A primer on oxygen fugacity and oxygen buffers (and their use in MELTS modeling)

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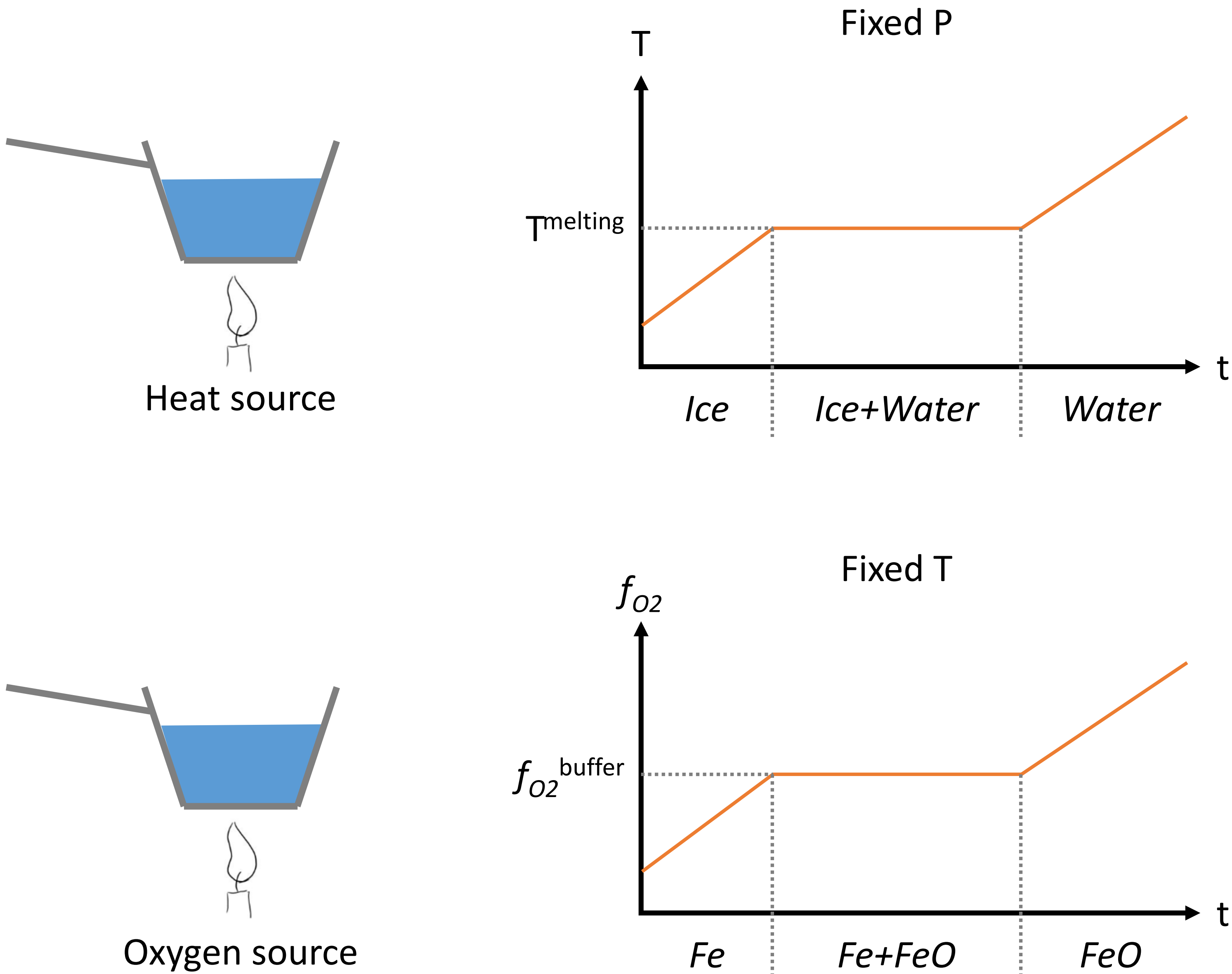
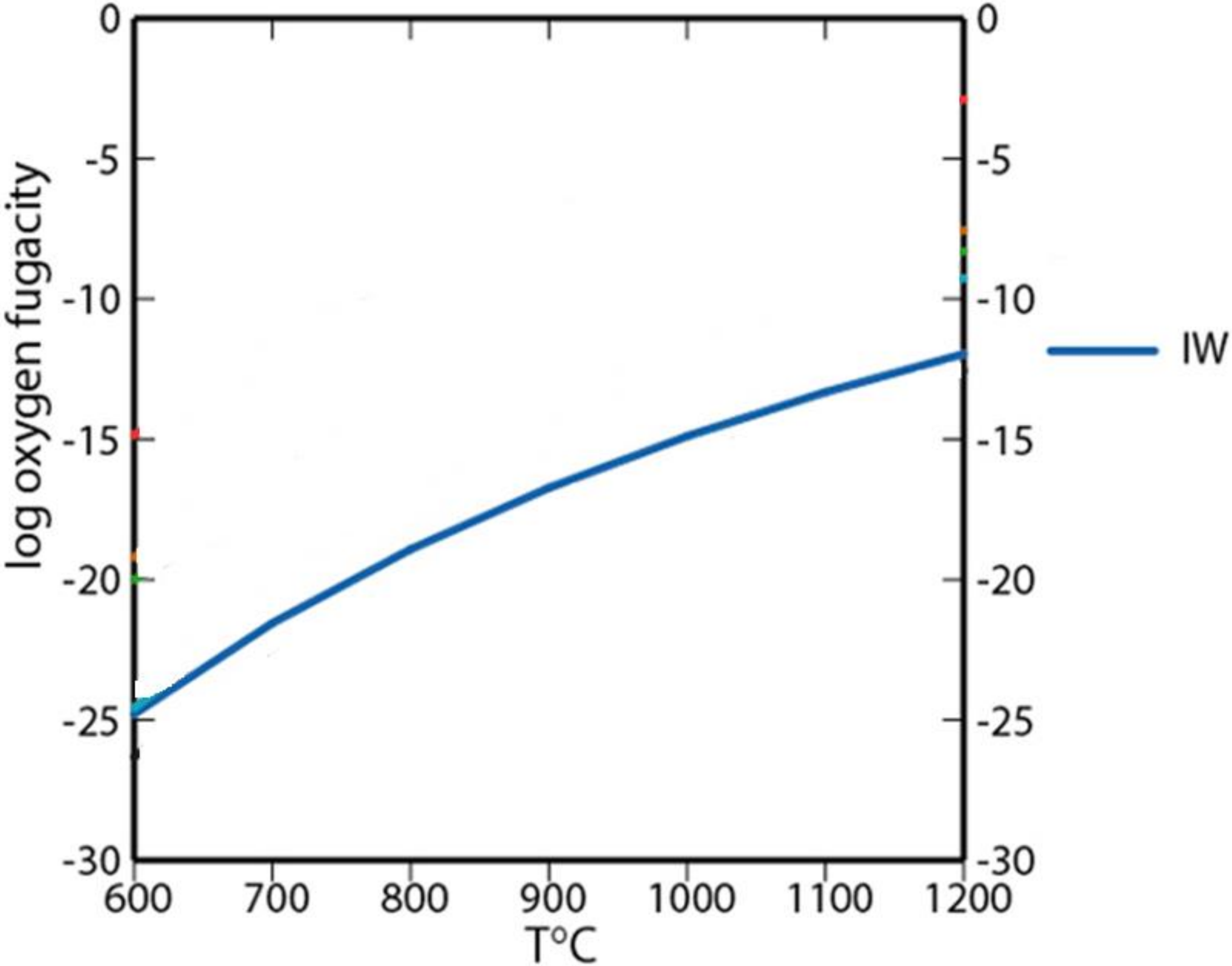
$$Fe + \frac{1}{2} O_2 \leftrightarrow FeO$$

$$K = \frac{a_{FeO}}{a_{Fe} * (a_{O_2})^{1/2}}$$

$$a_{O_2} \propto f_{O_2}$$


Heat source
Fixed P
T
$T^{melting}$
t
Ice
Ice+Water
Water
Oxygen source
Fixed T
f_{O2}
f_{O2}^{buffer}
t
Fe
Fe+FeO
FeO



