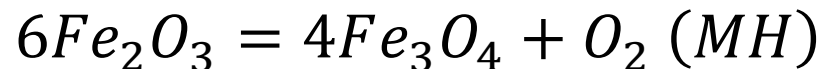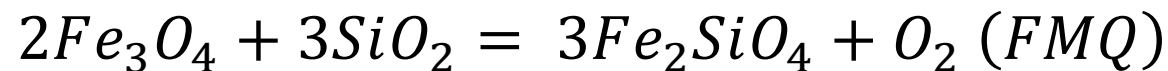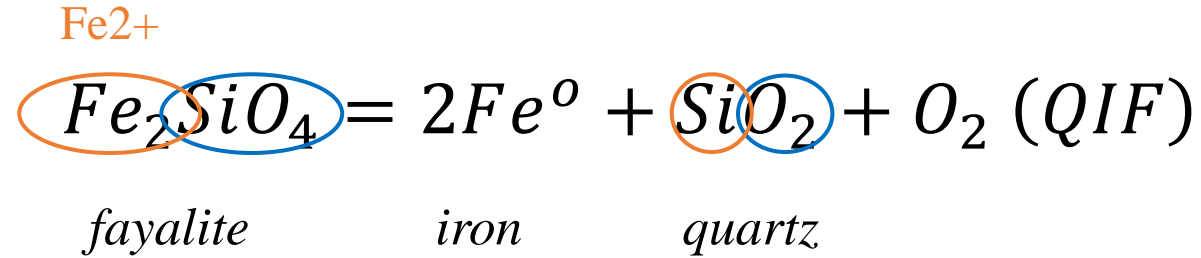# Oxygen Fugacityについて

Shobuzako kensuke

Topic

1. The importance of Oxygen Fugacity in petrology
2. Calibration of Oxygen Fugacity
3. Common Oxygen Buffer reactions
4. Some common misconceptions

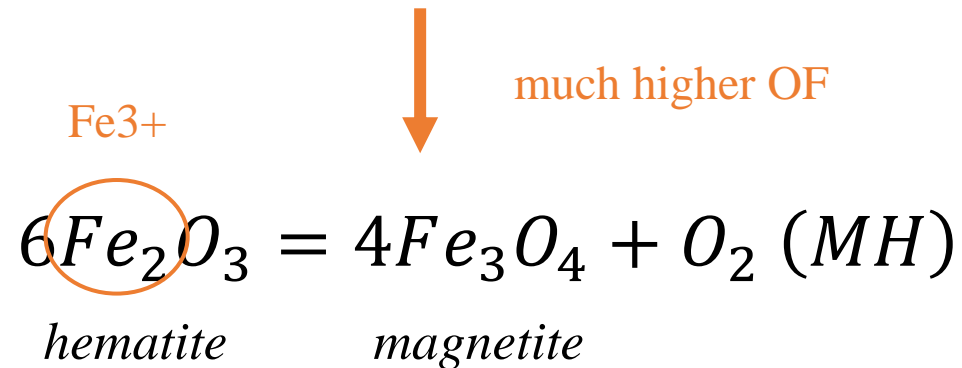# 1. The importance of Oxygen Fugacity(OF) in petrology

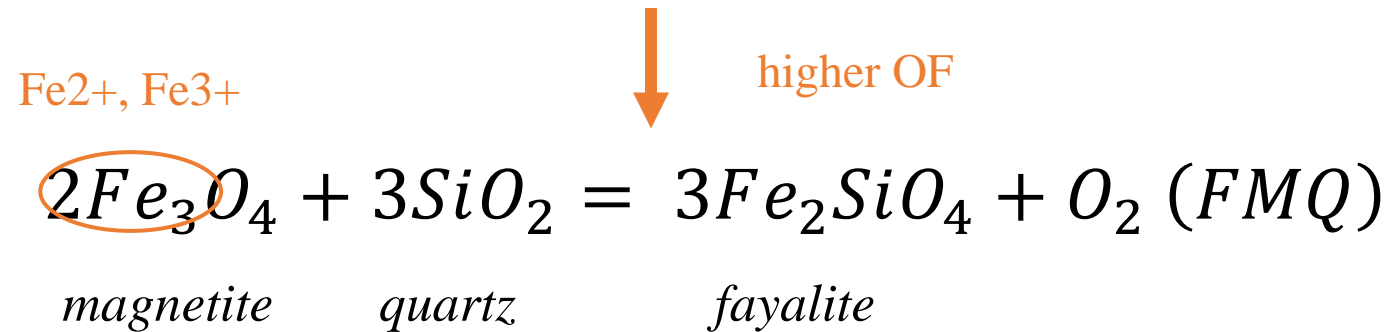- as a variable in determining the stability and compositions of oxides
- At very *low* OF(in the Earth's core), iron presents as a metal(Fe0)
- At *higher* OF, iron becomes the ferrous(divalent, Fe2+) and the ferric(trivalent,Fe3+)

