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Novel mineralogical quantitative phase analysis methodology applied to Canadian oil sands for ore characterization, processability prediction and optimization of froth treatment technologies

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Topics for the talk

Part 1

Background
- Strategic importance of Alberta oil sands to World Oil Reserves
- Goal: Reduce energy intensity and environmental footprint of production

Part 2

Novel methodology developed for quantitative phase analysis (QPA)
- Merging of weighted experimental results from various kinds of analyses
- Singular-value decomposition (SVD) of the QPA least-squares matrix to identify ***family of solutions*** consistent with all experimental observations

Part 3

Applications to oil sands R&D
- Mineralogy of fines (<44 μm solids) as potential indicators for ore characterization and processability predictions
- Optimization of bituminous froth treatment processes

Part 4

Concluding remarks
- Completeness of SVD-based least-squares QPA approach developed
- Next step in methodology development

Alberta Oil Sands

Syncrude's oil sands operations

- an open-pit mine north of Fort McMurray
- produced/shipped 105.8 millions bbl of synthetic crude oil in 2008

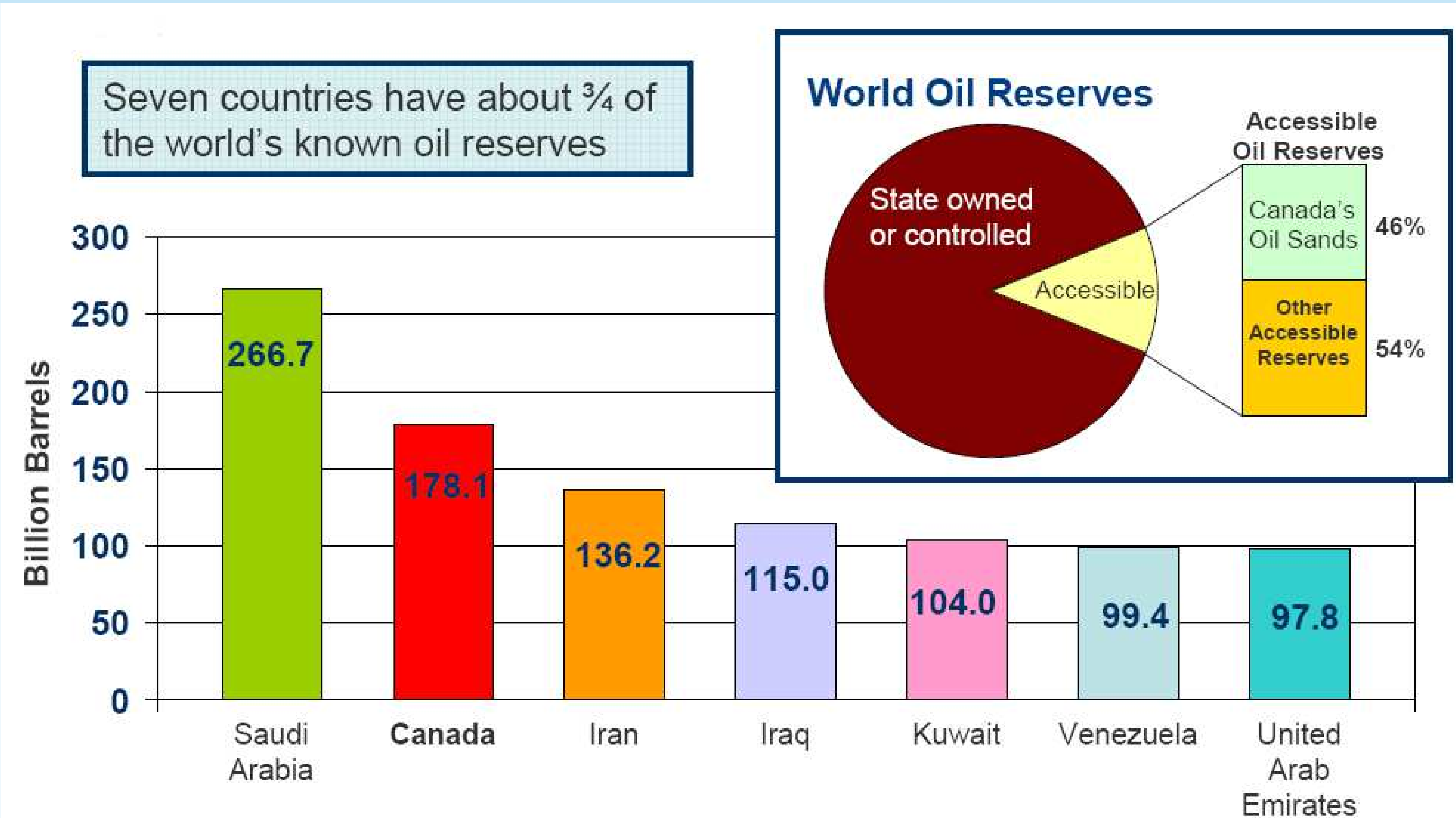
Oil sands are composed of :
- coarse sand, silt and clay solids (80–85 wt%),
- bitumen (5–15 wt%), and
- water (1–5 wt%)

Photographs taken from National Geographic, March 2009

Canada's oilsands potential is vast and largely untapped…

proven reserves | 1.7 trillions bbl oil in place

…placing Canada 2nd in proven oil reserves recoverable with today's technology



Source: Reserve data, Oil and Gas Journal, December 22, 2008 - "World Reserves" image, CAPP

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Research focused on Processability Issues…

Current Standards:

- Fines content (<44 µm solids)
- Bitumen content (ore grade)
- Ore blending:
  - fines, grade, D50, facies

From assessment of ore properties and process conditions

Research to address knowledge gaps

Known detrimental effects of:

-- clays & ultra-fines (mineralogy/chemistry/size)

-- organic rich solids (ORS)

Knowledgebase to predict:

- bitumen recovery
- tailings discharge
- bitumen froth & crude quality

Could results of quantitative mineralogical analyses be used as processability markers to:

-- Reduce energy intensity?

