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Metal saturation in the upper mantle

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- The uppermost mantle is oxidized.
  - From samples and partial melts [Wallace, Green 1988, Matveev et al. 1997]
  - It may contain H_2O, CO_2, CO_3^{2-}.
- fO_2 (shallow mantle) = fO_2 (whole of upper mantle)?

An experimental determination of primary carbonatite magma composition

M.E. Wallace & D.H. Green 1988

- Our experiments on the phase relationships of carbonate and amphibole-bearing peridotite (containing 0.3% H2O and 0.5–2.5% CO2) show that **sodic dolomitic carbonatite magma coexists with an amphibole lherzolite** assemblage in a field ranging from **2.1-3.0 GPa, 930-1,080 °C**,

- Their obtained **similar carbonatite melt composition and structure as preserved in natural samples** from Oldoinyo Lengai, Homa mountains, Tanzania and Kaiserstuhl, Germany.

Volatiles in the Earth's mantle: I. Synthesis of CHO fluids at 1273 K and 2.4 GPa

Matveev at al. 1997

- We have synthesized **graphite-saturated CHO fluids at 1000C and 2.4 GPa over 7.5 orders of magnitude in fO_2.**
- **H/O = 1.78 (H_2O-CO_2 stability field).**
- **H/O = 1330 (Si-SiC buffer).**

Using high-pressure experiments, we show here that large parts of the asthenosphere are likely to be metal-saturated.

- Pyroxene and garnet at P > 7 GPa in equilibrium with metallic Fe can incorporate sufficient Fe^{3+} that the mantle at >250 km depth is so reduced that an (Fe,Ni)-metal phase may be stable.

- Only shallow mantle (<250 km) oxidized.

- At the time of **core melt segregation** the silicate Earth was highly reduced and in equilibrium with Fe melt.
  - fO_2 was **2 log < Fe-FeO.**

- **Earth's upper mantle** is **now** oxidized.
  - Uppermantle rocks and mantle-derived melts range from **3 to 6 log > the Fe-FeO.**

- Shallow upper mantle seems to have experienced oxidation by 5 to 8 orders of magnitude in fO_2 .

- In the shallow mantle, fO_2 is monitored by equilibria:
  - $6Fe_2SiO_4$ (Ol) + O_2 = **$2Fe_3O_4$ (Sp)** + $3Fe_2Si_2O_6$ (Px);
  - $4Fe_2SiO_4$ (Ol) + Fe2Si2O6 (Px) + O_2 = **$2Fe^{2+}3Fe^{3+}{}_2Si_3O_{12}$ (Grt)**.
- Pressure increase stabilizes phases that fractionate Fe^{3+} (such as spinel or garnet)
- Pressure lowers activities of the Fe^{3+}, causing reduction.
- The general fO_2–depth trend in the mantle is believed to be towards reduction.

- To establish a redox profile through the upper mantle, we have equilibrated a model mantle composition in Fe-metal capsules to 14 GPa, corresponding to a depth of about 450 km.

- The starting composition was depleted relative to primitive mantle15 by 30% in normative olivine and enriched in FeO to a molar Mg/(Mg1Fe) bulk ratio of 0.5, to stabilize ferric-iron-fractionating phases like pyroxene and garnet and to raise the iron detection limit for electron energy loss spectroscopy (EELS) analysis.

- Before experimentation, the starting composition was sintered at 1,150C in CO–CO2 atmosphere at an fO2 near Fe-FeO, to render it free of ferric iron. All experiments were performed in Fe metal capsules from 1 to 14 GPa and 1,220 to 1,650 C. The fO2 at run conditions, ranging from 0.5 to 1.3 log units below Fe-FeO equilibrium, was deduced from the FeO contents of pyroxene and garnet in equilibrium with metallic Fe, assuming ideal ionic solution models.
- Run products were analysed for major elements and then thinned to electron transparency. Pyroxene, garnet and majorite solid solutions were then analysed for their Fe3+/ΣFe ratios using EELS.

