Glass Properties Course: Lecture 4

Density, Volume, and Packing: Part 3
Tuesday, September 9, 2008

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see http://www.lehigh.edu/imi/GlassPropertiesCourse.htm for archived version of lecture

Packing in Glass

- We will now examine the packing fractions (pf) obtained in glasses. This will provide a dimensionless parameter that displays some universal trends.
- We will need a good knowledge of the ionic radii. This will be provided next.

$$pf = \frac{\frac{4}{3}\pi \sum r_i^3 N_i}{V_f}$$

Ion Coordination, Radii, and Volumes

	Ca	Ba	Li	Na	K	Rb	Cs	O	Si	^{III}B	^{IV}B
Coordination	7-8	9	4	6	8	9	10	2	4	3	4
Radius (Å)	1.23	1.61	.73	1.16	1.65	1.77	1.95	1.21	.40	.15	.25
Radial Uncertainty (Å)	0.05	0.05	.05	.03	.02	.02	.02	.01	.01	.01	.01
Volume (Å^3)	7.80	17.48	1.63	6.54	14.71	19.16	31.06	7.42	.25	.01	.07
Volume Uncertainty(Å^3)	0.95	1.63	.34	.51	.60	.80	1.00	.37	.02	.003	.008
Fractional Volume Uncertainty	.12	.09	.21	.08	.04	.04	.03	.05	.08	.30	.11

Packing Fraction of Simple Cubic Lattice

- The packing fraction would be

$(4/3)\pi r^3/d^3$

r is related to d, $r = d/2$

Therefore, the packing is
$(4/3)\ \pi(d/2)^3/d^3 = 4\pi/24 = \pi\ /6 = 0.52$

Comparison of packing fractions of the units: Li

	Unit	Borate	Silicate
Li	f_1, Q_4	0.34	0.33
	f_2, Q_3	0.65	0.38
	f_3, Q_2	0.39	0.41
	f_4, Q_1	0.41	0.42

Comparison of packing fractions of the units: Na

	Unit	Borate	Silicate
Na	f_1, Q_4	0.35	0.33
	f_2, Q_3	0.62	0.42
	f_3, Q_2	0.41	0.46
	f_4, Q_1	0.46	0.48

Packing Fraction, pf

$$pf = \frac{\frac{4}{3}\pi \sum r_i^3 N_i}{V_f}$$

$$p = \sum \frac{\left(\frac{4}{3}\pi r_i^3 n_i\right)}{\text{Molar volume}}$$

$$= Density * \sum \frac{\left(\frac{4}{3}\pi r_i^3 n_i\right)}{\text{Molar mass}}$$

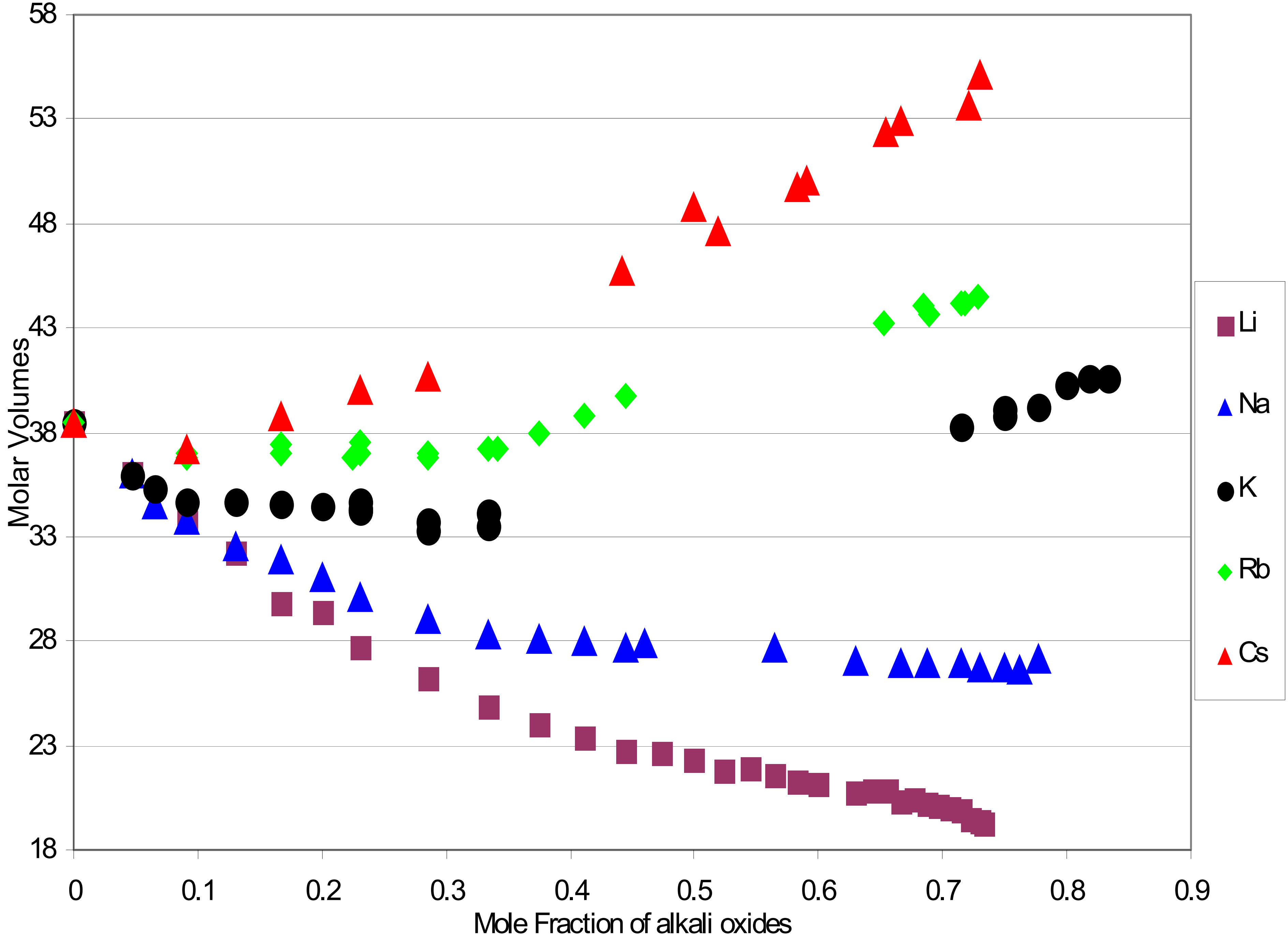
Packing Fraction of Glassy Boron Oxide (B_2O_3)

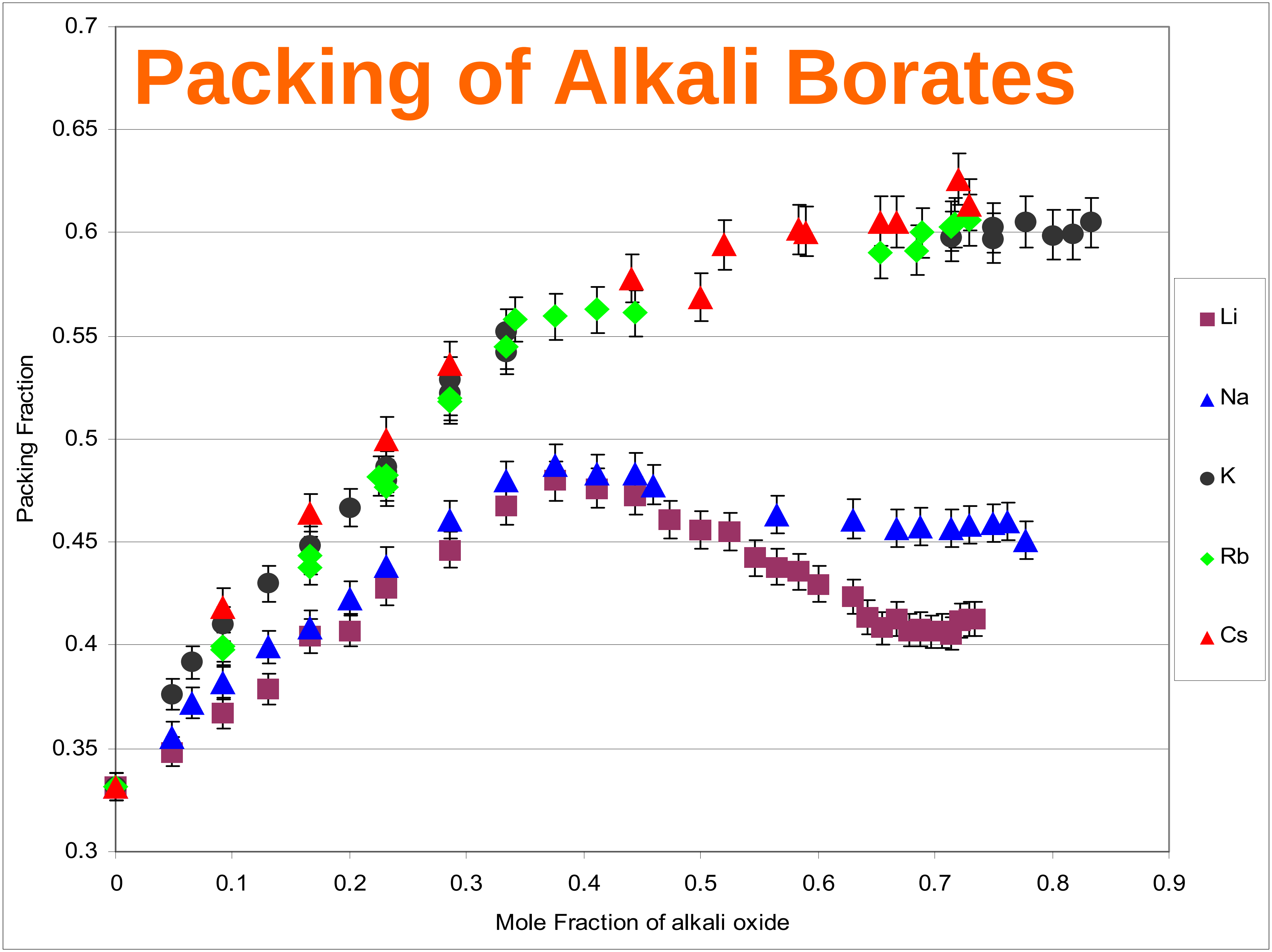
$$pf = Density * \sum \frac{\left(\frac{4}{3}\pi r_i^3 n_i\right)}{\text{Molar mass}}$$

$pf = (1.823)(4/3\pi)(2r_B^3 + 3r_O^3)6.02\times10^{23}/69.62$

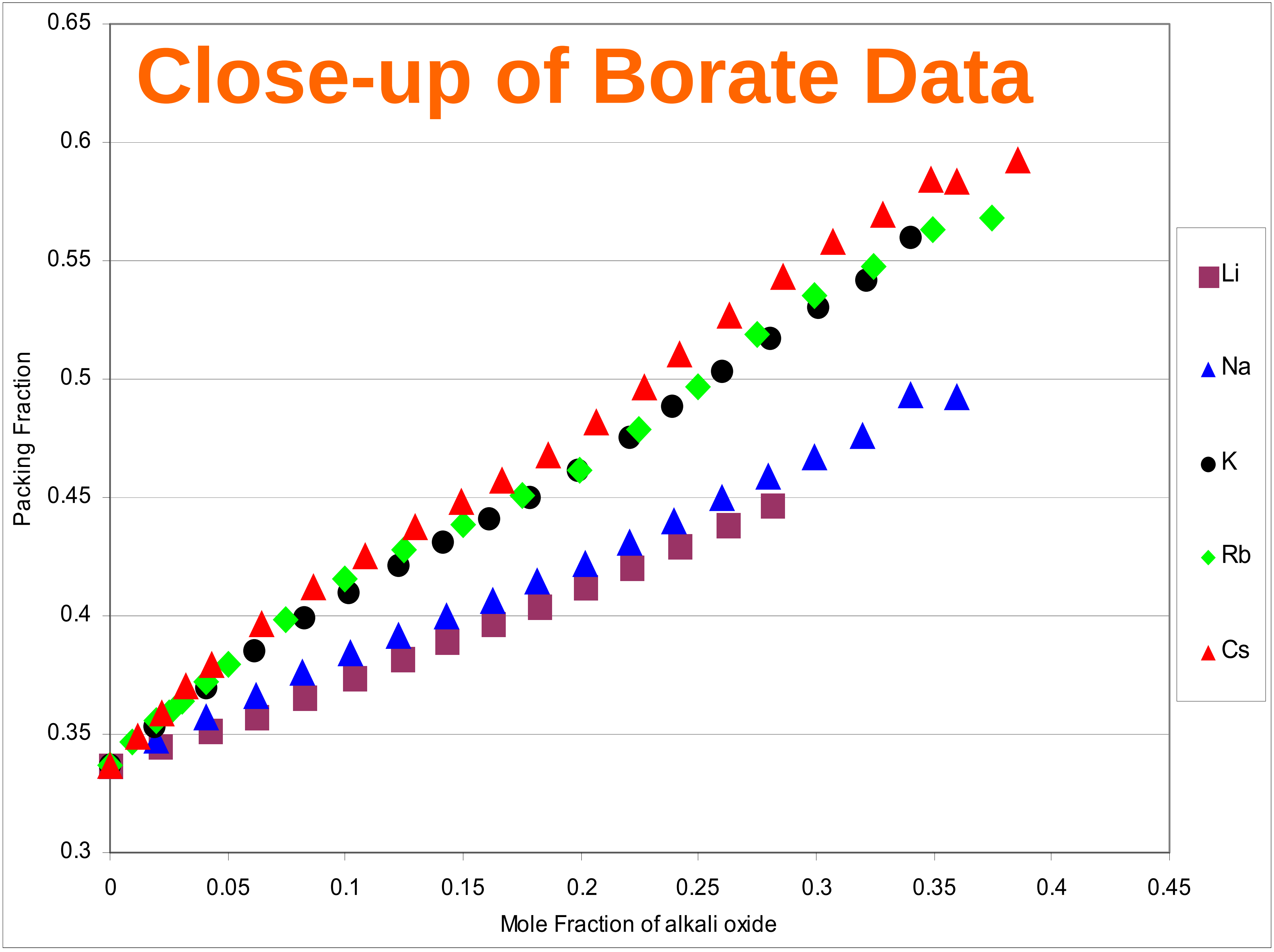
$pf = (1.823)(4/3\pi)(2(0.15\times10^{-8})^3 + 3(1.21\times10^{-8})^3)6.02\times10^{23}/69.62$