-- Decrease environmental footprint?

2. Novel methodology developed for quantitative phase analysis (QPA)

Incorporate experimental results from:

-- K, Al, Si, Fe, Ca, Mg, Ti, and Zr concentrations from XRF spectrometry

-- C and S concentrations from elemental analysis

-- mineral mass ratios of crystalline phases from XRD powder patterns

into a **single weighted linear least-squares refinement for QPA**

2.1

Mineral phases typically observed in oil sands ore

QPA by
least-squares solution
of a linear system of
weighted equations where
variables are the
phase concentrations of:

-- 18 minerals
-- "organic C"
-- "organic S"

(i.e., C and S unaccounted for by the mineral phases)

Mineral	Chemical formula	Density (kg/m^3) [÷ 1000 = g/cm^3]
Quartz	SiO_2	2,664
Clay minerals:		
Illite	$K_{0.8}Al_{2.8}Si_{3.2}O_{10}(OH)_2$	2,794
Kaolinite	$Al_2Si_2O_5(OH)_4$	2,599
Chlorite	$Mg_{2.5}Fe_{2.5}Al_2Si_3O_{10}(OH)_8$	2,982
Ca-Mg Carbonates:		
calcite	$CaCO_3$	2,713
dolomite	$CaMg(CO_3)_2$	2,868
ankerite	$CaFe_{2/3}Mg_{1/3}(CO_3)_2$	3,133
Heavy minerals:		
Siderite	$FeCO_3$	3,944
Pyrite	FeS_2	5,016
Zircon	$ZrSiO_4$	4,675
Rutile	TiO_2	4,249
Anatase	TiO_2	3,895
Ilmenite	$FeTiO_3$	4,787
Lepidocrocite	$FeO(OH)$	4,008
Calcium sulphates:		
Gypsum	$CaSO_4 \cdot 2\,H_2O$	2,339
Bassanite	$CaSO_4 \cdot 0.5\,H_2O$	2,715
Feldspars:		
Anorthite	$CaAl_2Si_2O_8$	2,762
Sanidine	$KAlSi_3O_8$	2,557

Construction of linear system of equations for least-squares solution

Analysis for each element K provides its weight fraction K^w in the sample, with uncertainty $\sigma(K^w)$, leading to a weighted equation of the type:

concentration of element K in phases P1, P2, …

$$[(M\_K / M\_P1)\, X\_P1 + (M\_K / M\_P2)\, X\_P2 + \ldots] \;/\; \sigma(K^w) \;=\; K^w / \sigma(K^w)$$

etc.

For each mineral mass ratio determined by Rietveld XRD (where two mineral phases P1 and P2 have similar density and micro-absorption), we have a weighted equation of the type:

$$[\,X\_P1 - (wt\_P1 / wt\_P2)\, X\_P2\,] \;/\; [\sigma(wt\_P1 / wt\_P2)] \;=\; 0$$

etc.

This gives a **linear system of weighted equations** that we symbolize as

$$\mathbf{A} \cdot \mathbf{x} = \mathbf{b}$$

with as many equations as there are elements analyzed and mineral mass ratios included.

From this, we create the ***normal system of equations***,
with dimension equal in number to the much smaller number of parameters in the model :
(here the 20 phase concentrations sought in the QPA)

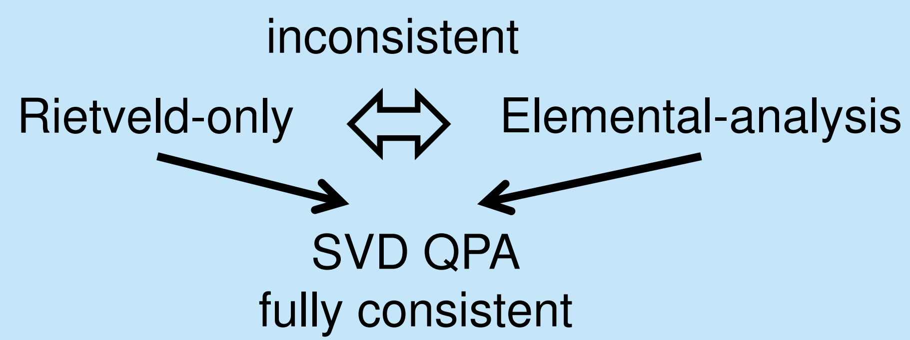
$$\mathbf{A}^T \cdot \mathbf{A} \cdot \mathbf{x} = \mathbf{A}^T \cdot \mathbf{b}$$

and solve it by ***singular value decomposition (SVD)*** based matrix inversion as:

$$\mathbf{x} = [\mathbf{A}^T \cdot \mathbf{A}]^{-1} \cdot \mathbf{A}^T \cdot \mathbf{b}$$