Table S1: Starting composition and representative electron microprobe analyses of run products.

		exp-10	exp-15	exp-15	zuII-4	zuII-4	zuIII-1	zuIII-1	zu-8	zu-8	zuII-3	zuII-3	zuIV-1	zuIV-1	zuIII-4
pressure (GPa)		1	3	3	6	6	7	7	8	8	10	10	12	12	14
temperature (°C)		1220	1400	1400	1400	1400	1450	1450	1650	1650	1500	1500	1500	1500	1500
run time (h)		48	24	24	4.5	4.5	6	6	1.5	1.5	3.5	3.5	10	10	4.5
ΔfO_2 (IW)		- 0.6(3)	- 0.5(3)	- 0.5(3)	- 0.5(3)	- 0.5(3)	- 0.6(3)	- 0.6(3)	- 1.1(3)	- 1.1(3)	- 0.7(1)	- 0.7(1)	-0.7(2)	-0.7(2)	- 1.3(3)
phase	start. comp.	cpx	grt	cpx	grt	cpx	grt	cpx	grt	cpx	grt	cpx	grt	cpx	grt
SiO_2	47.5	48.8	39.4	50.6	40.4	52.3	40.6	51.8	43.9	54.8	43.5	52.3	43.8	52.7	50.5
TiO_2	0.29	0.18	0.56	0.28	0.81	0.20	0.70	0.23	0.40	0.11	0.68	0.16	0.46	0.16	0.36
Al_2O_3	6.45	4.76	21.2	4.38	20.7	2.45	18.3	2.78	18.1	2.12	15.2	1.50	14.0	1.63	8.40
Cr_2O_3	0.56	0.74	1.30	0.50	1.26	0.36	1.02	0.34	0.96	0.27	0.87	0.29	1.10	0.33	0.69
FeO[a]	26.2	26.4	23.6	24.0	25.0	26.5	23.4	22.7	13.7	13.1	22.1	23.5	20.3	19.7	9.77
Fe_2O_3[a]	–	0.3	1.38	0.82	1.16	0.09	2.26	1.05	2.68	1.10	3.67	3.23	4.61	3.26	5.59
MgO	14.7	13.5	9.21	14.2	9.93	14.9	11.4	15.3	18.4	21.5	12.9	15.6	12.4	15.3	19.4
CaO	3.80	6.01	4.01	4.10	3.82	4.34	3.10	4.43	3.41	6.44	2.91	4.46	2.72	5.11	5.25
Na_2O	0.50	0.16	0.03	0.85	0.04	0.67	0.16	1.18	0.19	1.01	0.14	0.74	0.32	1.15	1.56
Total	100.0	100.9	100.7	99.7	102.0	101.8	100.9	99.8	101.7	100.5	102.0	101.8	99.7	99.3	101.5
Mg/(Mg+Fe)[a]	0.5	0.48(1)	0.41(1)	0.51(1)	0.41(1)	0.50(1)	0.47(1)	0.55(1)	0.71(3)	0.75(2)	0.51(3)	0.54(2)	0.52(1)	0.58(1)	0.78(2)
$Fe^{3+}/\Sigma Fe$ (EELS)		0.01(3)	0.05(3)	0.03(3)	0.04(2)	0.00(3)	0.08(3)	0.04(3)	0.15(4)	0.07(3)	0.13(2)	0.11(3)	0.17(5)	0.13(4)	0.34(6)
Si (per formula unit)		1.88(1)	3.01(1)	1.93(2)	3.06(2)	1.98(1)	3.11(2)	1.97(1)	3.18(2)	2.00(1)	3.28(2)	1.99(1)	3.36(2)	2.02(1)	3.67(1)
Al (per formula unit)		0.22(2)	1.91(2)	0.20(2)	1.76(2)	0.11(1)	1.65(4)	0.13(1)	1.55(2)	0.09(1)	1.35(3)	0.07(1)	1.27(1)	0.07(1)	0.72(3)