0
-5
-10
-15
-20
-25
-30
log oxygen fugacity
600
700
800
900
1000
1100
1200
T°C
IW

$$Fe + \frac{1}{2} O_2 \leftrightarrow FeO$$

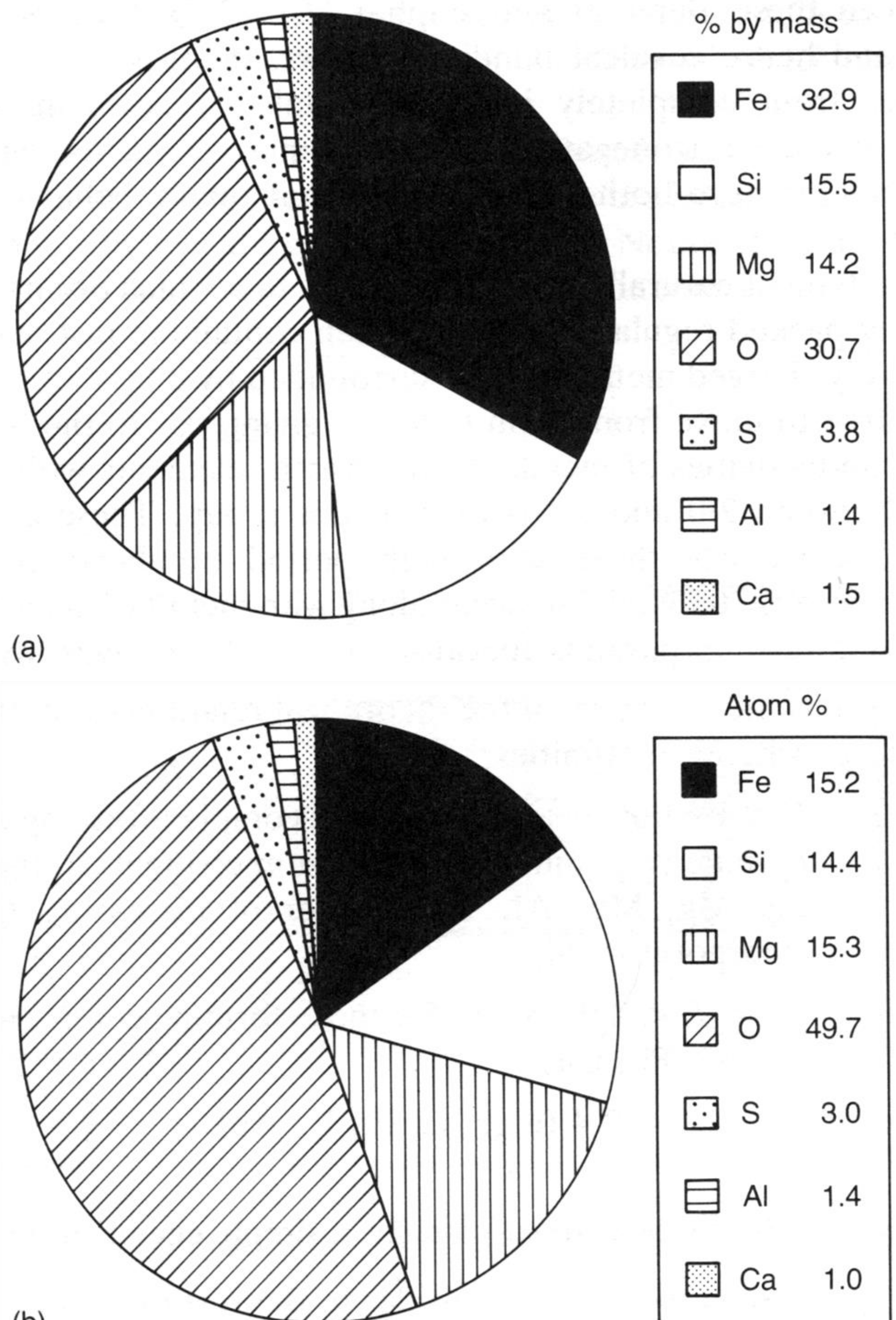
(Iron-Wustite: IW)

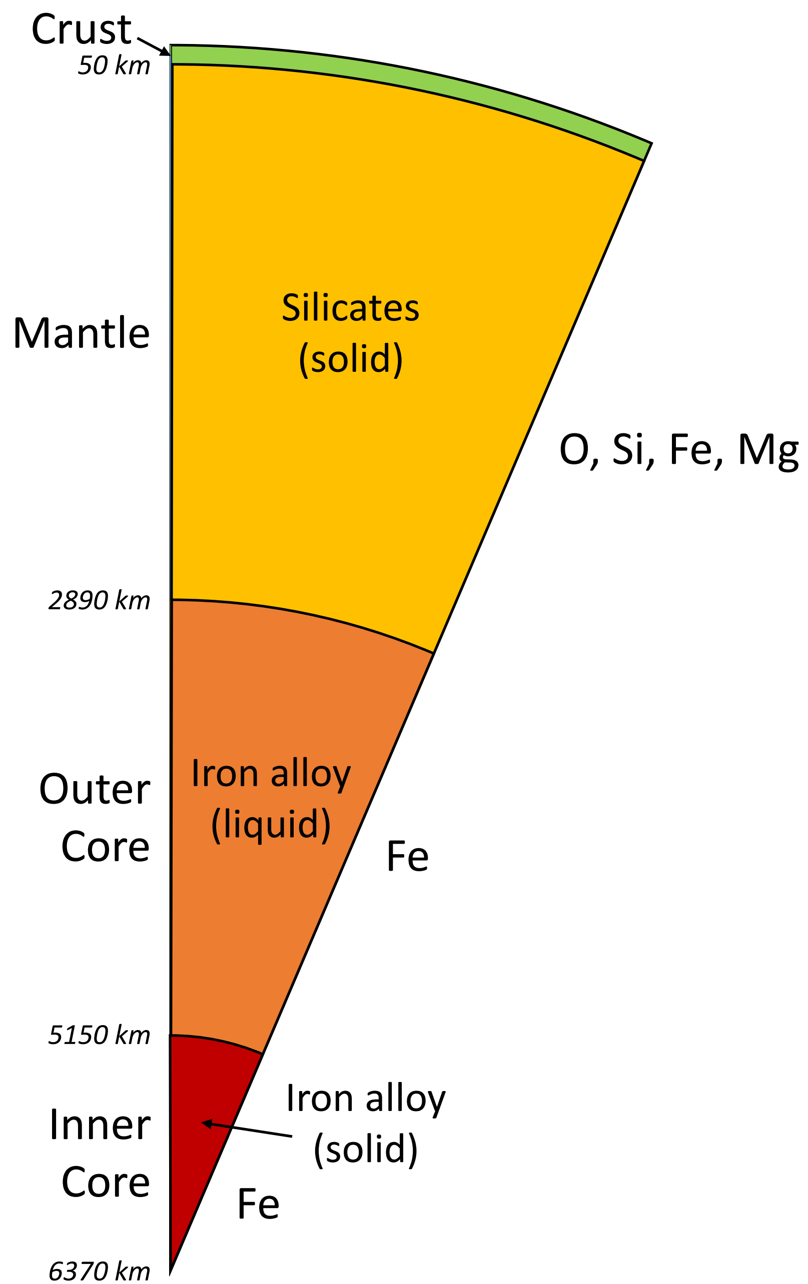
$$3\ FeO + \frac{1}{2} O_2 \leftrightarrow Fe_3O_4$$

(Wustite-Magnetite: WM)