$pf = 0.35$

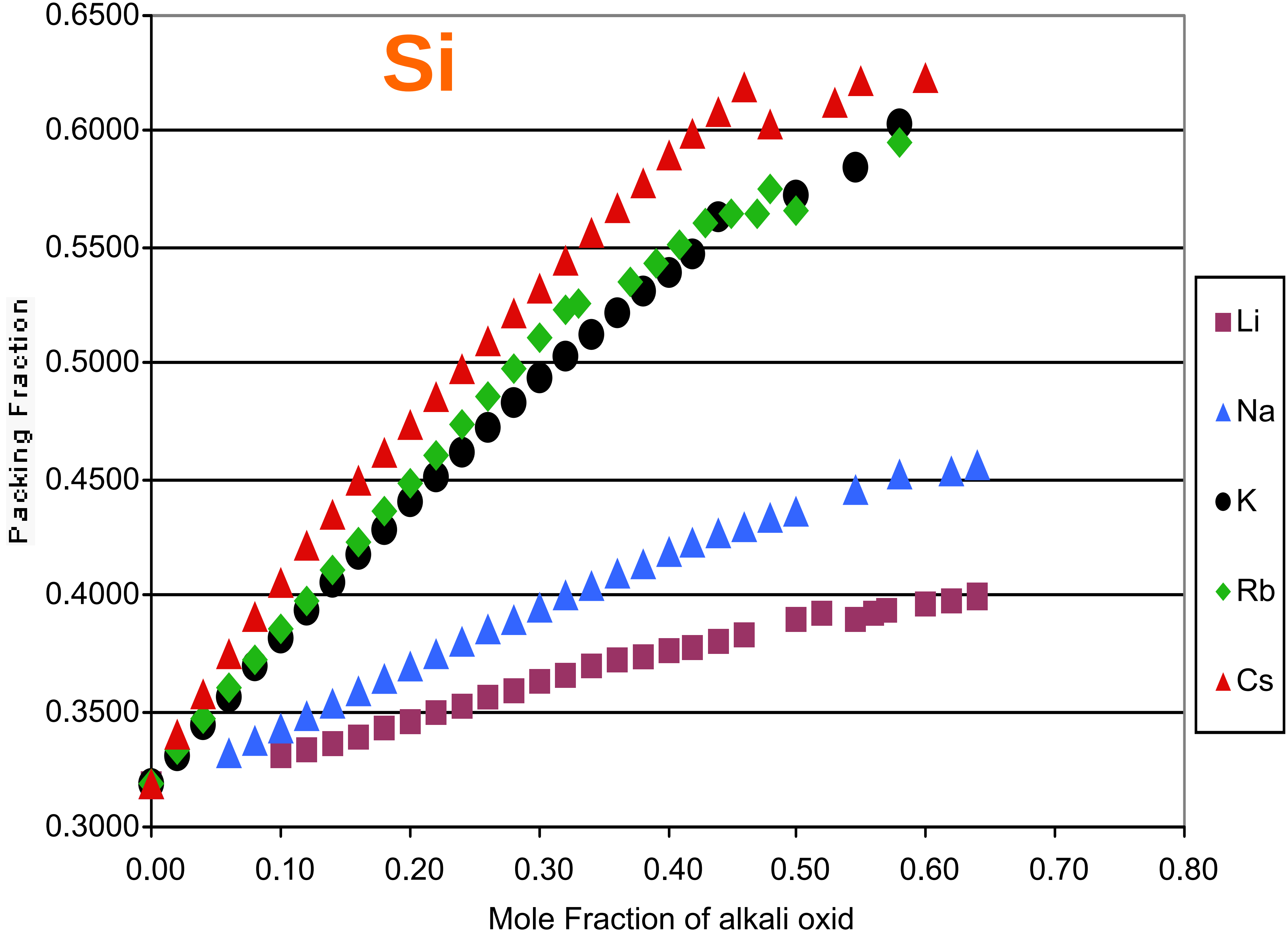

58
53
48
43
38
33
28
23
18
Molar Volumes
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Mole Fraction of alkali oxides
Li
Na
K
Rb
Cs



Packing of Alkali Borates
Packing Fraction
Mole Fraction of alkali oxide
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
Li
Na
K
Rb
Cs



Close-up of Borate Data
Packing Fraction
Mole Fraction of alkali oxide
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
Li
Na
K
Rb
Cs



Si
Packing Fraction
0.6500
0.6000
0.5500
0.5000
0.4500
0.4000
0.3500
0.3000
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
Mole Fraction of alkali oxid
Li
Na
K
Rb
Cs

Q_i Units: Si, Ge, P tetrahedra with i bridging oxygens

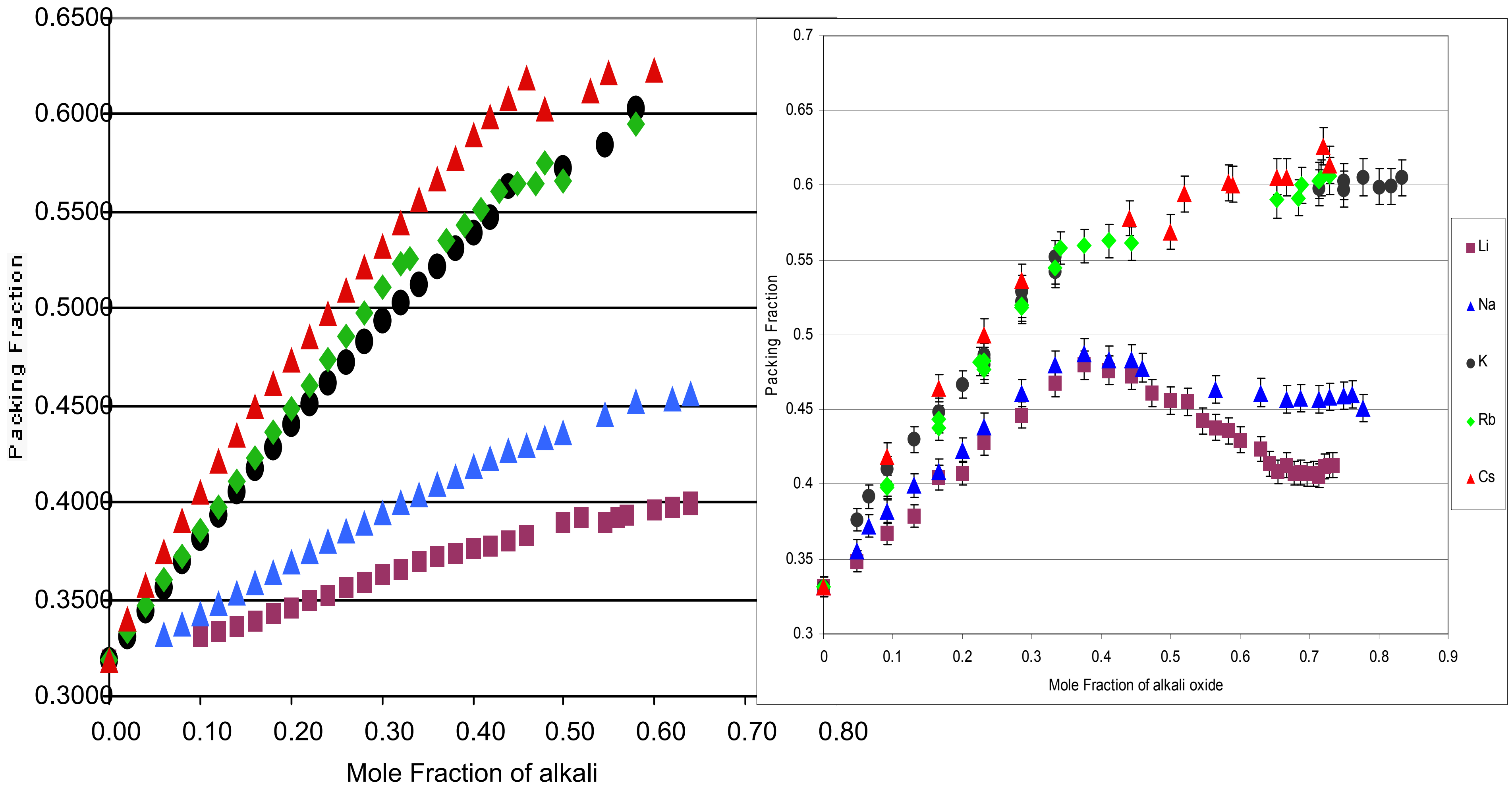
F_i Units: Borate units with trigonal borons with varying numbers of bridging oxygens (F_1,F_3,F_4,F_5) or tetrahedra with four bridging oxygens (F_2)

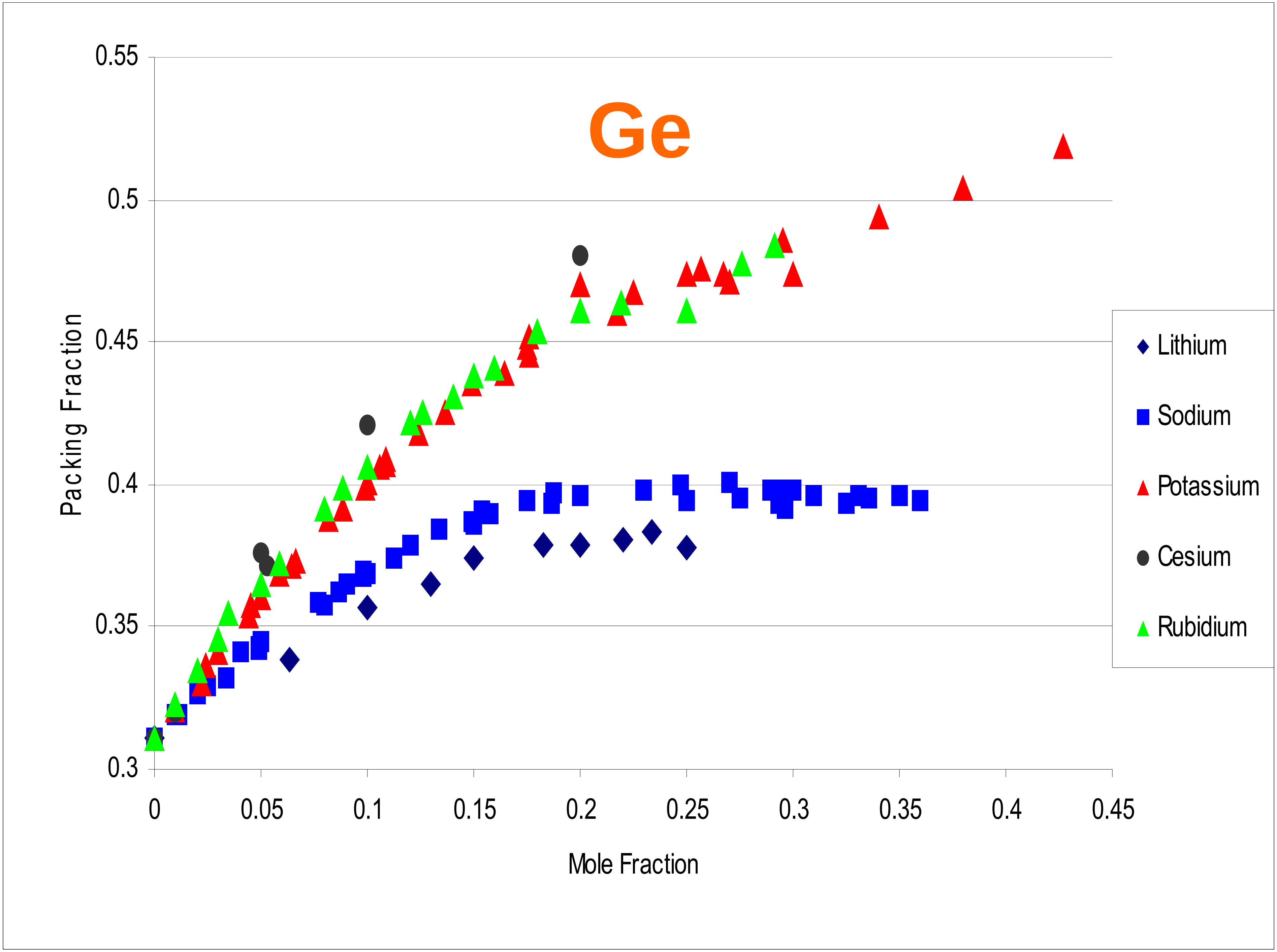
Similarities and differences between borates and silicates

a) splitting of packing fractions into two groups in both cases

b) No peak in Li or Na silicates (Q_i units versus F_i units)