  $\Rightarrow$ modelled as following reactions

$$Fe_2SiO_4 = 2Fe^o + SiO_2 + O_2 \ (QIF)$$

$$2Fe_3O_4 + 3SiO_2 = 3Fe_2SiO_4 + O_2 \ (FMQ)$$

$$6Fe_2O_3 = 4Fe_3O_4 + O_2 \ (MH)$$

Modelled Redox Reaction

Fe2+

$$Fe_2SiO_4 = 2Fe^o + SiO_2 + O_2 \ (QIF)$$

fayalite *iron* *quartz*

O = -2
O2 molecule = 0

higher OF

Fe2+, Fe3+

$$2Fe_3O_4 + 3SiO_2 = 3Fe_2SiO_4 + O_2 \ (FMQ)$$

magnetite *quartz* *fayalite*

much higher OF

Fe3+

$$6Fe_2O_3 = 4Fe_3O_4 + O_2 \ (MH)$$
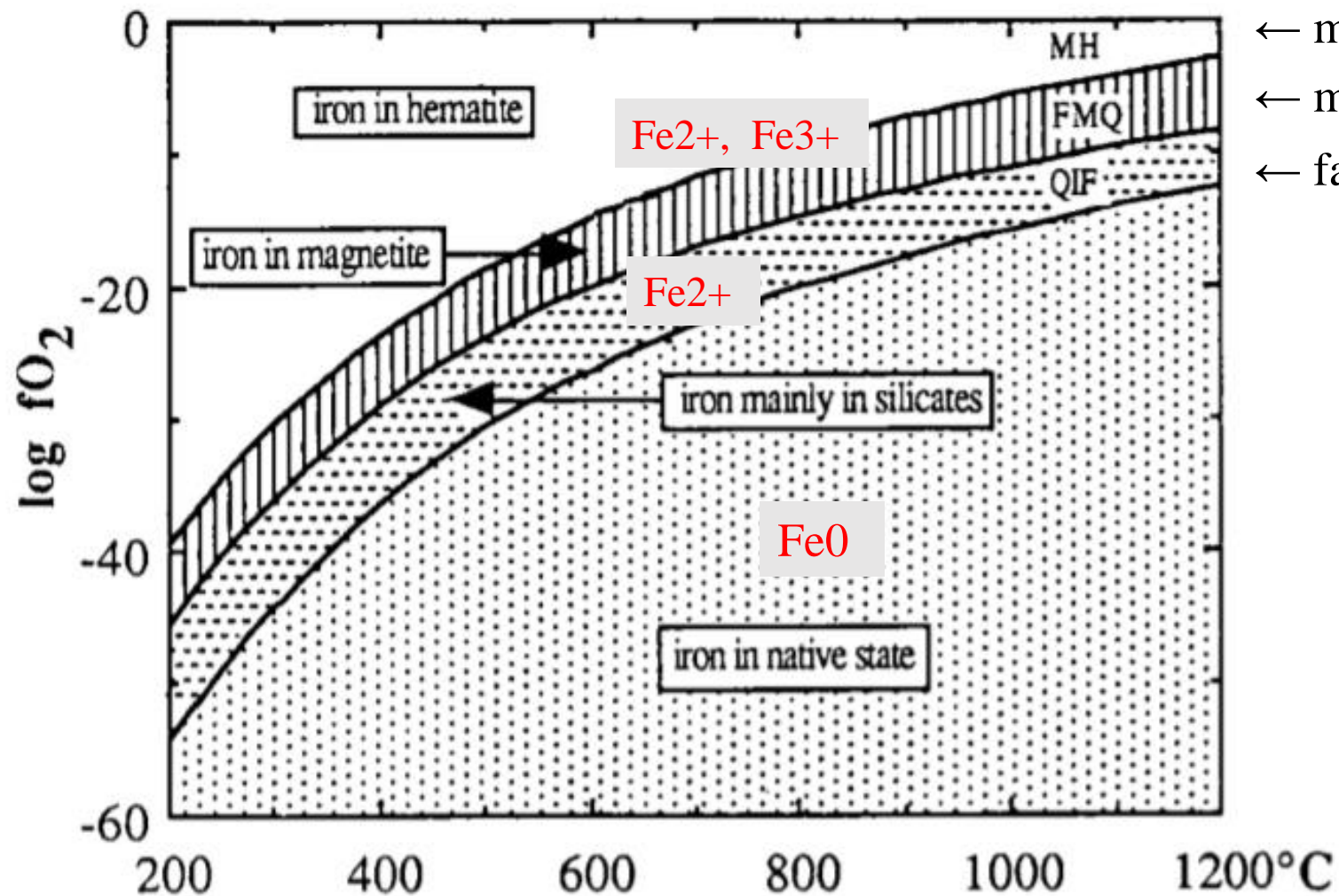
hematite *magnetite*

