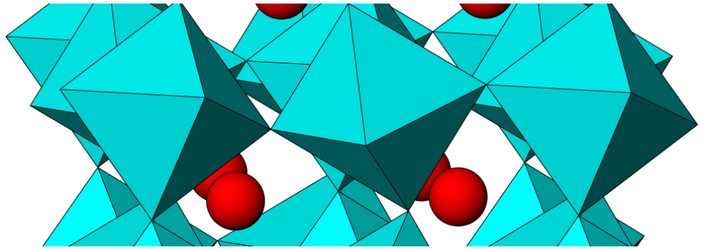
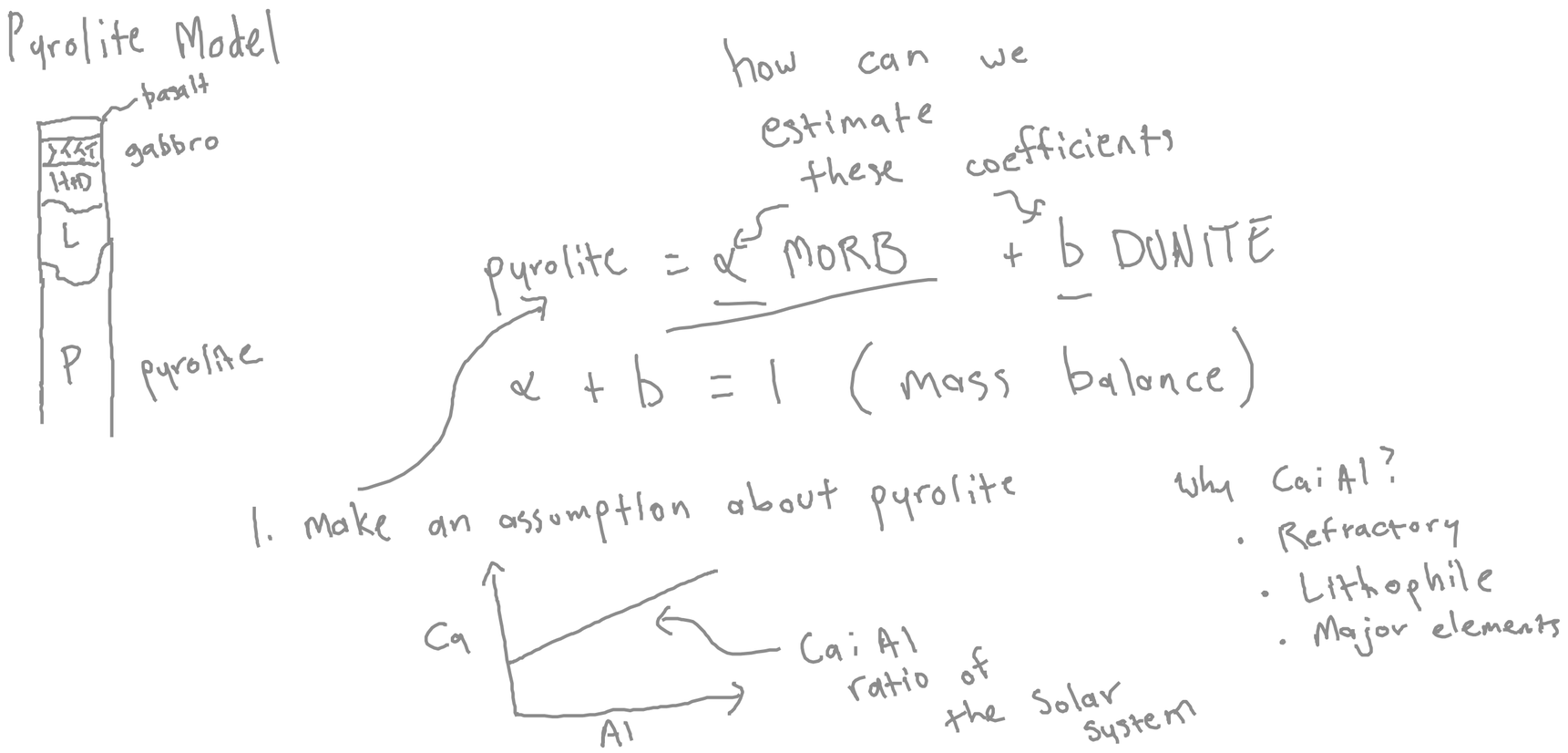