Comparison with Standard Rietveld-only QPA

	Rietveld QPA	SVD QPA value	SVD QPA 1-sigma s.u.
Quartz	72.58	53.5	4.5
Ilmenite	0.00	0.00	0.03
Illite	7.81	20.2	2.7
Kaolinite	12.53	15.5	6.9
Chlorite	1.01	1.3	0.5
Siderite	0.66	3.0	3.6
Calcite	0.00	-0.5	1.6
Dolomite	0.49	1.4	1.1
Pyrite	0.39	0.2	1.2
Zircon	0.00	0.28	0.05
Rutile	2.20	0.685	0.009
Anatase	2.14	0.666	0.009
Anorthite	0.00	0.0	6.4E-05
Gypsum	0.00	0.0	6.0E-05
Sanidine	0.00	0.0	1.0E-04
C organic	0.00	0.8	0.8
S organic	0.00	0.0	0.0
Ankerite	0.18	0.5	0.5
Bassanite	0.00	0.00	0.00
Lepidocrocite	0.00	0.00	0.00



		Rietveld QPA	SVD QPA	Measured concentration value	Measured concentration 1-sigma s.u.
K	(wt%)	0.6	1.6	1.7	0.1
Si	(wt%)	38.6	33.3	33.3	0.8
Al	(wt%)	4.3	7.3	7.7	0.5
Fe	(wt%)	0.8	1.9	1.9	0.6
Mg	(wt%)	0.2	0.3	0.3	0.1
Ca	(wt%)	0.1	0.2	0.2	0.3
Ti	(wt%)	2.60	0.81	0.81	0.03
Zr	(wt%)	0.0	0.1	0.1	0.1
C	(wt%)	0.2	1.3	1.3	0.5
S	(wt%)	0.2	0.1	0.1	0.5

Singularity of Quantitative Phase Analysis Problems

Singularity problems arise in QPA of multiphase geological systems because:

-- Standard Rietveld-only QPA analysis is SINGULAR in the presence of amorphous phases. It can at best derive RELATIVE proportions of CRYSTALLINE phases.

-- Elemental-analysis only QPA of soils with this complexity is also SINGULAR as we deal practically with 20 phases and 10 chemical elements.

-- Any claim to have extracted a single solution from a singular system can be shown mathematically to be optimistic at best (i.e., non-unique solution), and more probably wrong.

Assessing Singularity of QPA Problems

Singular value decomposition (SVD) of least-squares matrix $[\mathbf{A}^T \bullet \mathbf{A}]$

LS normal matrix

diagonal

Singular or not

$$[\mathbf{A}^T \bullet \mathbf{A}] = [\mathbf{R}] \cdot [\mathbf{D}] \cdot [\mathbf{R}]^T$$

orthonormal

columns of $[\mathbf{R}] \equiv \mathbf{R}_i \equiv$ singular vectors

elements of $[\mathbf{D}] \equiv D_i \equiv$ singular values

Family of solutions compatible with observations are identified by plotting vectors:

$$\mathbf{x} + k\,\mathbf{R}_i$$

where $\mathbf{x} = [\mathbf{A}^T \bullet \mathbf{A}]^{-1} \bullet \mathbf{A}^T \bullet \mathbf{b}$ and k is a scalar linear factor.

Typical example of performing SVD on least-squares matrix $[\mathbf{A}^T \cdot \mathbf{A}]$

No3

Singular values:	21073.108	21072.969	21071.649	21071.452	11982.921	10004.000	803.734	189.060	34.831	20.507
Qtz	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0005	0.0000	0.0057
Ilm	0.0000	0.0000	0.0000	0.0000	0.0003	0.0000	-0.3647	0.0015	0.9306	0.0000
Ill	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0001	0.0000	0.0030
Kao	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0787	0.0008	0.0029
Chl	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0002	0.9969	-0.0017	0.0001
Sid	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0003	0.0019	0.0172	0.0000
Cal	-0.0001	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0000
Dol	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0040	0.0001	0.0000
Pyr	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	-0.0003	0.0018	0.0171	0.0000
Zir	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0002	0.0000	1.0000
Rut	0.0000	0.0000	0.0000	0.0000	-0.6966	0.0000	-0.6681	-0.0005	-0.2613	0.0000
Ana	0.0000	0.0000	0.0000	0.0000	0.7174	0.0000	-0.6486	-0.0005	-0.2542	0.0000
Anor	-0.3498	-0.0702	-0.9336	0.0320	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Gyp	-0.5161	-0.3395	0.2445	0.7474	0.0000	-0.0001	0.0000	0.0000	0.0000	0.0000
SanM	-0.5068	0.8528	0.1256	-0.0037	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Corg	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0003	0.0000
Sorg	-0.0001	-0.0001	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000
Ank	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0001	0.0019	0.0067	0.0000
Bas	-0.5953	-0.3905	0.2297	-0.6636	0.0000	-0.0001	0.0000	0.0000	0.0000	0.0000
Lep	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0003	0.0025	0.0235	0.0000