Uncertainties in parenthesis are standard errors of the mean (95% confidence). (a) Recalculated based on $Fe^{3+}/\Sigma Fe$ ratio (EELS). Electron microprobe analyses at 15 kV and 15 nA using natural silicates as standards. Run products were thinned to electron transparency with a Gatan Duo-Mill ion milling system. Pyroxene, garnet, and majorite$_{ss}$ were analyzed for $Fe^{3+}/\Sigma Fe$ ratios with a Zeiss Libra 200 FE transmission electron microscope equipped with an in-column Omega energy filter and operated at 200 kV. The energy resolution was about 1 eV, measured as full width at half maximum of the zero loss peak. Molar $Fe^{3+}/\Sigma Fe$ was calculated from the iron $L_{2/3}$ spectra using the calibration of van Aken & Liebscher[16]. Background subtraction followed the procedure described by van Aken et al.[17]. fO_2 values calculated from ferrosilite (in cpx) and almandine (in grt) activities using ideal ionic solution models. Note that the 8 GPa and 14 GPa runs may have suffered some melt loss at run conditions, causing silicates to be more magnesian and Mg/(Mg+Fe) atomic ratios more variable. In the high pressure runs > 8 GPa some chemical variation may also be owed to the small amount of starting material (~ 5 mg) that can be equilibrated (c.f. elevated sodium content in grt at 14 GPa).

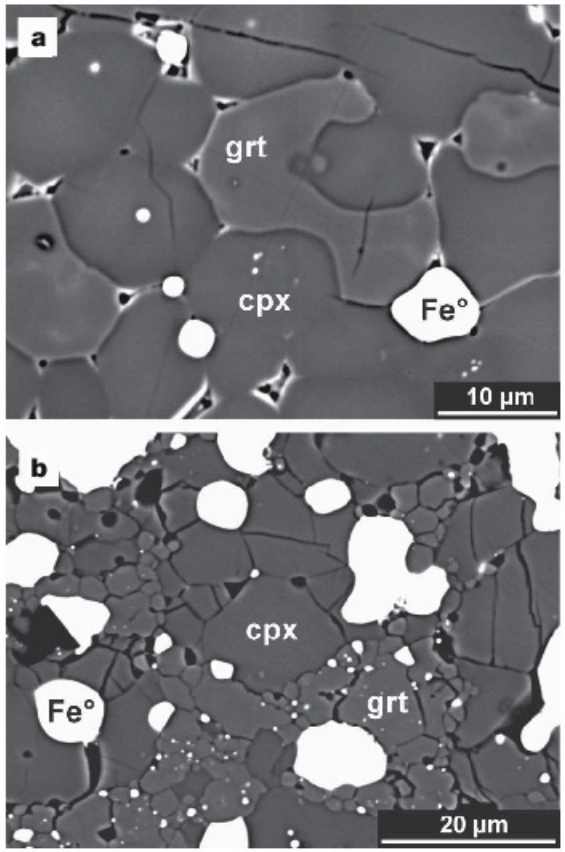

Figure 1 | Backscattered images of run products. **a**, 3 GPa experiment. **b**, 12 GPa experiment. Phases present are clinopyroxene (cpx), garnet (grt), metallic iron (Fe°) and minor amounts of partial melt.

- **1 GPa Ol + two Px+Fe**.
- **3 - 6 GPa**, **subcalcic Px + Grt +Fe**.
- Al^{3+} in Px falls with increasing pressure and modal Grt increases according to
  - MAl_2SiO_6 (CPx)+$M_2Si_2O_6$ (CPx) = $M_3Al_2Si_3O_{12}$ (Grt),
  - where M=Mg^{2+}, Fe^{2+} and Ca^{2+}.
- **7 GPa**, **Px → Grt**:
  - $2xM_2Si_2O_6$ (CPx) + $M_3Al_2Si_3O_{12}$(Grt) = [$M_3Al_2Si_3O_{12}$×$xM_3(MSi)Si_3O_{12}$] (Mj)
- **14 GPa**, **Mj + Fe**.