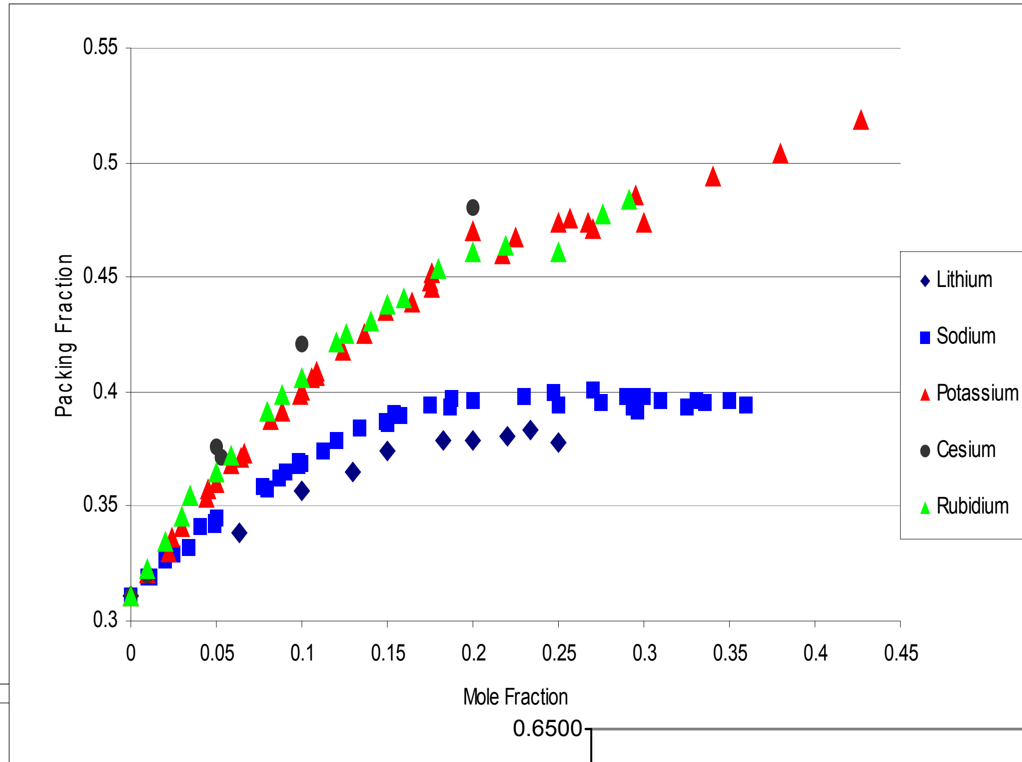
Silicates versus Borates

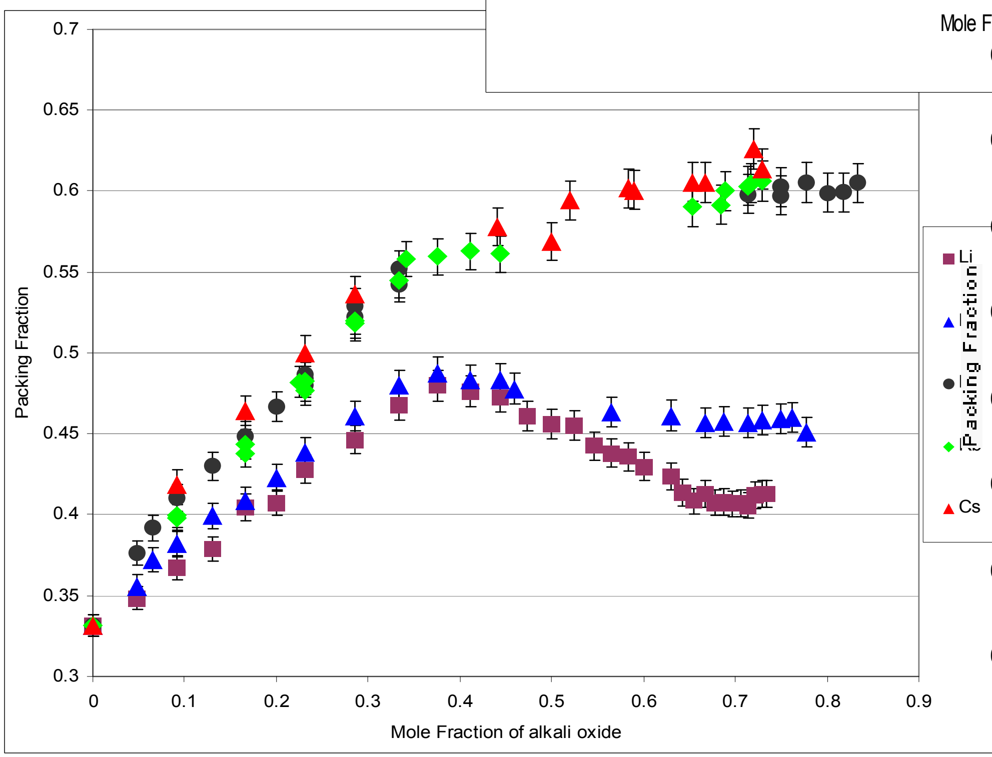


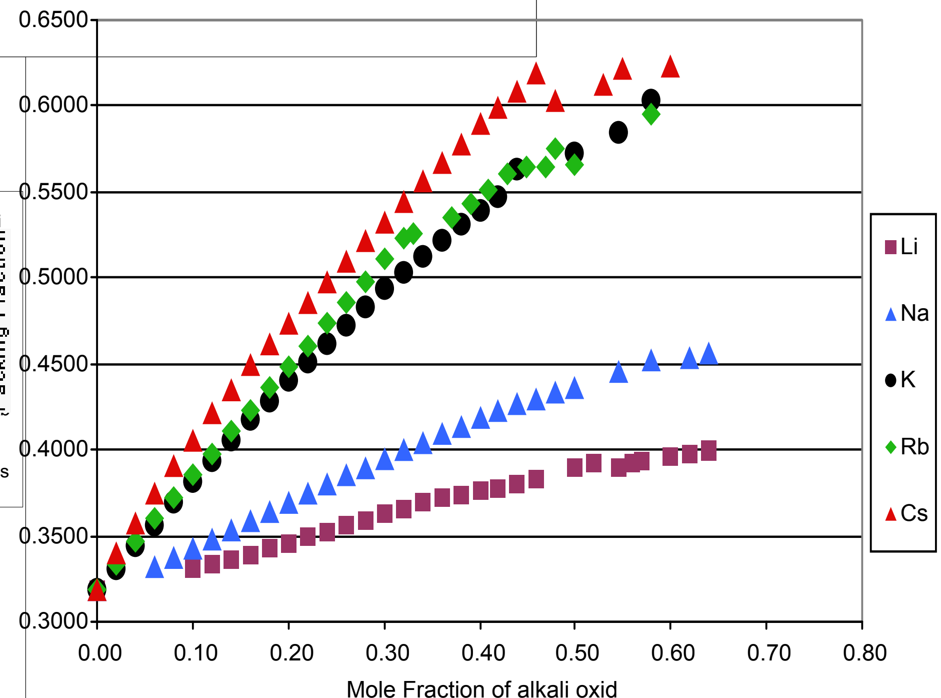


Ge
Packing Fraction
Mole Fraction
0.55
0.5
0.45
0.4
0.35
0.3
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45
Lithium
Sodium
Potassium
Cesium
Rubidium

Ge vs Si and B


Packing Fraction
Mole Fraction
Lithium
Sodium
Potassium
Cesium
Rubidium
0.55
0.5
0.45
0.4
0.35
0.3
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
0.45

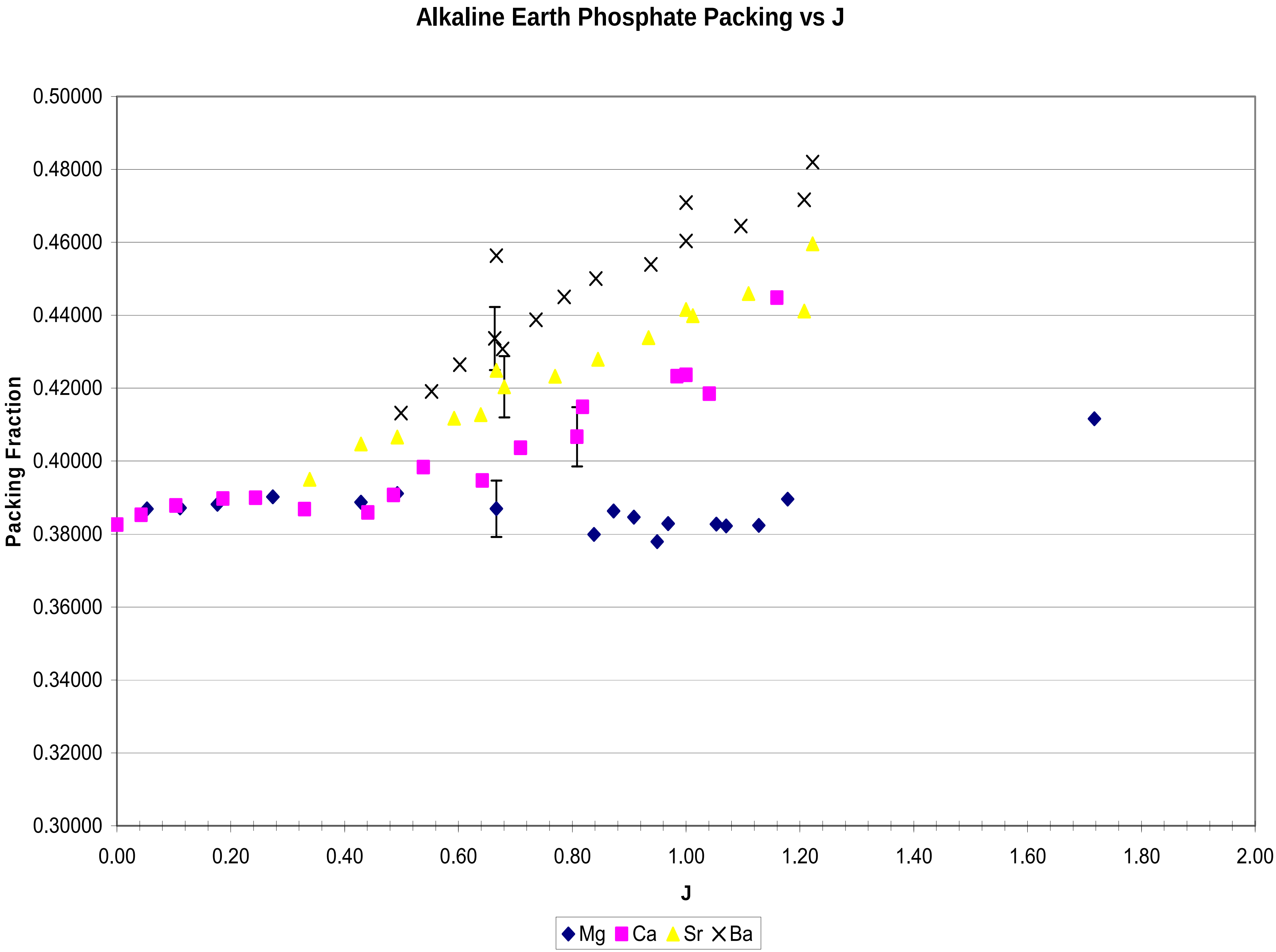

Packing Fraction
Mole Fraction of alkali oxide
Li
Cs
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9


Mole Fraction of alkali oxid
Li
Na
K
Rb
Cs
0.6500
0.6000
0.5500
0.5000
0.4500
0.4000
0.3500
0.3000
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80