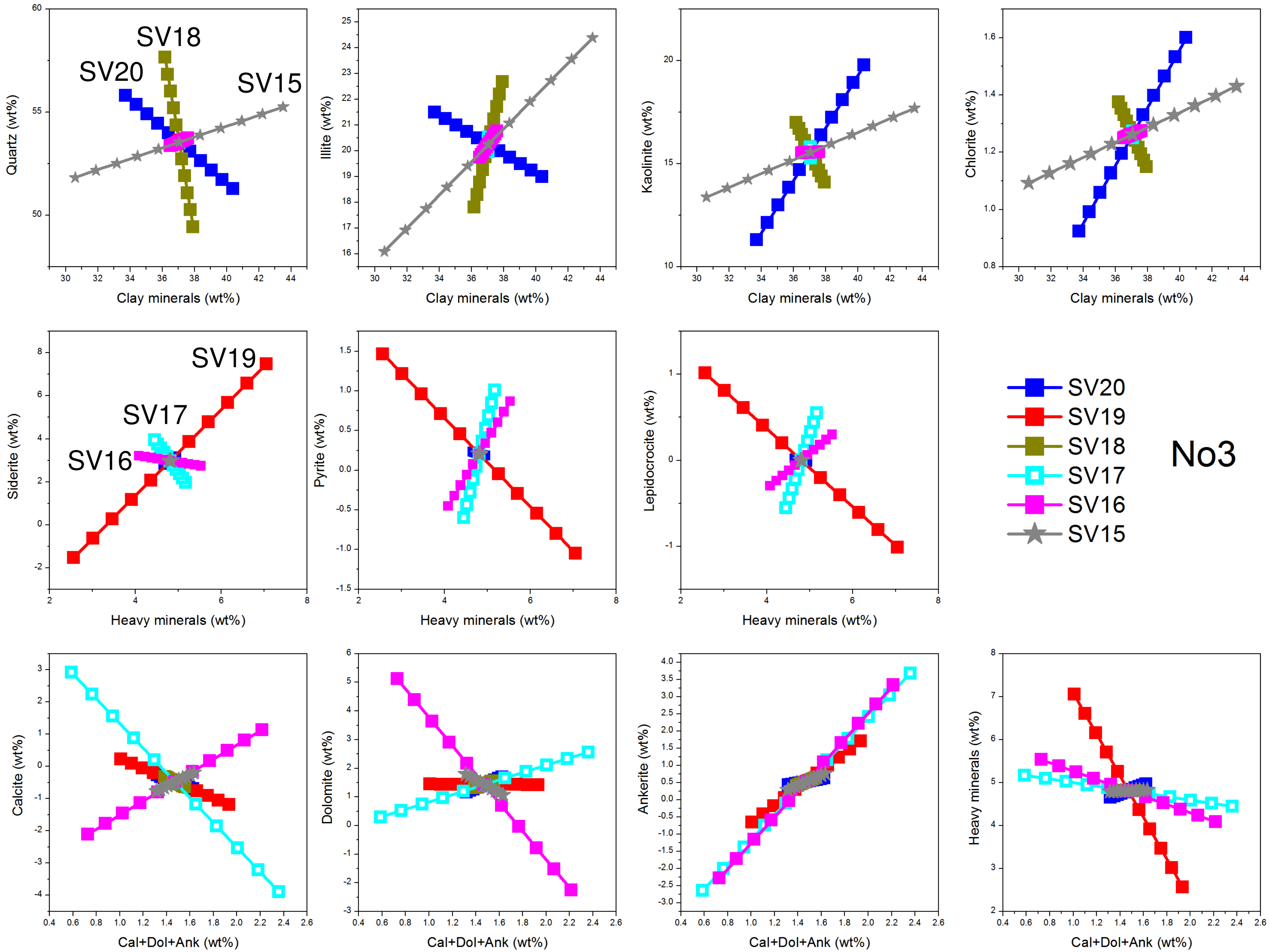
	4.617	3.970	2.355	1.342	0.981	0.841	0.514	0.308	0.254	0.125
Qtz	-0.0004	0.0005	-0.0018	0.0013	-0.3418	0.0374	-0.0049	0.8216	0.0331	-0.4533
Ilm	0.0166	-0.0269	-0.0008	-0.0034	0.0000	-0.0008	-0.0021	-0.0001	0.0045	0.0001
Ill	-0.0008	0.0010	-0.0036	0.0027	-0.8283	0.1011	-0.0570	-0.4876	-0.0021	-0.2503
Kao	-0.0110	0.0106	-0.0196	0.0049	-0.4303	0.0047	0.0539	0.2901	-0.0165	0.8489
Chl	0.0023	-0.0018	0.0011	0.0001	-0.0337	0.0025	0.0024	0.0226	-0.0010	0.0675
Sid	-0.2407	0.2631	0.0612	0.1245	-0.0002	0.0474	0.1980	0.0127	-0.9000	-0.0403
Cal	-0.2461	-0.1081	-0.5763	-0.0232	0.0576	0.3240	-0.6809	0.0326	-0.1424	0.0417
Dol	-0.2479	-0.1216	-0.5631	-0.0539	-0.0725	-0.7374	0.2264	-0.0253	-0.0020	-0.0524
Pyr	-0.2066	0.4204	0.0294	0.8204	-0.0013	-0.1321	-0.1604	-0.0045	0.2514	0.0049
Zir	0.0000	0.0000	0.0001	0.0000	0.0056	-0.0005	0.0000	-0.0041	-0.0001	0.0009
Rut	-0.0045	0.0072	0.0002	0.0009	0.0000	0.0002	0.0005	0.0000	-0.0012	0.0000
Ana	-0.0043	0.0070	0.0002	0.0009	0.0000	0.0002	0.0005	0.0000	-0.0012	0.0000
Anor	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Gyp	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
SanM	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Corg	-0.7681	-0.4536	0.4398	-0.0162	-0.0039	-0.0170	-0.0484	0.0009	0.0886	0.0086
Sorg	0.0000	-0.0001	0.0000	-0.0002	0.0000	0.0000	0.0000	0.0000	-0.0001	0.0000
Ank	-0.2705	0.0419	-0.3823	0.0655	0.0468	0.5621	0.6319	-0.0239	0.2369	-0.0197
Bas	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
Lep	-0.3373	0.7205	0.0784	-0.5509	-0.0004	-0.0597	-0.1108	-0.0035	0.2026	0.0042

