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Supplement of

Graulichite-(La), $LaFe_3^{3+}(AsO_4)_2(OH)_6$, a new addition to the alunite supergroup from the Patte d'Oie mine, Bou Skour mining district, Morocco

Cristian Biagioni et al.

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```
data_shelx

_audit_creation_method           'SHELXL-2018/1'
_shelx_SHELXL_version_number     '2018/1'
_chemical_name_mineral           'graulichite-(La)'
_chemical_compound_source        'Bou Skour, Morocco'
_chemical_formula_analytical
;
Al0.45 As0.86 Ca0.11 Ce0.25 Cu0.18 Fe2.38 H6.04
K0.05 La0.43 O14 P0.48 Pb0.06 S0.66 Sr0.10
;
_chemical_formula_sum
 'As1.40 Fe2.82 La0.95 O14'
_chemical_formula_weight         617.48

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 _atom_type_description
 _atom_type_scat_dispersion_real
 _atom_type_scat_dispersion_imag
 _atom_type_scat_source
 'As'  'As'   0.0499   2.0058
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'Fe'  'Fe'   0.3463   0.8444
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'La'  'La'  -0.2871   2.4523
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'
 'O'  'O'   0.0106   0.0060
 'International Tables Vol C Tables 4.2.6.8 and 6.1.1.4'

_space_group_crystal_system      trigonal
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_space_group_IT_number 166

_space_group_name_H-M_alt 'R -3 m :H'

_space_group_name_Hall '-R 3 2"'

_shelx_space_group_comment

;

The symmetry employed for this shelxl refinement is uniquely defined

by the following loop, which should always be used as a source of

symmetry information in preference to the above space-group names.

They are only intended as comments.

;

loop_

_space_group_symop_operation_xyz

'x, y, z'

'-y, x-y, z'

'-x+y, -x, z'

'x-y, -y, -z'

'y, x, -z'

'-x, -x+y, -z'

'x+2/3, y+1/3, z+1/3'

'-y+2/3, x-y+1/3, z+1/3'

'-x+y+2/3, -x+1/3, z+1/3'

'x-y+2/3, -y+1/3, -z+1/3'

'y+2/3, x+1/3, -z+1/3'

'-x+2/3, -x+y+1/3, -z+1/3'

'x+1/3, y+2/3, z+2/3'

'-y+1/3, x-y+2/3, z+2/3'

'-x+y+1/3, -x+2/3, z+2/3'

'x-y+1/3, -y+2/3, -z+2/3'

'y+1/3, x+2/3, -z+2/3'

'-x+1/3, -x+y+2/3, -z+2/3'

'-x, -y, -z'

'y, -x+y, -z'

'x-y, x, -z'

'-x+y, y, z'

'-y, -x, z'

'x, x-y, z'

'-x+2/3, -y+1/3, -z+1/3'

'y+2/3, -x+y+1/3, -z+1/3'

'x-y+2/3, x+1/3, -z+1/3'

'-x+y+2/3, y+1/3, z+1/3'

'-y+2/3, -x+1/3, z+1/3'

'x+2/3, x-y+1/3, z+1/3'

'-x+1/3, -y+2/3, -z+2/3'

'y+1/3, -x+y+2/3, -z+2/3'

'x-y+1/3, x+2/3, -z+2/3'

'-x+y+1/3, y+2/3, z+2/3'

'-y+1/3, -x+2/3, z+2/3'

'x+1/3, x-y+2/3, z+2/3'

_cell_length_a 7.252(13)

_cell_length_b 7.252(13)

_cell_length_c 16.77(3)

_cell_angle_alpha 90

_cell_angle_beta 90

_cell_angle_gamma 120

_cell_volume 764(3)

_cell_formula_units_Z 3

_cell_measurement_temperature 293(2)

_cell_measurement_reflns_used 41

_cell_measurement_theta_min 5.62

_cell_measurement_theta_max 15.82

_exptl_crystal_description 'anhedral'

_exptl_crystal_colour 'yellow'

_exptl_crystal_density_meas 'not measured'

_exptl_crystal_density_method ?