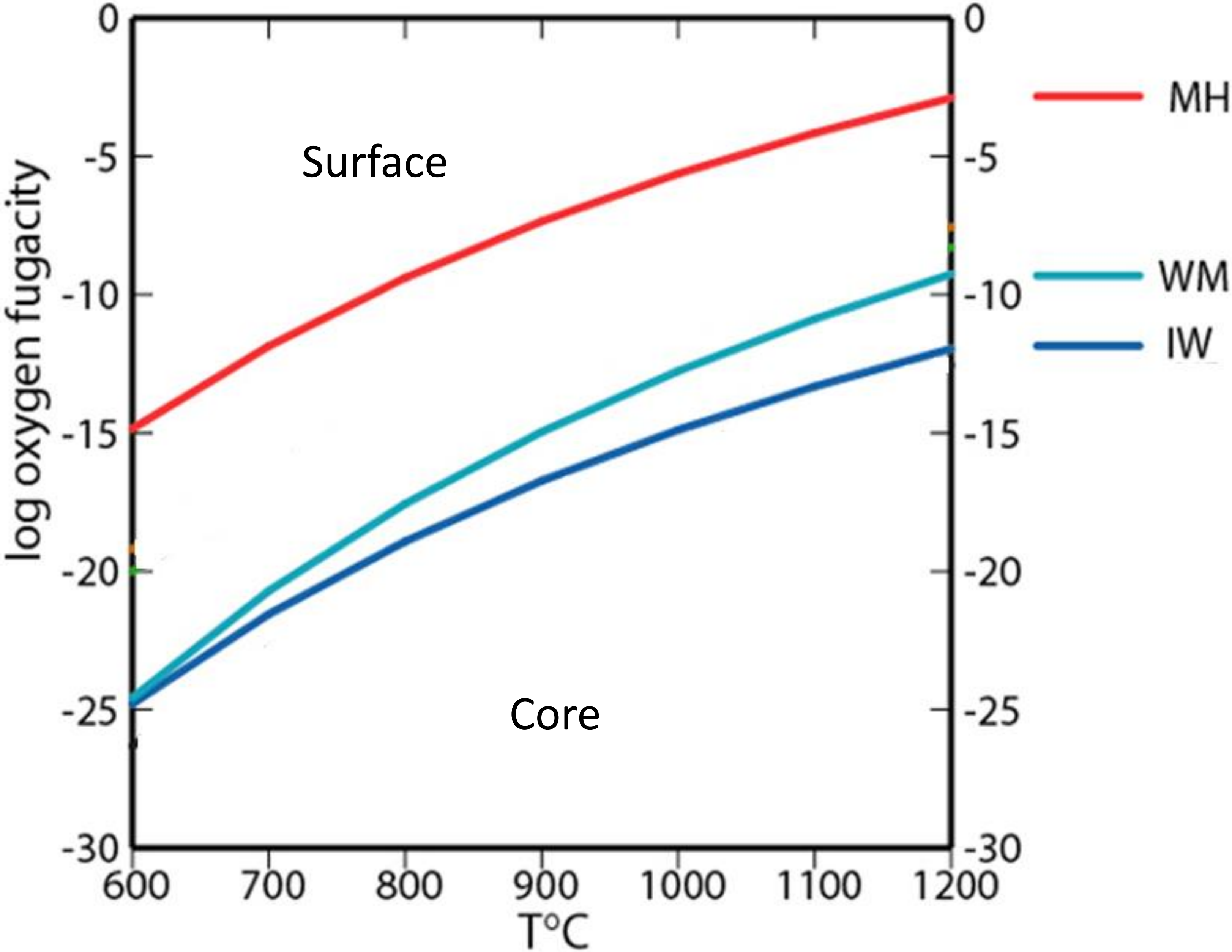
$$2\ Fe_3O_4 + \frac{1}{2} O_2 \leftrightarrow 3\ Fe_2O_3$$

(Magnetite-Hematite: MH)


% by mass
Fe 32.9
Si 15.5
Mg 14.2
O 30.7
S 3.8
Al 1.4
Ca 1.5
(a)
Atom %
Fe 15.2
Si 14.4
Mg 15.3
O 49.7
S 3.0
Al 1.4
Ca 1.0
(b)



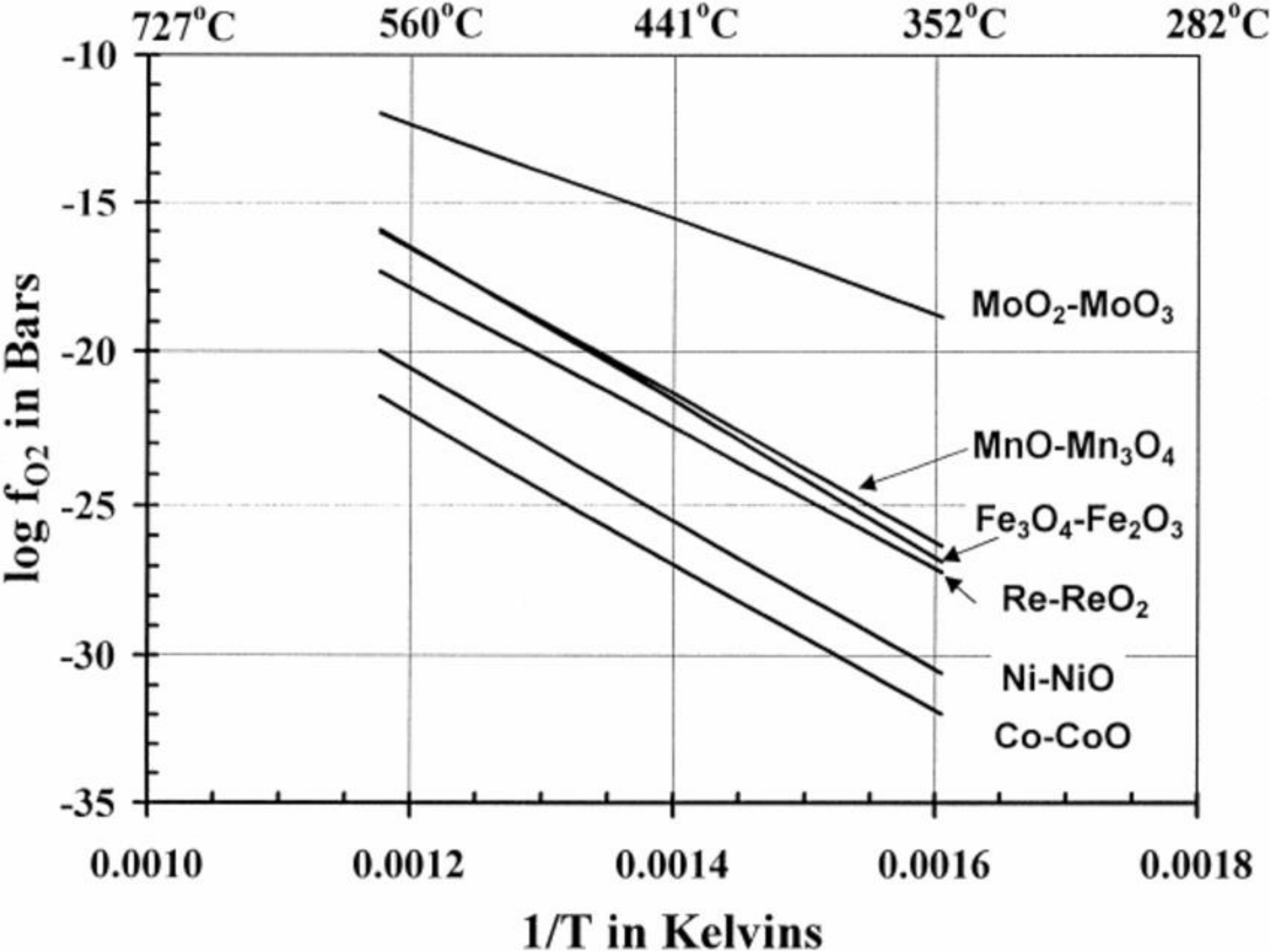
Crust
50 km
Mantle
Silicates
(solid)
O, Si, Fe, Mg
2890 km
Outer
Core
Iron alloy
(liquid)
Fe
5150 km
Inner
Core
Iron alloy
(solid)
Fe
6370 km

