

The crystal chemistry of sherwoodite, a calcium 14-vanadoaluminate heteropoly complex

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Abstract

The crystal structure of sherwoodite (tetragonal, space group $I4_1/amd$; $a = 28.06$, $c = 13.56$ Å) has been determined from 848 counter-measured intensity data (MoK α radiation). Difficulties with disorder and variability of crystal water as well as poor crystal quality prevented refinement below $R = 0.22$, but the essential structure is clearly revealed. Aluminum is found to play an essential role as the nucleus atom in the heteropoly complex molecule found in the structure: 14-vanadoaluminate, $(AlV_{14}O_{46})^{n-}$. There are 8 molecules in the unit cell joined by Ca²⁺ ions into chains along body diagonals, cross-linked to form an open framework of zeolitic character. The remaining Ca atoms and H₂O molecules could not be resolved and are presumably in disordered array in the intermolecular channels. The vanadium is partially reduced, and the ideal formula that best fits the determined structure and chemical analysis is $Ca_{4.5}(AlV_{12}V_2^VO_{46}) \cdot 28H_2O$. The molecule has $4/mmm$ symmetry and consists of 14 VO₆ octahedra condensed by edge-sharing around the central AlO₆ octahedron. The V-O distances vary from 1.58 to 2.36 Å.

Introduction

In 1958, Thompson *et al.* published a description of a new calcium vanadate mineral which was found at the Peanut Mine, Montrose County, Colorado. This rare species occurs as soft, greenish-black, tetragonal crystals up to 1 mm on fracture surfaces in Colorado Plateau sandstones bearing partially-oxidized vanadium minerals. The discrete nature of the mineral species was clearly established by its characteristic physical and crystallographic properties, but a wholly satisfactory chemical description could not be given. The best formula that could be derived from a microchemical analysis and crystallographic studies was $Ca_3V_8O_{22} \cdot 15H_2O$. The analysis also showed minor amounts of Al, Fe, and Mg. Thompson *et al.* (1958) recognized that the true chemical nature of sherwoodite could only be learned from a crystal structure analysis.

Such a structure determination has now been undertaken. Although still incomplete, it has clearly revealed that sherwoodite contains isolated molecules of a 14-vanadoaluminate heteropoly complex. The mineral is the first known occurrence in nature of this type of chemical complex. Although experimental difficulties have prevented full refinement of the

structure of this mineral to a degree that is nowadays considered desirable, the results obtained at this point are considered to be sufficiently noteworthy to warrant making this preliminary report.

Experimental procedure

A flat, square fragment of a euhedral crystal $0.07 \times 0.06 \times 0.025$ mm in size (from the Peanut Mine) was used for structure analysis. Precession photography confirmed the earlier space-group determination, given as $I4_1/amd$ (No. 141). Careful measurement of the 20.0.0 and 0.0.12 reflections in the plus and minus 2θ regions on the Picker automatic diffractometer using MoK α radiation gave cell constants $a = 28.06(3)$ and $c = 13.56(2)$ Å for this crystal. Intensities were measured for all allowed independent reflections with $2\theta < 45$ degrees; of 1783 measured, 848 had $F > 3\sigma$ based on counting statistics, and were used for the structure analysis.

The reflection 962 was used to monitor the primary beam during the run, and the intensity of this reflection showed somewhat greater than expected variation. As a consequence (and because of difficulties encountered in the structure refinement) the data set was measured a second time, but with no apparent

Table 2. Observed and calculated structure factors for sherwoodite
 The three columns are: h, F(obs), F(calc).

| H,0,0 | | | 28 | 227 | -208 | H,20,0 | | |
|--------|-----|------|--------|-----|------|--------|-----|------|
| 4 | 389 | 362 | | | | | | |
| 8 | 273 | 365 | | | | | | |
| 10 | 746 | -662 | | | | | | |
| 14 | 395 | 300 | | | | | | |
| 16 | 772 | 671 | | | | | | |
| 18 | 821 | 762 | | | | | | |
| 20 | 750 | 694 | | | | | | |
| 22 | 393 | 289 | | | | | | |
| 24 | 185 | 169 | | | | | | |
| | | | | | | | | |
| H,2,0 | | | H,8,0 | | | H,0,1 | | |
| 6 | 447 | -500 | 12 | 518 | -476 | 5 | 466 | -401 |
| 8 | 276 | -260 | 16 | 502 | 417 | 7 | 199 | -83 |
| 10 | 267 | 228 | 18 | 367 | -273 | 9 | 480 | 370 |
| 14 | 225 | 132 | 20 | 150 | 118 | 11 | 463 | -395 |
| 16 | 556 | 486 | 22 | 89 | 98 | 13 | 153 | -129 |
| 18 | 478 | 428 | 24 | 89 | -26 | 15 | 392 | 411 |
| 20 | 475 | 457 | 26 | 188 | -174 | 17 | 385 | 359 |
| 24 | 93 | 6 | 28 | 245 | 206 | 19 | 281 | 254 |
| 30 | 134 | -105 | | | | 21 | 472 | 451 |
| | | | | | | 23 | 185 | -127 |
| H,4,0 | | | H,10,0 | | | H,1,1 | | |
| 4 | 86 | -271 | 10 | 122 | -150 | 2 | 377 | -578 |
| 6 | 114 | 105 | 12 | 128 | -77 | 6 | 229 | 167 |
| 8 | 401 | -429 | 14 | 142 | 92 | 8 | 444 | 345 |
| 10 | 255 | -210 | 16 | 235 | 225 | 10 | 283 | -260 |
| 12 | 161 | 132 | 18 | 770 | 610 | 12 | 138 | -67 |
| 14 | 241 | -202 | 22 | 140 | -95 | 14 | 132 | 143 |
| 16 | 262 | -217 | 28 | 287 | -252 | 24 | 252 | 189 |
| 18 | 194 | 205 | | | | 30 | 101 | 51 |
| 22 | 124 | -132 | | | | | | |
| 24 | 308 | -297 | | | | | | |
| 26 | 178 | 158 | | | | | | |
| 30 | 242 | -170 | | | | | | |
| | | | | | | | | |
| H,6,0 | | | H,12,0 | | | H,2,1 | | |
| 6 | 583 | -544 | 14 | 231 | 176 | 5 | 129 | -88 |
| 10 | 122 | -167 | 16 | 398 | 305 | 7 | 146 | 185 |
| 12 | 168 | -222 | 18 | 228 | 245 | 9 | 309 | -294 |
| 14 | 383 | -349 | 20 | 116 | 53 | 13 | 87 | 26 |
| 16 | 107 | -131 | 24 | 230 | -228 | 17 | 283 | 243 |
| 18 | 97 | 52 | | | | 19 | 365 | 349 |
| 20 | 339 | -252 | | | | 23 | 161 | 152 |
| 22 | 244 | -256 | | | | | | |
| 24 | 100 | 25 | | | | | | |
| | | | | | | | | |
| H,18,0 | | | H,14,0 | | | H,3,1 | | |
| 18 | 128 | -137 | 14 | 183 | -125 | 4 | 105 | -94 |
| 22 | 136 | 79 | 16 | 295 | 226 | 6 | 226 | -132 |
| 24 | 149 | 85 | 18 | 117 | 86 | 8 | 119 | 103 |
| | | | 22 | 275 | -235 | 10 | 209 | 170 |
| | | | | | | 12 | 128 | -128 |
| | | | | | | 18 | 226 | -175 |