_exptl_crystal_density_diffrn 4.026

_exptl_crystal_F_000 855.9

_exptl_transmission_factor_min 0.571

_exptl_transmission_factor_max 0.652

_exptl_crystal_size_max 0.040

_exptl_crystal_size_mid 0.035

_exptl_crystal_size_min 0.030

_exptl_absorpt_coefficient_mu 12.412

_shelx_estimated_absorpt_T_min ?

_shelx_estimated_absorpt_T_max ?

_exptl_absorpt_correction_type 'multi-scan'

_exptl_absorpt_correction_T_min ?

_exptl_absorpt_correction_T_max ?

_exptl_absorpt_process_details 'SADABS (Sheldrick, 2015)'

_exptl_absorpt_special_details ?

_diffrn_ambient_temperature 293(2)

_diffrn_radiation_wavelength 0.71073

_diffrn_radiation_type MoK\a

_diffrn_radiation_source 'fine-focus sealed tube'

_diffrn_radiation_monochromator graphite

_diffrn_measurement_device_type 'Bruker Apex II'

_diffrn_reflns_number 116

_diffrn_reflns_av_unetI/netI 0.0726

_diffrn_reflns_av_R_equivalents 0.0563

_diffrn_reflns_limit_h_min -5

_diffrn_reflns_limit_h_max 5

_diffrn_reflns_limit_k_min -4

_diffrn_reflns_limit_k_max 4

_diffrn_reflns_limit_l_min -12

_diffrn_reflns_limit_l_max 12

_diffrn_reflns_theta_min 3.645

_diffrn_reflns_theta_max 15.873

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_diffrn_reflns_Laue_measured_fraction_max 0.770

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_diffrn_reflns_point_group_measured_fraction_max 0.770

_diffrn_reflns_point_group_measured_fraction_full 0.770

_reflns_number_total 47

_reflns_number_gt 36

_reflns_threshold_expression 'I > 2\s(I)'

_reflns_Friedel_coverage 0.000

_reflns_Friedel_fraction_max .

_reflns_Friedel_fraction_full .

_reflns_special_details

;

Reflections were merged by SHELXL according to the crystal

class for the calculation of statistics and refinement.

_reflns_Friedel_fraction is defined as the number of unique

Friedel pairs measured divided by the number that would be

possible theoretically, ignoring centric projections and

systematic absences.

;

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_computing_cell_refinement 'Apex3 (Bruker AXS Inc., 2016)'

_computing_data_reduction 'Apex3 (Bruker AXS Inc., 2016)'

_computing_structure_refinement 'SHELXL-2018/1 (Sheldrick, 2018)'

_computing_molecular_graphics ?

_computing_publication_material ?

_refine_special_details ?

_refine_ls_structure_factor_coef Fsqd

_refine_ls_matrix_type full

_refine_ls_weighting_scheme calc

_refine_ls_weighting_details

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_atom_sites_solution_hydrogens .