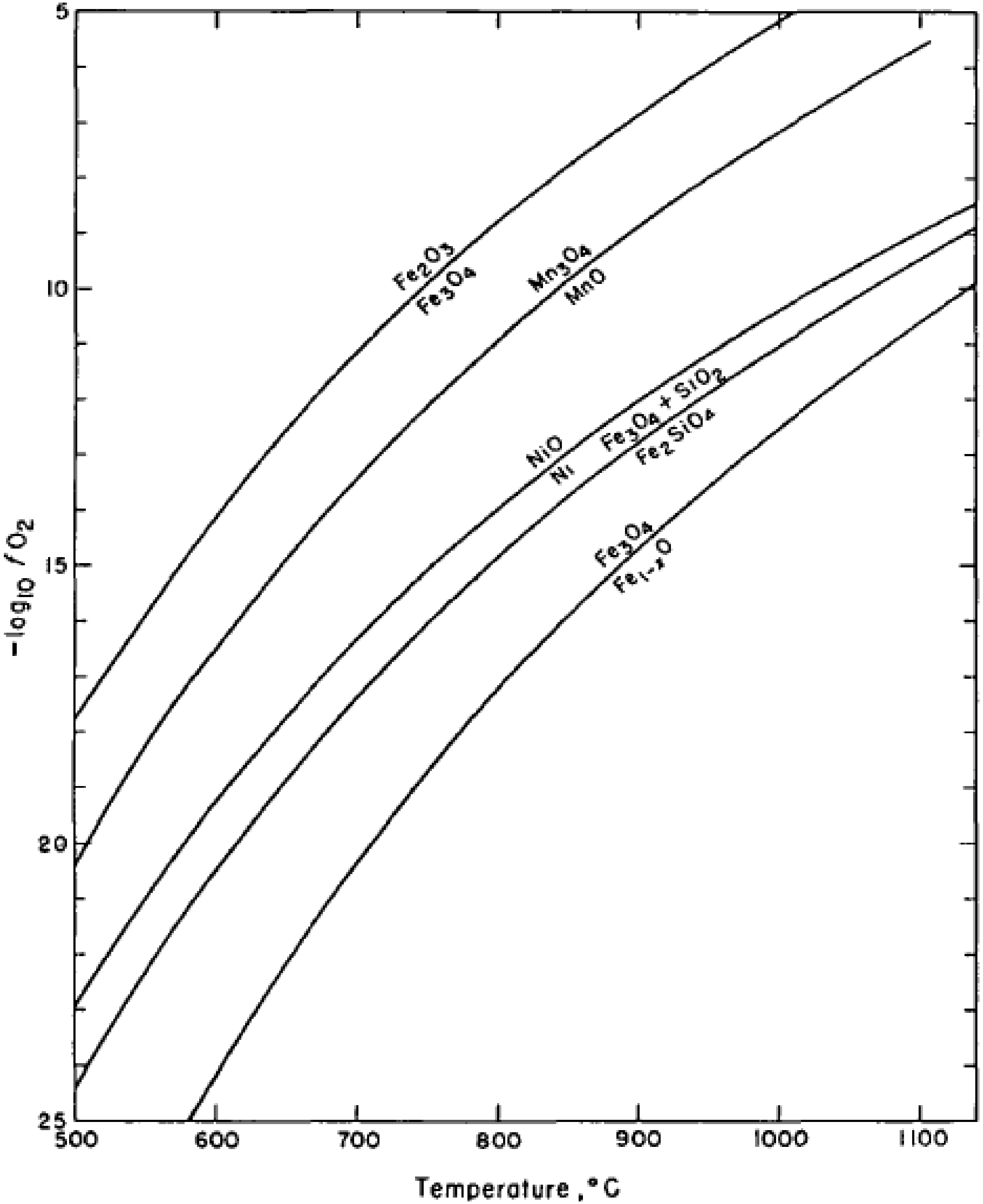


0
-5
-10
-15
-20
-25
-30
log oxygen fugacity
Surface
Core
MH
WM
IW
600
700
800
900
1000
1100
1200
T°C

$$Ni + \frac{1}{2} O_2 \leftrightarrow NiO$$

(Nickel-Nickel Oxide: NNO)


727°C
560°C
441°C
352°C
282°C
-10
-15
-20
-25
-30
-35
0.0010
0.0012
0.0014
0.0016
0.0018
log f_{O2} in Bars
1/T in Kelvins
MoO_2-MoO_3
MnO-Mn_3O_4
Fe_3O_4-Fe_2O_3
Re-ReO_2
Ni-NiO
Co-CoO



Fe2O3
Fe3O4
Mn3O4
MnO
NiO
Ni
Fe3O4 + SiO2
Fe2SiO4
Fe3O4
Fe1-xO
-log10 fO2
Temperature, °C
5
10
15
20
25
500
600
700
800
900
1000
1100

$$3\ Fe_2SiO_4 + O_2 \leftrightarrow 2\ Fe_3O_4 + 3\ SiO_2$$

(Fayalite-Magnetite+Quartz: FMQ or QFM)

$$3\ CaFeSi_2O_6 + 3\ FeTiO_3 + O_2 \leftrightarrow 3\ CaTiSiO_5 + 2\ Fe_3O_4 + 3\ SiO_2$$

(Hedenbergite+Ilmenite-Titanite+Magnetite+Quartz)

$$6\ Ca_2Fe_5Si_8O_{22}(OH)_2 + 12\ FeTiO_3 + 7\ O_2 \leftrightarrow 12\ CaTiSiO_5 + 14\ Fe_3O_4 + 36\ SiO_2 + 6\ H_2O$$

(Amphibole+Ilmenite-Titanite+Magnetite+Quartz: TMQAI)

