Mineral indicators of potassium activity in the upper mantle: a review

O. G. Safonov

Institute of Experimental Mineralogy, Chernogolovka, Russia

Department of Petrology, Moscow State University, Moscow, Russia

"High-Pressure Mineralogy: Theory and Experiment", Moscow, MSU, October 22, 2015

MANTLE METASOMATISM

compositional changes in the mantle wall-rock due to interaction with mantle fluids (Lloyd & Bailey, 1973)

Cryptic metasomatism

(Dawson, 1984): changes in composition (especially, trace elements) without addition of new phases

Stealth metasomatism

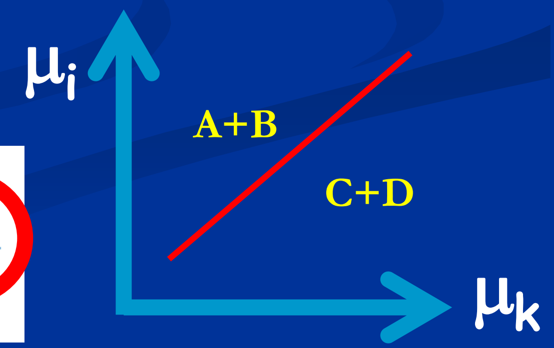
(O'Reilly & Griffin, 2013): addition of new phases, which are indistinguishable mineralogically from the common peridotite phases

Modal (patent) metasomatism

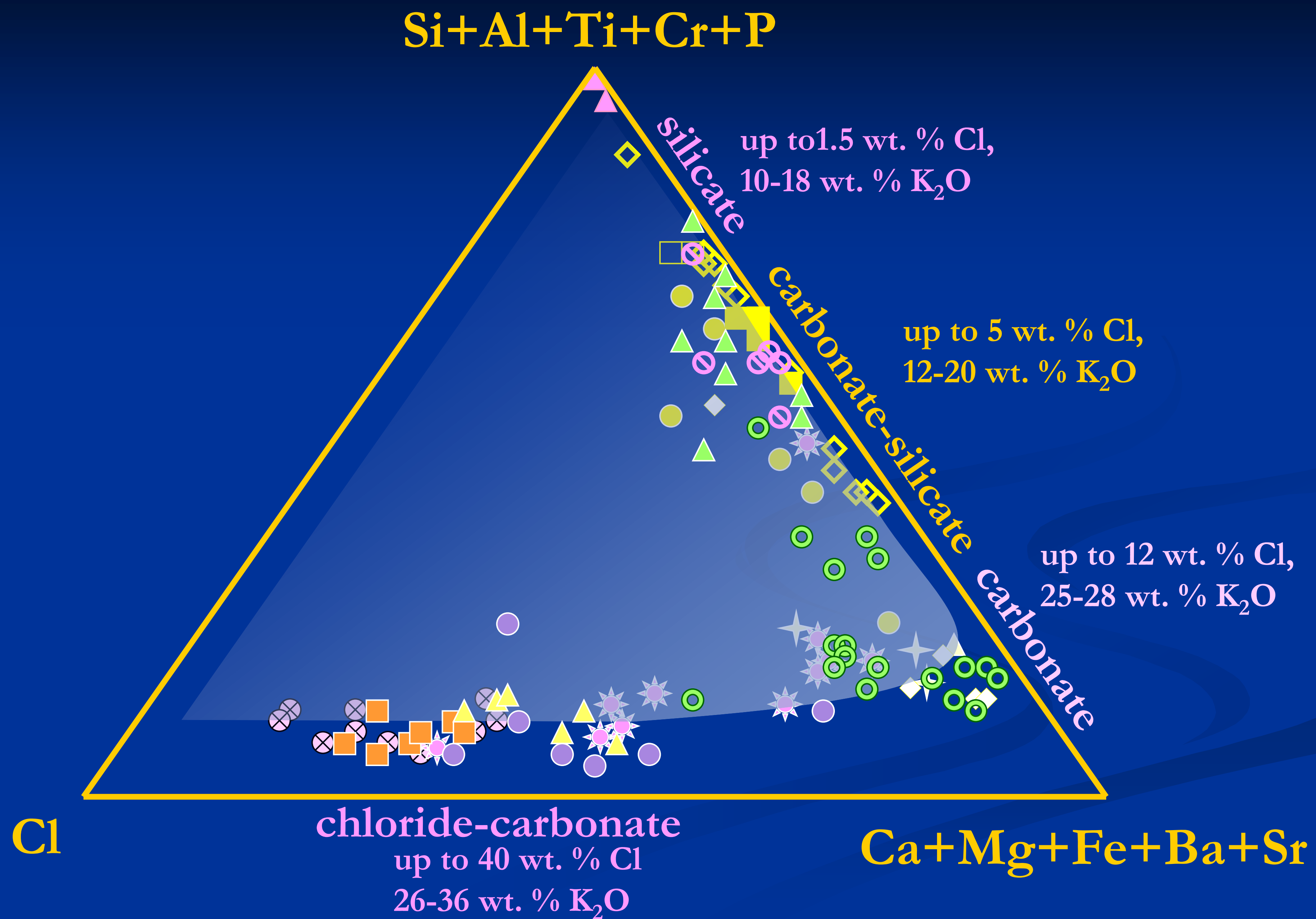
(Harte, 1983): "the presence of minerals additional to those seen commonly in peridotites"