_refine_ls_hydrogen_treatment undef

_refine_ls_extinction_method none

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_refine_ls_number_reflns 47

_refine_ls_number_parameters 7

_refine_ls_number_restraints 0

_refine_ls_R_factor_all 0.1222

_refine_ls_R_factor_gt 0.0956

_refine_ls_wR_factor_ref 0.2162

_refine_ls_wR_factor_gt 0.2074

_refine_ls_goodness_of_fit_ref 1.237

_refine_ls_restrained_S_all 1.237

_refine_ls_shift/su_max 0.000

_refine_ls_shift/su_mean 0.000

loop_

_atom_site_label

_atom_site_type_symbol

_atom_site_fract_x

_atom_site_fract_y

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 _atom_site_U_iso_or_equiv
 _atom_site_adp_type
 _atom_site_occupancy
 _atom_site_site_symmetry_order
 _atom_site_calc_flag
 _atom_site_refinement_flags_posn
 _atom_site_refinement_flags_adp
 _atom_site_refinement_flags_occupancy
 _atom_site_disorder_assembly
 _atom_site_disorder_group
La La 0.000000 0.000000 0.000000 0.030 Uiso 0.9457 12 d S U P . .
Fe Fe 0.500000 0.500000 0.500000 0.015 Uiso 0.94 4 d S U P . .
As As 0.000000 0.000000 0.3163(13) 0.020 Uiso 0.6982 6 d S U P . .
O1 O 0.000000 0.000000 0.415(5) 0.025 Uiso 1 6 d S U P . .
O2 O 0.219(4) -0.219(4) -0.052(3) 0.025 Uiso 1 2 d S U P . .
OH O 0.120(5) -0.120(5) 0.132(2) 0.025 Uiso 1 2 d S U P . .

_geom_special_details
;
 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
 into account individually in the estimation of esds in distances, angles
 and torsion angles; correlations between esds in cell parameters are only
 used when they are defined by crystal symmetry.  An approximate (isotropic)
 treatment of cell esds is used for estimating esds involving l.s. planes.
;

loop_
 _geom_bond_atom_site_label_1
 _geom_bond_atom_site_label_2
 _geom_bond_distance
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_geom_bond_site_symmetry_2

_geom_bond_publ_flag

La OH 2.67(5) 19 ?

La OH 2.67(5) 20 ?

La OH 2.67(5) 2 ?

La OH 2.67(5) . ?

La OH 2.67(5) 21 ?

La OH 2.67(5) 3 ?

La O2 2.88(5) . ?

La O2 2.88(5) 21 ?

La O2 2.88(5) 3 ?

La O2 2.88(5) 20 ?

La O2 2.88(5) 2 ?

La O2 2.88(5) 19 ?

Fe OH 1.958(19) 33 ?

Fe OH 1.958(19) 9 ?

Fe OH 1.958(19) 32 ?

Fe OH 1.958(19) 8 ?

Fe O2 2.03(4) 13 ?

Fe O2 2.03(4) 25 ?

As O2 1.56(5) 8_445 ?

As O2 1.56(5) 9 ?

As O2 1.56(5) 7_455 ?

As O1 1.65(9) . ?

loop_

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_geom_angle_atom_site_label_2

_geom_angle_atom_site_label_3

_geom_angle

_geom_angle_site_symmetry_1

_geom_angle_site_symmetry_3

_geom_angle_publ_flag

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OH La OH 122(2) 19 2 ?

OH La OH 180.0(18) 20 2 ?

OH La OH 180.0 19 . ?

OH La OH 122(2) 20 . ?

OH La OH 58(2) 2 . ?

OH La OH 58(2) 19 21 ?

OH La OH 58(2) 20 21 ?

OH La OH 122(2) 2 21 ?

OH La OH 122(2) . 21 ?

OH La OH 122(2) 19 3 ?

OH La OH 122(2) 20 3 ?

OH La OH 58(2) 2 3 ?

OH La OH 58(2) . 3 ?

OH La OH 180(4) 21 3 ?

OH La O2 106.6(16) 19 . ?

OH La O2 58.8(7) 20 . ?

OH La O2 121.2(7) 2 . ?

OH La O2 73.4(16) . . ?

OH La O2 58.8(7) 21 . ?

OH La O2 121.2(7) 3 . ?

OH La O2 121.2(7) 19 21 ?

OH La O2 121.2(7) 20 21 ?

OH La O2 58.8(7) 2 21 ?

OH La O2 58.8(7) . 21 ?

OH La O2 73.4(16) 21 21 ?

OH La O2 106.6(16) 3 21 ?

O2 La O2 68.7(8) . 21 ?

OH La O2 58.8(7) 19 3 ?

OH La O2 58.8(7) 20 3 ?

OH La O2 121.2(7) 2 3 ?

OH La O2 121.2(7) . 3 ?

OH La O2 106.6(16) 21 3 ?

OH La O2 73.4(16) 3 3 ?