Lecture 6: Making the Earth (Trace elements edition)

1. The primitive mantle (pyrolite model)
2. Trace element definitions
    A. Compatibility and partition coefficients
    B. General trends in compatibility
    C. The relationship between partition coefficients and equilibrium constants
3. Thermodynamic basis for compatibility

We acknowledge and respect the lək^{w} əŋən peoples on whose traditional territory the university stands and the Songhees, Esquimalt and W̱SÁNEĆ peoples whose historical relationships with the land continue to this day.



Pyrolite Model: Ringwood, A.E., 1962. **A model for the upper mantle**. *Journal of Geophysical Research*.

Practice problem

The observed chondritic mass abundances for Calcium and Aluminum are:

Element	wt % in Chondrite	Atomic Mass
Ca	0.92	40.1
Al	0.85	27
O		16

The average wt % of CaO and Al_2O_3 in Basalt and Harzburgite:

Oxide	wt % in Basalt	wt % in Harzburgite
CaO	11.3	6.1
Al_2O_3	15.1	5.1

What ratio do you need to mix basalt and harzburgite back together to get the composition of the mantle before melt was removed? Assumptions:

- Pyrolite is a combination of melt (basalt) and melted mantle (harzburgites)
- Earth has the same Refractory Lithophile Elemental (RLE) abundances as Chondrites

Solution.