Most problematic family of solutions compatible with observations will be those

$$\mathbf{x} + k\,\mathbf{R}_i$$

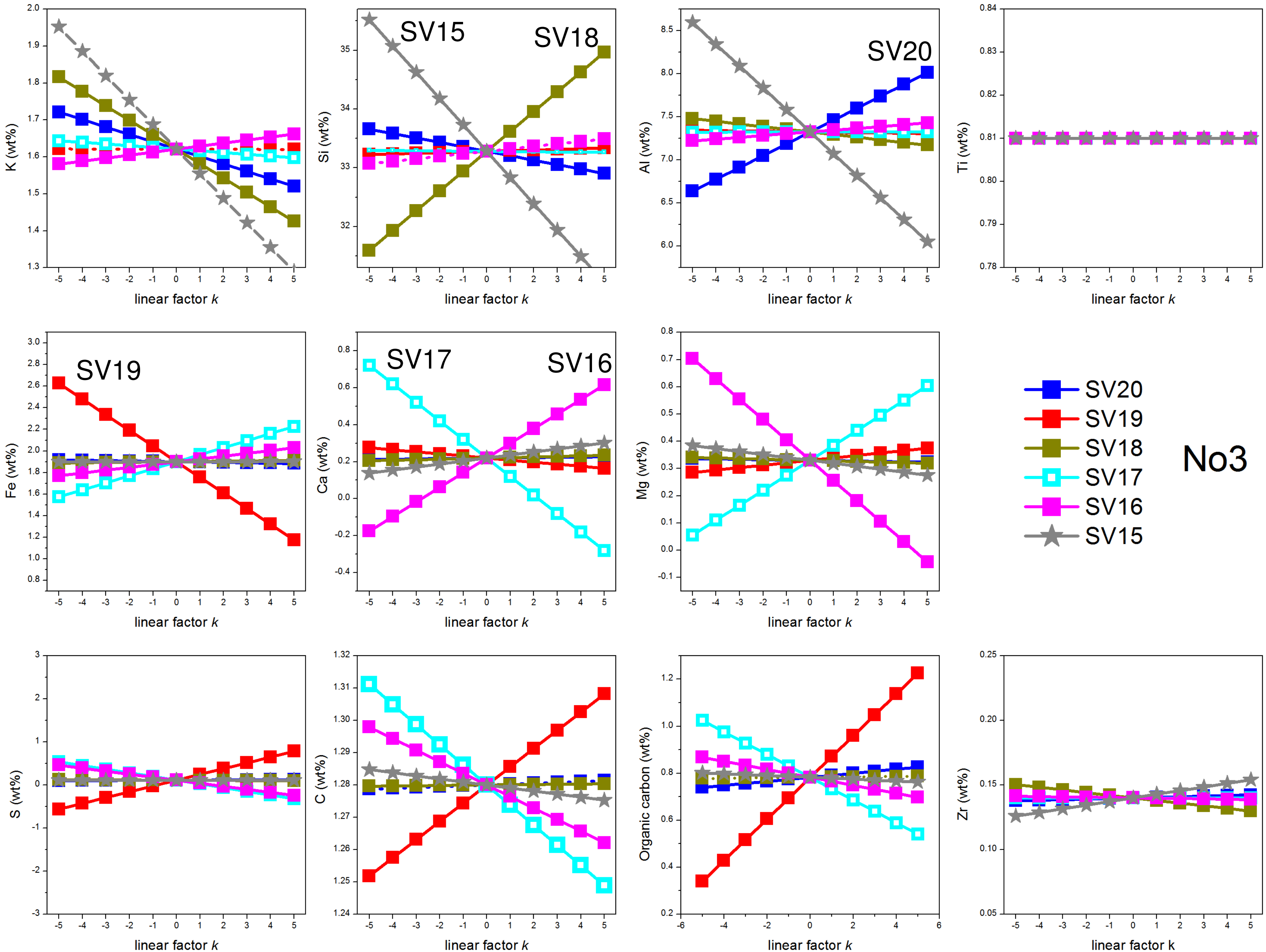
where R_i correspond to the smallest singular values.