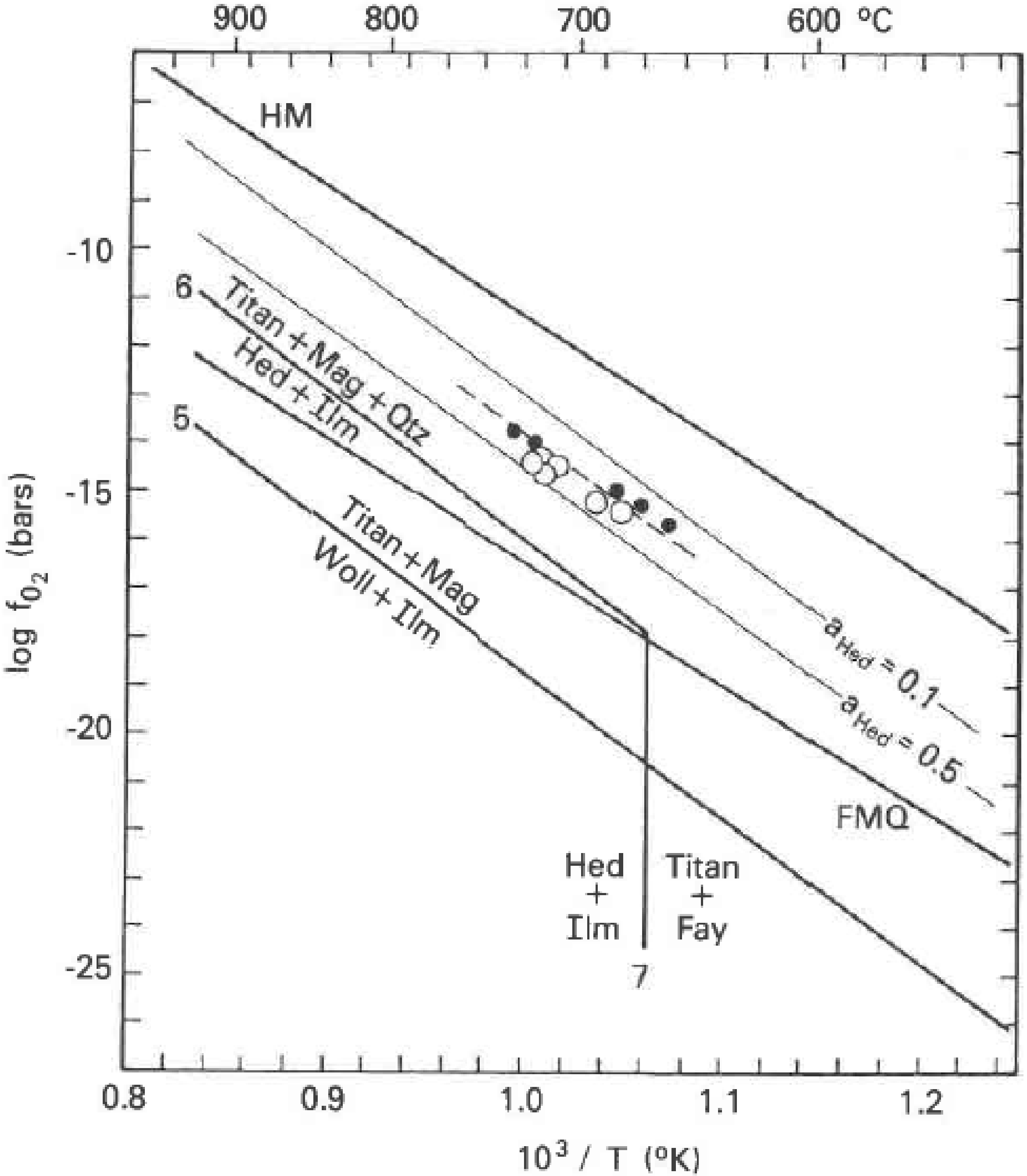
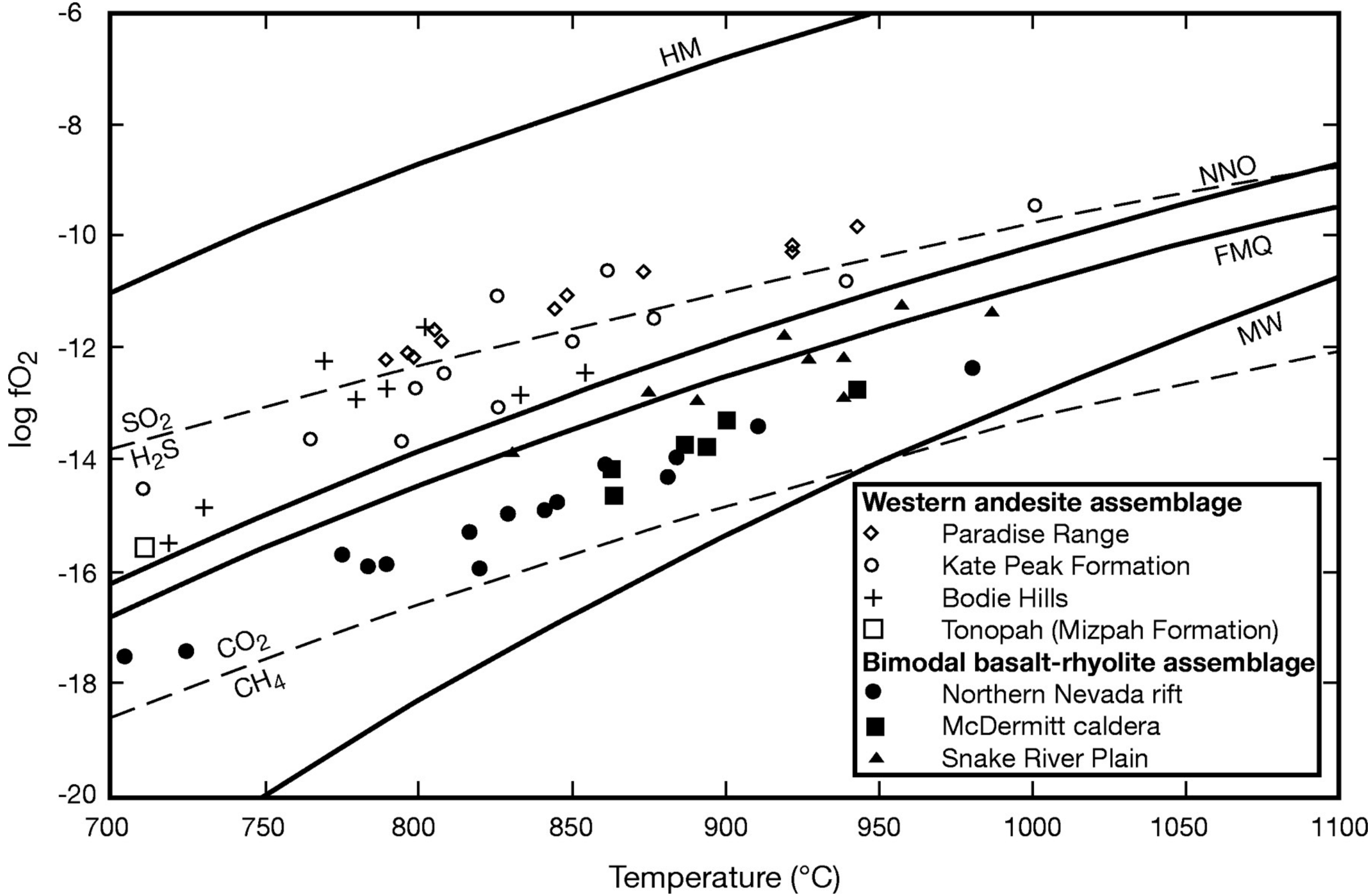
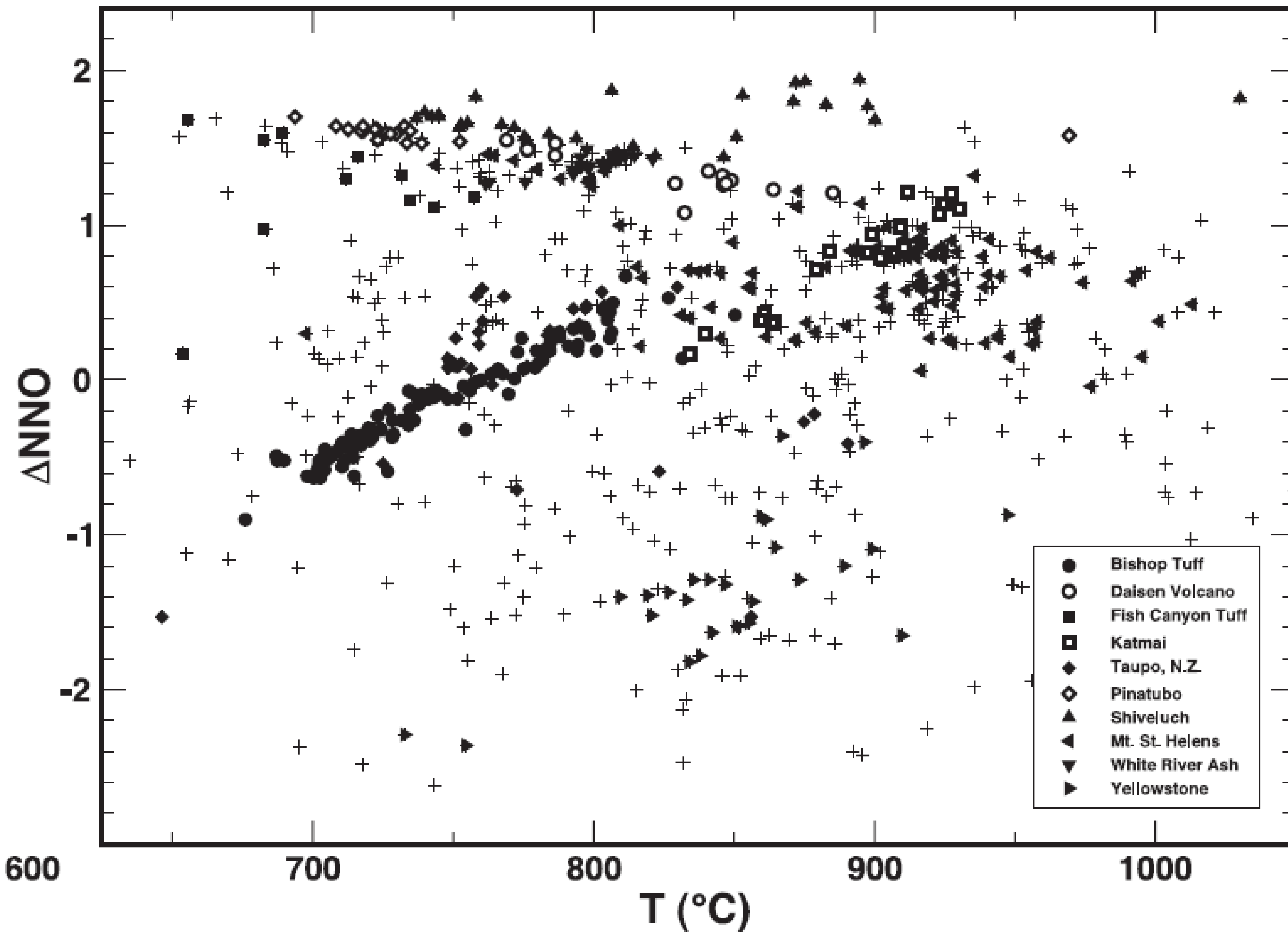
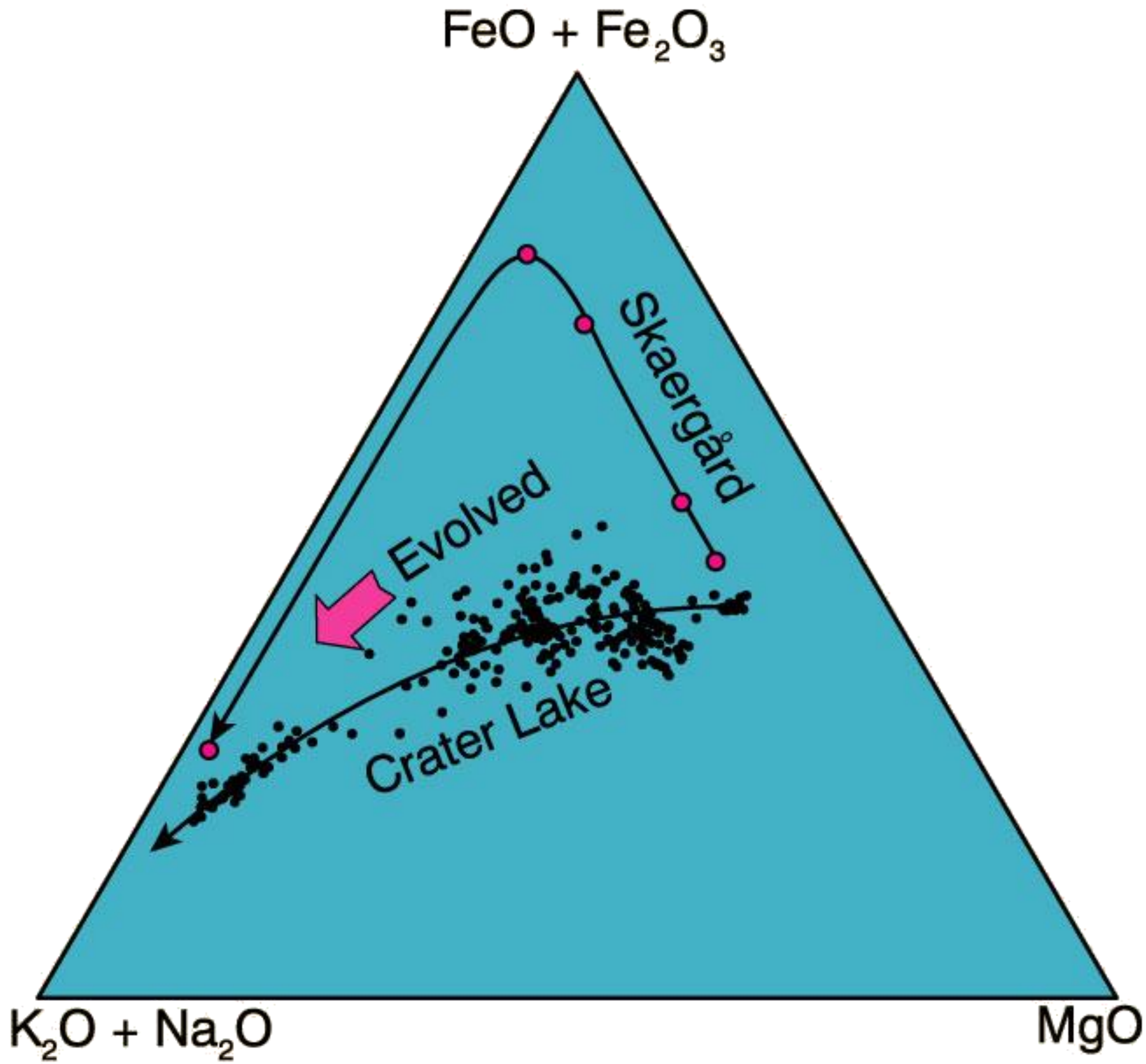