Basalt $\frac{CaO}{Al_2O_3}$ ratio: M 0.75

Harz. $\frac{CaO}{Al_2O_3}$ ratio: H 1.2

$0.8 = \alpha\, 0.75 + (1-\alpha)\, 1.2$

$\alpha = 0.89$

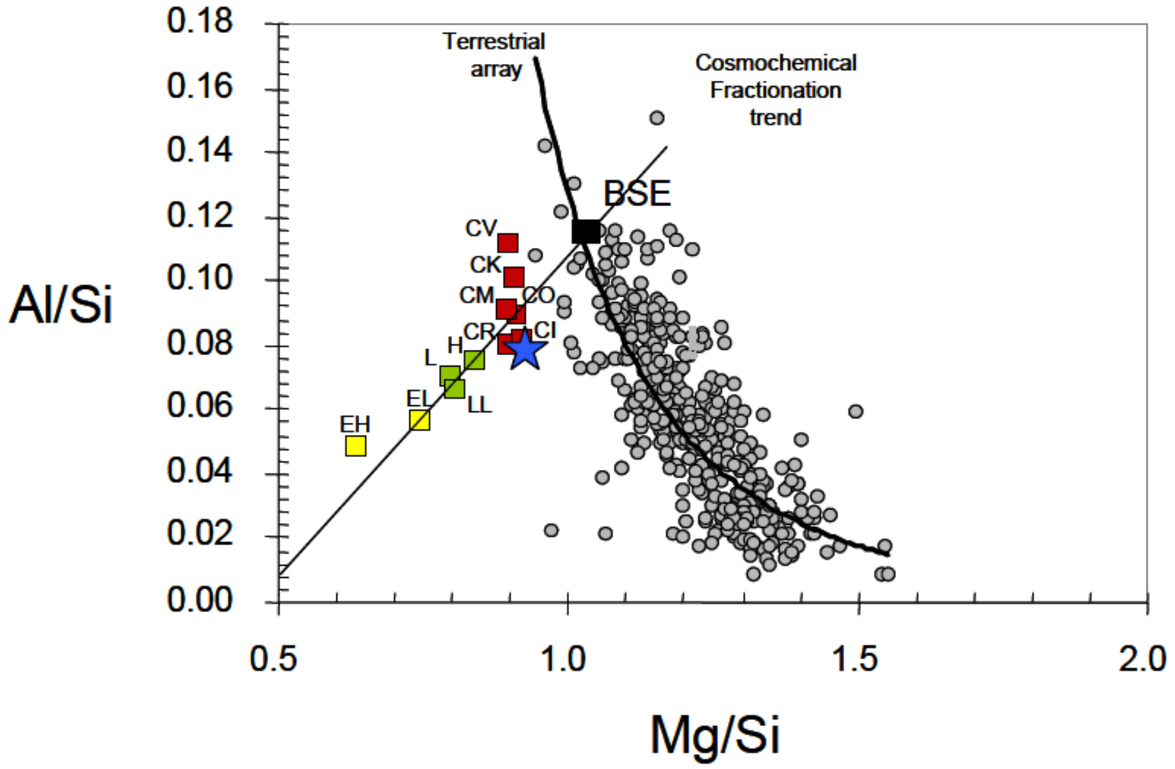
Chondrite

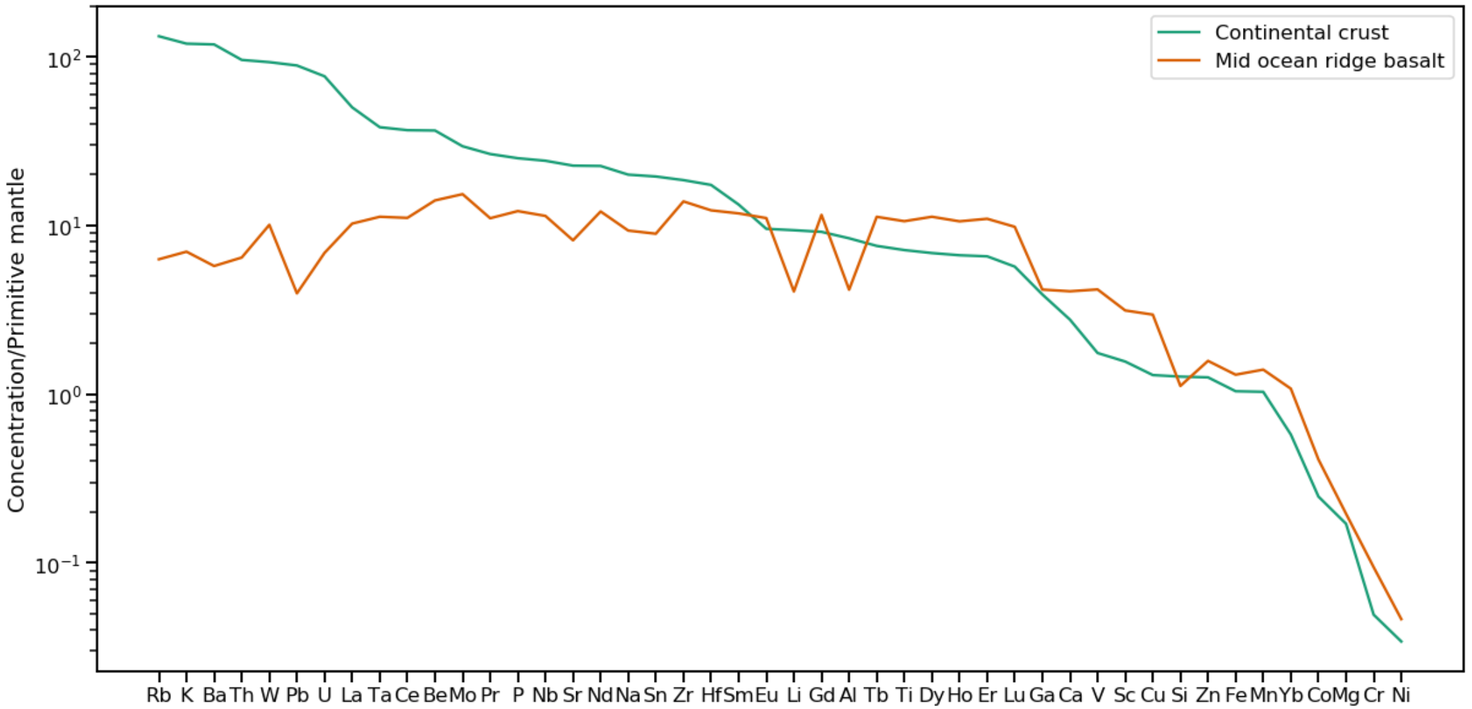
$$0.85\,g\,Al \left(\frac{1\,mol\,Al}{27\,g\,Al}\right)\left(\frac{1\,mol\,Al_2O_3}{2\,mol\,Al}\right)\left(\frac{(27\times2)+(16\times3)\,g}{1\,mol\,Al_2O_3}\right) = 1.6\,g\,Al_2O_3$$

