c axis. This property was recognized to be the result of a change in stacking sequence of the Fe_8S_{14} clusters, which are a prominent feature of these structures. The structure analysis showed that other factors, including cation substitutions and vacancies, also are significant in the crystal chemistry of bartonite.

Experimental and computational details

The crystal selected for intensity measurements was cut from a larger crystal to obtain an irregular fragment about 0.1 mm in longest dimension, slightly elongated in an oblique direction. The unit cell parameters determined by Czamanske *et al.* (1981) are given in Table 1. The c axis was oriented parallel to the ϕ axis of a Picker single-crystal diffractometer and 1742 reflections in the angular range 5° to 60° 2θ were measured in Nb-filtered Mo$K\alpha$ radiation. A standard reflection was monitored after each 30 measurements; no significant variation was noted during the data collection. Following correction of intensities for Lorentz and polarization effects and conversion to $|F_o|$, the symmetry-equivalent reflections ($hkl = khl$) were averaged and a set of 817 data was obtained, of which 504 with $|F_o| > 3\sigma(F)$ (where σ was based on counting statistics) were used for the structure analysis. No absorption corrections were made because the crystal shape was irregular al-

0003–004X/81/0304–0376$02.00

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OBSERVED AND CALCULATED STRUCTURE FACTORS FOR BARTONITE

E, * denote data excluded from least squares analysis.

Reflections marked * were measured less than $3\sigma(F)$, and set to zero.

OBSERVED AND CALCULATED STRUCTURE FACTORS COMPARED FOR BARTONITE

0,0,L

2	109E	-192
4	0*	-45
6	243	236
8	134	-151
10	185	183
12	260	258
14	218	-204
16	795	798
18	0*	37
20	62	-69
22	0*	27
24	0*	-57
26	96	104
28	165	168

1,0,L

1	182	-206
3	105	-109
5	135	128
7	230	223
9	113	103
11	46	50
13	61	-59
15	155	-155
17	105	-104
19	49	52
21	63	50

2,0,L

0	0*	-25
2	0*	-2
4	0*	31
6	128	121
8	65	60
10	92	-105
12	0*	33
14	123	125
16	0*	-35
18	60	-58
20	0*	19
22	54	64
24	61	51

3,0,L

1	242	239
3	154	156
5	0*	38
7	159	-151
9	220	-220
11	45	44
13	200	202
15	136	136
17	57	34
19	0*	48
21	0*	-27
23	62	-70
25	66	-48

4,0,L

0	129	-141
2	167	154
4	86	80
6	198	-187
8	1105E	1146
10	91	-93
12	71	-69
14	76	82
16	127	-127
18	103	115
20	197	201
22	153	-157
24	367	380

5,0,L

1	161	160
3	42	-31
5	133	-139
7	99	-109
9	97	-96
11	0*	-32
13	47	23
15	0*	30
17	55	52
19	62	47
21	74	-87
23	100	-104

6,0,L

0	223	227
2	0*	3
4	0*	13
6	141	141
8	66	-69
10	0*	-7
12	0*	69
14	64	71
16	99	98
18	0*	-31
20	0*	-12
22	67	74

7,0,L

1	188	-185
3	0*	25
5	198	198
7	156	159
9	56	30
11	57	69
13	0*	40
15	104	-95
17	127	-135
21	103	103
23	71	79

8,0,L

0	812	812
2	154	-152
4	0*	-29
6	89	78
8	127	-136
10	0*	37
12	137	131
14	129	-138
16	456	459
18	55	-25
20	64	-55

9,0,L

1	0*	-2
3	80	-84
5	0*	-17
7	84	79
9	86	79
11	0*	18
13	80	-78
15	85	-71
17	59E	7
19	55	33

OBSERVED AND CALCULATED STRUCTURE FACTORS COMPARED FOR BARTONITE

10,0,L

0	75	-49
2	66	64
4	0*	7
6	0*	35
8	172	174
10	0*	-11
12	0*	-13
14	88	80
16	0*	-51
18	0*	24
20	65	41

11,0,L

1	0*	33
3	74	71
5	0*	22
7	108	-109
9	156	-159
11	0*	10
13	99	118
15	0*	63
17	65	-26