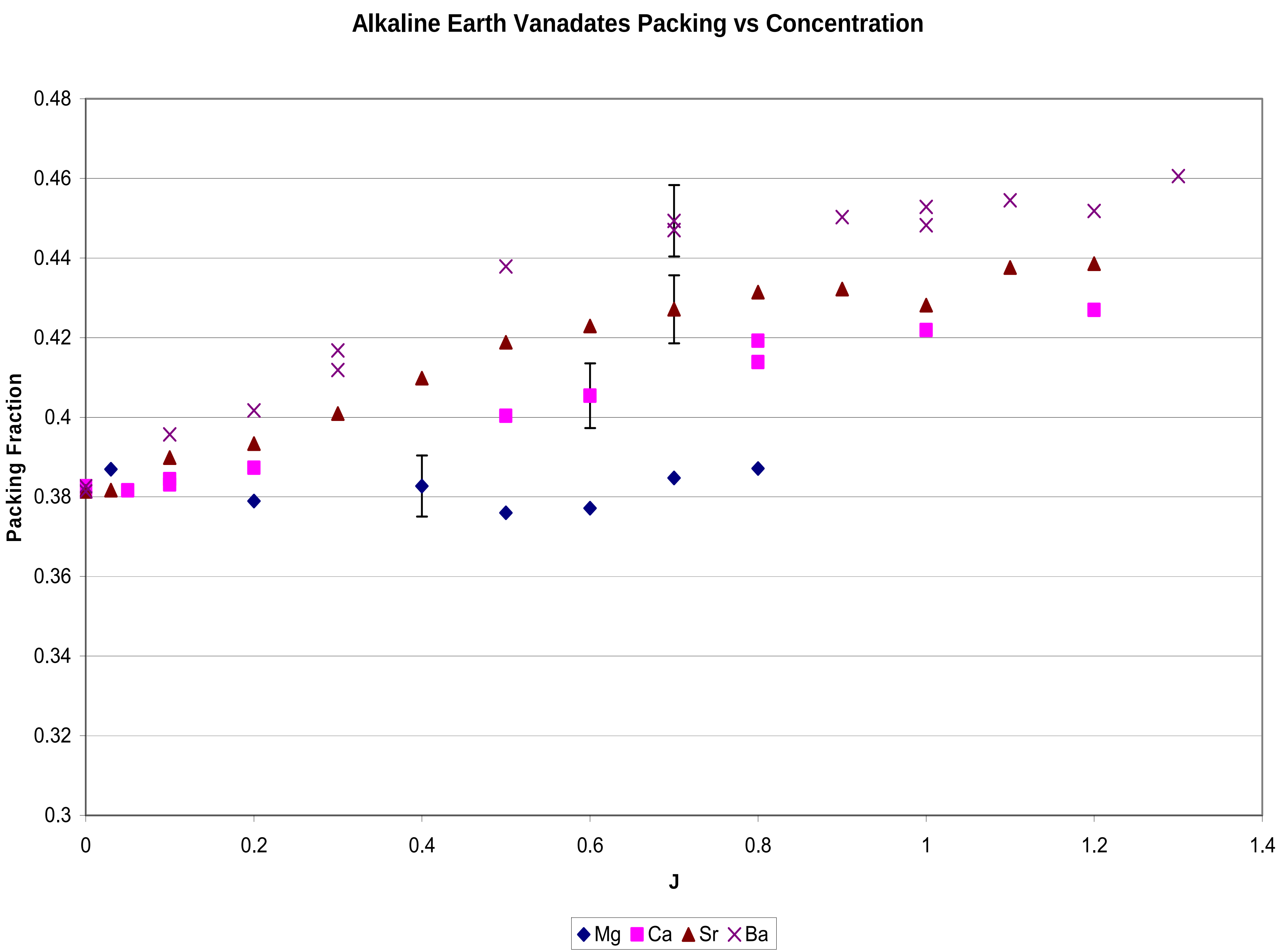
Two Types of Packing

1. *Ionic*: K, Rb, Cs
2. *Covalent*: Li and Na

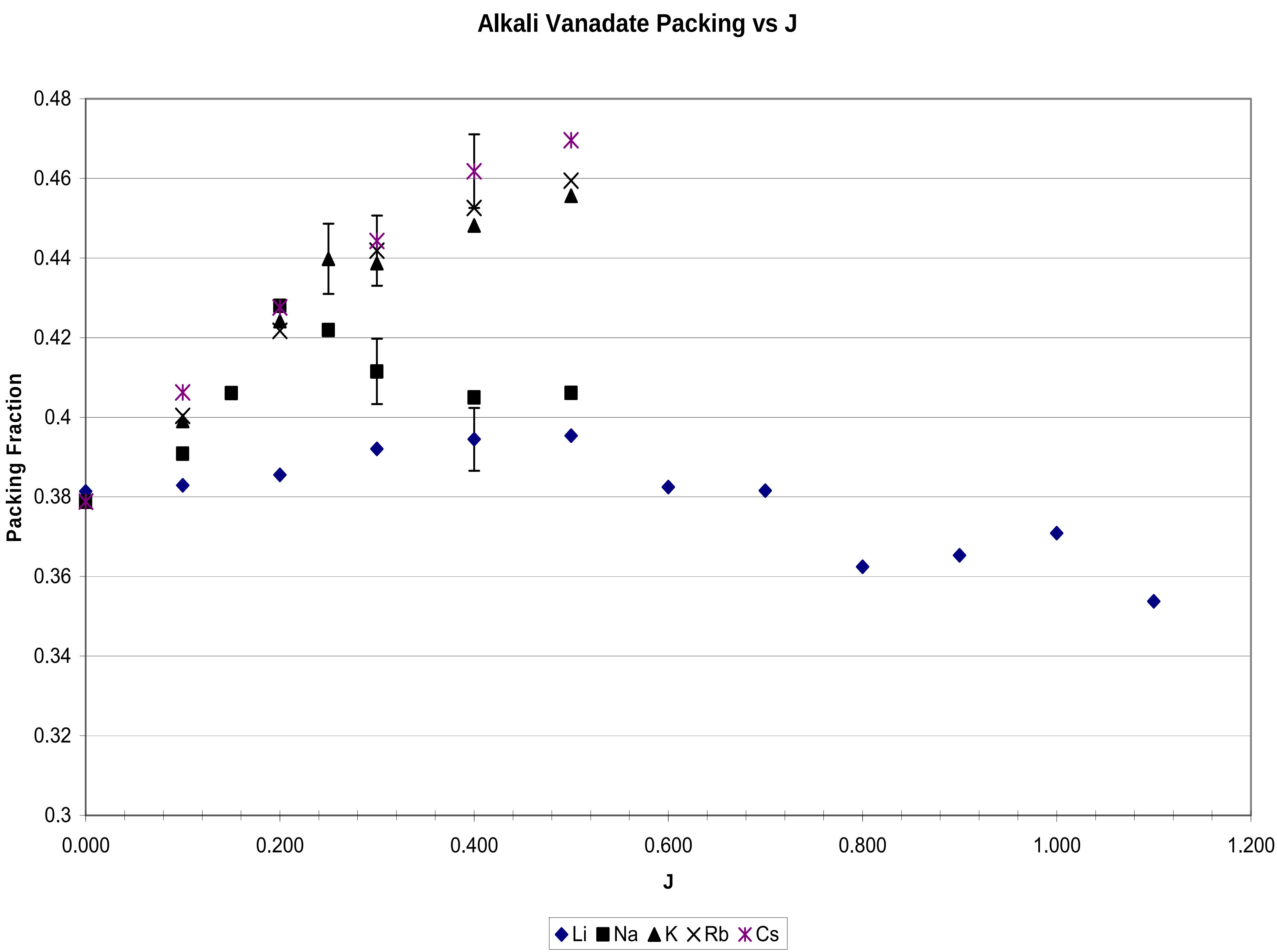
V(Li, Na) < V(O) < V(K, Rb, Cs)



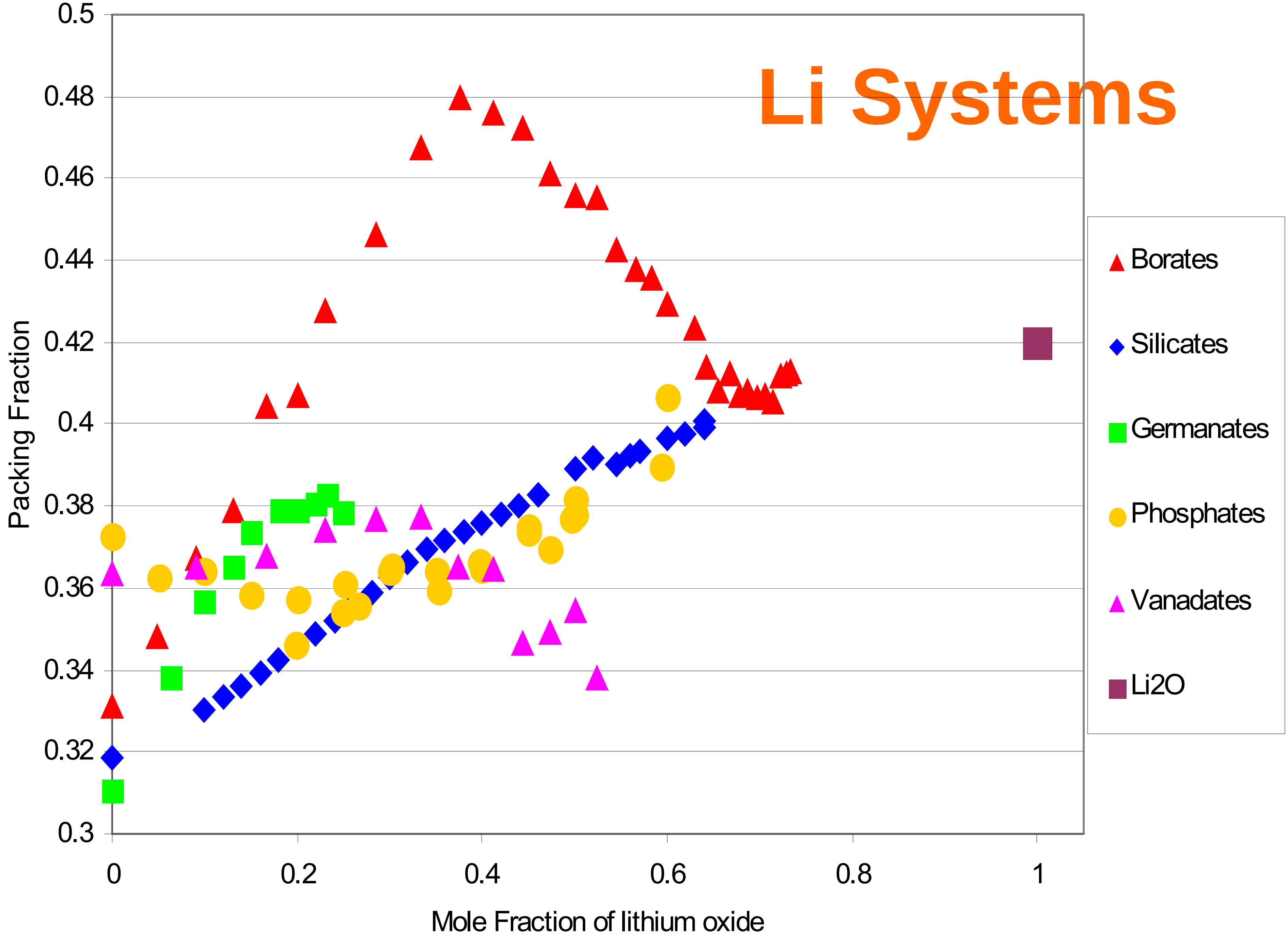
Alkaline Earth Phosphate Packing vs J
Packing Fraction
0.50000
0.48000
0.46000
0.44000
0.42000
0.40000
0.38000
0.36000
0.34000
0.32000
0.30000
0.00
0.20
0.40
0.60
0.80
1.00
1.20
1.40
1.60
1.80
2.00
J
Mg
Ca
Sr
Ba