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| | | | | | | | | |
|---------|-----|------|----------|-----|------|----------|-----|------|
| H, 4, 1 | | | H, 9, 1 | | | H, 17, 1 | | |
| 5 | 301 | -294 | 10 | 709 | -510 | 22 | 149 | -170 |
| 9 | 248 | 190 | 12 | 287 | -216 | | | |
| 11 | 125 | -81 | 14 | 153 | 161 | H, 18, 1 | | |
| 13 | 88 | 38 | 16 | 252 | 426 | 21 | 252 | -186 |
| 15 | 144 | -129 | 18 | 88 | -107 | 23 | 182 | 194 |
| 19 | 120 | 61 | 20 | 301 | 257 | | | |
| 21 | 225 | -117 | 22 | 96 | 111 | H, 19, 1 | | |
| 23 | 271 | -211 | 24 | 184 | -170 | 20 | 142 | -47 |
| 27 | 178 | 121 | 26 | 207 | -172 | | | |
| H, 5, 1 | | | H, 10, 1 | | | H, 20, 1 | | |
| 8 | 210 | -228 | 17 | 503 | 538 | 21 | 95 | 63 |
| 12 | 91 | -42 | 23 | 94 | 89 | | | |
| 14 | 112 | 94 | H, 11, 1 | | | H, 0, 2 | | |
| 16 | 263 | -259 | 16 | 342 | 273 | 4 | 199 | -209 |
| 22 | 99 | -33 | 24 | 153 | 150 | 10 | 282 | 237 |
| 24 | 247 | -231 | 28 | 143 | -112 | 12 | 88 | -54 |
| H, 6, 1 | | | H, 12, 1 | | | 14 | 160 | -170 |
| 9 | 411 | 354 | 15 | 156 | 111 | 20 | 245 | -221 |
| 11 | 144 | 211 | 19 | 155 | 219 | 22 | 212 | 139 |
| 13 | 160 | -161 | 21 | 96 | -90 | 24 | 382 | -302 |
| 15 | 217 | -189 | 23 | 255 | -222 | 26 | 427 | 367 |
| 19 | 233 | -217 | H, 13, 1 | | | 28 | 154 | -111 |
| 23 | 139 | -63 | 14 | 429 | 306 | H, 1, 2 | | |
| 25 | 183 | 108 | 26 | 101 | 61 | 3 | 168 | -113 |
| 29 | 116 | 26 | H, 14, 1 | | | 5 | 101 | 142 |
| H, 7, 1 | | | 17 | 224 | 130 | 7 | 195 | 175 |
| 8 | 617 | -535 | 21 | 287 | -261 | 9 | 566 | 430 |
| 10 | 170 | -154 | H, 15, 1 | | | 11 | 166 | -182 |
| 12 | 120 | 78 | 16 | 115 | 62 | 15 | 258 | 231 |
| 14 | 196 | -178 | H, 16, 1 | | | 19 | 206 | -228 |
| 18 | 472 | 382 | 17 | 136 | 16 | 21 | 289 | 281 |
| 22 | 122 | -117 | 19 | 219 | -219 | 23 | 107 | -55 |
| 26 | 97 | -53 | | | | 25 | 148 | 123 |
| 28 | 270 | -224 | | | | 27 | 119 | 83 |
| H, 8, 1 | | | | | | H, 2, 2 | | |
| 11 | 86 | 110 | | | | 4 | 594 | -415 |
| 17 | 143 | -125 | | | | 6 | 157 | 153 |
| 19 | 112 | 221 | | | | 8 | 288 | 209 |
| 23 | 115 | 85 | | | | 16 | 124 | -132 |
| | | | | | | 18 | 100 | -53 |