Figure 1: Log oxygen fugacity-T diagram showing the relative stabilities of the various oxidation states of iron in the system Fe-Si-O.

In naturel system…

The abundances of Mg and Ti is significant.

Ex 1) In hematite, Fe2+ become stable to solute Mg into iron silicates

Ex2)   Fe2+ and Ti substitute for Fe3+

Although Oxygen fugacity is a variable to determine the stability and the composition of iron oxides, Oxygen fugacity is <u>a function of Fe/Mg ratio and Ti content of the oxides</u>.

Thus, Oxygen fugacity is governed by the mineral assemblages in the rocks, and also <u>Oxygen fugacity may be a dependent variable, rather than imposed from the environment</u>.

2. Calibration of Oxygen Fugacity

○ History of Oxygen Fugacity

- Eugster (1925-1987) introduced Oxygen Fugacity to petrology.
- He developed the oxygen-controlling equilibria experiment in order to control <u>oxygen potential</u>.
- He define such equilibria as <u>Oxygen buffer</u> (for example, QIF,FMQ,MH).
- Applied Oxygen buffer to petrology, he use <u>the partial pressure of oxygen</u> (P_{O2}).
- In the condensed system, however, since P_{O2} cannot be defined, the <u>Oxygen Fugacity</u>, which is associated with <u>the chemical potential</u>, was introduced

Oxygen Fugacity for FMQ,

Ideal state

$$K_{FMQ} = \frac{(a_{fay})^3}{(a_{SiO_2})^3 (a_{mt})^2} (a_{O_2})$$

$$K_{FMQ} = a_{O_2} = \frac{f_{O_2}}{f_{O_2}^o}$$

$$K_{FMQ} = f_{O_2}$$

$$\log K = -\frac{\Delta G_{FMQ}^o}{2.303RT}$$

$$\log f_{O_2} = -\frac{\Delta G_{FMQ}^o}{2.303RT}$$

Real state
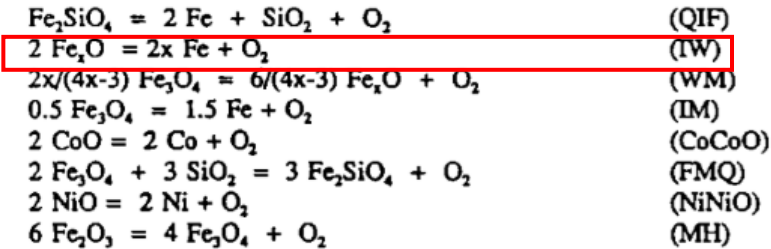
⇒ FMQ reaction doesn't have pure end-member composition.
In natural rock, we must know how the compositions of the phases relate to activity.