$$dG = -SdT + Vdp + \sum_{j}^{l} \mu_i dm_i + \sum_{i}^{k} m_i d\mu_i$$

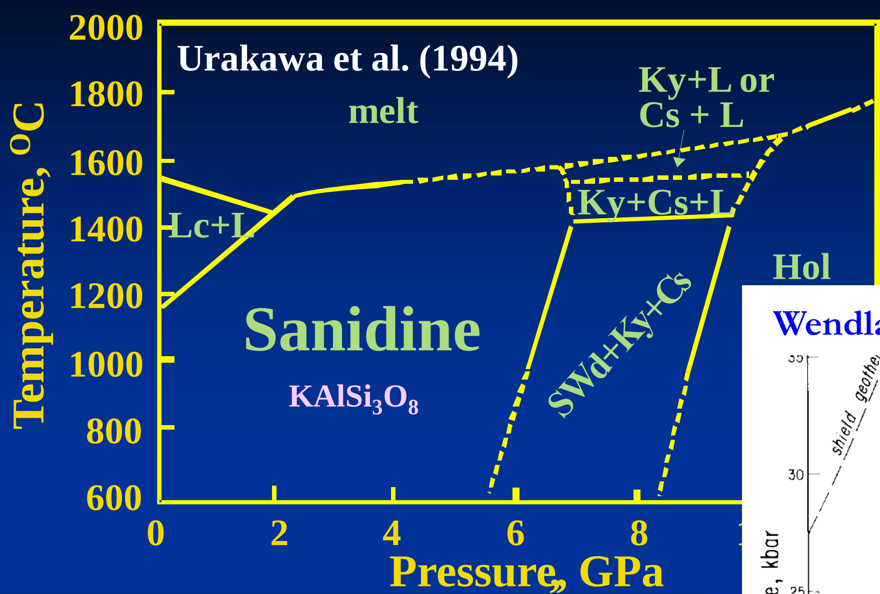
perfectly mobile components

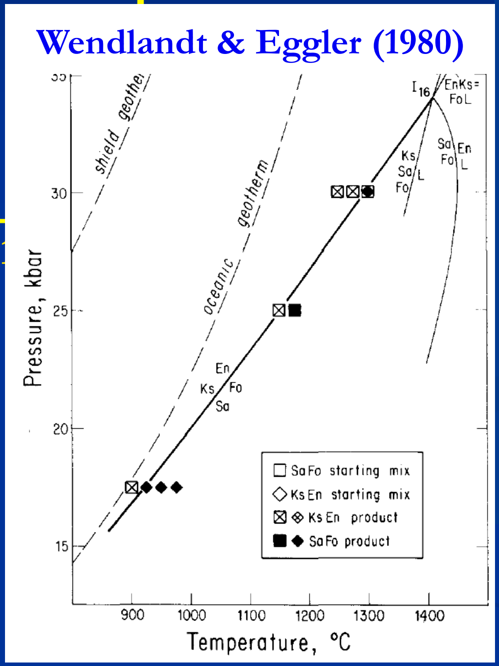


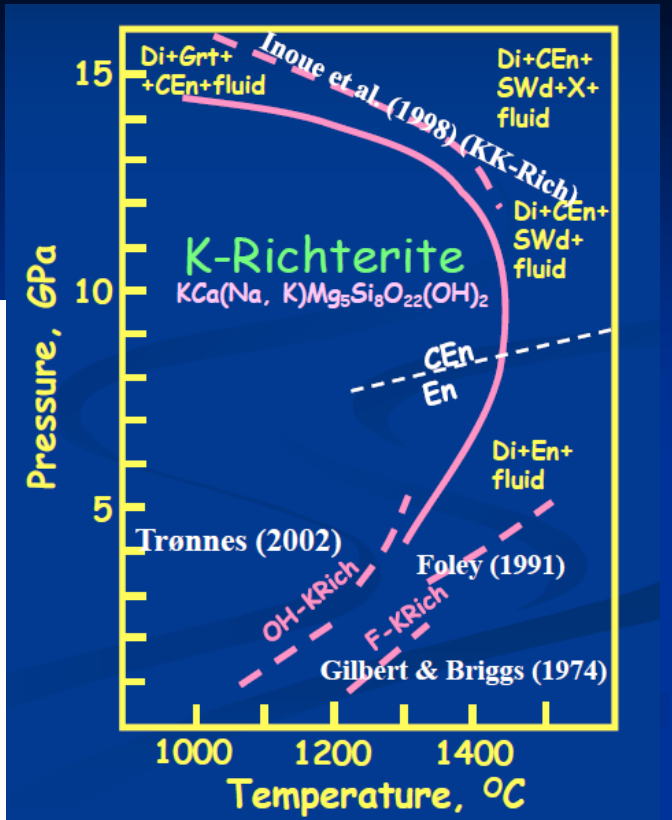
Alkaline fluids in the upper mantle

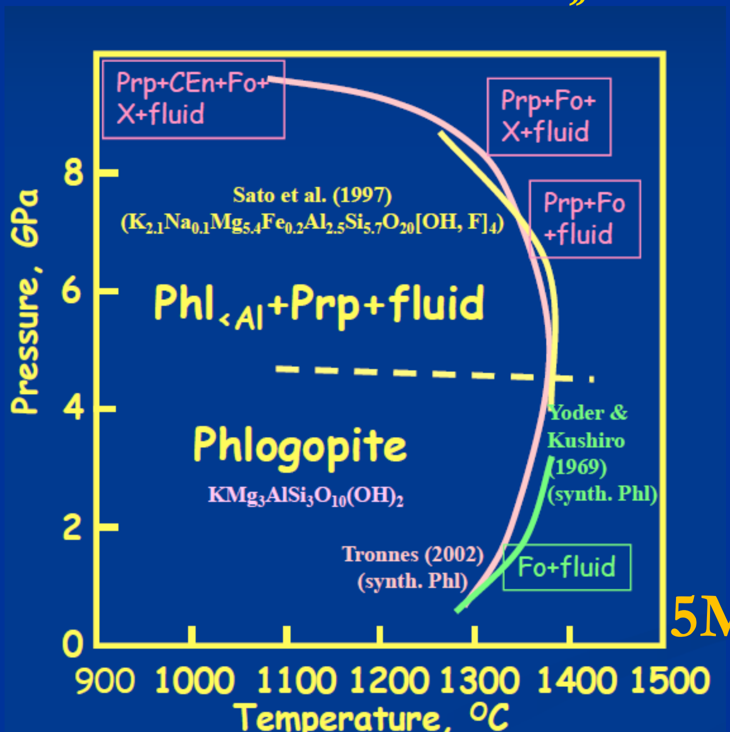


K-bearing minerals in the upper mantle









Origin of Phlogopite and Potassic Richterite Bearing Peridotite Xenoliths from South Africa

Ken-ichiro Aoki — Contrib. Mineral. Petrol. 53, 145 – 156 (1975)

$$5MgSiO_3 + CaMg_2Al_2Si_3O_{12} + 2H_2O + K_2O =$$
$$= K_2Mg_6Al_2Si_6O_{20}(OH)_4 + CaMgSi_2O_6$$