Fig. 1. Logarithmic plot of f_{O_2} versus T, showing stability of several mineral assemblages: FMQ, $Fe_2SiO_4 + Fe_3O_4 + SiO_2$; HM, $Fe_2O_3 + Fe_3O_4$; 5, $CaSiO_3 + FeTiO_3 + CaTiSiO_5 + Fe_3O_4$; 6, $CaFeSi_2O_6 + FeTiO_3 + CaTiSiO_5 + Fe_3O_4 + SiO_2$; 7, $CaTiSiO_5 + Fe_2SiO_4 + CaFeSi_2O_6 + FeTiO_3$. Light curves labeled $a_{Hed} = 0.5$ and 0.1 depict shift in Equilibrium 6 as a result of lowered activity of hedenbergite (greater diopside component) in clinopyroxene. Circles, f_{O_2}-T values determined by ilmenite-magnetite geothermometry for tuffs containing abundant clinopyroxene, ilmenite, and magnetite; dots, f_{O_2}-T values for tuffs from the same sequence that contain titanite, magnetite, and sparse ilmenite (Lipman, 1971); dashes, position of Equilibrium 6 calculated on the basis of the compositions of clinopyroxene, ilmenite, and magnetite in the tuffs ($a_{titanite}$ taken as 1).


HM
NNO
FMQ
MW
SO2
H2S
CO2
CH4
log fO2
Temperature (°C)
-6
-8
-10
-12
-14
-16
-18
-20
700
750
800
850
900
950
1000
1050
1100
Western andesite assemblage
Paradise Range
Kate Peak Formation
Bodie Hills
Tonopah (Mizpah Formation)
Bimodal basalt-rhyolite assemblage
Northern Nevada rift
McDermitt caldera
Snake River Plain