⇒ defined from thermodynamic equilibration constant (アトキンスp.263)

3. Common Oxygen buffer reactions

TABLE 1

SOME COMMON PETROLOGIC BUFFERS

Equilibria

$Fe_2SiO_4 = 2 Fe + SiO_2 + O_2$ (QIF)

$2 Fe_xO = 2x Fe + O_2$ (IW)

$2x/(4x-3) Fe_3O_4 = 6/(4x-3) Fe_xO + O_2$ (WM)

$0.5 Fe_3O_4 = 1.5 Fe + O_2$ (IM)

$2 CoO = 2 Co + O_2$ (CoCoO)

$2 Fe_3O_4 + 3 SiO_2 = 3 Fe_2SiO_4 + O_2$ (FMQ)

$2 NiO = 2 Ni + O_2$ (NiNiO)

$6 Fe_2O_3 = 4 Fe_3O_4 + O_2$ (MH)

Equilibrium Expressions*

buffer	A	B	C	Temp. range (°C)	Ref
αQIF	-29,435.7	7.391	.044	150 - 573	1
βQIF	-29,520.8	7.492	.050	573 - 1200	1
IW	-27,489	6.702	.055	565 - 1200	1,2
WM	-32,807	13.012	.083	565 - 1200	1,2
IM	-28,690.6	8.13	.056	300 - 565	3
CoCoO	-24,332.6	7.295	.052	600 - 1200	4
FMαQ	-26,455.3	10.344	.092	400 - 573	1
FMβQ	-25,096.3	8.735	.110	573 - 1200	1
NiNiO	-24,930	9.36	.046	600 - 1200	5
MH	-25,497.5	14.330	.019	300 - 573	1
MH	-26,452.6	15.455	.019	573 - 682	1
MH	-25,700.6	14.558	.019	682 - 1100	1

* where $\log fO_2 = A/T + B + C(P-1)/T$ (T in Kelvins)

Note: temperature of the alpha - beta quartz transition is approximated by the expression: T(°C) = 573 + 0.025P(bars).

Caution: The buffers may be strongly curved at low pressures and it is advised not to extrapolate these expressions below the limits indicated.