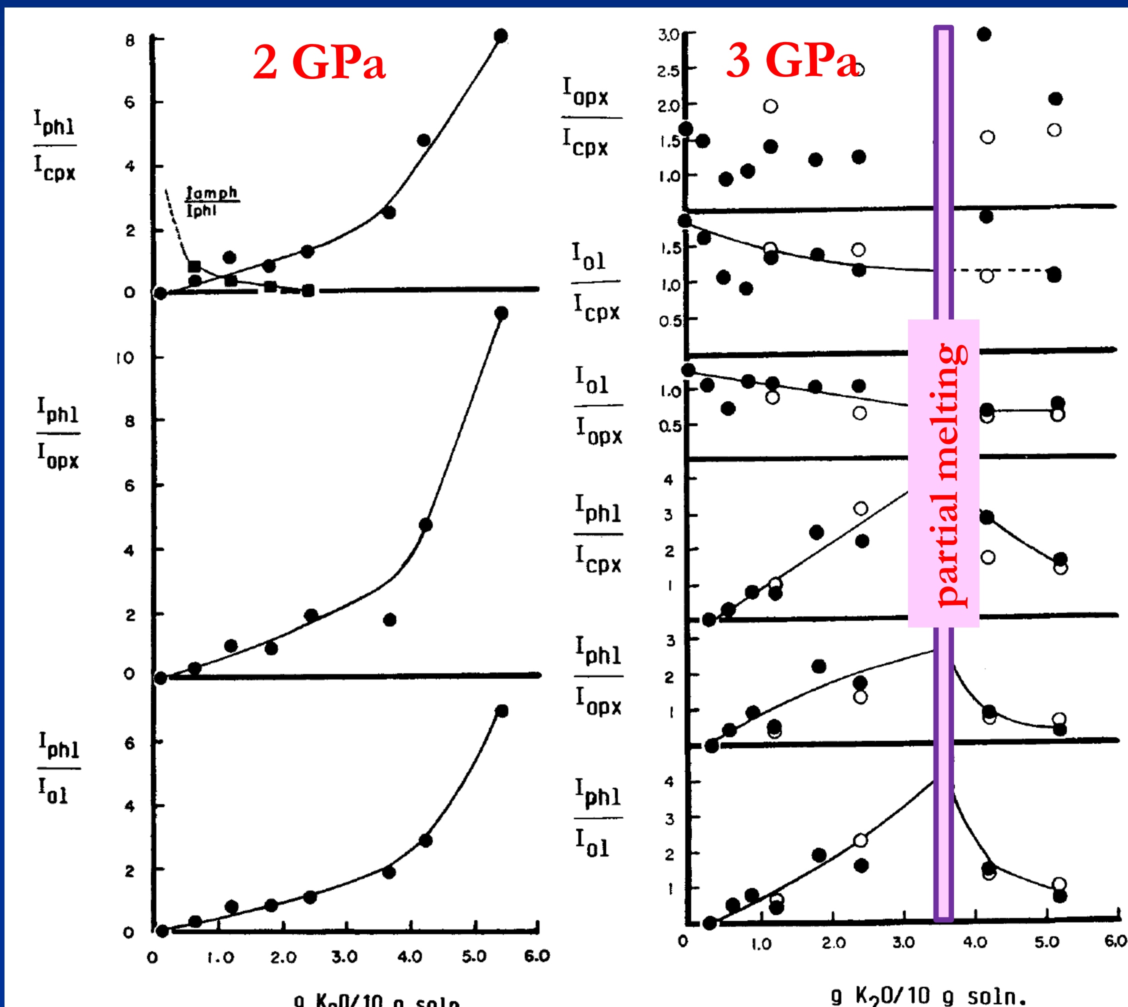
Pyrolite-K_2CO_3-H_2O system

Patent mantle-metasomatism: Inferences based on experimental studies

Proc. Indian Acad. Sci. (Earth Planet. Sci.), Vol. 99, No. 1, March 1990, pp. 21–37.

Y THIBAULT and A D EDGAR

2 – 3 GPa, 850-950^{O}C



With the increase of the K content of the fluid

- ✓ Amount of phlogopite systematically increases relative to Ol, Opx and Cpx (decrease at 3 GPa is related to the beginning of partial melting).
- ✓ Al for phlogopite is provided by garnet.
- ✓ Amount of amphibole rapidly decreases at 2 GPa.
- ✓ Increase of the Cpx/Opx and Ol/Opx ratios at 2 GPa.