Chondrite

$$0.92\,g\,Ca \left(\frac{1\,mol\,Ca}{40.1\,g\,Ca}\right)\left(\frac{1\,mol\,CaO}{1\,mol\,Ca}\right)\left(\frac{40.1+16}{1\,mol\,CaO}\right) = 1.29\,g\,CaO$$

$\frac{g\,CaO}{g\,Al_2O_3} = 0.8$

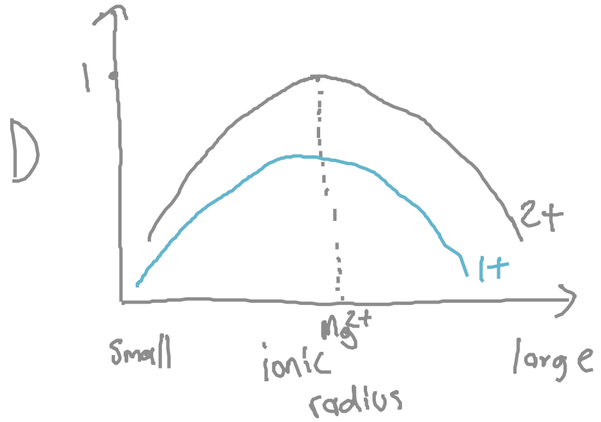

Al/Si
Mg/Si
0.18
0.16
0.14
0.12
0.10
0.08
0.06
0.04
0.02
0.00
0.5
1.0
1.5
2.0
Terrestrial
array
Cosmochemical
Fractionation
trend
BSE
CV
CK
CM
CO
CR
CI
H
L
LL
EL
EH


Continental crust
Mid ocean ridge basalt
Concentration/Primitive mantle
10^{2}
10^{1}
10^{0}
10^{-1}
Rb K Ba Th W Pb U La Ta Ce Be Mo Pr P Nb Sr Nd Na Sn Zr Hf Sm Eu Li Gd Al Tb Ti Dy Ho Er Lu Ga Ca V Sc Cu Si Zn Fe Mn Yb Co Mg Cr Ni

Trace elements, compatibility, and general trends.

Trace elements are < 0.1 wt% of a rock/mineral

- concentrations are too low to dictate phase
- trace elements passively substitute into phases



The partition coefficient: D

$D_i = \frac{C_i^{solid}}{C_i^{Liquid}}$ at equilibrium

(i: a trace element)

$D > 1$ compatible, trace element prefers solid phase

$D < 1$ incompatible, trace element prefers liquid phase

$0.1 - 1$: moderately incompatible

Equilibrium constants and partition coefficients. Ni exchange in olivine.

$$wA + xB \overset{K}{\rightleftharpoons} yC + zD$$

$$K_{eq} \simeq \frac{[C]^y [D]^z}{[A]^w [B]^x}$$

recall:

$$\Delta G = -RT \ln K$$

gas constant; T in Kelvin

$$\Delta G \simeq -RT \ln D_i$$

X_{Ni} = molar fraction of nickel

$$Mg_2SiO_4 \text{ (olivine)} + Ni_2SiO_4 \text{ (melt)} \longleftrightarrow$$

$$Ni_2SiO_4 \text{ (olivine)} + Mg_2SiO_4 \text{ (melt)}$$

$$K = \frac{X_{Ni}^2 \, X_{Mg}^2}{X_{Mg}^2 \, X_{Ni}^2}$$

red = melt

$$1 \simeq \frac{X_{Mg}^2 \text{ melt}}{X_{Mg}^2 \text{ solid}}$$

$$K = \frac{X_{Ni}^2}{X_{Ni}^2}$$

$$D \simeq \frac{C_s}{C_L}$$

Thermodynamic model for compatibility. Energy to displace lattice:

$W = f \cdot d$

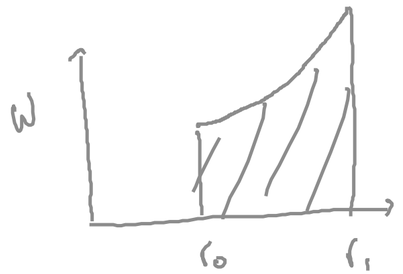
$\dot{\varepsilon}$ = strain = relative deformation = $\frac{r_1 - r_0}{r} = \frac{dr}{r}$

E = Young's modulus = $\frac{\sigma}{\dot{\varepsilon}}$ = resisting change

$\sigma = F/A$ = stress

$$W = f \cdot d = \frac{F}{A} \cdot A \cdot d = \sigma \cdot A \cdot d$$
$$= \frac{\sigma}{\dot{\varepsilon}} \dot{\varepsilon} A d$$
$$W = E \cdot \dot{\varepsilon} A d$$
$$W = E \frac{dr}{r} A d$$
$$W = E 4\pi r^2 \frac{dr}{r} \cdot d$$
$$W = E 4\pi r^2 \frac{dr}{r} (r - r_0)$$

$A = 4\pi r^2$ surface area of a sphere



Integral.

$$W = E\,4\pi r\,(r - r_0)\,dr$$

$$W = E\,4\pi r \int_{r_0}^{r} r(r - r_0)\,dr$$

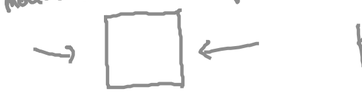
$$W = E\,4\pi \int_{r_0}^{r} (r^2 - r r_0)\,dr$$

$$W = E\,4\pi \left(\frac{r^3}{3} - \frac{r_0 r^2}{2} \right) \Bigg|_{r_0}^{r}$$

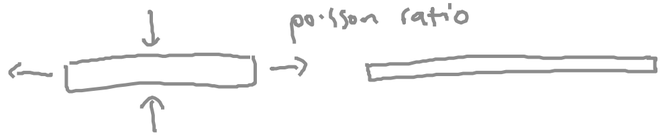
$$W = E\,4\pi \left(\frac{1}{3}(r - r_0)^3 - \frac{r_0}{2}(r - r_0)^2 = \Delta G_{\text{strain lattice}} \right)$$

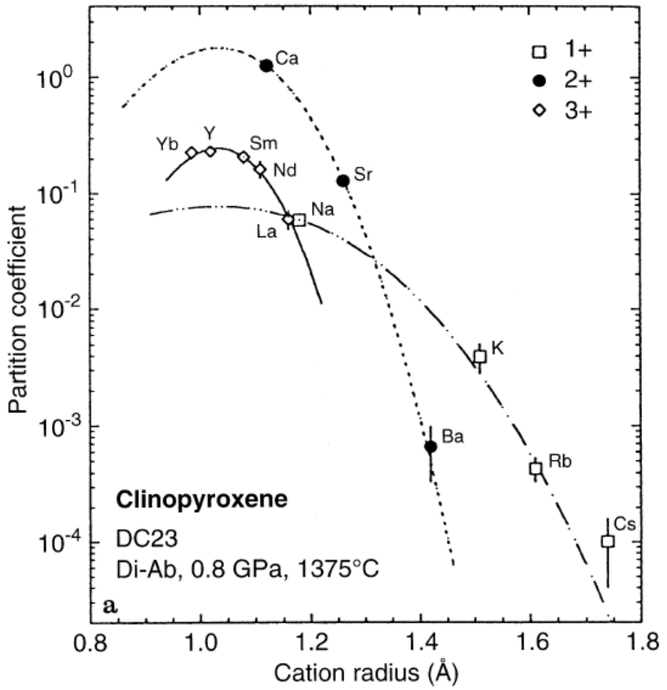
E = Young's modulus $\simeq \frac{3K}{1-2\sigma}$ ← Bulk modulus; ← poisson ratio

