

SUPPLEMENTARY MATERIALS

Quantitative XRD phase analysis of poorly ordered nontronite clay in nickel laterites

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Synopsis

Modified PONKCS models developed to quantify turbostratically disordered nontronite in laterite ores.

Abstract

Studies of the extraction of nickel from low grade laterite ores require a much better quantitative understanding of the poorly ordered mineral phases present including turbostratically disordered nontronite. Whole pattern refinements with nontronite x-ray diffraction data from a Western Australian nickel deposit (Bulong) using a nontronite lattice model (Pawley phase) with two space groups P3 and C2/m and a peaks phase group model were performed to improve the accuracy of quantitative X-ray diffraction of nickel laterite ore samples. Modifications were applied when building the new models to accommodate asymmetric peak shape and anisotropic peak broadening due to the turbostratic disorder. Spherical harmonics were used as convolution factors to represent anisotropic crystal size and strain, and asymmetric peak shape when using the lattice model. A peaks phase group model was also developed to fit the anisotropic peak broadening in the nontronite pattern. The quantitative results of the new Pawley phase and peaks phase group model were compared and verified with synthetic mixtures of nontronite, quartz and goethite simulating various Western Australian laterite ore compositions. The models developed in this paper demonstrate adequate accuracy for quantification of nontronite in the synthesized reference materials and should be generally applicable to quantitative phase analysis of nontronite in nickel laterite ore samples.

Appendix A. Supercell model for turbostratically disordered smectite in TOPAS syntax

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'turbostratically disordered smectite d(001) approx. 15 Å
'structure of TOT layer (cis-vacant) by: Tsipurski et al., Clay Minerals 19(1984), 177-193 (modified)
'model for turbostratic disorder by: Ufer et al., Z. Kristallogr. 219(2004), 519-527
str
prm scnon 0.00008`_0.00000 min 0.0000001 max 1 'scale factor
prm mshkl 0.01991`_0.05020_LIMIT_MIN_0.005 min 0.005 max 0.2 'strain of non-basal reflection
prm ms001 1.00000`_0.38944_LIMIT_MIN_0.001 min 0.001 max 2 'strain of basal reflection
prm cshkl 28.54665`_1.35020 min 0.0000001 max 1000 'size of non-basal reflections
prm cs001 5.76015`_0.09071 min 0.0000001 max 20 'size of basal reflections

'occupancies of cations
prm !pMg 0.02 min 0 max 1 prm !pFe 0.7 min 0.5 max 1 prm pAl =1-pMg-pFe;; 0.28 min 0 max 1
'octahedral position, Mg fixed, Fe Al refinable. total 1.
prm ptrans 0.5 min 0 max 1 'mixing parameter for cis- and trans-vacancy; 0 => trans-vacant.
prm !altet 0.05 min 0 max 1 prm sitet =1-altet-fetet; prm fetet 0.01 min 0 max 0.5 'Al fixed, Fe Si
refinable. total 1.
prm pCa 0.1 min 0 max 0.3 prm pH2O =pCa;; 0.1 min 0 'interlayer H2O Ca occ max 0.3

'atom absolute position in c direction to avoid a stretching/shortening of the TOT layer by varying c0
prm !zT 2.7135
prm !zO11 1.0955
prm !zO12 1.0553
prm !zO2 3.3668

prm !layer 9 'layer: supercell factor for elongation in c direction
prm cnon 15 min 14 max 15.8 'subcell c

lor_fwhm = If(And(H==0,K==0), 0.1 Rad Lam/(Cos(Th) cs001), 0.1 Rad Lam/(Cos(Th) cshkl));
'thinner in 001 direction
lor_fwhm = If(And(H==0,K==0), ms001 Tan(Th), Sqrt((mshkl Tan(Th))^2 + L^2/(Get(c)^2 L^2 +
Get(c)^4 ((H/Get(a))^2+(K/Get(b))^2))); 'aniso strain and additional l-dependent broadening to
avoid "ripples"
scale_pk = If(And(H==0,K==0),If(Mod(L,layer),0,layer),1); 'scaling of classes (001 and hkl) and
removal of redundant 001 reflections
scale = scnon;

r_bragg 1.53469955
phase_name "nontronite-15A"
MVW( 0,0,0) 'value will be upadte after refinement
space_group 5
Phase_LAC_1_on_cm( 18.08806`_17.77692)
Phase_Density_g_on_cm3( 0.23902`_0.18477)
a_anon 5.3 min 5.25 max 5.35
b_bnon 9.15 min 9.1 max 9.2
c=layer*cnon; 'supercell c
be !benon 100.2