12,0,L

0	89	-78
2	0*	21
4	85	54
6	67	-80
8	371	373
10	79	-78
12	0*	-9
14	60	44

13,0,L

1	65	68
3	0*	-4
5	65	-44
7	0*	11
9	0*	29

14,0,L

0	158	152
2	0*	-9
4	0*	-43
6	0*	46
8	70	-52

1,1,L

0	152	-149
2	312E	275
4	31	1
6	280	-277
8	74	69
10	238	-242
12	0*	26
14	258	252
16	125	-121
18	79	69
20	73	58
22	140	-141

2,1,L

1	0*	6
3	0*	6
5	74	61
7	0*	-6
9	73	-65
11	0*	16
13	91	91
15	0*	-21
17	0*	-13
19	0*	44
21	52	34
23	0*	-25

3,1,L

0	204	190
2	300	-296
4	45	42
6	424	424
8	125	-123
10	171	168
12	107	101
14	189	-187
16	48	44
18	70	-76
20	0*	28
22	168	169
24	0*	-46

4,1,L

1	159	157
3	0*	8
5	84	-95
7	160	-162
9	183	-185
11	0*	-20
13	78	82
15	64	62
17	53	28
19	0*	32
21	74	-69
23	86	-97
25	58	-38

5,1,L

0	77	72
2	236	-243
4	44	-44
6	213	205
8	126	-119
10	58	59
12	48	35
14	152	-154
16	0*	-3
18	70	-69
20	0*	8
22	83	87

6,1,L

1	0*	13
3	0*	22
5	92	102
7	74	67
9	0*	18
11	62	54
13	68	68
15	0*	-19
17	0*	1
19	80E	50
21	56	58
23	0*	5

7,1,L

0	95	-89
2	240	235

OBSERVED AND CALCULATED STRUCTURE FACTORS COMPARED FOR BARTONITE

7,1,L

4	0*	47
6	188	-181
8	72	80
10	162	-158
12	61	41
14	241	240
16	88	-87
18	86	72
20	62	59
22	118	-113

8,1,L

1	141	-144
3	85	-85
5	0*	14
7	67	64
9	0*	12
11	0*	-11
13	63	-59
15	115	-116
17	95	-92
19	0*	13
21	0*	13

9,1,L

0	0*	-32
2	70	76
4	0*	3
6	59	-78
8	49	30
10	91	-80
12	0*	18
14	82	89
16	0*	-48
18	0*	32
20	0*	35

10,1,L

1	68	68
3	55	54
5	67	43
7	0*	15
9	0*	2
11	0*	36
13	85	83
15	0*	30
17	0*	31
19	65	46

11,1,L

0	0*	50
2	137	-145
4	0*	3
6	165	168
8	89	-87
10	72	69
12	0*	36
14	111	-113
16	0*	16
18	72	-57

12,1,L

1	63	26
3	0*	-15
5	0*	-37
7	73	-71
9	103	-86
11	0*	-15

13,1,L

0	0*	42
2	0*	-24
4	0*	17
6	62	62

2,2,L

0	0*	38
2	44	30
4	711	-698
6	0*	24
8	0*	-33
10	54	50
12	397	-380
14	0*	-37
16	75	-58
18	102	90
20	221	-212
22	84	-63
24	0*	-45
26	0*	72
28	109	-112

3,2,L

1	97	96
3	0*	1
5	56	57
7	88	89
9	55	58
11	49	55
13	51	47
15	0*	-15
17	50	41
19	60	76
21	0*	28
23	0*	-17
25	0*	50
27	72	50

4,2,L

0	86	79
2	42	-50
4	0*	-25
6	89	86
8	0*	-52
10	88	-84
12	0*	26
14	65	69
16	0*	19
18	0*	-63
20	0*	-12
22	57	56

5,2,L

1	79	-85
3	0*	-1
5	88	83
7	0*	-29
9	99	-102
11	0*	7
13	88	91
15	53	-39
17	0*	-61
19	0*	11
21	65	58