Reference: 1: linear fit to Hass (personal comm.); 2. Huebner (1971); 3. $\log K_{IM} = 1/4(\log K_{FMQ} + 3 \log K_{IQF})$; 4. Holmes, et al., (1986); 5. Huebner and Sato (1970)
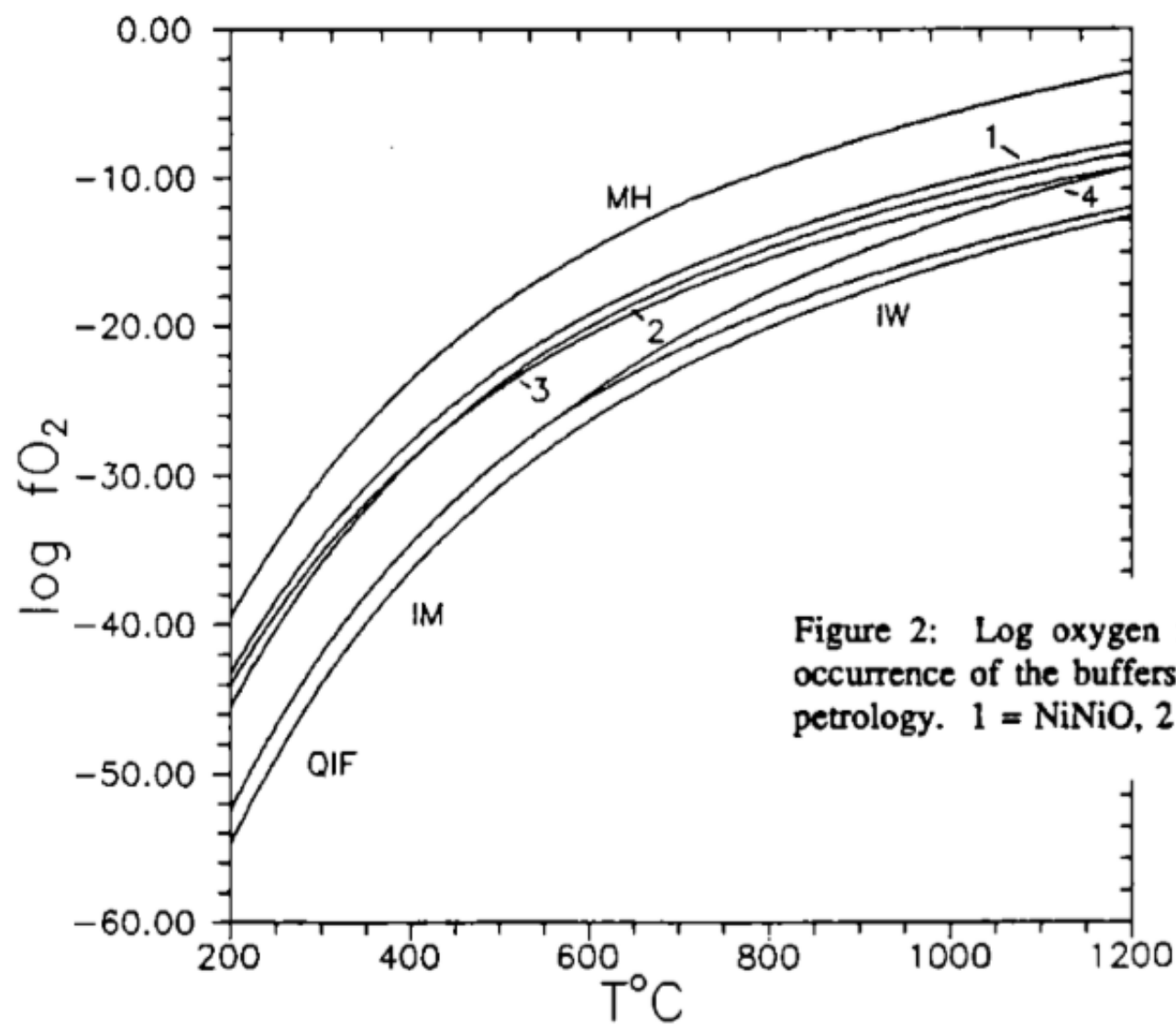
Figure 2: Log oxygen fugacity-T diagram showing the occurrence of the buffers commonly used in experimental petrology. 1 = NiNiO, 2 = FMQ, 3 = CoCoO, 4 = WM.
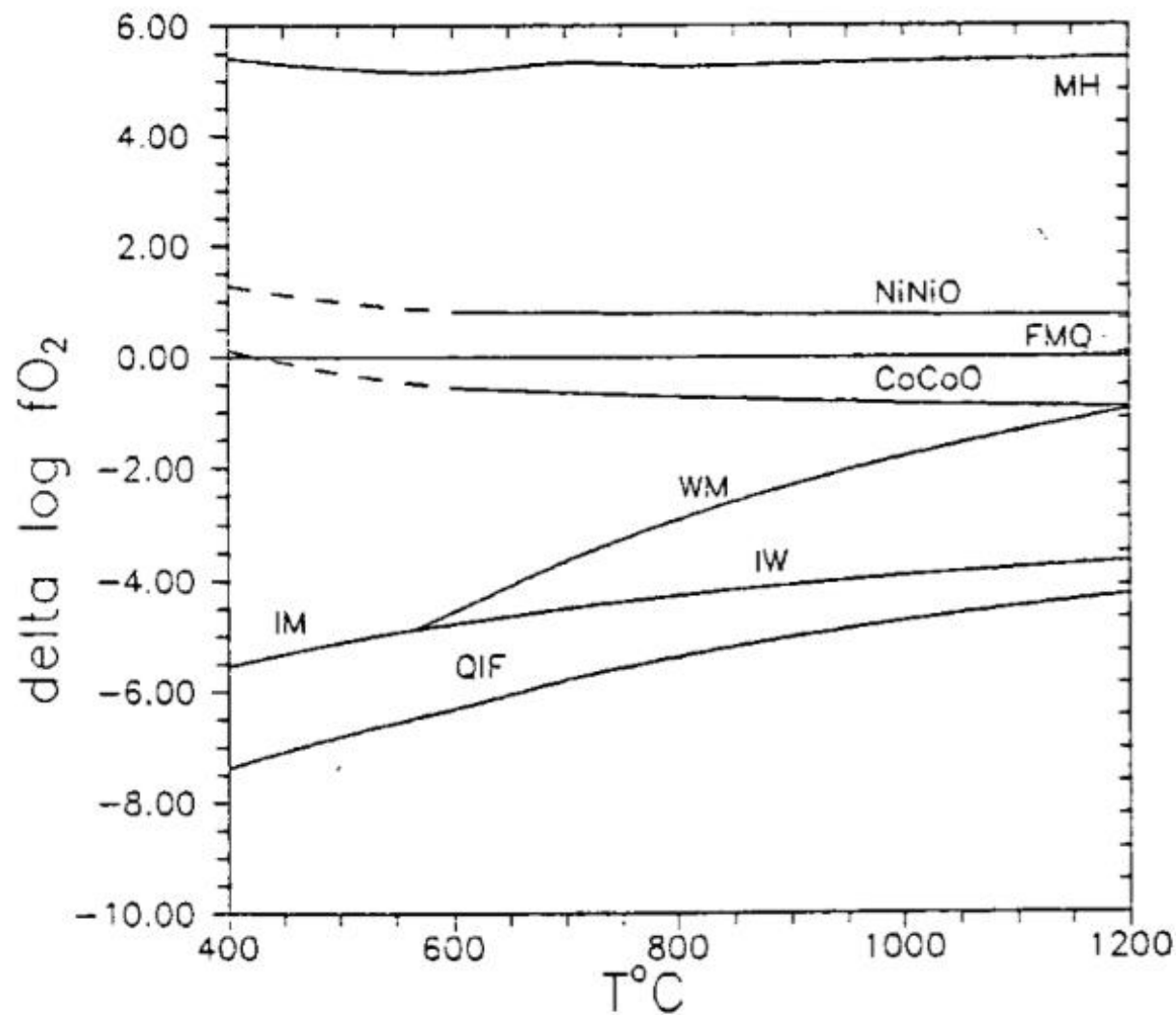
Figure 3: Δ log fO_2 - T diagram showing the common petrologic buffers as normalized to the oxygen fugacity of the FMQ buffer. Portions of the NiNiO and CoCoO buffers that lie outside of the range of experimental calibration are dashed.