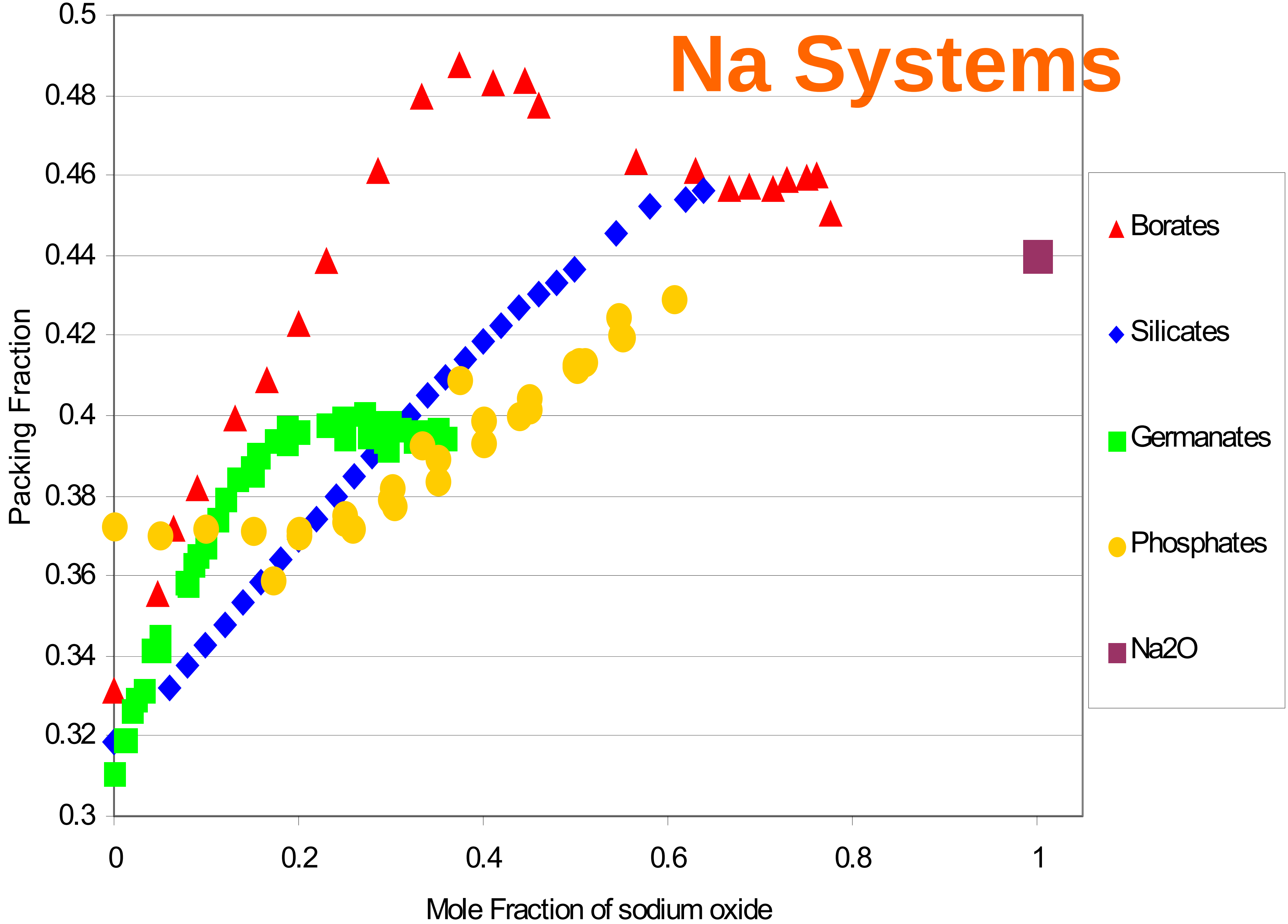


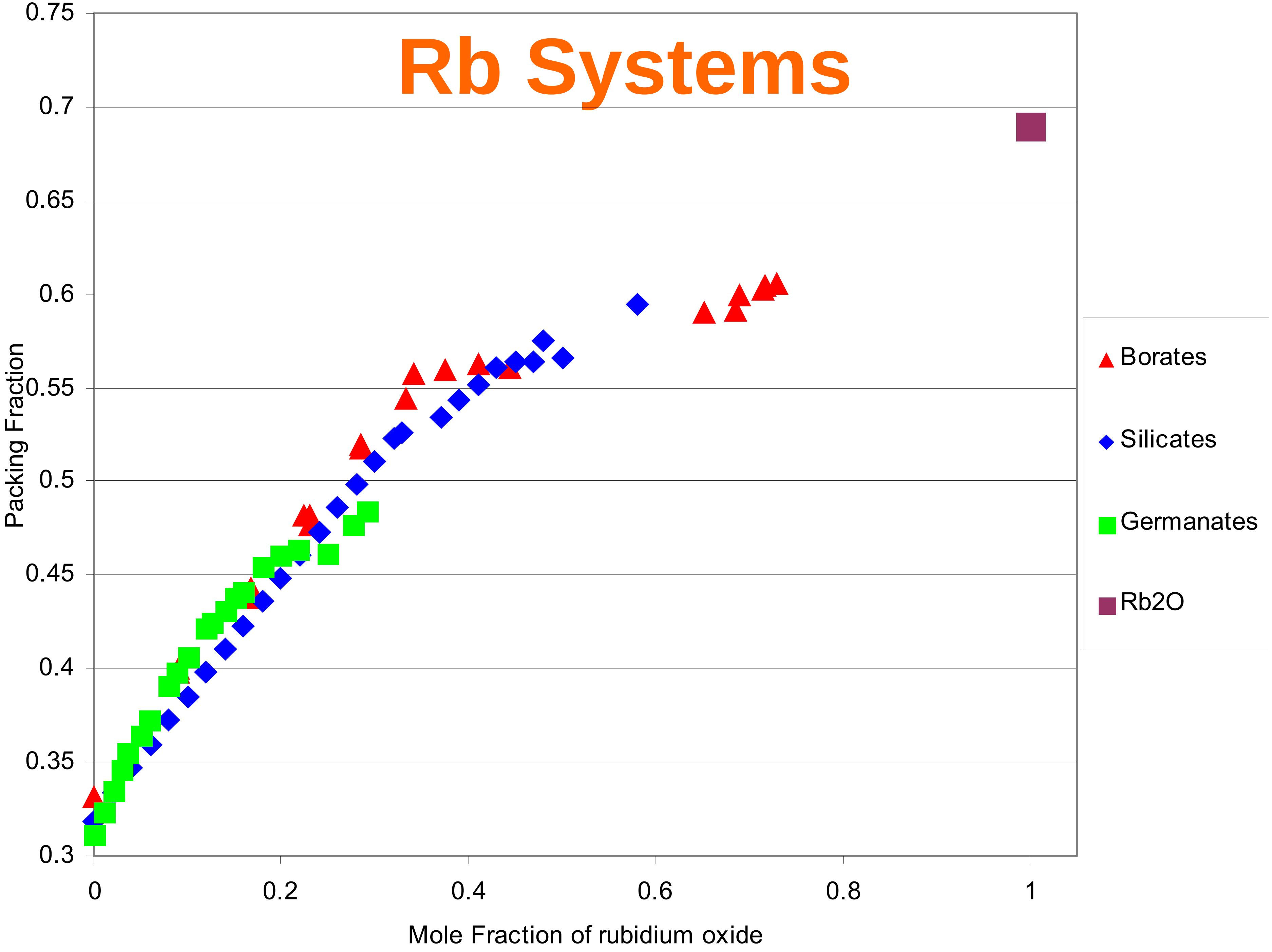
Alkaline Earth Vanadates Packing vs Concentration
Packing Fraction
0.48
0.46
0.44
0.42
0.4
0.38
0.36
0.34
0.32
0.3
0
0.2
0.4
0.6
0.8
1
1.2
1.4
J
Mg
Ca
Sr
Ba



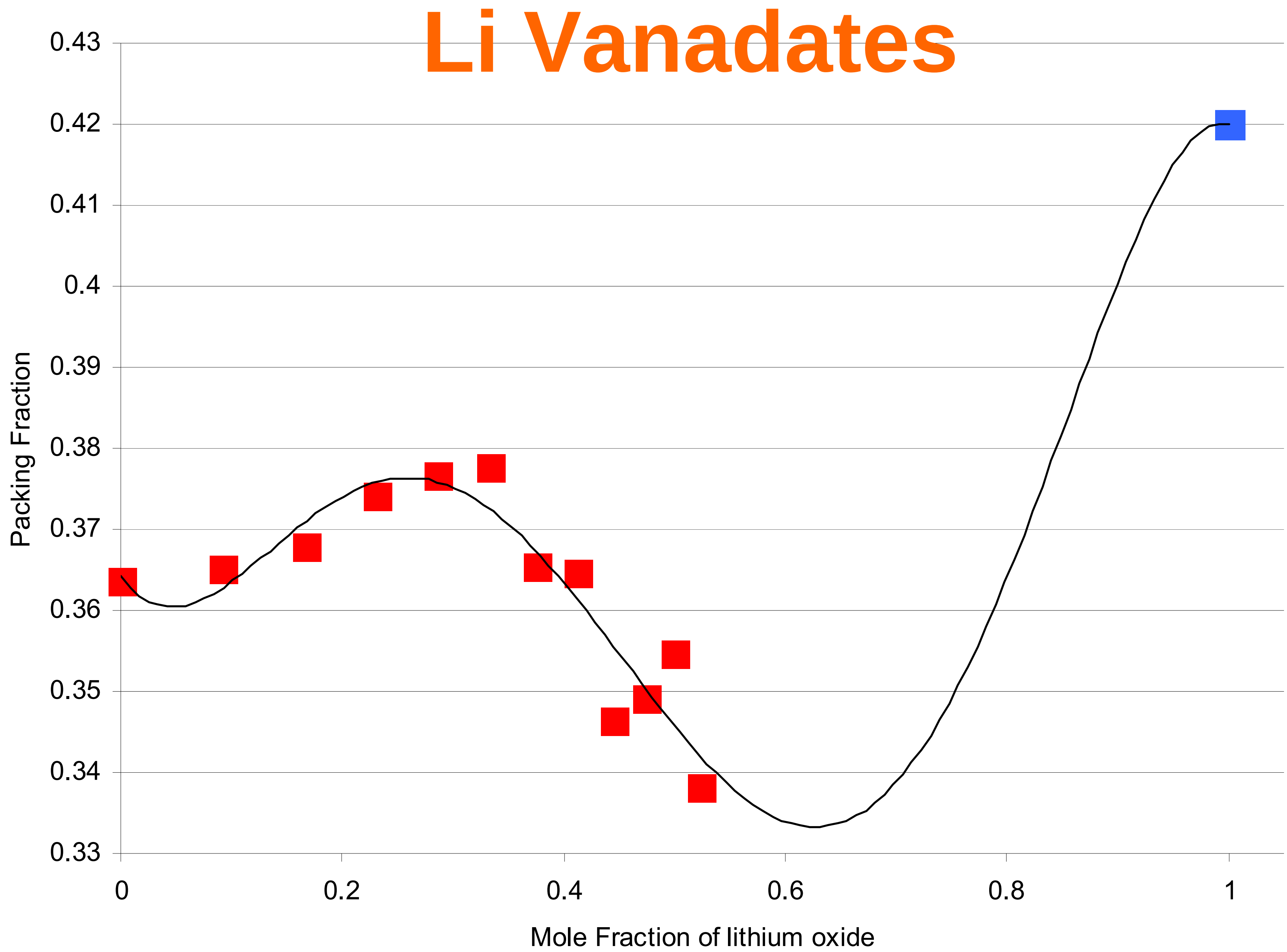
Alkali Vanadate Packing vs J
Packing Fraction
0.48
0.46
0.44
0.42
0.4
0.38
0.36
0.34
0.32
0.3
0.000
0.200
0.400
0.600
0.800
1.000
1.200
J
Li
Na
K
Rb
Cs


Li Systems
Packing Fraction
0.5
0.48
0.46
0.44
0.42
0.4
0.38
0.36
0.34
0.32
0.3
0
0.2
0.4
0.6
0.8
1
Mole Fraction of lithium oxide
Borates
Silicates
Germanates
Phosphates
Vanadates
Li2O


Na Systems
Packing Fraction
Mole Fraction of sodium oxide
0.5
0.48
0.46
0.44
0.42
0.4
0.38
0.36
0.34
0.32
0.3
0
0.2
0.4
0.6
0.8
1
Borates
Silicates
Germanates
Phosphates
Na2O



Rb Systems
0.75
0.7
0.65
0.6
0.55
0.5
0.45
0.4
0.35
0.3
Packing Fraction
0
0.2
0.4
0.6
0.8
1
Mole Fraction of rubidium oxide
Borates
Silicates
Germanates
Rb2O



Li Vanadates
Packing Fraction
0.43
0.42
0.41
0.4
0.39
0.38
0.37
0.36
0.35
0.34
0.33
0
0.2
0.4
0.6
0.8
1
Mole Fraction of lithium oxide