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| | | | | | | | | |
|----|---------|------|----|----------|-------|----|----------|------|
| | H, 2, 2 | | 24 | 93 | 48 | 17 | 374 | 309 |
| | | | 26 | 316 | 267 | 19 | 102 | -138 |
| 20 | 85 | -28 | 28 | 103 | 86 | 23 | 159 | 95 |
| 22 | 319 | -228 | | | | 27 | 168 | -134 |
| 24 | 206 | 191 | | H, 7, 2 | | | | |
| | H, 3, 2 | | 7 | 1002 | -818 | | H, 12, 2 | |
| | | | 9 | 147 | -104 | 14 | 289 | -247 |
| 5 | 210 | 247 | 11 | 419 | -362 | 16 | 125 | 163 |
| 7 | 521 | 471 | 13 | 268 | -204 | 22 | 158 | -176 |
| 9 | 305 | 230 | 15 | 149 | -120 | | | |
| 11 | 79 | 128 | 17 | 283 | 198 | | H, 13, 2 | |
| 15 | 238 | 206 | 21 | 105 | 92 | 13 | 262 | 161 |
| 23 | 347 | 291 | 23 | 250 | -223 | 15 | 135 | 55 |
| 25 | 138 | 129 | 25 | 95 | -115 | | | |
| 29 | 145 | 119 | 27 | 111 | -82 | | H, 14, 2 | |
| | | | 29 | 156 | -131 | | | |
| | H, 4, 2 | | | H, 8, 2 | | 16 | 120 | -115 |
| 6 | 117 | 130 | 10 | 1092 | 962 | 22 | 158 | -131 |
| 8 | 427 | 303 | 12 | 307 | 214 | | | |
| 10 | 93 | 54 | 18 | 258 | 161 | | H, 15, 2 | |
| 14 | 310 | -283 | 20 | 163 | -97 | 15 | 149 | -124 |
| 16 | 130 | 107 | 24 | 175 | 181 | 21 | 171 | -173 |
| 18 | 119 | -110 | 26 | 174 | 129 | | | |
| 20 | 181 | -161 | 28 | 161 | 116 | | H, 16, 2 | |
| 24 | 172 | 123 | | | | 20 | 205 | -212 |
| 26 | 184 | 140 | | H, 9, 2 | | | | |
| 23 | 148 | 108 | 9 | 1395 | -1279 | | H, 17, 2 | |
| | | | 11 | 339 | -296 | | | |
| | H, 5, 2 | | 13 | 158 | -132 | 19 | 172 | -138 |
| 5 | 165 | 176 | 15 | 120 | 67 | | | |
| 7 | 188 | 178 | 19 | 309 | 302 | | H, 21, 2 | |
| 9 | 168 | -158 | 23 | 130 | -74 | | | |
| 11 | 95 | 63 | 25 | 149 | -151 | 21 | 203 | 139 |
| 13 | 197 | 182 | 27 | 209 | -201 | | | |
| 17 | 84 | -74 | | | | | H, 0, 3 | |
| 19 | 164 | 131 | | H, 10, 2 | | 1 | 293 | -259 |
| 23 | 155 | -61 | 12 | 201 | 242 | 5 | 169 | 228 |
| 27 | 161 | 105 | 16 | 196 | 173 | 7 | 222 | 250 |
| | | | 28 | 112 | 68 | 9 | 219 | 251 |
| | H, 6, 2 | | | | | 11 | 142 | 224 |
| 8 | 707 | 627 | | H, 11, 2 | | 13 | 140 | 163 |
| 10 | 461 | 381 | 11 | 635 | -669 | 15 | 463 | -425 |
| 14 | 106 | 80 | 13 | 153 | -135 | 21 | 283 | -229 |
| 16 | 82 | -97 | 15 | 360 | 308 | 23 | 100 | -29 |
| 18 | 137 | -121 | | | | | | |
| 22 | 145 | -23 | | | | | | |

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| | | |
|---------|-----|-----|
| H, 0, 3 | | |
| 25 | 421 | 310 |
| 29 | 118 | -2 |

| | | |
|---------|-----|-----|
| H, 1, 3 | | |
| 6 | 188 | 210 |
| 8 | 335 | 328 |
| 14 | 165 | 194 |
| 20 | 101 | -90 |
| 22 | 186 | 134 |
| 26 | 311 | 284 |

| | | |
|---------|-----|------|
| H, 2, 3 | | |
| 7 | 367 | 350 |
| 9 | 149 | 201 |
| 13 | 147 | -187 |
| 17 | 132 | -125 |
| 19 | 130 | -54 |
| 23 | 89 | -15 |
| 27 | 384 | 281 |
| 29 | 117 | -45 |

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|---------|-----|------|
| H, 3, 3 | | |
| 6 | 515 | 561 |
| 8 | 133 | 208 |
| 12 | 91 | 9 |
| 18 | 121 | -98 |
| 20 | 117 | -125 |
| 22 | 184 | 150 |
| 24 | 310 | 217 |
| 26 | 133 | 103 |
| 28 | 139 | 126 |

| | | |
|---------|-----|------|
| H, 4, 3 | | |
| 7 | 166 | 186 |
| 11 | 259 | -282 |
| 13 | 170 | -183 |
| 17 | 81 | 57 |
| 23 | 196 | 143 |
| 25 | 314 | 184 |
| 29 | 101 | 3 |