2.7



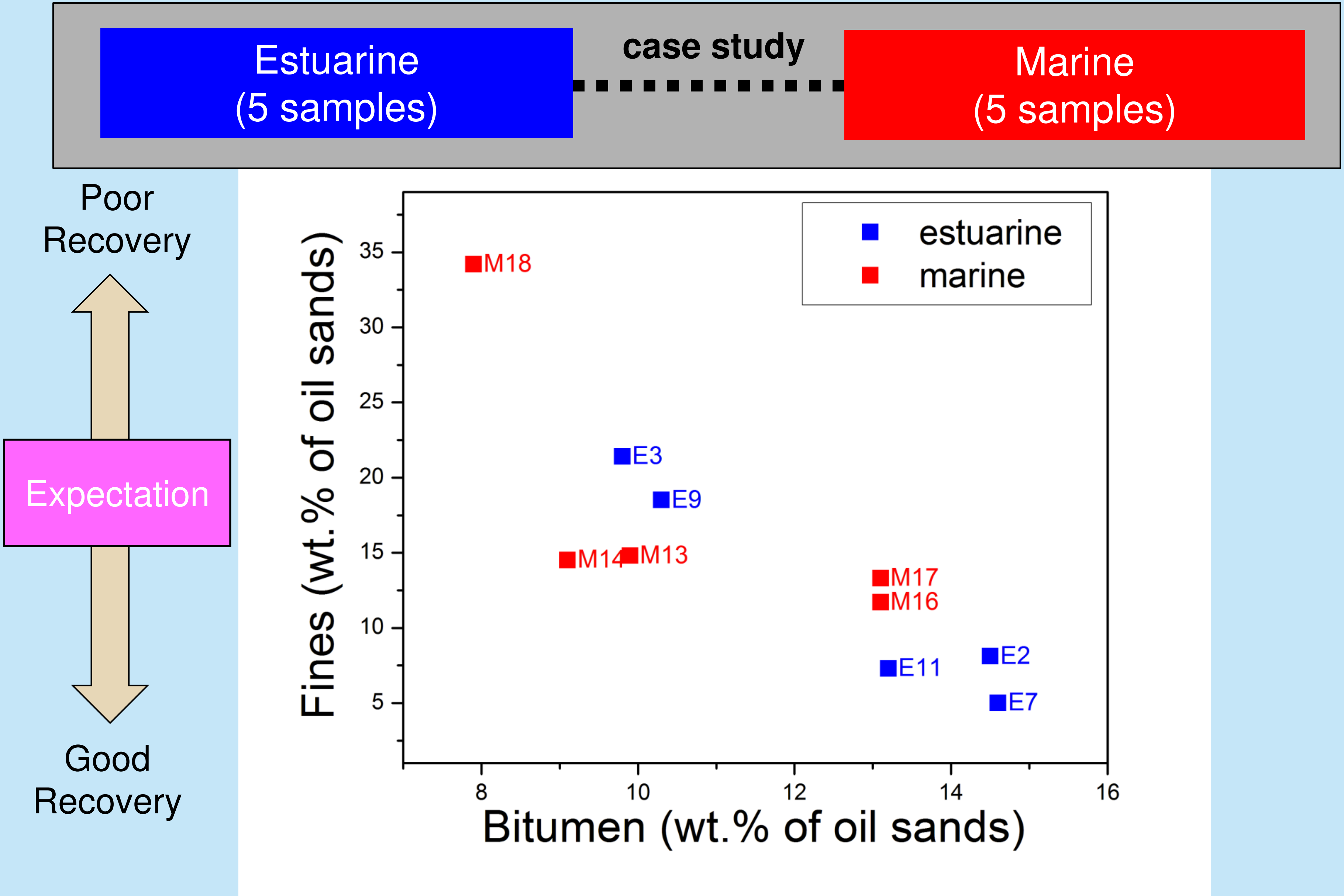
SV18
SV20
SV15
Quartz (wt%)
Illite (wt%)
Kaolinite (wt%)
Chlorite (wt%)
Clay minerals (wt%)
SV19
SV17
SV16
Siderite (wt%)
Pyrite (wt%)
Lepidocrocite (wt%)
Heavy minerals (wt%)
SV20
SV19
SV18
SV17
SV16
SV15
No3
Calcite (wt%)
Dolomite (wt%)
Ankerite (wt%)
Heavy minerals (wt%)
Cal+Dol+Ank (wt%)

2.8



K (wt%)
Si (wt%)
Al (wt%)
Ti (wt%)
Fe (wt%)
Ca (wt%)
Mg (wt%)
S (wt%)
C (wt%)
Organic carbon (wt%)
Zr (wt%)
linear factor k
SV15
SV18
SV20
SV19
SV17
SV16
SV20
SV19
SV18
SV17
SV16
SV15
No3