Some Definitions for Borosilicates

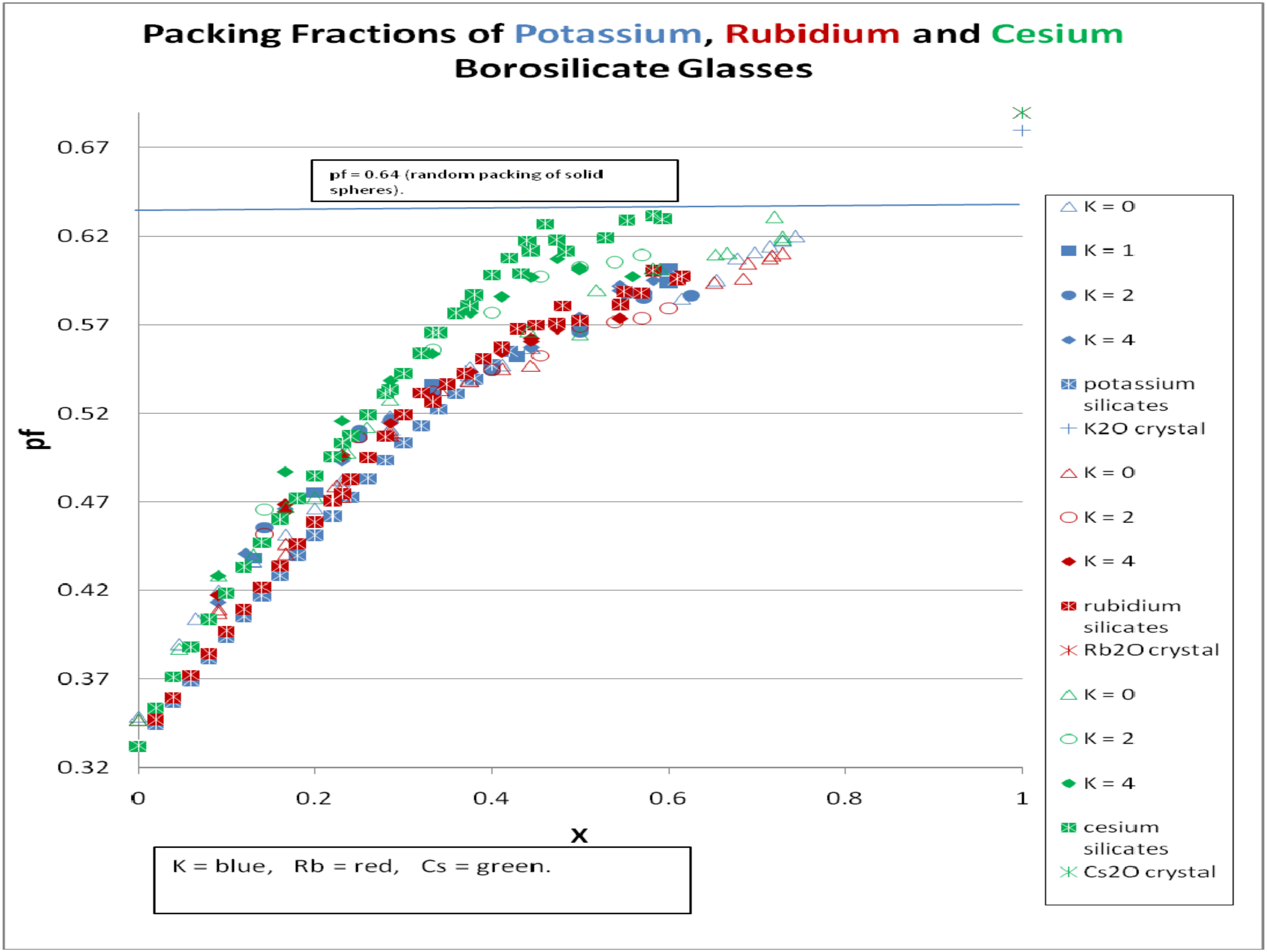
- $RM_2O.B_2O_3.KSiO_2$

R = molar ratio of M_2O to B_2O_3

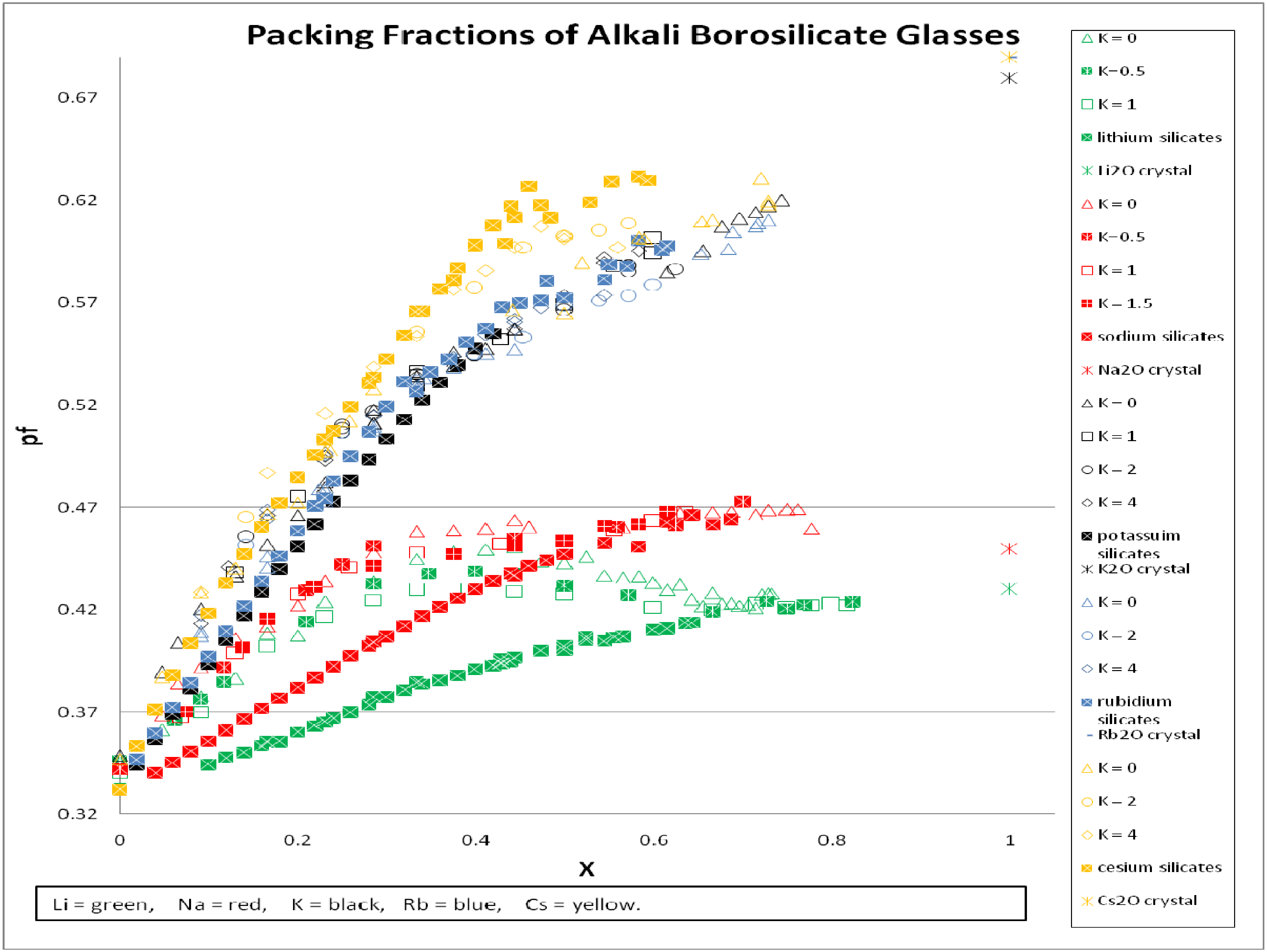
K = molar ratio of SiO_2 to B_2O_3

$x = R/(R+1+K)$

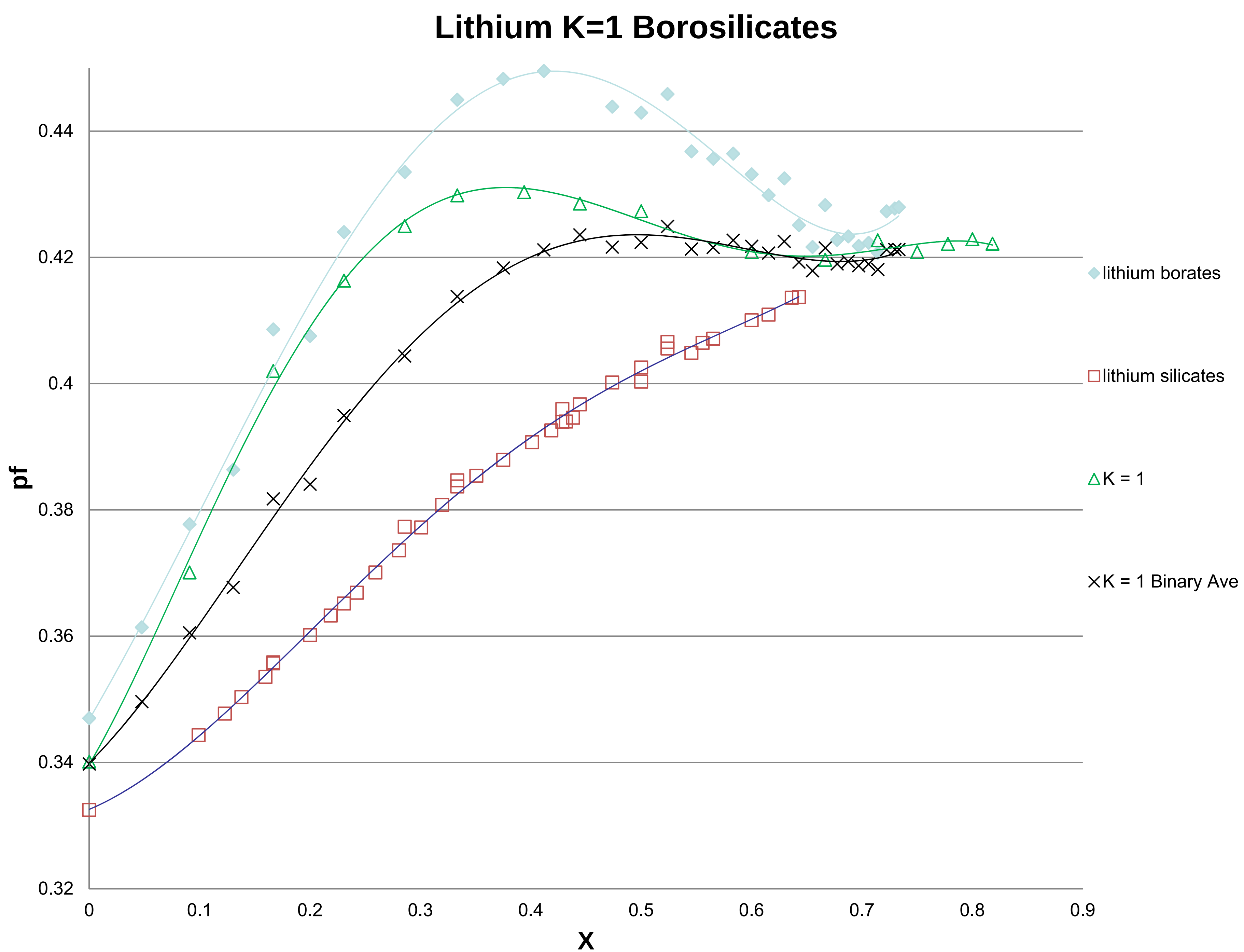
Works also for MO instead of M_2O



Packing Fractions of Potassium, Rubidium and Cesium Borosilicate Glasses
pf = 0.64 (random packing of solid spheres).
pf
0.32
0.37
0.42
0.47
0.52
0.57
0.62
0.67
0
0.2
0.4
0.6
0.8
1
x
K = blue, Rb = red, Cs = green.
K = 0
K = 1
K = 2
K = 4
potassium silicates
K2O crystal
K = 0
K = 2
K = 4
rubidium silicates
Rb2O crystal
K = 0
K = 2
K = 4
cesium silicates
Cs2O crystal



Packing Fractions of Alkali Borosilicate Glasses
pf
X
0.67
0.62
0.57
0.52
0.47
0.42
0.37
0.32
0
0.2
0.4
0.6
0.8
1
K = 0
K = 0.5
K = 1
lithium silicates
Li2O crystal
K = 0
K = 0.5
K = 1
K = 1.5
sodium silicates
Na2O crystal
K = 0
K = 1
K = 2
K = 4
potassuim silicates
K2O crystal
K = 0
K = 2
K = 4
rubidium silicates
Rb2O crystal
K = 0
K = 2
K = 4
cesium silicates
Cs2O crystal
Li = green, Na = red, K = black, Rb = blue, Cs = yellow.


Lithium K=1 Borosilicates
pf
0.32
0.34
0.36
0.38
0.4
0.42
0.44
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
X
lithium borates
lithium silicates
K = 1
K = 1 Binary Ave

Sharing Models of the Modifier

- Proportional
- Dell and Bray
- Martin and Feller

Proportional:

$R = R_B + R_{Si}$

$R_B = R(1/(1+K))$ $R_{Si} = R(K/(1+K))$

Sharing Models of the Modifier

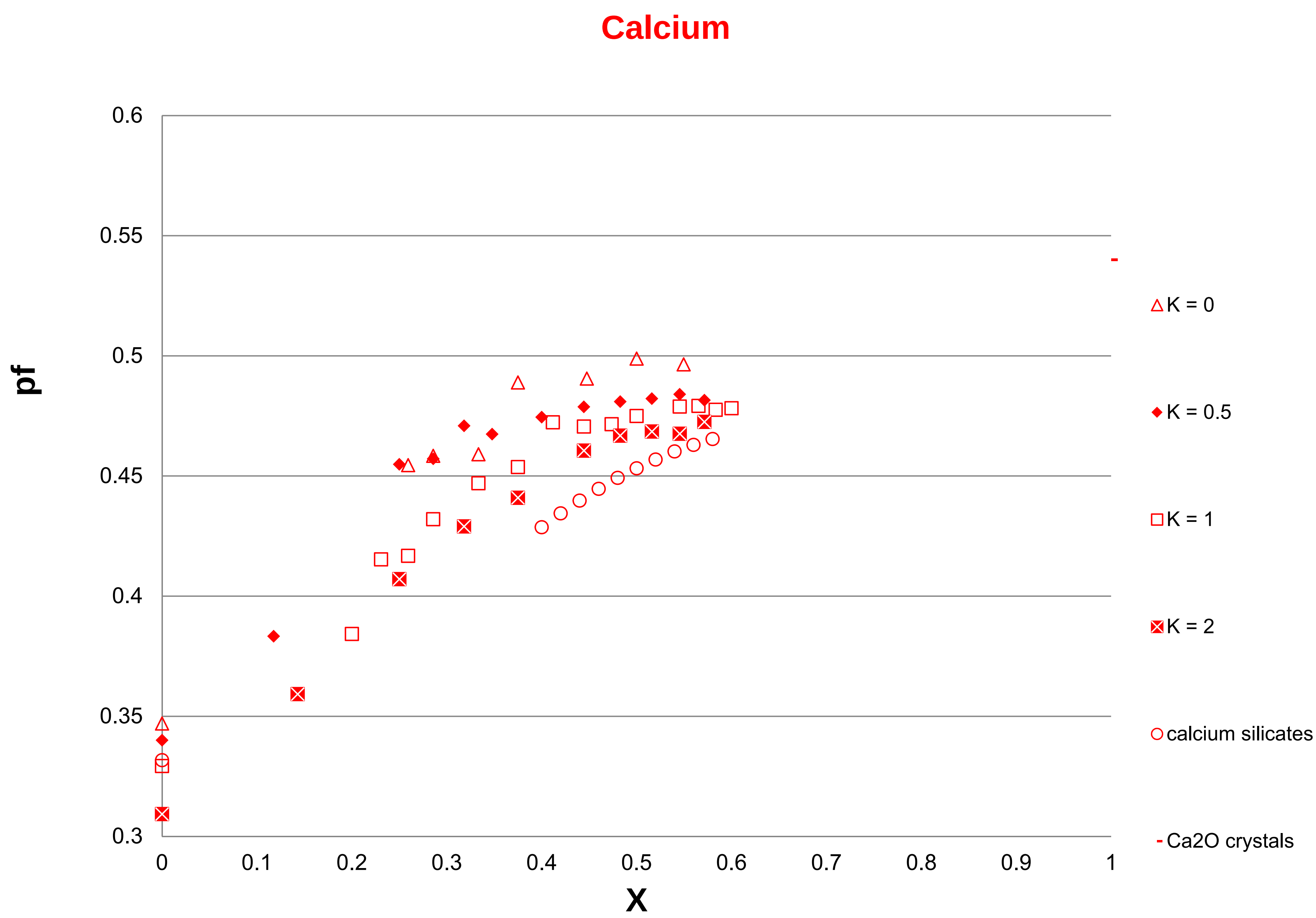
- Proportional
- Dell and Bray
- Martin and Feller