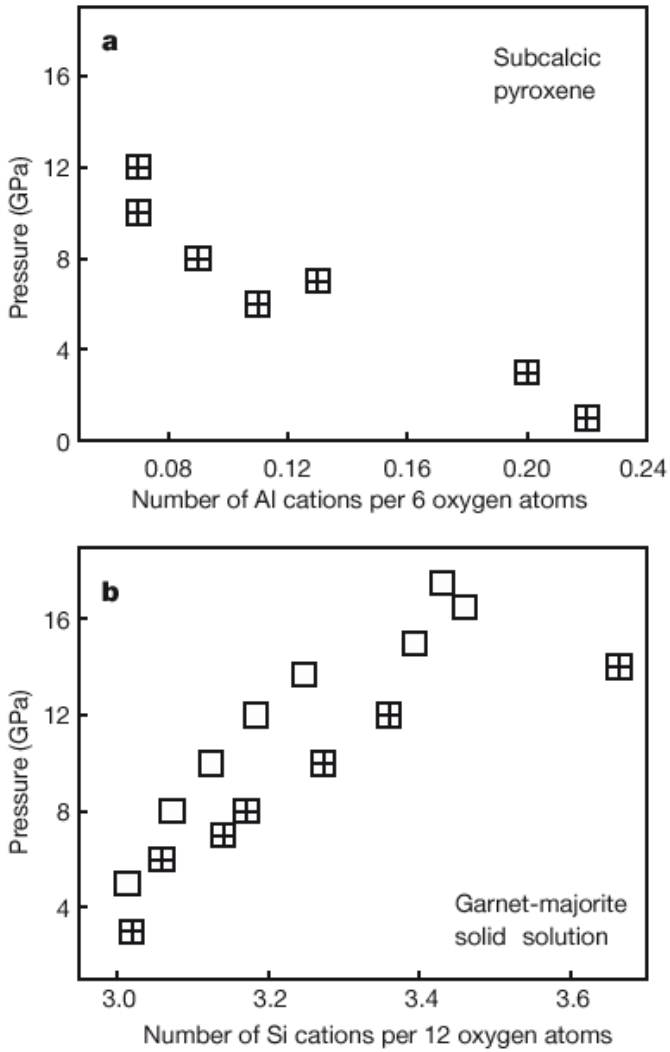

Figure 2 | Experimental clinopyroxene (a) and garnet–majorite compositions (b). Crossed symbols, this study (bulk Mg/(Mg+Fe) = 0.5); open symbols, ref. 18 with bulk Mg/(Mg+Fe) = 0.9. Onset of majorite substitution in garnet at about 7 GPa is independent of bulk Mg/(Mg+Fe).

- < 6 GPa, Fe^{3+} contents are pressureinsensitive.
- > 7 GPa, $Fe^{3+}/\Sigma Fe$ increases, up to 0.34 at 14 GPa.

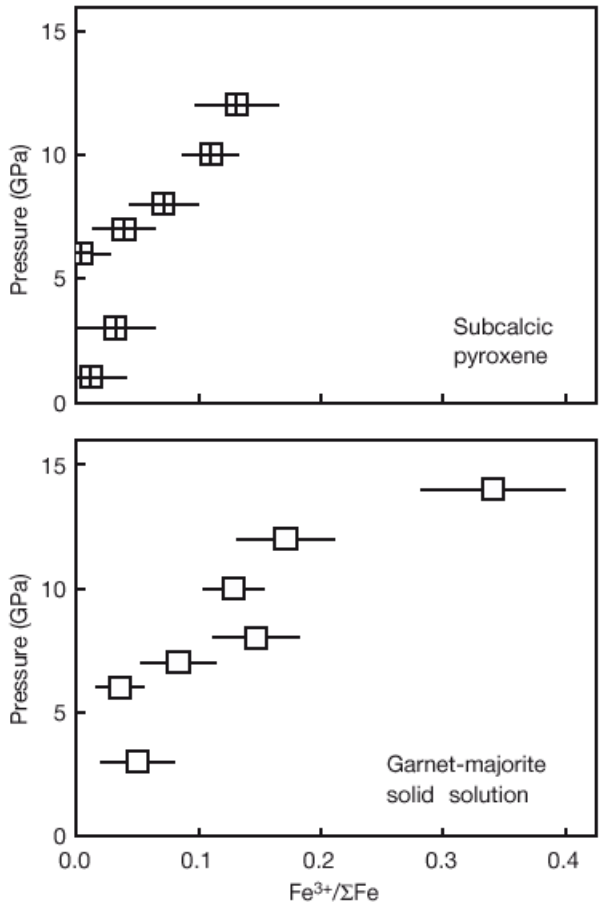

Figure 3 | Pressure effect on the $Fe^{3+}/\Sigma Fe$ atomic ratios of pyroxene and garnet (redox equilibrium with metallic Fe). Averages of 8 to 15 analyses per symbol. Error bars are standard errors of the mean with 95% confidence interval and include variations among analyses and uncertainties of the universal curve parameters of ref. 16.