3. Applications to Oil Sands R&D



Correlation with Jar Test and BEU Assessments of Bitumen Recovery

estuarine

2

3

9

7

11

marine


13


14

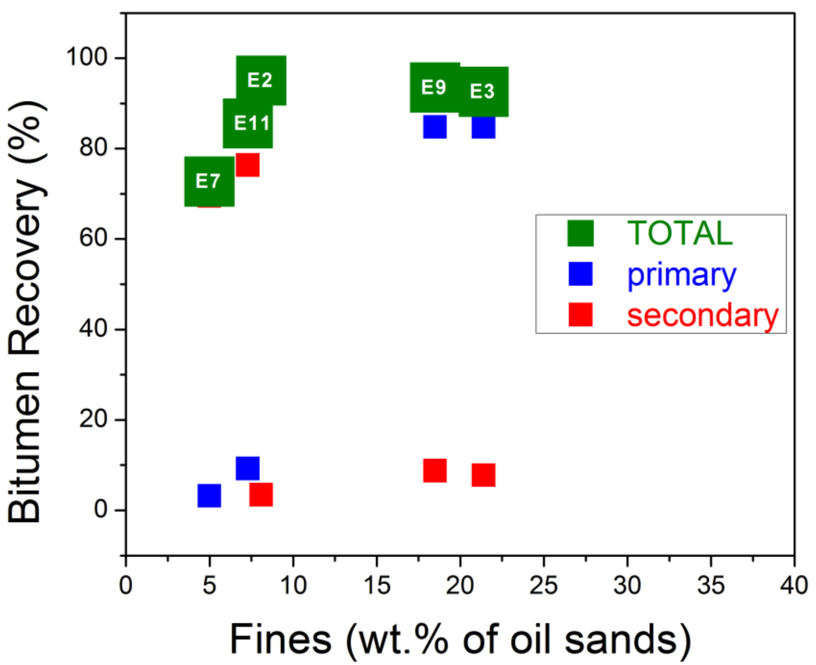

16


17

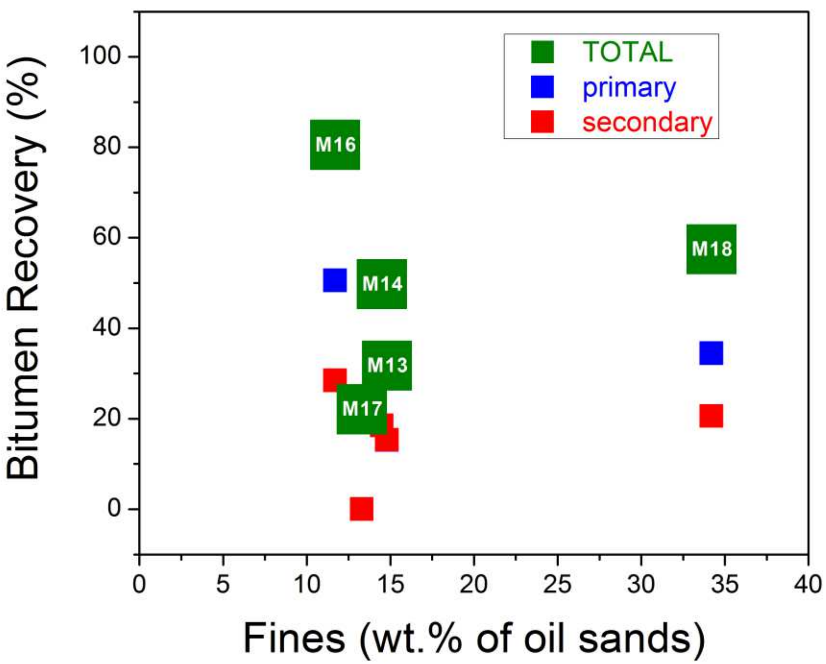

18

Bitumen Recovery vs. Fines Content (Process Water A = Constant Caustic)