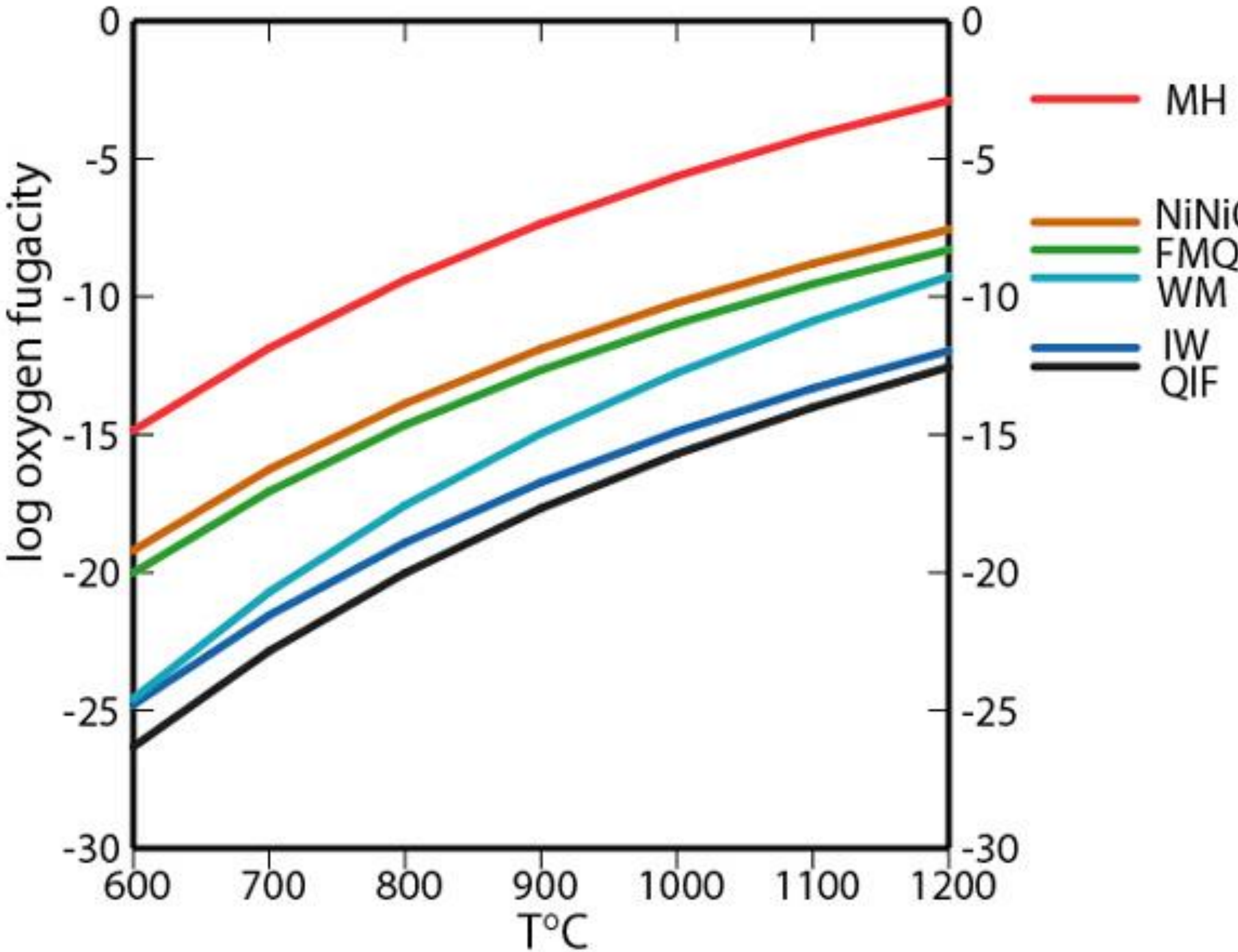


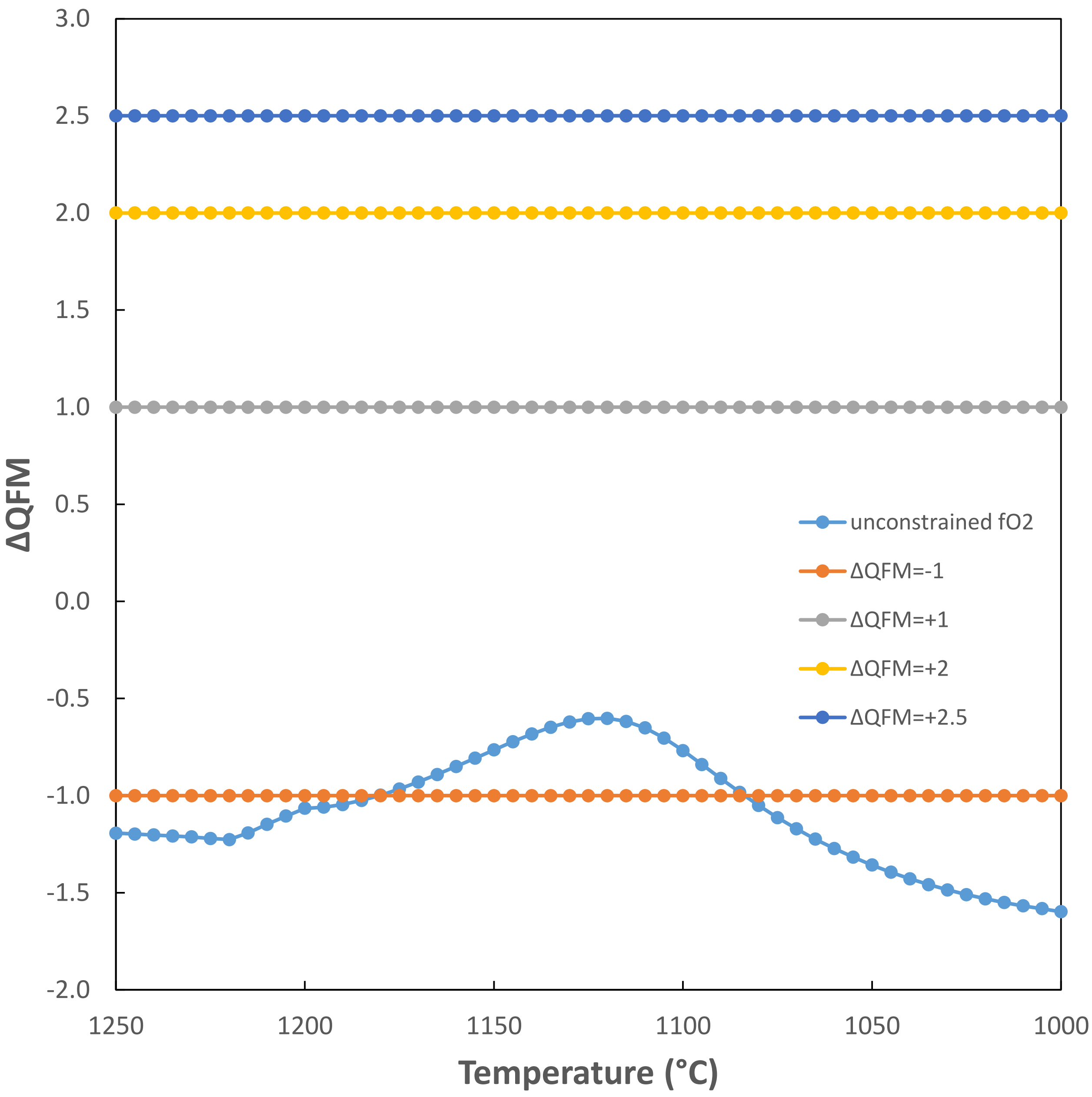
2
1
0
-1
-2
ΔNNO
600
700
800
900
1000
T (°C)
Bishop Tuff
Daisen Volcano
Fish Canyon Tuff
Katmai
Taupo, N.Z.
Pinatubo
Shiveluch
Mt. St. Helens
White River Ash
Yellowstone