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|---------|-----|-----|
| H, 5, 3 | | |
| 6 | 109 | 115 |

| | | |
|----|-----|------|
| 8 | 125 | 218 |
| 10 | 99 | -121 |
| 12 | 160 | 112 |
| 18 | 159 | -131 |
| 20 | 147 | 101 |
| 24 | 105 | 100 |
| 26 | 94 | 104 |
| 28 | 101 | 110 |

| | | |
|---------|-----|------|
| H, 6, 3 | | |
| 7 | 138 | 219 |
| 15 | 205 | -149 |
| 17 | 89 | 25 |
| 19 | 87 | -46 |
| 21 | 161 | -81 |
| 25 | 184 | 150 |
| 29 | 114 | 15 |

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|---------|-----|------|
| H, 7, 3 | | |
| 8 | 83 | -129 |
| 10 | 415 | -403 |
| 14 | 249 | -245 |
| 20 | 118 | 26 |
| 22 | 89 | -107 |
| 24 | 97 | -78 |

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|---------|-----|------|
| H, 8, 3 | | |
| 9 | 738 | 649 |
| 11 | 252 | 215 |
| 13 | 230 | -236 |
| 15 | 101 | 58 |
| 17 | 226 | -184 |
| 21 | 106 | -91 |
| 23 | 88 | -42 |
| 27 | 250 | 196 |

| | | |
|---------|-----|------|
| H, 9, 3 | | |
| 10 | 115 | -82 |
| 12 | 614 | -537 |
| 14 | 238 | 256 |
| 16 | 221 | -155 |
| 18 | 169 | 109 |
| 28 | 105 | -103 |

| | | |
|----------|--|--|
| H, 10, 3 | | |
|----------|--|--|

| | | |
|----|-----|------|
| 11 | 445 | 367 |
| 13 | 138 | 180 |
| 15 | 513 | -450 |
| 17 | 209 | 150 |
| 21 | 110 | -76 |
| 23 | 103 | -68 |
| 25 | 166 | 136 |

| | | |
|----------|-----|------|
| H, 11, 3 | | |
| 12 | 104 | -87 |
| 16 | 224 | 189 |
| 18 | 155 | -28 |
| 20 | 155 | -126 |
| 22 | 171 | 105 |
| 24 | 103 | 23 |

| | | |
|----------|-----|------|
| H, 12, 3 | | |
| 13 | 169 | -162 |
| 15 | 276 | 198 |
| 19 | 89 | -59 |
| 21 | 144 | -65 |
| 23 | 118 | 95 |
| 25 | 157 | 71 |

| | | |
|----------|-----|------|
| H, 13, 3 | | |
| 14 | 126 | -53 |
| 16 | 124 | -132 |
| 18 | 186 | -155 |
| 24 | 121 | 96 |
| 26 | 101 | 92 |

| | | |
|----------|-----|-----|
| H, 14, 3 | | |
| 15 | 154 | 163 |
| 23 | 99 | 40 |

| | | |
|----------|-----|------|
| H, 15, 3 | | |
| 16 | 225 | -215 |
| 24 | 108 | 101 |

| | | |
|----------|-----|------|
| H, 16, 3 | | |
| 17 | 185 | 180 |
| 19 | 232 | 153 |
| 21 | 134 | -122 |

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| | | | | | | | | |
|----------|-----|------|---------|-----|------|----------|-----|------|
| H, 20, 3 | | | H, 4, 4 | | | 15 | 307 | 480 |
| 21 | 119 | -108 | 12 | 266 | -375 | 17 | 208 | -276 |
| H, 0, 4 | | | 14 | 83 | 54 | 21 | 106 | -17 |
| 0 | 75 | 63 | 16 | 302 | 355 | H, 10, 4 | | |
| 2 | 285 | -327 | 18 | 171 | 183 | 16 | 253 | -306 |
| 4 | 474 | 482 | 20 | 131 | -149 | 24 | 137 | -162 |
| 6 | 429 | -354 | 22 | 179 | 212 | 26 | 163 | 149 |
| 10 | 268 | 221 | 28 | 94 | -67 | H, 11, 4 | | |
| 12 | 139 | 152 | H, 5, 4 | | | 13 | 286 | 345 |
| 14 | 539 | -426 | 11 | 83 | 86 | 15 | 185 | -300 |
| 16 | 327 | 252 | 13 | 106 | -113 | 17 | 160 | 196 |
| 18 | 220 | -235 | 15 | 117 | -146 | 19 | 132 | -72 |
| 20 | 136 | 137 | 17 | 156 | -167 | 25 | 261 | 178 |
| 22 | 186 | -147 | 19 | 114 | -111 | H, 12, 4 | | |
| 28 | 178 | 126 | H, 6, 4 | | | 16 | 230 | 228 |
| H, 1, 4 | | | 8 | 100 | 98 | 20 | 265 | -220 |
| 3 | 502 | -459 | 10 | 103 | -178 | 24 | 211 | 101 |
| 5 | 281 | 249 | 12 | 151 | -208 | H, 13, 4 | | |
| 7 | 91 | 60 | 14 | 162 | 154 | 25 | 169 | 91 |
| 13 | 153 | 147 | 16 | 221 | 174 | H, 14, 4 | | |
| 15 | 460 | -378 | 18 | 125 | 86 | 14 | 232 | 137 |
| 17 | 338 | 317 | 20 | 139 | 130 | H, 15, 4 | | |
| 19 | 340 | -327 | 26 | 116 | 54 | 17 | 321 | -378 |
| 25 | 257 | 191 | H, 7, 4 | | | 23 | 158 | 73 |
| H, 2, 4 | | | 11 | 179 | -224 | H, 16, 4 | | |
| 2 | 97 | 107 | 13 | 185 | 262 | 16 | 221 | 247 |
| 4 | 289 | -240 | 15 | 244 | -286 | H, 17, 4 | | |
| 6 | 98 | 123 | 17 | 105 | 67 | 19 | 358 | -297 |
| | | 108 | 25 | 143 | 147 | H, 18, 4 | | |
| 1 | | -94 | H, 8, 4 | | | 18 | 265 | 320 |
| 16 | | -131 | 8 | 190 | -211 | H, 9, 4 | | |
| 18 | 261 | 256 | 12 | 92 | 141 | 13 | 155 | -258 |
| 22 | 125 | -139 | 14 | 331 | -429 | | | |
| 26 | 178 | 132 | 16 | 161 | 196 | | | |
| 28 | 118 | -26 | 18 | 160 | 95 | | | |
| H, 3, 4 | | | 22 | 206 | -257 | | | |
| 5 | 124 | -144 | 26 | 126 | -25 | | | |
| 7 | 257 | 308 | H, 9, 4 | | | | | |
| 13 | 146 | -101 | | | | | | |
| 17 | 404 | -404 | | | | | | |
| 27 | 175 | 174 | | | | | | |