O2 La O2 111.3(8) . 3 ?

O2 La O2 180(2) 21 3 ?

OH La O2 121.2(7) 19 20 ?

OH La O2 73.4(16) 20 20 ?

OH La O2 106.6(16) 2 20 ?

OH La O2 58.8(7) . 20 ?

OH La O2 121.2(7) 21 20 ?

OH La O2 58.8(7) 3 20 ?

O2 La O2 68.7(8) . 20 ?

O2 La O2 111.3(8) 21 20 ?

O2 La O2 68.7(8) 3 20 ?

OH La O2 58.8(7) 19 2 ?

OH La O2 106.6(16) 20 2 ?

OH La O2 73.4(16) 2 2 ?

OH La O2 121.2(7) . 2 ?

OH La O2 58.8(7) 21 2 ?

OH La O2 121.2(7) 3 2 ?

O2 La O2 111.3(8) . 2 ?

O2 La O2 68.7(8) 21 2 ?

O2 La O2 111.3(8) 3 2 ?

O2 La O2 180(2) 20 2 ?

OH La O2 73.4(16) 19 19 ?

OH La O2 121.2(7) 20 19 ?

OH La O2 58.8(7) 2 19 ?

OH La O2 106.6(16) . 19 ?

OH La O2 121.2(7) 21 19 ?

OH La O2 58.8(7) 3 19 ?

O2 La O2 180.0 . 19 ?

O2 La O2 111.3(8) 21 19 ?

O2 La O2 68.7(8) 3 19 ?

O2 La O2 111.3(8) 20 19 ?

O2 La O2 68.7(8) 2 19 ?

OH Fe OH 180.0 33 9 ?

OH Fe OH 83(3) 33 32 ?

OH Fe OH 97(3) 9 32 ?

OH Fe OH 97(3) 33 8 ?

OH Fe OH 83(3) 9 8 ?

OH Fe OH 180.0 32 8 ?

OH Fe O2 86.5(16) 33 13 ?

OH Fe O2 93.5(16) 9 13 ?

OH Fe O2 86.5(16) 32 13 ?

OH Fe O2 93.5(16) 8 13 ?

OH Fe O2 93.5(16) 33 25 ?

OH Fe O2 86.5(16) 9 25 ?

OH Fe O2 93.5(16) 32 25 ?

OH Fe O2 86.5(16) 8 25 ?

O2 Fe O2 180.0 13 25 ?

OH Fe La 130.5(14) 33 7 ?

OH Fe La 49.5(14) 9 7 ?

OH Fe La 130.5(14) 32 7 ?

OH Fe La 49.5(14) 8 7 ?

O2 Fe La 124.4(15) 13 7 ?

O2 Fe La 55.6(15) 25 7 ?

OH Fe La 49.5(14) 33 13 ?

OH Fe La 130.5(14) 9 13 ?

OH Fe La 49.5(14) 32 13 ?

OH Fe La 130.5(14) 8 13 ?

O2 Fe La 55.6(15) 13 13 ?

O2 Fe La 124.4(15) 25 13 ?

La Fe La 180.0 7 13 ?

O2 As O2 106.7(19) 8_445 9 ?

O2 As O2 106.7(19) 8_445 7_455 ?

O2 As O2 106.7(19) 9 7_455 ?

O2 As O1 112.1(18) 8_445 . ?

O2 As O1 112.1(18) 9 . ?

O2 As O1 112.1(18) 7_455 . ?

As O2 Fe 131(3) 13_544 7_444 ?

As O2 La 140(2) 13_544 . ?

Fe O2 La 88.9(19) 7_444 . ?

Fe OH Fe 136(3) 15_554 14_544 ?

Fe OH La 96.6(16) 15_554 . ?

Fe OH La 96.6(16) 14_544 . ?