- In natural Grt-peridotites: $Fe^{3+}/\Sigma Fe$ (Grt) > $Fe^{3+}/\Sigma Fe$ (Px).
- In experiment: $Fe^{3+}/\Sigma Fe$ ~ CMj in Grt.

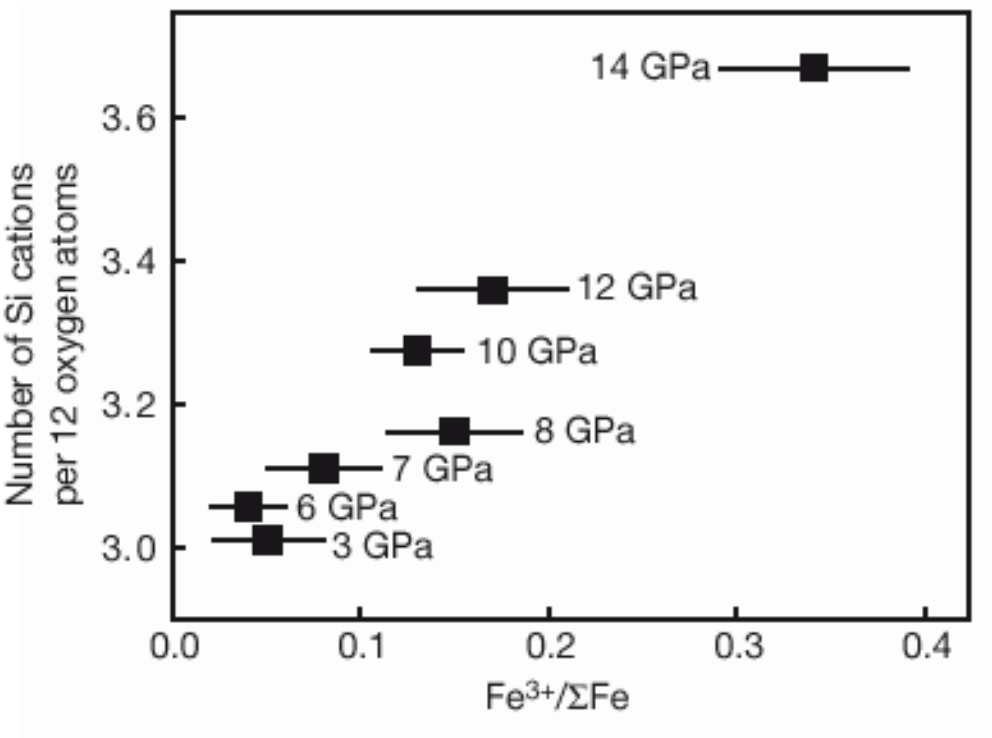

Figure 4 | Correlation between the $Fe^{3+}/\Sigma Fe$ atomic ratio and the Si_{3+x} excess in garnet–majorite solid solutions. Error bars are standard errors of the mean with 95% confidence interval and include variations among analyses and uncertainties of the universal curve parameters of ref. 16.

- **We suggest that not only the lower mantle and the transition zone, but also the lower half of the upper mantle is metal-saturated.**
- **Fe-metal saturation will set in when the mantle silicates in equilibrium with metallic Fe can fractionate more Fe2 O3 than is present in the fertile upper mantle**.
- We can approximate the depth at which this is likely to happen. At 8 GPa, fertile mantle with 4.5 wt% Al2 O3 and 3.7 wt% CaO (ref. 15) will crystallize about 20 wt% majoritic garnet, 15 wt% subcalcic clinopyroxene, and 65 wt% olivine (assuming all Al2 O3 fractionates into garnet and all CaO into pyroxene). A typical iron content in garnet from garnet peridotite, calculated as FeO, is 8 to 10 wt%. In our 8 GPa garnets, 15 mol% of total Fe is ferric iron. Therefore, 20 wt% majori-tic garnet with an average 9 wt% FeO may fractionate about 2,400 p.p.m. Fe2 O3 , and this is in equilibrium with metallic Fe. Fertile upper mantle at shallow pressure contains about 2,000 p.p.m. Fe2 O3 and about 8 wt% FeO.
- **Hence, that same composition compressed to 7 to 8 GPa will be Fe-metal-saturated.**