Martin and Feller:

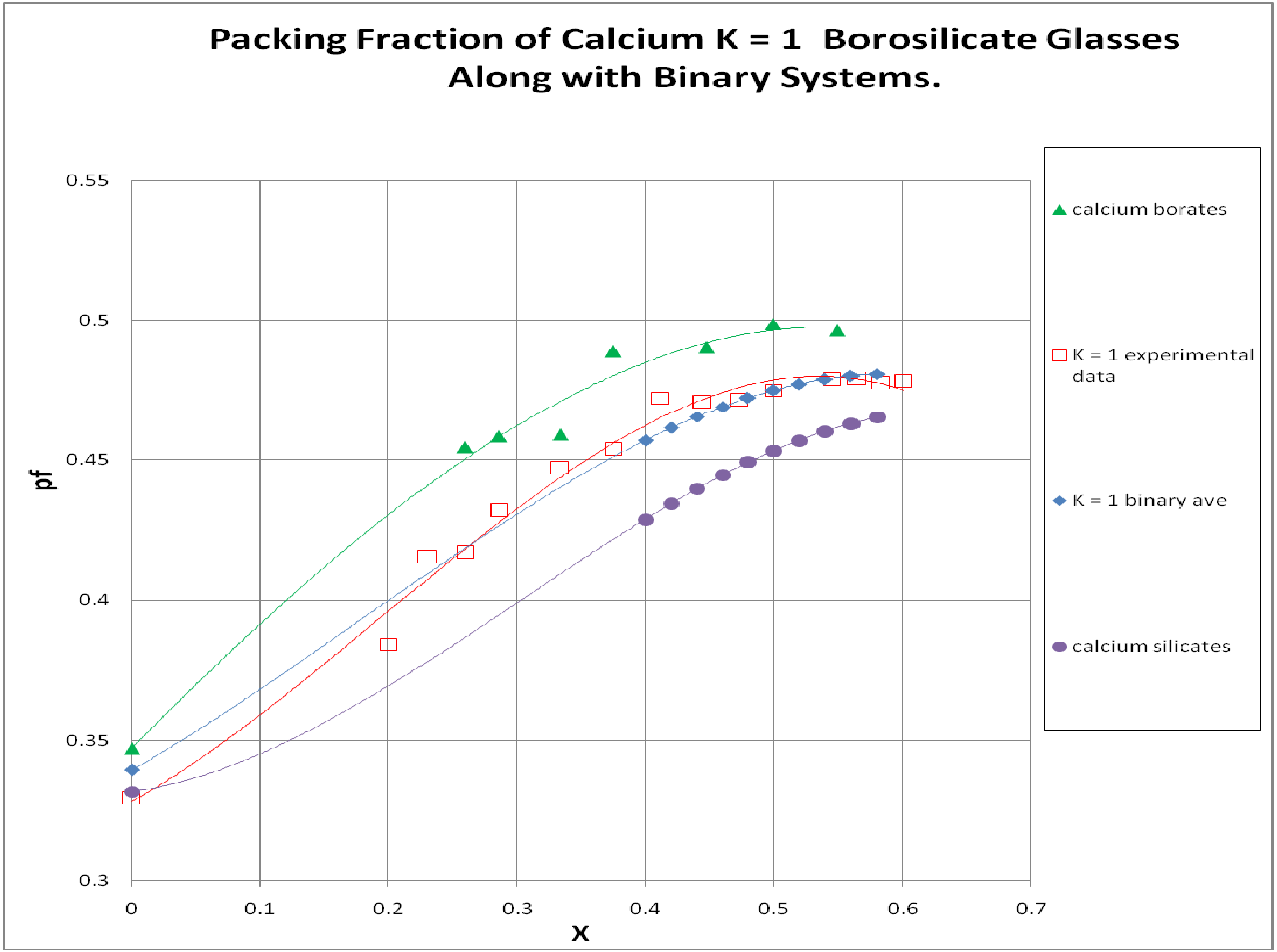
$R < Ro \quad R_B = R, R_{Si} = 0.$

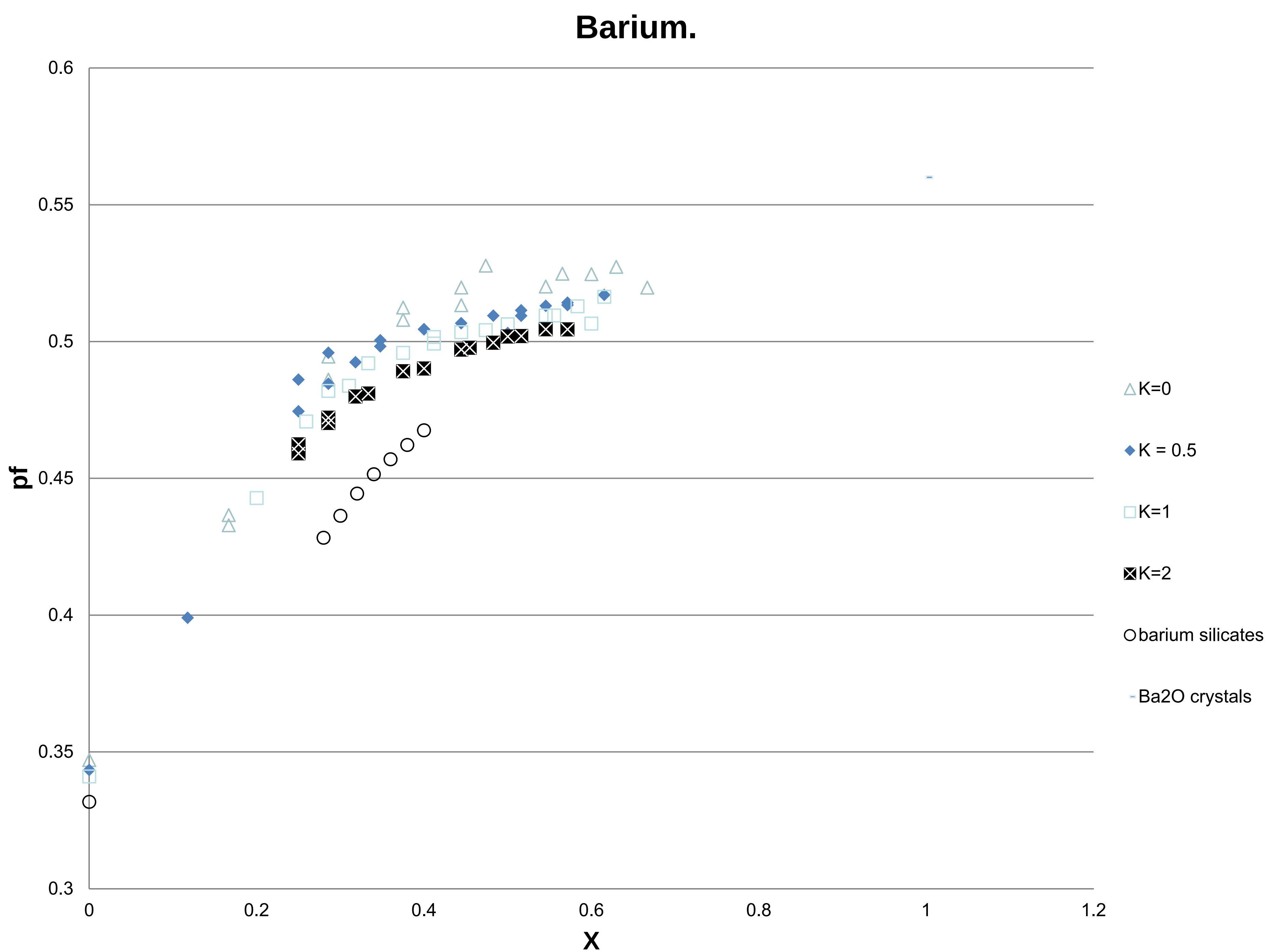
$R > Ro$

$R_B = Ro + (R-Ro)(1/(1+K)) \quad R_{Si} = (R-Ro)(K/(1+K))$



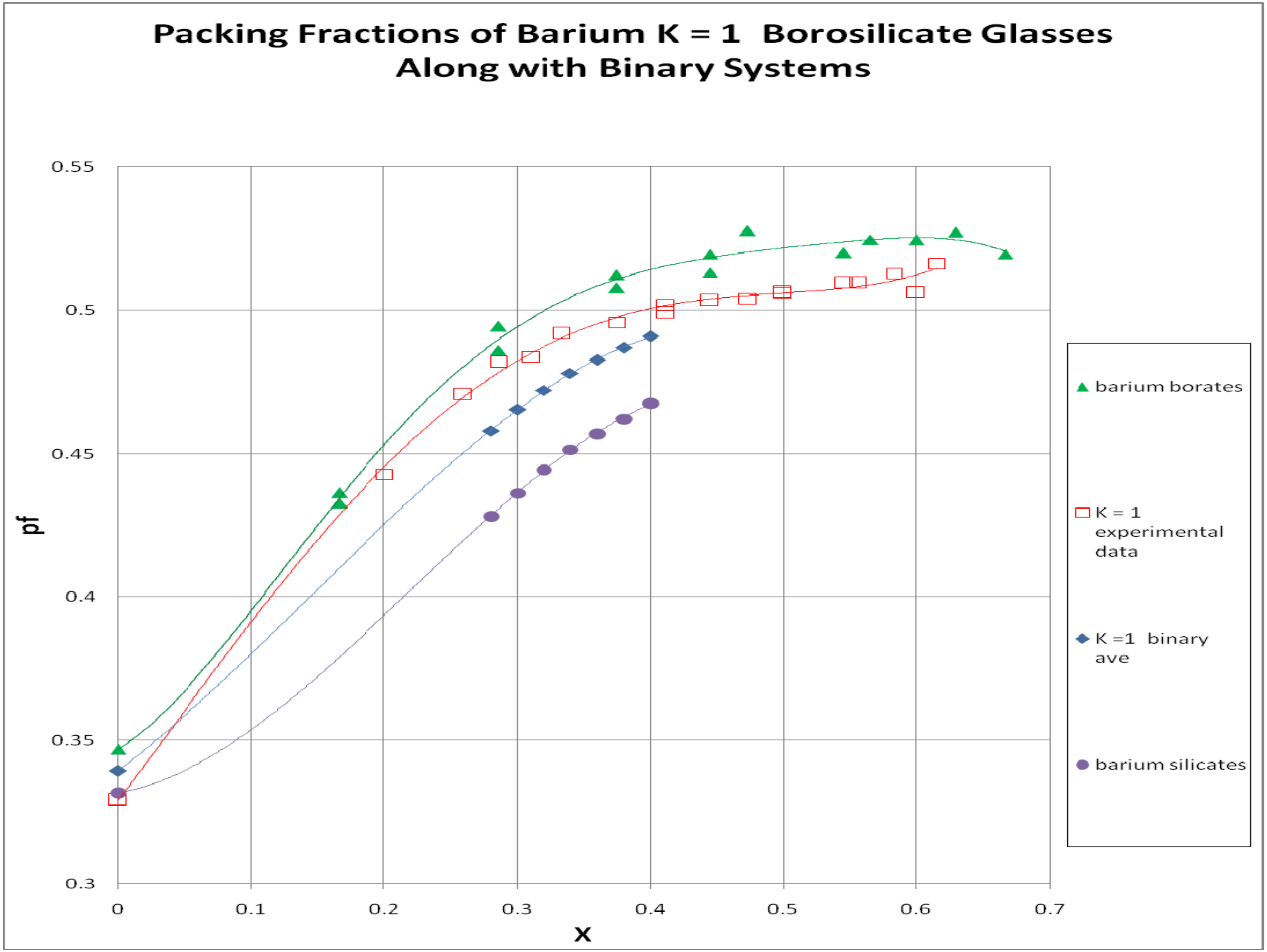
Calcium
0.6
0.55
0.5
0.45
0.4
0.35
0.3
pf
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
X
K = 0
K = 0.5
K = 1
K = 2
calcium silicates
Ca2O crystals