4.   Some common misconceptions

I.   Oxygen buffer reactions doesn't exist in natural system.

II. Because free Oxygen is so rare in natural system, one cannot explain with only using Oxygen buffer reactions.

III. Ferrous/Ferric ratio have been used to indicate "oxidation state" of rocks, but this is not equal to Oxygen Fugacity.
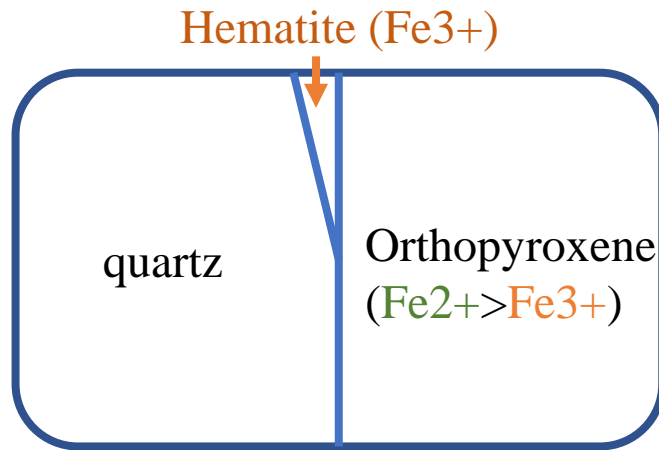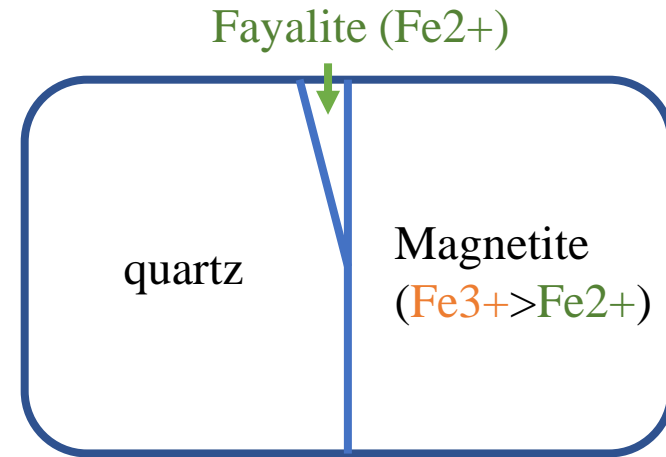

Rock(1): Orthopyroxene(XFe=0.20) 50%
               Quartz 49%
               Hematite 1%

Rock(2): Magnetite 50%
               Quartz 49%
               Fayalite(XFe=1.0?) 1%

the end