$FeO + Fe_2O_3$
Skaergård
Evolved
Crater Lake
$K_2O + Na_2O$
MgO

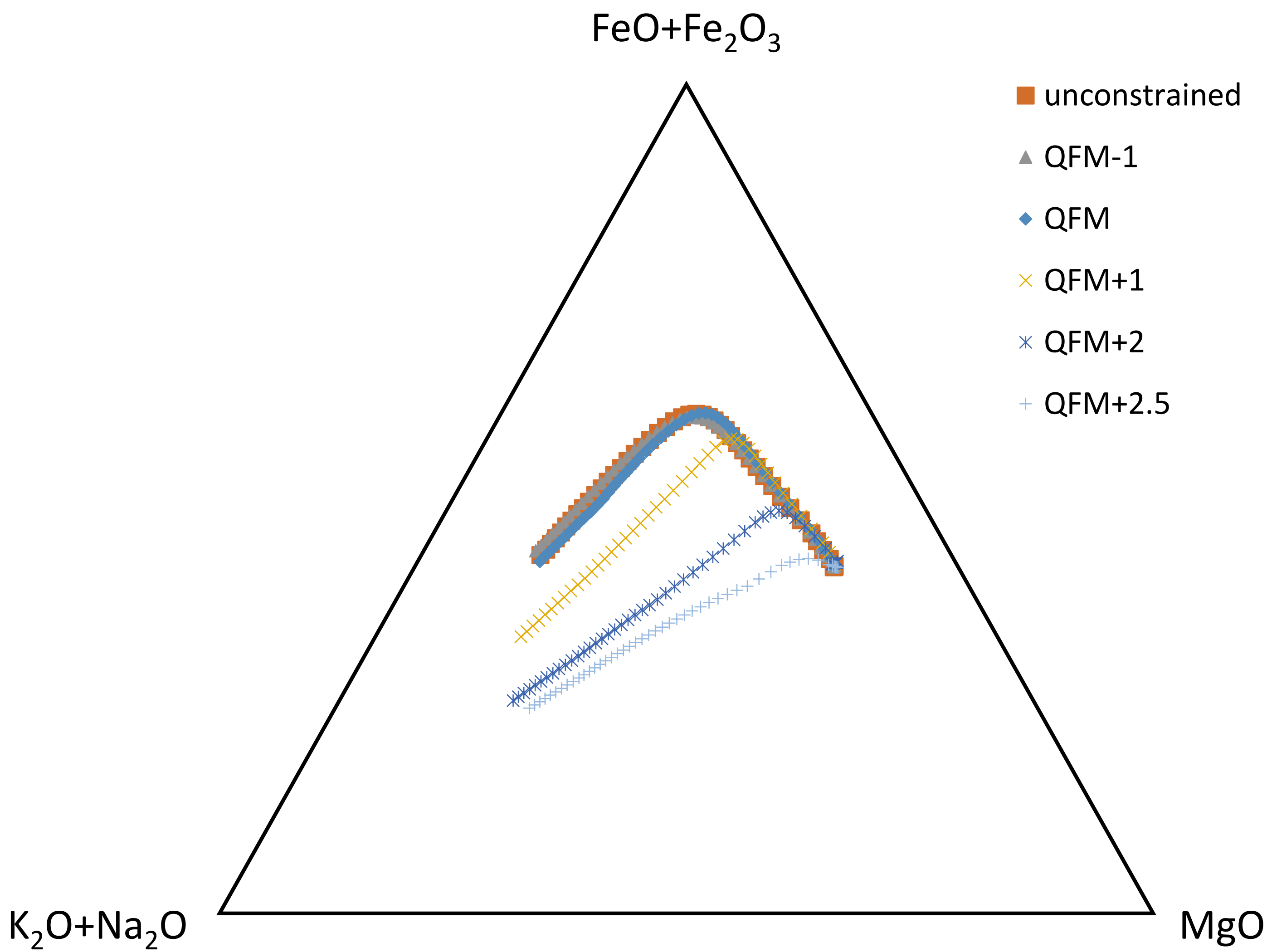
Issues:

1. Need to constrain f_{O2} relevant for the system of interest:
   - Can use Fe^{2+} and Fe^{3+} in the system, but there are challenges to doing so with natural samples
   - Can use assemblage to constrain state of oxidation
   - Can use oxybarometers to constrain state of oxidation
2. Need to capture the possible ranges of f_{O2} evolution over the course of crystallization or melting
   - Requires starting at the correct f_{O2} condition
   - Requires maintaining the correct f_{O2} condition over the course of crystallization or melting
   - Imprecisions in calculations can lead to large deviations from expected f_{O2} condition variations, especially when FeO_T and MgO concentrations are low

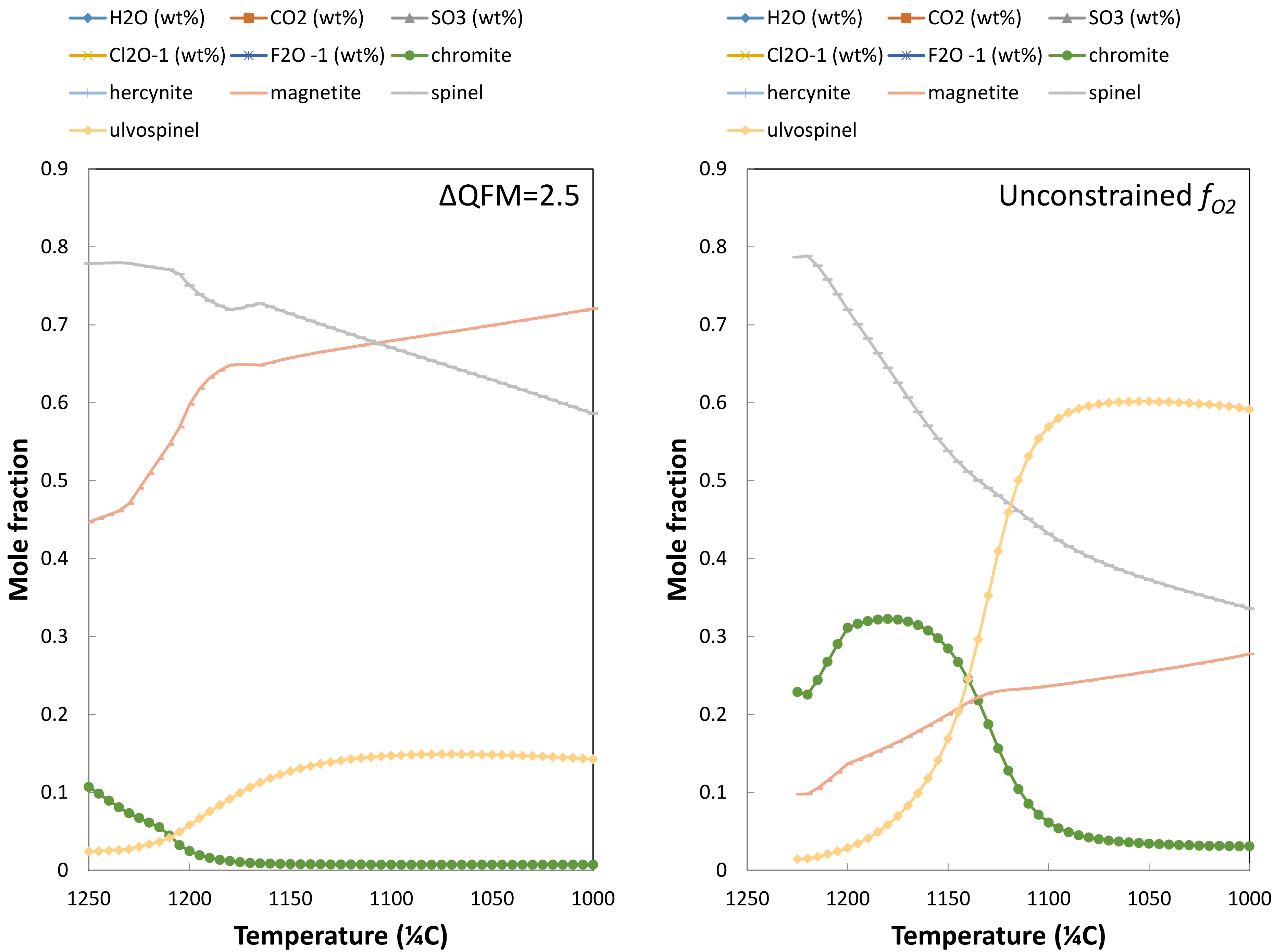

0
-5
-10
-15
-20
-25
-30
log oxygen fugacity
600
700
800
900
1000
1100
1200
T°C
MH
NiNiO
FMQ
WM
IW
QIF



3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
ΔQFM
1250
1200
1150
1100
1050
1000
Temperature (°C)
unconstrained fO2
ΔQFM=-1
ΔQFM=+1
ΔQFM=+2
ΔQFM=+2.5



FeO+Fe2O3
K2O+Na2O
MgO
unconstrained
QFM-1
QFM
QFM+1
QFM+2
QFM+2.5



H2O (wt%)
CO2 (wt%)
SO3 (wt%)
Cl2O-1 (wt%)
F2O -1 (wt%)
chromite
hercynite
magnetite
spinel
ulvospinel
ΔQFM=2.5
Mole fraction
Temperature (¼C)
1250
1200
1150
1100
1050
1000
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
H2O (wt%)
CO2 (wt%)
SO3 (wt%)
Cl2O-1 (wt%)
F2O -1 (wt%)
chromite
hercynite
magnetite
spinel
ulvospinel
Unconstrained f_{O2}
Mole fraction
Temperature (¼C)