OBSERVED AND CALCULATED STRUCTURE FACTORS COMPARED FOR BARTONITE

	6,2,L	
0	0*	21
2	54	63
4	399	-390
6	0*	59
8	0*	5
10	79	59
12	263	-263
14	0*	14
16	0*	-42
18	80	80
20	165	-156
22	60	-29
24	0*	-22
26	62	59
	7,2,L	
1	125	110
3	0*	-5
5	0*	-11
7	52	57
9	66	68
11	45	36
13	0*	15
15	0*	4
17	63	67
19	57	72
	8,2,L	
0	0*	-15
2	0*	-37
4	60	-52
6	0*	5
8	0*	28
10	63	-71
12	60E	-25
14	49	28
16	58	-27
18	59	-37
	9,2,L	
1	55	-48
3	50	47
5	80	90
7	52	-24
9	67	-80
11	0*	20
13	113	107
	10,2,L	
0	0*	15
2	0*	52
4	203	-208
6	80	70
8	0*	-23
10	61	46
12	152	-147
14	0*	35
16	0*	-18
18	0*	46
20	104	-102
	11,2,L	
1	0*	51
3	64	-34
5	0*	-28
7	0*	39
9	0*	53
11	0*	12
13	0*	-27
	12,2,L	
0	64	58
2	0*	-23
4	59	-49
6	0*	3
8	0*	11
10	0*	-21
12	0*	-17
	13,2,L	
1	0*	-22
3	56	47
5	72	80
7	0*	-2
9	0*	-37
	14,2,L	
0	0*	-37
2	0*	28
4	115	-105
6	68	38
	3,3,L	
0	0*	-36
2	399	395
4	76	73
6	231	-231
8	170	176
10	176	-170
12	69	62
14	316	322
16	79	-81
18	131	128
20	84	83
22	146	-147
24	68	50
	4,3,L	
1	193	-193
3	37	-24
5	164	162
7	177	183
9	52	61
11	58	54
13	0*	-5
15	128	-124
17	115	-125
19	49	44
21	74	77
23	67	57
	5,3,L	
0	112	-108
2	186	181
4	39	45
6	155	-159
8	0*	37
10	163	-171
12	52	46
14	207	208
16	85	-93
18	0*	41
20	60	55
22	89	-89

OBSERVED AND CALCULATED STRUCTURE FACTORS COMPARED FOR BARTONITE

	6,3,L	
1	127	127
3	58	63
5	49	51
7	55	52
9	52	37
11	70	57
13	82	91
15	0*	38
17	54	59
19	70	74
	7,3,L	
0	195	192
2	191	-193
4	0*	15
6	321	324
8	49	-57
10	187	183
12	65	69
14	158	-176
16	67	71
18	51	-35
20	0*	20
22	150	150
	8,3,L	
1	84	77
3	0*	17
5	50	-37
7	119	-120
9	143	-148
11	0*	-4
13	67	68
15	51	48
17	0*	6
19	0*	14
21	0*	-39
23	69	-67
	9,3,L	
0	0*	34
2	85	-89
4	53	49
6	145	148
8	60	-62
10	56	39
12	67	69
14	54	-41
16	0*	4
18	61	-45
20	0*	27
22	81	85
	10,3,L	
1	0*	35
3	0*	34
5	84	87
7	70	85
9	61	60
11	58	58
13	0*	46
15	0*	2
17	0*	23
	11,3,L	
0	0*	-46
2	150	155
4	0*	-5
6	129	-145
8	68	77
10	87	-95
12	0*	-2
14	150	151
16	68	-59
18	62	72
	12,3,L	
1	80	-73
3	0*	-27
5	0*	16
7	0*	47
9	0*	19
11	0*	2
13	0*	-24
15	74	-64
	4,4,L	
0	1144	1162
2	178	-179
4	53	-53
6	123	119
8	169	-172
10	73	80
12	173	167
14	177	-175
16	576	591
18	0*	-6
20	79	-67
22	0*	18
24	71	-54
26	68	65
	5,4,L	
1	91	-106
3	126	-129
5	0*	-10
7	82	89
9	56	53
11	0*	-2
13	93	-96
15	116	-125
17	62	-57
	6,4,L	
0	46	-56
2	48	34
4	0*	9
6	62	49
8	142	134
10	49	-51
12	0*	-2
14	78	92
16	0*	-51
18	0*	-13
20	0*	31
22	0*	27
24	68	65
	7,4,L	
1	88	94
3	81	87
5	0*	21
7	127	-129
9	180	-183
11	0*	21
13	138	143
15	93	88

OBSERVED AND CALCULATED STRUCTURE FACTORS COMPARED FOR BARTONITE

8,4,L

0	127	-130
2	0*	34
4	53	35
6	127	-140
8	584	595
10	98	-103
12	0*	-47
14	0*	38
16	89	-91
18	0*	36
20	122	119
22	106	-108

9,4,L

1	75	78
3	0*	-27
5	86	-86
7	49	-36

10,4,L

0	181	182
2	0*	-4
4	0*	-23
6	66	78
8	64	-57
10	0*	20
12	0*	31
14	0*	17
16	100	96

11,4,L

1	141	-134
3	0*	-4
5	72	90
7	54	55
9	0*	-17
11	0*	25
13	0*	10
15	62	-74
17	98	-103