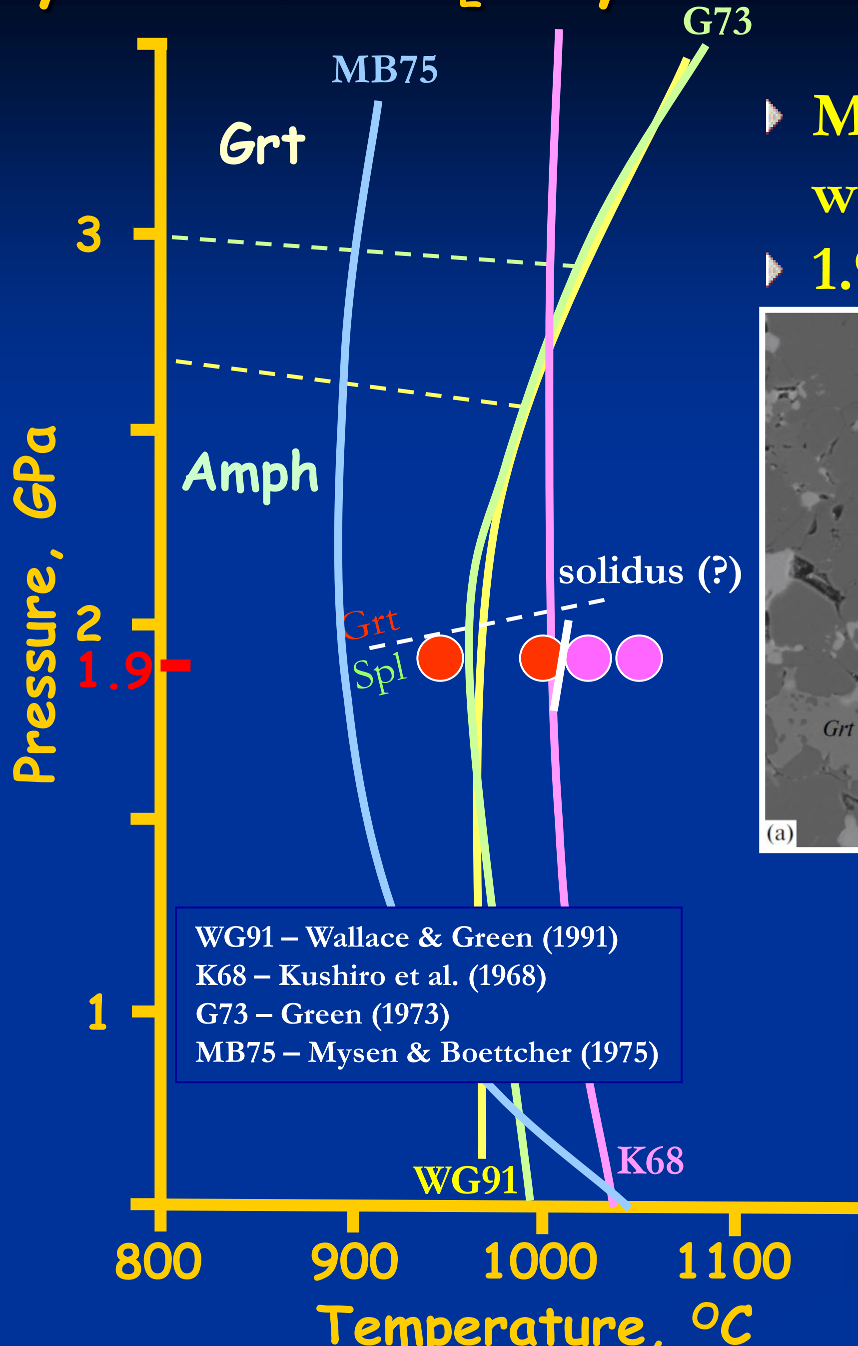
Patent K-metasomatism at depths 20-30 kbar will rapidly result in the disappearance of garnet, and decline in amounts of spinel, amphibole and orthopyroxene.