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_refine_diff_density_rms 0.357

_shelx_res_file

;

TITL 2046_0m in R-3m

shelx.res

created by SHELXL-2018/1 at 08:30:55 on 05-Mar-2022

CELL 0.71073 7.25170 7.25170 16.76730 90.0000 90.0000 120.0000

ZERR 6.00 0.01320 0.01320 0.03170 0.0000 0.0000 0.0000

LATT 3

SYMM -y,x-y,z

SYMM -x+y,-x,z

SYMM x-y,-y,-z

SYMM y,x,-z

SYMM -x,-x+y,-z

SFAC As Fe La O

UNIT 3 6 6 24

ACTA

```
L.S. 10
OMIT -1 1 1
OMIT 0 1 2
FMAP 2
BOND
WGHT    0.052900  514.500183
FVAR       0.09073
LA    3    0.000000    0.000000    0.000000    10.07881   10.03000
FE    2    0.500000    0.500000    0.500000    10.23499   10.01500
AS    1    0.000000    0.000000    0.316340    10.11636   10.02000
O1    4    0.000000    0.000000    0.414803    10.16667   10.02500
O2    4    0.218590   -0.218590   -0.051919    10.50000   10.02500
OH    4    0.119689   -0.119689    0.131920    10.50000   10.02500
HKLF 4



REM  2046_0m in R-3m
REM R1 =  0.0956 for      36 Fo > 4sig(Fo)  and  0.1222 for all      47 data
REM      7 parameters refined using      0 restraints

END

WGHT      0.0520    516.4087

REM Highest difference peak  1.683,  deepest hole -1.495,  1-sigma level  0.357
Q1    1   0.0543  0.1086  0.0013  10.50000  0.05    1.68
Q2    1   0.0616  0.1232  0.3258  10.50000  0.05    1.56
Q3    1  -0.0679 -0.1358  0.0806  10.50000  0.05    1.19
Q4    1  -0.0543 -0.1086  0.3353  10.50000  0.05    1.14
Q5    1   0.0508 -0.2841 -0.0359  11.00000  0.05    0.95
```

```
Q6    1  -0.0659 -0.1318  0.3955  10.50000  0.05    0.92
Q7    1   0.0087 -0.3701 -0.0444  11.00000  0.05    0.90
Q8    1   0.3259  0.0316 -0.0377  11.00000  0.05    0.76
Q9    1   0.0000  0.0000  0.1614  10.16667  0.05    0.76
Q10   1   0.0600 -0.4700 -0.0362  10.50000  0.05    0.65
Q11   1   0.0000  0.0000  0.5000  10.08333  0.05    0.58
Q12   1   0.5295  0.4705  0.5416  10.50000  0.05    0.52
Q13   1   0.4194  0.4065  0.5349  11.00000  0.05    0.49
Q14   1   0.0590 -0.2844  0.1119  11.00000  0.05    0.49
Q15   1   0.0813 -0.0813  0.1835  10.50000  0.05    0.48
Q16   1   0.1761 -0.1761 -0.0260  10.50000  0.05    0.45
Q17   1   0.3670  0.4721  0.4598  11.00000  0.05    0.37
Q18   1   0.1624 -0.1624  0.0207  10.50000  0.05    0.37
Q19   1   0.2116 -0.2116  0.1913  10.50000  0.05    0.28
Q20   1   0.1106 -0.3585  0.1286  11.00000  0.05    0.25
;
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_shelx_hkl_file
;
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  2  -1   0  430.88   18.23
 -4   2   0 1000.00   27.09
 -5   1   0   52.83   18.67
 -1   1   1    5.08    5.41
 -3   2   1   70.88   10.13
  3  -2  -1   63.71   14.68
  4   0   1   80.77   14.99
 -4   1   1   50.81   12.97
  4  -3   1   43.34   16.30
 -5   2  -1   33.94   16.42
  5  -3  -1   49.22   18.00
```