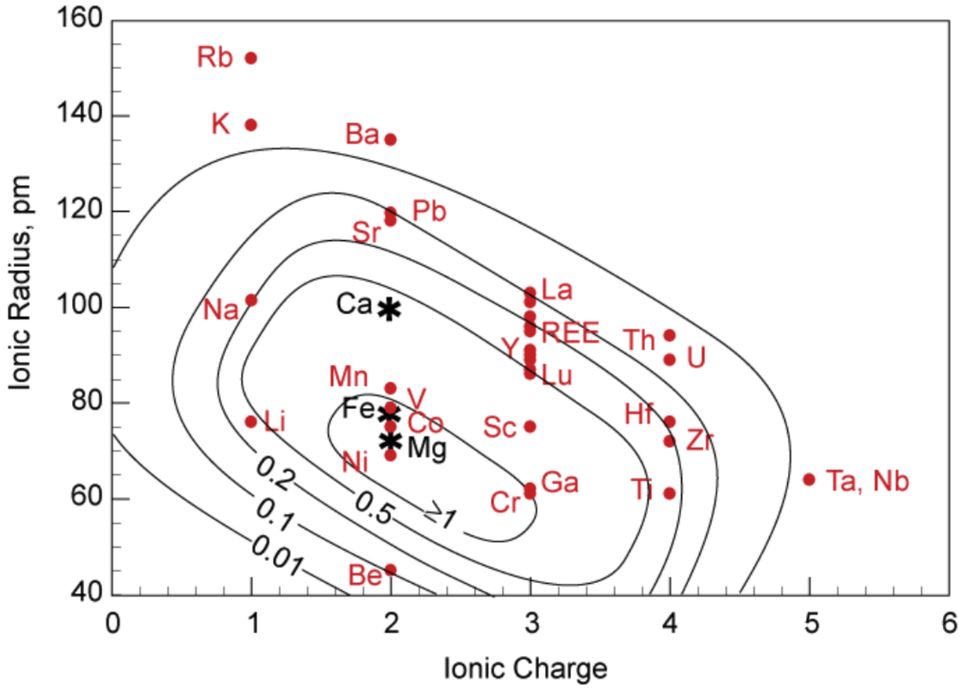
Bulk modulus ↓ compression



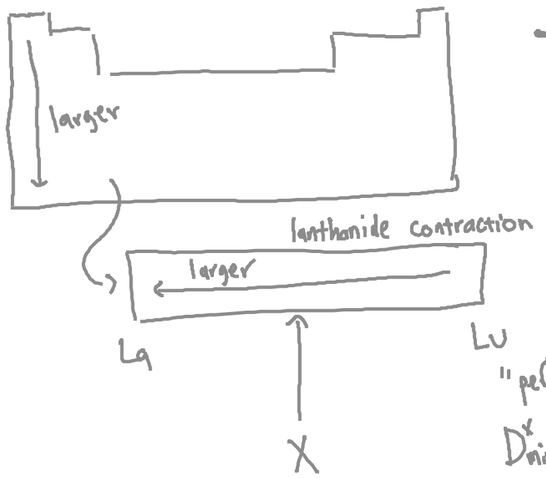
$$K \simeq \frac{z_a z_c e^2 (n-1)}{V_0}$$




1+
2+
3+
Ca
Yb
Y
Sm
Nd
Sr
Na
La
K
Ba
Rb
Cs
Clinopyroxene
DC23
Di-Ab, 0.8 GPa, 1375°C
a
Partition coefficient
Cation radius (Å)
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
0.8
1.0
1.2
1.4
1.6
1.8


Ionic Radius, pm
Ionic Charge
160
140
120
100
80
60
40
0
1
2
3
4
5
6
Rb
K
Ba
Pb
Sr
Na
Ca
La
REE
Y
Lu
Th
U
Mn
V
Fe
Co
Mg
Li
Sc
Hf
Zr
Ni
Ga
Cr
Ti
Ta, Nb
Be
0.2
0.1
0.01
0.5
≥1

Periodic table, general patterns in ion size



ionic radius

- more shells, generally large ions
- as Z, atomic number, increases along a row
  - ionic radius decreases

- $r_{cation} < r_{neutral}^{ot} < r_{anion}$

"perfect size"

$D^{x}_{min} = 1$ $\quad D^{Lu}_{min} \leq D^{x}_{min}$