'atom positions
site Al1 num_posns 2 x=0;:0.00000 y=0;:0.00000 z=0;:0.00000 occ Al+3 =ptrans*pAl; beq
0.5 'octahedral trans
```

site Mg1 num_posns 2 x =0;:0.00000 y =0;:0.00000 z =0;:0.00000 occ Mg+2
 =ptrans*pMg; beq 0.5 'octahedral trans
 site Fe1 num_posns 2 x =0;:0.00000 y =0;:0.00000 z =0;:0.00000 occ Fe+3 =ptrans*pFe; beq
 0.5 'octahedral trans
 site Al2 num_posns 2 x =0;:0.00000 y 0.6540 z =0;:0.00000 occ Al+3 =(1-ptrans)*pAl;
 beq 0.5 'octahedral cis
 site Mg2 num_posns 2 x =0;:0.00000 y 0.6540 z =0;:0.00000 occ Mg+2 =(1-
 ptrans)*pMg; beq 0.5 'octahedral cis
 site Fe2 num_posns 2 x =0;:0.00000 y 0.6540 z =0;:0.00000 occ Fe+3 =(1-ptrans)*pFe;
 beq 0.5 'octahedral cis
 site Al3 num_posns 2 x =0;:0.00000 y 0.3210 z =0;:0.00000 occ Al+3 =pAl; beq
 0.5 'octahedral cis
 site Mg3 num_posns 2 x =0;:0.00000 y 0.3210 z =0;:0.00000 occ Mg+2 =pMg;
 beq 0.5 'octahedral cis
 site Fe3 num_posns 2 x =0;:0.00000 y 0.3210 z =0;:0.00000 occ Fe+3 =pFe; beq
 0.5 'octahedral cis
 site Si1 num_posns 4 x 0.4320 y =1/3;:0.33333 z =zT/(layer*cnon); occ Si+4
 =sitet; beq 0.4 'tetrahedral
 site Al4 num_posns 4 x 0.4320 y =1/3;:0.33333 z =zT/(layer*cnon); occ Al+3
 =altet; beq 0.4 'tetrahedral
 site Fe4 num_posns 4 x 0.4320 y =1/3;:0.33333 z =zT/(layer*cnon); occ Fe+3
 =fetet; beq 0.4 'tetrahedral
 site Si2 num_posns 4 x 0.4320 y 0.662 z =zT/(layer*cnon); occ Si+4 =sitet;
 beq 0.4 'tetrahedral
 site Al5 num_posns 4 x 0.4320 y 0.662 z =zT/(layer*cnon); occ Al+3 =altet;
 site Fe5 num_posns 4 x 0.4320 y 0.662 z =zT/(layer*cnon); occ Fe+3 =fetet;
 site O7 num_posns 4 x 0.1730 y 0.7250 z =zO2/(layer*cnon); occ O-2 1 beq
 0.8
 site O8 num_posns 4 x 0.1700 y 0.2680 z =zO2/(layer*cnon); occ O-2 1 beq
 0.8
 site O9 num_posns 4 x 0.4170 y 0.6560 z =zO11/(layer*cnon); occ O-2 1 beq
 0.8
 site O10 num_posns 4 x 0.3430 y 0.3470 z =zO11/(layer*cnon); occ O-2 1
 beq 0.8
 site O11 num_posns 4 x =1/3;:0.33333 y 0.9760 z =zO12/(layer*cnon); occ O-2 1
 beq 0.8
 site O12 num_posns 4 x 0.4890 y 0.4960 z =zO2/(layer*cnon); occ O-2 1
 beq 0.8

 site Ca num_posns 4 x 0 y 0 z 0 occ Ca+2 =pCa; beq 0.8 'atom positions defined in rigid
 body, will be updated after refinement.
 site O1 num_posns 4 x 0 y 0 z 0 occ O-2 =pH2O; beq 2.5 'atom positions defined in rigid
 body, will be updated after refinement.
 site O2 num_posns 4 x 0 y 0 z 0 occ O-2 =pH2O; beq 2.5 'atom positions defined in rigid
 body, will be updated after refinement.
 site O3 num_posns 4 x 0 y 0 z 0 occ O-2 =pH2O; beq 2.5 'atom positions defined in rigid
 body, will be updated after refinement.
 site O4 num_posns 4 x 0 y 0 z 0 occ O-2 =pH2O; beq 2.5 'atom positions defined in rigid
 body, will be updated after refinement.
 site O5 num_posns 4 x 0 y 0 z 0 occ O-2 =pH2O; beq 2.5 'atom positions defined in rigid
 body, will be updated after refinement.

site O6 num_posns 4 x 0 y 0 z 0 occ O-2 =pH2O; beq 2.5 'atom positions defined in rigid body, will be updated after refinement.

'rigid body of the interlayer complex

prm !dCaO 2.41

rigid

point_for_site Ca

point_for_site O1 uz = dCaO;

point_for_site O2 uz =-dCaO;

point_for_site O3 ux = dCaO;

point_for_site O4 ux =-dCaO;

point_for_site O5 uy = dCaO;

point_for_site O6 uy =-dCaO;

rotate 45 qx 1 operate_on_points "O*"

rotate =180/Pi*ArcSin(1/Sqrt(3)); qy 1 operate_on_points "O*" 'this rotation angle in original "supercell" model is ArcCos(1/Sqrt(3)), because BGMMN use Eulerian angle to describe rigid body rotation.

rotate -18.42 qz 1 operate_on_points "O*"

translate tx 6.892 ty 2.092 tz=0.5*cnon*Sin(benon Deg); operate_on_points "O* Ca"