12,4,L

0	392	380
2	95	-91
4	0*	6
6	0*	37
8	68	-72
10	0*	2
12	74	79

5,5,L

0	0*	-59
2	77	72
4	64	-63
6	163	-158
8	43	29
10	126	-125
12	0*	-21
14	91	79
16	64	-75
18	0*	38
20	0*	23
22	100	-106

6,5,L

1	0*	5
3	47	45
5	56	62
7	0*	-14
9	49	-53
11	0*	23
13	97	102

7,5,L

0	0*	33
2	165	-158
4	48	47
6	207	210
8	116	-110
10	76	57
12	69	73
14	88	-86
16	0*	4
18	82	-76
20	0*	19
22	122	123

8,5,L

1	54	34
3	50	-41
5	88	-88
7	88	-96
9	94	-101

9,5,L

0	49	67
2	76	-78
4	53	-41
6	0*	62
8	0*	-18
10	54	36
12	0*	5
14	78	-78

10,5,L

1	0*	3
3	0*	18
5	0*	65
7	0*	38
9	0*	16

11,5,L

0	99	-95
2	89	77
4	0*	32
6	95	-87
8	0*	-9
10	109	-107
12	0*	24
14	111	122
16	83	-72

12,5,L

1	65	-67
3	0*	-42
5	0*	-1
7	0*	15
9	0*	-11

13,5,L

0	0*	21
2	0*	34
4	0*	-7
6	0*	-21

OBSERVED AND CALCULATED STRUCTURE FACTORS COMPARED FOR BARTONITE

13,5,L

8	62	39

6,6,L

0	56	60
2	59	65
4	268	-272
6	76	85
8	0*	-17
10	70	71
12	180	-184
14	0*	26
16	0*	-5
18	59	68
20	133	-126

7,6,L

1	63	66
3	0*	9
5	46	48
7	82	90
9	75	81
11	50	53
13	0*	17
15	0*	-3
17	69	46
19	75	61

8,6,L

0	127	113
2	0*	-28
4	52	-37
6	50	44
8	52	-46
10	0*	-22
12	0*	10
14	0*	14
16	67	54

9,6,L

1	0*	-21
3	0*	39
5	81	88
7	0*	11
9	0*	-29
11	0*	35
13	78	78

10,6,L

0	0*	-15
2	69	67
4	154	-156
6	68	58
8	0*	22
10	0*	42
12	121	-121

11,6,L

1	57	63
3	0*	3
5	0*	-17
7	0*	20

12,6,L

0	0*	-4
2	0*	3
4	0*	-24

13,6,L

1	0*	-1
3	75	46
5	65	59

7,7,L

0	0*	-15
2	227	224
4	0*	-3
6	170	-172
8	133	131
10	96	-92
12	0*	4
14	182	191
16	0*	-51
18	98	111

8,7,L

1	122	-123
3	0*	-20
5	68	62
7	68	69
9	0*	11
11	0*	17
13	0*	-11
15	76	-84
17	76	-92

9,7,L

0	74	-71
2	61	77
4	58	68
6	0*	-38
8	0*	-7
10	88	-83
12	0*	55
14	114	125

10,7,L

1	61	76
3	55	46
5	0*	28
7	0*	25
9	0*	19
11	0*	33

11,7,L

0	96	109
2	118	-118
4	0*	-34
6	143	151
8	69E	-35
10	101	106

8,8,L

0	469	472
2	122	-121
4	60	-25
6	0*	27
8	91	-92
10	0*	-2
12	92	76
14	94	-105
16	289	291

OBSERVED AND CALCULATED STRUCTURE FACTORS COMPARED FOR BARTONITE

	9,8,L	
1	57	-37
3	72	-60
5	0*	-15
7	0*	24

	10,8,L	
0	0*	-42
2	0*	22
4	0*	-13
6	0*	5
8	99	100
10	0*	-23
12	0*	-22

	11,8,L	
1	0*	20
3	67E	19
5	0*	-13
7	79	-80
9	98	-102

	9,9,L	
0	0*	28
2	0*	37
4	0*	-31

	10,9,L	
1	0*	22
3	0*	37
5	0*	37

	11,9,L	
0	0*	-17
2	0E	-63
4	0*	41
6	76	84

	10,10,L	
0	71	40
2	0*	37
4	101	-106