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| | | | | | | | |
|----|----------|------|----|---------|------|----|----------|
| | H, 19, 4 | | 15 | 263 | 299 | | H, 11, 5 |
| | | | 17 | 275 | 335 | | |
| 21 | 237 | -121 | | | | 12 | 84 78 |
| | H, 0, 5 | | | H, 5, 5 | | 14 | 103 65 |
| | | | 14 | 90 | 33 | 16 | 119 -73 |
| 1 | 306 | -285 | 16 | 164 | -164 | 24 | 204 -159 |
| 5 | 178 | 103 | 24 | 133 | 57 | 26 | 150 110 |
| 7 | 465 | -601 | | | | | H, 12, 5 |
| 9 | 94 | 145 | | | | | |
| 13 | 245 | -177 | | | | 15 | 112 -69 |
| 17 | 165 | -179 | 9 | 136 | -113 | 21 | 151 -168 |
| 19 | 174 | 200 | 11 | 140 | -87 | 23 | 102 10 |
| 21 | 242 | -158 | 15 | 204 | 334 | 25 | 119 114 |
| 23 | 153 | -155 | 17 | 273 | 341 | | |
| | | | 19 | 159 | 197 | | H, 13, 5 |
| | H, 1, 5 | | 21 | 128 | 101 | | |
| | | | 23 | 140 | -86 | 16 | 108 -30 |
| 2 | 290 | -214 | 25 | 128 | -121 | 20 | 117 -112 |
| 4 | 288 | 337 | | | | | |
| 6 | 218 | -379 | | | | | H, 14, 5 |
| 8 | 187 | 206 | | | | | |
| 14 | 124 | -136 | 14 | 112 | 175 | 17 | 100 47 |
| 16 | 112 | 138 | 20 | 156 | 149 | | |
| 18 | 230 | -319 | 22 | 335 | 265 | | H, 15, 5 |
| 20 | 159 | 106 | 24 | 187 | -149 | | |
| | | | 26 | 111 | 71 | 22 | 119 -22 |
| | | | | | | 24 | 175 117 |
| | H, 2, 5 | | | | | | |
| | | | | | | | H, 16, 5 |
| 3 | 112 | -195 | | | | | |
| 5 | 239 | -279 | 9 | 150 | -99 | 19 | 115 161 |
| 9 | 166 | -89 | 17 | 274 | 358 | 21 | 106 21 |
| 17 | 204 | 247 | 19 | 262 | 258 | | |
| 27 | 155 | -25 | | | | | |
| | | | | | | | H, 17, 5 |
| | H, 3, 5 | | | | | | |
| | | | 12 | 201 | 224 | 18 | 198 -216 |
| 6 | 146 | 197 | 14 | 115 | -127 | | |
| 8 | 138 | -160 | 16 | 101 | 131 | | H, 18, 5 |
| 10 | 127 | -48 | 18 | 143 | 82 | | |
| 12 | 124 | 184 | 20 | 230 | 157 | 19 | 148 153 |
| 16 | 200 | -259 | 22 | 221 | -187 | 21 | 147 36 |
| 22 | 125 | -136 | 24 | 285 | 238 | | |
| 26 | 167 | 37 | 26 | 183 | -132 | | H, 19, 5 |
| 28 | 220 | 67 | | | | | |
| | | | | | | 20 | 118 -96 |
| | | | | | | | |
| | H, 4, 5 | | | | | | |
| | | | 13 | 89 | -148 | | |
| 7 | 100 | 121 | 15 | 163 | 136 | | |
| 11 | 119 | -240 | | | | | |