Pyrolite-KCl-H_2O system

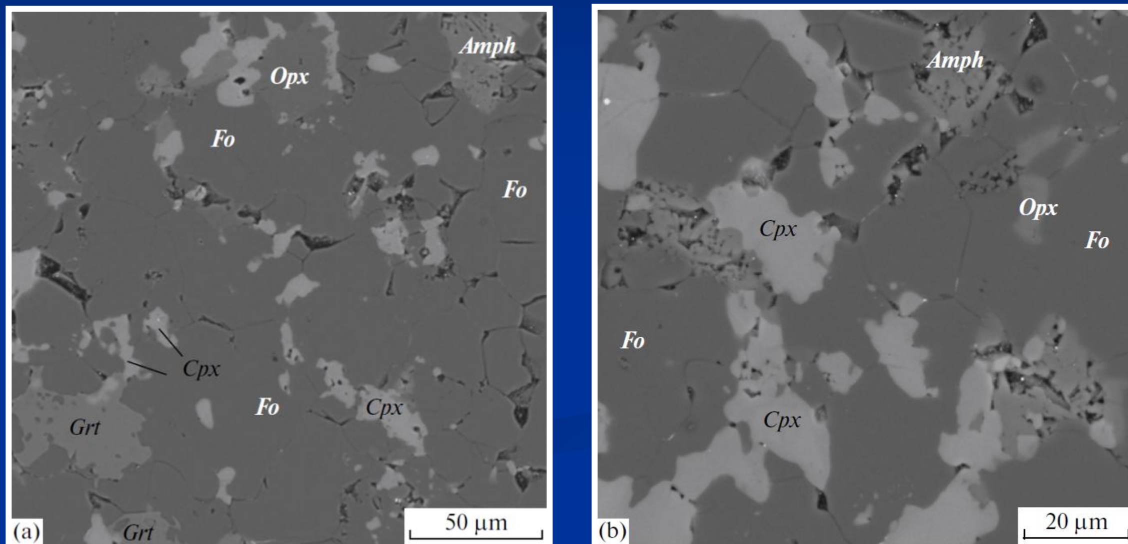
Interaction of Model Peridotite with H_2O–KCl Fluid: Experiment at 1.9 GPa and Its Implications for Upper Mantle Metasomatism

Petrology, 2013, Vol. 21, No. 6, pp. 599–615.

O. G. Safonov[a, b, c] and V. G. Butvina[a]

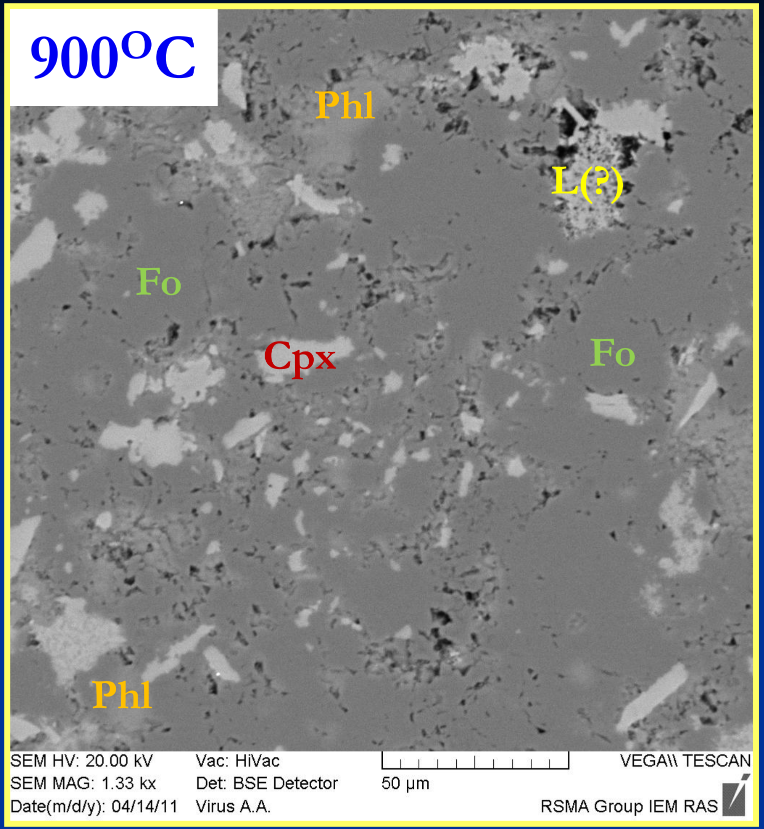


- Model peridotite $Fo_{57}En_{17}Prp_{14}Di_{12}$ + 0.3 wt. % Na_2O + 4.4 wt. % H_2O
- 1.9 GPa.