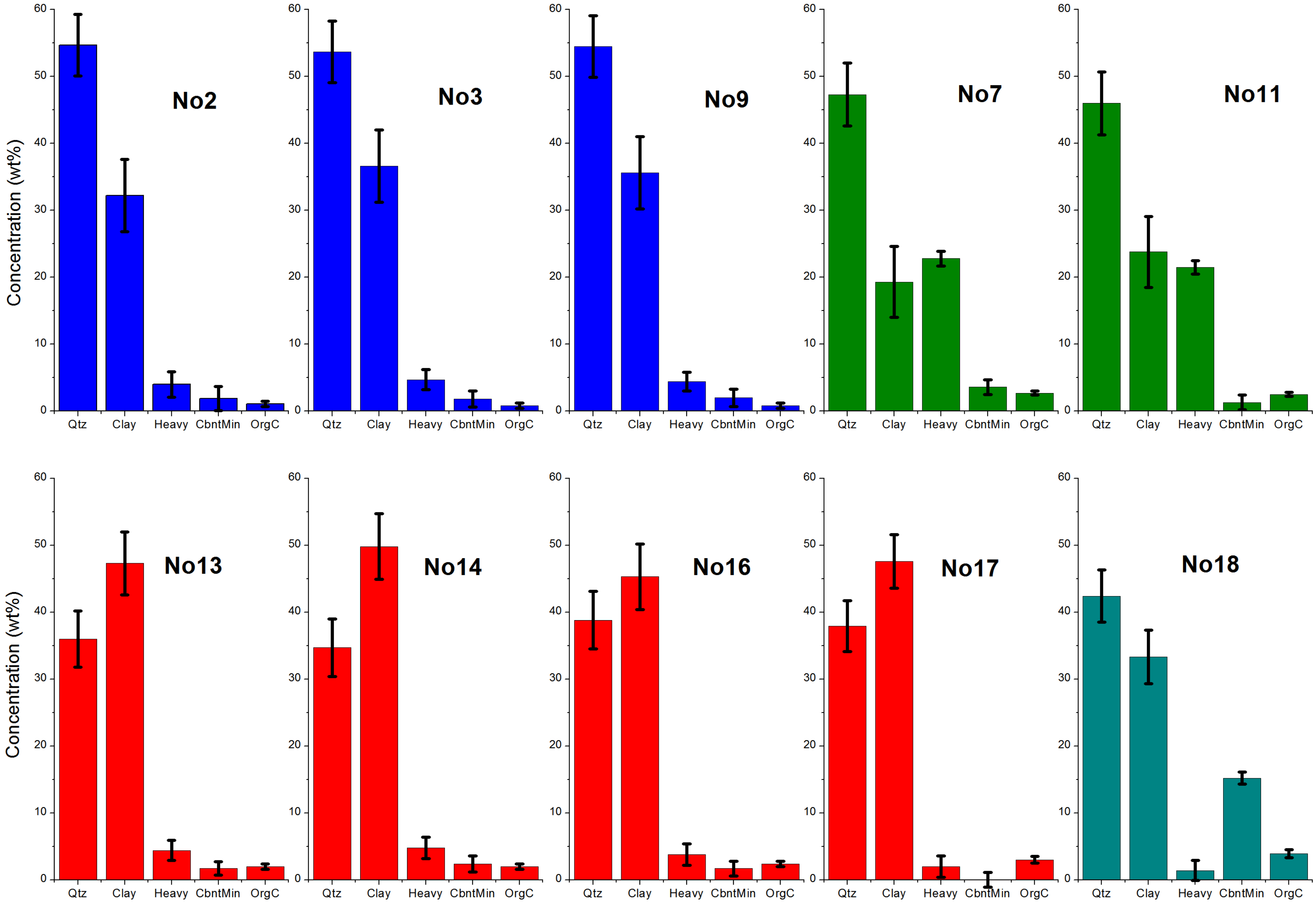
Estuarine



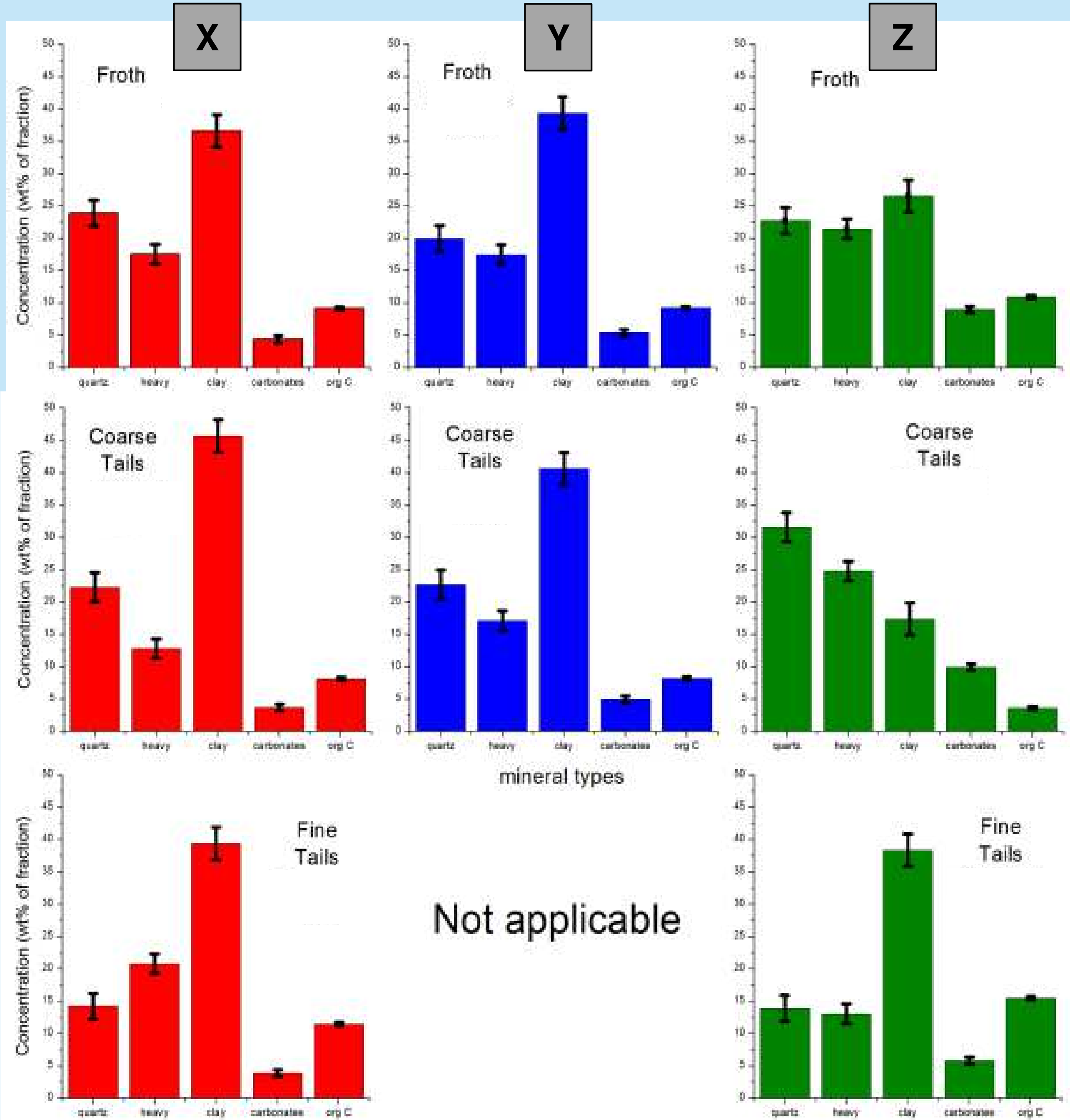
Marine



No relationship between bitumen recovery and fines (or bitumen) content was noted for the 10 oil sands tested in this case study


Concentration (wt%)
0
10
20
30
40
50
60
Qtz
Clay
Heavy
CbntMin
OrgC
No2
No3
No9
No7
No11
No13
No14
No16
No17
No18

Bituminous Froth Treatment Processes



QPA results with novel methodology

- Showed measurable differences in froth solids composition do occur
- Allowed assessment of relative advantages/ disadvantages between different froth treatment processes

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4. Concluding Remarks

Limitations of traditional approaches to QPA

-- Standard Rietveld-only QPA analysis is SINGULAR in the presence of amorphous phases. It can at best derive RELATIVE proportions of CRYSTALLINE phases.

-- Elemental-analysis only QPA of soils with this complexity is also SINGULAR as we deal practically with 20 phases and 10 chemical elements.

-- Any claim to extract a single solution from a singular system can be shown mathematically to be optimistic at best.

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4. Concluding Remarks

Superiority of SVD-based least-squares QPA approach developed

-- Rietveld data and elemental-analysis data can be merged into a linear system of weighted observations where ABSOLUTE phase abundance are the unknowns.

-- The corresponding least-squares system is usually NOT SINGULAR, even in the presence of 20 phases like here, where some phases are crystalline and others amorphous.

-- The SVD solution of this system would flag any singularity and pinpoint its origin, leading to least-squares results objectively and uniquely expressed in terms of abundance of COMBINATIONS of phases.

-- Any additional analytical result (e.g. magnetic measurements) that can be expressed in terms of phase abundance can be merged into the above SVD-based least-squares approach, increasing the accuracy of numerical results.

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