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| | | | | | | | | |
|----|-------|------|----|--------|------|----|--------|------|
| | H,0,6 | | 13 | 85 | -123 | 12 | 143 | 157 |
| | | | 17 | 212 | 205 | 14 | 137 | -126 |
| 4 | 398 | -369 | 19 | 159 | 100 | 16 | 117 | -39 |
| 6 | 449 | 522 | 21 | 142 | 150 | 20 | 117 | 30 |
| 8 | 243 | -406 | 23 | 236 | 206 | 22 | 157 | -183 |
| 10 | 158 | 199 | 27 | 103 | -79 | 24 | 179 | 211 |
| 12 | 108 | -145 | | | | | | |
| 16 | 194 | -195 | | H,6,6 | | | H,11,6 | |
| 20 | 118 | -175 | 8 | 187 | -183 | 11 | 213 | -324 |
| 26 | 137 | 86 | 16 | 229 | 235 | 13 | 88 | 123 |
| | | | 18 | 303 | 358 | 15 | 146 | -172 |
| | H,1,6 | | 20 | 170 | 118 | 23 | 207 | -214 |
| 1 | 211 | -209 | 26 | 128 | -95 | | | |
| 3 | 115 | -50 | | | | | H,13,6 | |
| 5 | 411 | 557 | | H,7,6 | | 13 | 203 | -243 |
| 7 | 492 | -735 | 7 | 86 | 93 | | | |
| 15 | 195 | -251 | 11 | 243 | -293 | | H,14,6 | |
| 17 | 133 | 146 | 13 | 274 | 301 | 20 | 127 | -55 |
| 21 | 108 | 4 | | | | | | |
| 23 | 116 | -112 | | H,9,6 | | | H,15,6 | |
| | | | 9 | 219 | -280 | 15 | 208 | 242 |
| | H,2,6 | | | | | 23 | 105 | 31 |
| 4 | 127 | 103 | | H,7,6 | | | | |
| 6 | 292 | -357 | 17 | 123 | 169 | | H,16,6 | |
| 8 | 191 | 283 | 19 | 134 | 165 | 18 | 209 | 273 |
| 12 | 171 | -236 | 21 | 310 | 378 | | | |
| 16 | 173 | 197 | | | | | H,17,6 | |
| 26 | 183 | 86 | | H,8,6 | | 17 | 324 | 361 |
| | | | 10 | 83 | 59 | 21 | 127 | 92 |
| | H,3,6 | | 12 | 209 | -310 | | | |
| 9 | 150 | -217 | 16 | 147 | 221 | | H,18,6 | |
| 13 | 107 | 73 | 18 | 131 | 182 | 20 | 130 | 88 |
| 17 | 178 | -208 | 20 | 92 | 66 | | | |
| 19 | 197 | 262 | 22 | 144 | 155 | | H,19,6 | |
| 23 | 186 | -128 | 24 | 219 | -216 | 19 | 120 | 205 |
| | | | | | | | | |
| | H,4,6 | | | H,9,6 | | | H,0,7 | |
| 6 | 94 | -86 | 11 | 155 | 239 | 5 | 180 | -243 |
| 10 | 93 | -123 | 13 | 187 | -220 | 7 | 526 | 794 |
| 16 | 183 | 262 | 19 | 158 | 235 | 9 | 309 | 343 |
| 18 | 167 | 164 | 23 | 112 | 73 | | | |
| 20 | 144 | 97 | | | | | | |
| | | | | H,10,6 | | | | |
| | H,5,6 | | | | | | | |
| 5 | 112 | -113 | | | | | | |

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| | | | | | | | | |
|---------|-----|------|----------|-----|------|----------|-----|------|
| H, 0, 7 | | | H, 6, 7 | | | H, 14, 7 | | |
| 11 | 95 | 72 | 7 | 84 | -166 | 17 | 117 | 116 |
| 13 | 115 | -83 | 13 | 301 | -318 | | | |
| 15 | 192 | 269 | 17 | 122 | 116 | H, 15, 7 | | |
| 17 | 96 | -177 | 21 | 135 | -61 | 16 | 226 | 229 |
| 19 | 205 | -159 | 23 | 130 | 34 | 20 | 114 | 84 |
| 23 | 111 | 132 | H, 7, 7 | | | H, 17, 7 | | |
| 25 | 116 | 133 | 10 | 109 | -174 | 18 | 239 | 298 |
| H, 1, 7 | | | 12 | 253 | 255 | H, 0, 8 | | |
| 2 | 75 | -98 | 16 | 123 | 127 | 4 | 178 | -158 |
| 8 | 199 | -356 | 18 | 110 | 91 | 6 | 220 | 263 |
| 16 | 95 | -190 | 22 | 148 | 141 | 8 | 626 | 713 |
| 22 | 130 | -130 | H, 8, 7 | | | 10 | 406 | 432 |
| H, 2, 7 | | | 9 | 98 | 91 | 12 | 189 | 132 |
| 5 | 121 | 218 | 11 | 208 | -265 | 14 | 133 | 27 |
| 9 | 298 | 439 | 13 | 85 | 73 | 16 | 122 | 180 |
| 11 | 177 | 209 | 17 | 85 | 91 | 18 | 233 | -243 |
| 13 | 100 | -32 | H, 9, 7 | | | 24 | 234 | 221 |
| 15 | 167 | -189 | 10 | 263 | 284 | H, 1, 8 | | |
| 17 | 141 | 177 | 12 | 203 | -240 | 7 | 233 | -217 |
| 25 | 164 | 228 | 14 | 119 | 104 | 9 | 168 | -124 |
| H, 3, 7 | | | 16 | 114 | 54 | 11 | 246 | -248 |
| 4 | 87 | 14 | 20 | 107 | 44 | 13 | 104 | -123 |
| 6 | 82 | -118 | 22 | 104 | 82 | 19 | 197 | -184 |
| 8 | 255 | -276 | 24 | 133 | -69 | 21 | 178 | 223 |
| 10 | 149 | -60 | H, 10, 7 | | | 25 | 108 | -136 |
| 12 | 117 | -203 | 11 | 197 | 215 | H, 2, 8 | | |
| 15 | 118 | 47 | 13 | 90 | -123 | 2 | 221 | -230 |
| 18 | 111 | 61 | H, 11, 7 | | | 4 | 87 | 60 |
| 24 | 117 | -154 | 12 | 129 | 132 | 8 | 369 | 419 |
| H, 4, 7 | | | 16 | 142 | -203 | 10 | 366 | 389 |
| 7 | 78 | 10 | H, 12, 7 | | | 12 | 184 | 209 |
| 19 | 105 | 130 | 15 | 173 | -149 | 14 | 112 | -120 |
| H, 5, 7 | | | 23 | 130 | -91 | 16 | 99 | -32 |
| 6 | 157 | -175 | H, 11, 8 | | | 18 | 125 | -18 |
| 10 | 87 | -122 | 15 | 173 | -149 | 20 | 144 | -158 |
| 16 | 110 | 125 | 23 | 130 | -91 | 22 | 117 | -12 |
| 20 | 196 | 172 | H, 12, 8 | | | | | |
| 26 | 120 | -87 | | | | | | |