5	-2	1	50.32	18.69
-1	0	2	-3.65	7.25
-3	1	2	73.31	11.07
-3	2	-2	123.65	17.51
3	-1	-2	63.57	10.57
-4	1	-2	4.28	15.75
4	-1	2	-14.44	15.92
-5	2	2	11.05	14.18
5	-2	-2	16.86	14.47
5	-3	2	12.19	18.28
0	0	3	15.46	7.12
0	0	-3	5.56	6.13
-2	1	3	854.22	22.87
-2	1	-3	766.88	28.57
2	-1	3	856.62	24.15
3	0	3	194.88	18.90
-3	0	-3	220.39	25.63
-4	2	3	12.10	12.15
-4	2	-3	6.94	15.00
4	-2	-3	7.84	10.61
-5	4	3	220.15	22.02
-5	1	-3	243.58	28.50
5	-1	3	239.70	25.82
5	-4	-3	220.45	21.61
-5	1	3	107.87	17.28
5	-1	-3	120.90	16.62
-1	0	-4	-2.86	9.50
-2	0	4	419.53	19.40
-3	2	4	41.82	14.69
-3	1	-4	-9.20	16.50
3	-1	4	28.80	15.17
-4	1	4	-8.37	13.28

4	-1	-4	1.49	10.42
-5	3	4	-5.03	15.54
-5	2	-4	31.57	18.49
5	-3	-4	-13.45	13.94
-1	0	5	7.93	10.77
0	1	5	-2.85	9.85
-2	2	5	-13.66	12.08
-2	0	-5	3.01	11.04
-3	1	5	68.59	15.66
-3	2	-5	33.25	13.59
-4	1	-5	120.94	19.11
-4	3	5	106.14	18.08
-5	2	5	-11.41	17.02
-5	3	-5	66.73	17.06
0	0	-6	931.53	23.90
0	0	6	921.79	24.37
-2	1	6	112.18	12.74
-2	1	-6	109.78	13.48
1	-2	-6	113.26	15.43
2	-1	6	92.53	12.96
-3	0	-6	83.43	13.75
3	0	6	84.74	16.87
-4	2	-6	588.83	25.52
-4	2	6	553.59	29.46
-1	0	-7	760.23	23.39
1	-1	-7	726.88	23.32
1	0	7	721.36	23.36
-1	1	7	748.79	24.76
-3	1	-7	145.24	18.82
-3	2	7	141.49	17.43
-3	2	7	153.48	18.87
-4	1	7	175.29	24.11

-4	3	-7	202.97	19.78
0	1	8	9.41	11.47
1	0	-8	7.47	11.80
1	-1	8	9.14	12.32
-1	1	-8	-12.17	11.69
0	-1	-8	2.95	12.25
-2	0	-8	151.26	17.14
-3	1	8	43.26	12.49
-3	1	8	40.17	20.47
-4	1	-8	21.40	15.97
-4	3	8	25.59	18.29
-4	3	8	31.23	18.93
0	0	9	18.48	11.50
0	0	-9	20.86	12.09
-2	1	-9	260.08	19.52
1	-2	-9	264.35	19.91
1	1	9	268.64	18.42
-2	1	9	249.82	22.43
-1	2	9	255.09	22.01
-4	2	-9	16.18	16.72
-4	2	9	16.48	21.47
-4	2	9	26.01	13.14
1	0	10	91.35	13.76
-1	0	-10	76.09	14.31
1	-1	-10	87.73	14.56
-1	1	10	82.14	14.97
-2	0	10	746.58	27.15
0	2	10	747.08	25.63
-3	2	10	28.16	15.56
-3	1	-10	18.34	15.00
-2	-1	-10	16.43	12.86
-1	1	-11	16.74	13.66

```
  0   1  11   27.61   14.27
 -1   0  11   13.57   13.14
  1   0 -11   10.20   13.47
  0  -1 -11   12.03   14.80
 -2   2  11  107.21   17.93
 -2   0 -11   97.72   15.03
  0   0  12  164.17   20.15
  0   0 -12  165.13   21.26
 -2   1  12  161.58   22.69
 -1   2  12  119.34   21.20
  0   0   0    0.00    0.00
;
_shelx_hkl_checksum   99437
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