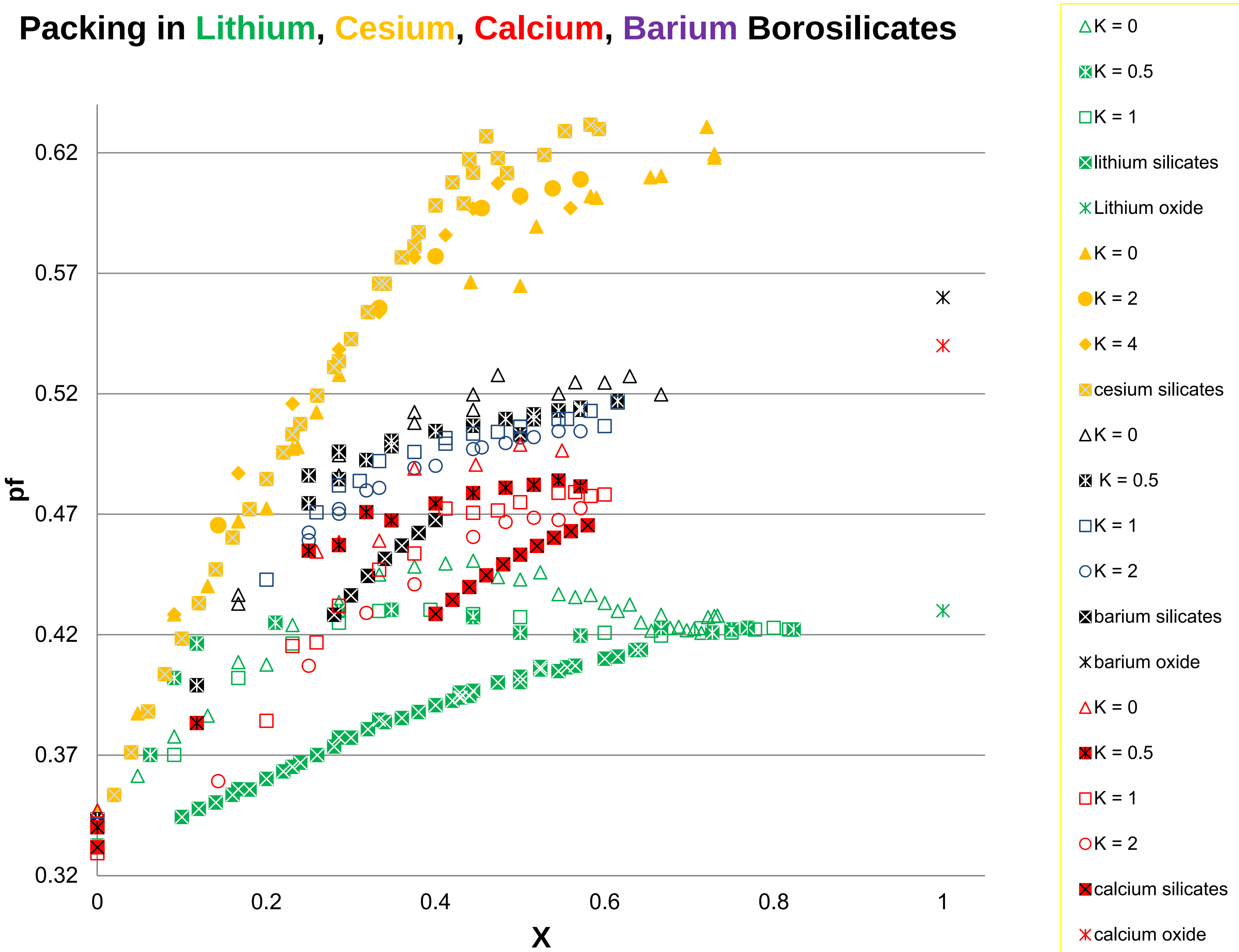

Packing Fraction of Calcium K = 1 Borosilicate Glasses
Along with Binary Systems.
pf
x
0.55
0.5
0.45
0.4
0.35
0.3
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
calcium borates
K = 1 experimental data
K = 1 binary ave
calcium silicates


Barium.
pf
X
0.6
0.55
0.5
0.45
0.4
0.35
0.3
0
0.2
0.4
0.6
0.8
1
1.2
K=0
K = 0.5
K=1
K=2
barium silicates
Ba2O crystals

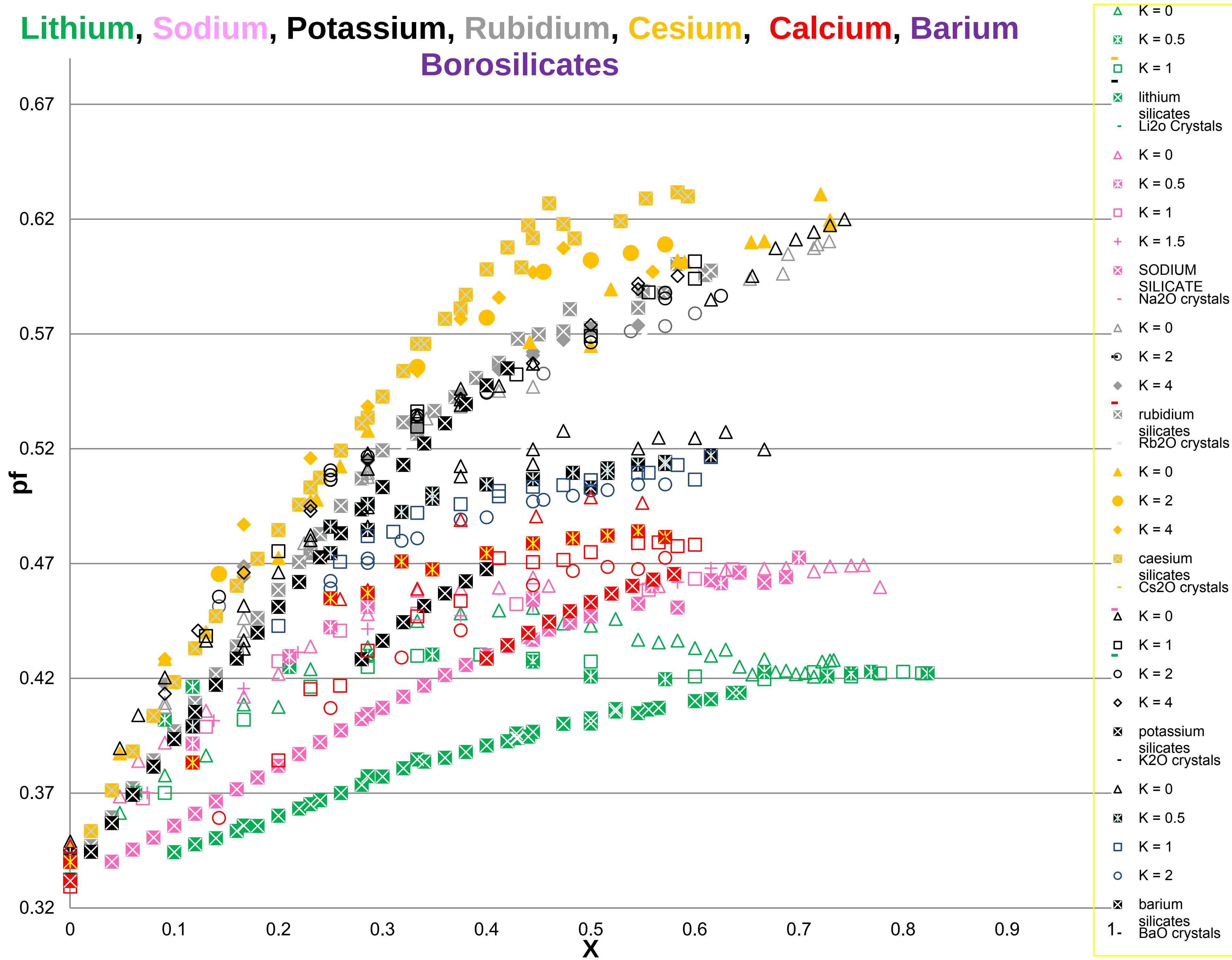
Problem

- Determine the packing fractions of the barium borate glass system.
- Using the known density of BaO compare the packing fraction of the crystal to the glasses.
- Plot all results.


Packing Fractions of Barium K = 1 Borosilicate Glasses
Along with Binary Systems
0.55
0.5
0.45
0.4
0.35
0.3
pf
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
x
barium borates
K = 1 experimental data
K =1 binary ave
barium silicates



Packing in Lithium, Cesium, Calcium, Barium Borosilicates
pf
X
0.62
0.57
0.52
0.47
0.42
0.37
0.32
0
0.2
0.4
0.6
0.8
1
K = 0
K = 0.5
K = 1
lithium silicates
Lithium oxide
K = 0
K = 2
K = 4
cesium silicates
K = 0
K = 0.5
K = 1
K = 2
barium silicates
barium oxide
K = 0
K = 0.5
K = 1
K = 2
calcium silicates
calcium oxide



Lithium, Sodium, Potassium, Rubidium, Cesium, Calcium, Barium
Borosilicates
pf
X
0.67
0.62
0.57
0.52
0.47
0.42
0.37
0.32
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
K = 0
K = 0.5
K = 1
lithium silicates
Li2o Crystals
K = 0
K = 0.5
K = 1
K = 1.5
SODIUM SILICATE
Na2O crystals
K = 0
K = 2
K = 4
rubidium silicates
Rb2O crystals
K = 0
K = 2
K = 4
caesium silicates
Cs2O crystals
K = 0
K = 1
K = 2
K = 4
potassium silicates
K2O crystals
K = 0
K = 0.5
K = 1
K = 2
barium silicates
BaO crystals

Mechanical Packing


5050
HIGH SPEED PAINT MIXER
Red Devil
WARNING!
CRAFTSMAN
Two Speed Band Saw

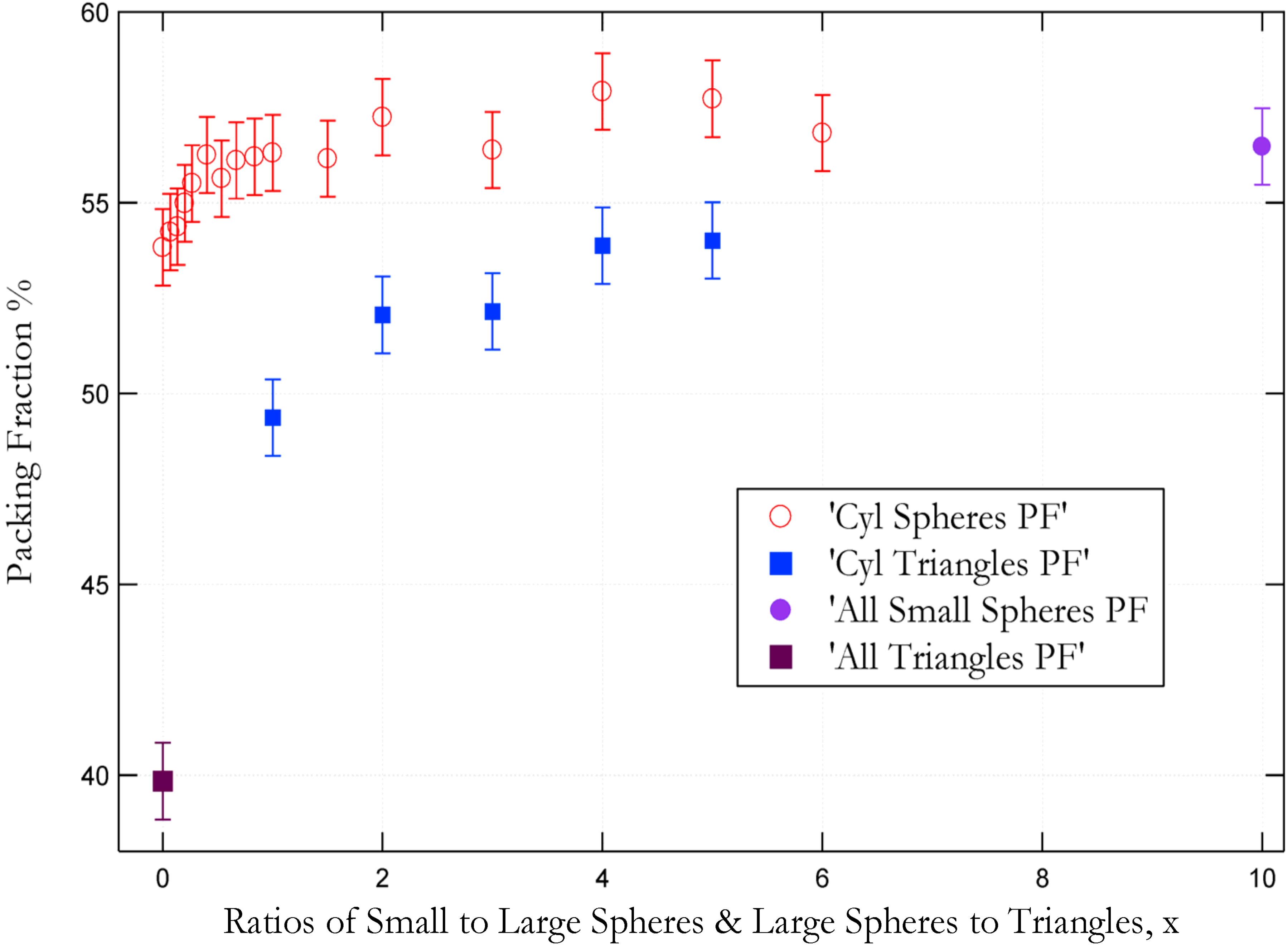

60
55
50
45
40
Packing Fraction %
0
2
4
6
8
10
Ratios of Small to Large Spheres & Large Spheres to Triangles, x
'Cyl Spheres PF'
'Cyl Triangles PF'
'All Small Spheres PF
'All Triangles PF'

Figure 5

Conclusions

1. Density leads to structural parameters:

   Molar Volume, Structural Volumes, Packing

2. Packing is a universal dimensionless measure of volume. More needs to be done here.

3. Real structural trends may often be noted.

4. Structural models may be tested but not absolutely verified.

Acknowledgements

- **Coe College for student housing, stipends, and much more**
- **NSF under various grants**
  - **RUI NSF 0502051**
  - **REU NSF 0649007**
  - **International Travel NSF 0813608**
  - **IMI-NSF New Functionality in Glass-**
    - **Lehigh/Penn State**