Table 2, page 9

| | | | | | | | | |
|---------|-----|------|----------|-----|------|---------|-----|------|
| H, 3, 8 | | | H, 9, 8 | | | H, 1, 9 | | |
| 5 | 217 | -157 | 11 | 228 | 224 | 6 | 107 | -93 |
| 7 | 152 | -217 | 13 | 90 | 7 | 10 | 307 | -343 |
| 9 | 418 | -377 | 17 | 177 | -128 | 16 | 149 | 47 |
| 11 | 313 | -288 | 21 | 122 | -86 | 18 | 137 | -58 |
| 13 | 169 | -159 | | | | 20 | 172 | 144 |
| 15 | 89 | -34 | H, 10, 8 | | | H, 2, 9 | | |
| 17 | 126 | 45 | 10 | 371 | 425 | 5 | 119 | -101 |
| 21 | 168 | -168 | 12 | 91 | -105 | 7 | 104 | -97 |
| 25 | 97 | -19 | 16 | 158 | 165 | 9 | 369 | 371 |
| H, 4, 8 | | | 20 | 141 | -95 | 13 | 93 | -23 |
| 4 | 242 | -258 | H, 11, 8 | | | 19 | 131 | -134 |
| 10 | 229 | 279 | 15 | 88 | -96 | 21 | 99 | 119 |
| 12 | 86 | -15 | H, 12, 8 | | | 23 | 115 | -40 |
| 14 | 111 | -88 | 16 | 201 | -246 | H, 3, 9 | | |
| 16 | 208 | -233 | H, 13, 8 | | | 6 | 132 | -156 |
| 20 | 106 | -62 | 17 | 110 | -20 | 8 | 216 | -226 |
| 22 | 99 | -86 | H, 14, 8 | | | 10 | 191 | -213 |
| 24 | 116 | -83 | 14 | 226 | -229 | 14 | 120 | -147 |
| H, 5, 8 | | | H, 15, 8 | | | 16 | 143 | 209 |
| 9 | 225 | -218 | 17 | 101 | 48 | 20 | 92 | -25 |
| 13 | 91 | 13 | H, 16, 8 | | | H, 4, 9 | | |
| H, 6, 8 | | | 16 | 164 | 147 | 5 | 148 | -155 |
| 10 | 213 | 268 | 18 | 117 | -94 | 9 | 130 | 92 |
| 12 | 143 | -161 | H, 17, 8 | | | 11 | 91 | 95 |
| 14 | 151 | -165 | 17 | 101 | 48 | 15 | 92 | -154 |
| 24 | 151 | 40 | H, 18, 8 | | | 23 | 119 | -84 |
| H, 7, 8 | | | 16 | 164 | 147 | H, 5, 9 | | |
| 9 | 371 | 353 | 18 | 117 | -94 | 6 | 102 | 46 |
| 11 | 90 | 36 | H, 19, 8 | | | 8 | 94 | -12 |
| 21 | 135 | 71 | 16 | 164 | 147 | 10 | 95 | -107 |
| 23 | 117 | 17 | H, 20, 8 | | | 14 | 93 | 109 |
| H, 8, 8 | | | 1 | 212 | 243 | 18 | 115 | 25 |
| 8 | 477 | 469 | 3 | 225 | -169 | 20 | 106 | 17 |
| 10 | 207 | -226 | 5 | 137 | -126 | H, 6, 9 | | |
| 12 | 94 | 119 | 7 | 312 | 379 | 7 | 139 | 133 |
| 14 | 92 | 12 | 9 | 120 | 72 | | | |
| 16 | 142 | 53 | 11 | 258 | 235 | | | |
| 22 | 112 | 9 | 15 | 93 | 83 | | | |
| | | | 19 | 189 | 186 | | | |
| | | | 21 | 185 | -218 | | | |

Table 2, page 10

H, 6, 9

| | | |
|----|-----|-----|
| 13 | 88 | -67 |
| 19 | 132 | 107 |

H, 7, 9

| | | |
|----|-----|------|
| 10 | 259 | 327 |
| 12 | 93 | 99 |
| 14 | 97 | -131 |
| 16 | 148 | -143 |

H, 8, 9

| | | |
|----|-----|------|
| 9 | 264 | 346 |
| 11 | 125 | -152 |
| 13 | 109 | 36 |
| 15 | 132 | 153 |
| 17 | 127 | 195 |
| 21 | 162 | 151 |

H, 9, 9

| | | |
|----|-----|------|
| 12 | 92 | 8 |
| 18 | 181 | -259 |
| 22 | 131 | -71 |

H, 10, 9

| | | |
|----|-----|------|
| 11 | 92 | 23 |
| 15 | 158 | 129 |
| 19 | 140 | 215 |
| 21 | 153 | -149 |

H, 11, 9

| | | |
|----|-----|------|
| 14 | 151 | -165 |
| 18 | 115 | -120 |
| 20 | 141 | -172 |

H, 12, 9

| | | |
|----|-----|----|
| 17 | 126 | 71 |
|----|-----|----|

H, 13, 9

| | | |
|----|-----|------|
| 14 | 110 | 107 |
| 16 | 139 | -127 |

H, 14, 9

| | | |
|----|-----|-----|
| 19 | 153 | -45 |
|----|-----|-----|

H, 0, 10

| | | |
|----|-----|------|
| 2 | 545 | 566 |
| 8 | 191 | -220 |
| 10 | 200 | 306 |
| 12 | 196 | -368 |
| 14 | 125 | 179 |
| 16 | 153 | 271 |
| 18 | 205 | 288 |

H, 1, 10

| | | |
|----|-----|------|
| 1 | 267 | 286 |
| 3 | 194 | -199 |
| 5 | 146 | 74 |
| 7 | 138 | 194 |
| 9 | 214 | -245 |
| 19 | 132 | 99 |

H, 2, 10

| | | |
|----|-----|------|
| 4 | 144 | 79 |
| 10 | 128 | -216 |
| 18 | 100 | 191 |

H, 3, 10

| | | |
|----|-----|-----|
| 3 | 233 | 253 |
| 13 | 119 | 5 |
| 15 | 144 | 212 |
| 17 | 120 | 152 |
| 21 | 129 | 129 |

H, 4, 10

| | | |
|----|-----|------|
| 6 | 162 | -242 |
| 14 | 96 | -187 |
| 16 | 149 | 118 |
| 20 | 116 | 31 |

H, 5, 10

| | | |
|----|-----|----|
| 5 | 102 | 83 |
| 11 | 144 | 74 |
| 13 | 108 | 51 |

H, 6, 10

| | | |
|----|-----|------|
| 12 | 102 | -163 |
| 14 | 97 | -5 |

H, 7, 10

| | | |
|----|-----|------|
| 15 | 134 | -158 |
| 19 | 111 | 68 |

H, 8, 10

| | | |
|----|-----|-----|
| 12 | 97 | 36 |
| 16 | 107 | 21 |
| 18 | 157 | 248 |

H, 9, 10

| | | |
|----|-----|------|
| 13 | 136 | -125 |
| 17 | 151 | -137 |
| 19 | 262 | -271 |

H, 10, 10

| | | |
|----|-----|------|
| 12 | 190 | -242 |
| 16 | 151 | 218 |

H, 11, 10

| | | |
|----|-----|------|
| 11 | 166 | -146 |
| 15 | 96 | -21 |
| 17 | 113 | -76 |

H, 12, 10

| | | |
|----|-----|------|
| 14 | 88 | -111 |
| 18 | 180 | 179 |

H, 0, 11

| | | |
|----|-----|------|
| 1 | 113 | 113 |
| 3 | 185 | 274 |
| 7 | 126 | -138 |
| 11 | 132 | -32 |
| 15 | 238 | 222 |
| 17 | 223 | 227 |
| 19 | 145 | 186 |

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| | | | | | | | | |
|--------|-----|------|---------|-----|------|---------|-----|------|
| H,1,11 | | | H,9,11 | | | 7 | 160 | -83 |
| 2 | 183 | 180 | 16 | 215 | -114 | 11 | 105 | -68 |
| 10 | 199 | 248 | | | | 15 | 98 | -1 |
| 12 | 249 | -322 | H,10,11 | | | H,6,12 | | |
| 14 | 211 | 221 | 11 | 122 | -56 | 6 | 126 | 237 |
| 16 | 104 | 67 | 15 | 102 | 136 | 14 | 91 | -48 |
| H,2,11 | | | H,11,11 | | | H,7,12 | | |
| 9 | 101 | -75 | 16 | 134 | 122 | 11 | 92 | -68 |
| 17 | 175 | 187 | H,12,11 | | | H,8,12 | | |
| 19 | 129 | 95 | 13 | 136 | -44 | 10 | 93 | 134 |
| H,3,11 | | | H,0,12 | | | H,10,12 | | |
| 4 | 130 | -58 | 0 | 250 | -226 | 10 | 143 | 7 |
| 6 | 144 | 123 | 4 | 90 | -42 | H,0,13 | | |
| 10 | 128 | -61 | 8 | 111 | -111 | 1 | 93 | -161 |
| 12 | 95 | 70 | 10 | 132 | -167 | H,1,13 | | |
| 16 | 142 | 86 | 12 | 175 | 175 | 4 | 97 | -13 |
| H,4,11 | | | 14 | 178 | -253 | H,2,13 | | |
| 9 | 109 | 116 | H,1,12 | | | H,5,13 | | |
| 11 | 100 | -52 | 13 | 104 | -128 | 10 | 115 | 88 |
| 15 | 107 | 52 | H,2,12 | | | 12 | 106 | -82 |
| 17 | 111 | 83 | 2 | 133 | -160 | H,2,14 | | |
| H,5,11 | | | 8 | 134 | 71 | 4 | 104 | -55 |
| 6 | 143 | -167 | 12 | 135 | -152 | H,3,14 | | |
| 10 | 103 | -112 | H,3,12 | | | 5 | 96 | 31 |
| 18 | 130 | 76 | 13 | 159 | 74 | H,4,14 | | |
| H,6,11 | | | H,4,12 | | | 6 | 100 | 4 |
| 7 | 111 | 111 | 4 | 127 | -202 | | | |
| 15 | 96 | -13 | 6 | 120 | 128 | | | |
| H,7,11 | | | 8 | 150 | 235 | | | |
| 16 | 115 | 78 | 10 | 142 | 213 | | | |
| H,8,11 | | | 16 | 96 | 7 | | | |
| 9 | 87 | 42 | H,5,12 | | | | | |
| 15 | 158 | -158 | | | | | | |
| 17 | 118 | 136 | | | | | | |