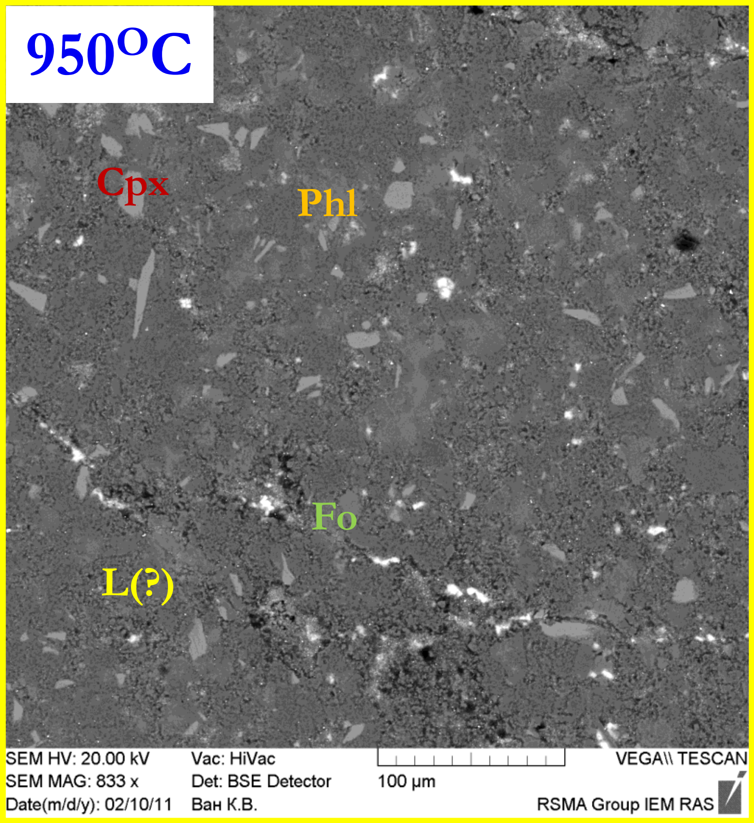


Phase	SiO_2	Al_2O_3	MgO	CaO	Na_2O
Ol	43.48	0.00	56.88	0.05	0.00
Cpx	57.37	0.13	18.94	24.98	0.09
Opx	56.83	6.99	37.74	0.43	0.09
Amph	47.41	15.77	21.04	12.09	2.79
Grt	45.58	25.44	23.81	7.95	0.00

$KCl/(KCl+H_2O) = 0.13$



$KCl/(KCl+H_2O) = 0.39$



Phl

Prp + 3En + {H_2O + 2KCl} = [Cl-Phl + Phl]

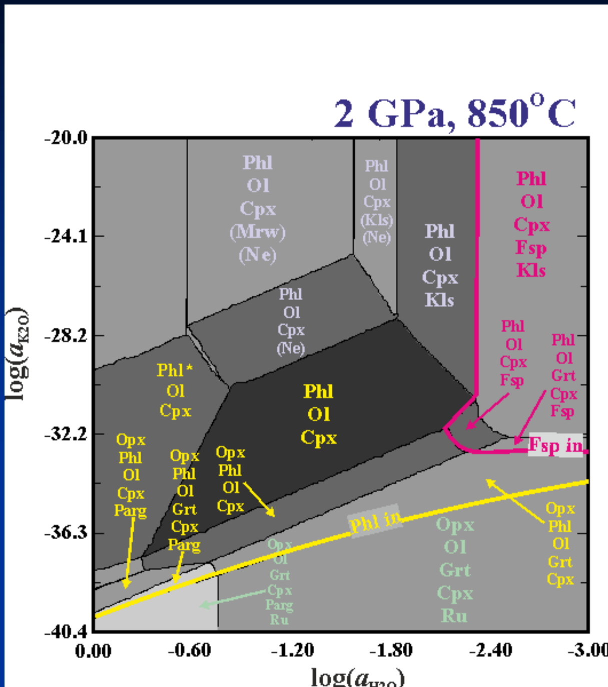
1/9Grs + En + {1/9H_2O + 2/9KCl} =1/3Di + [1/9Cl-Phl + 1/9Phl]

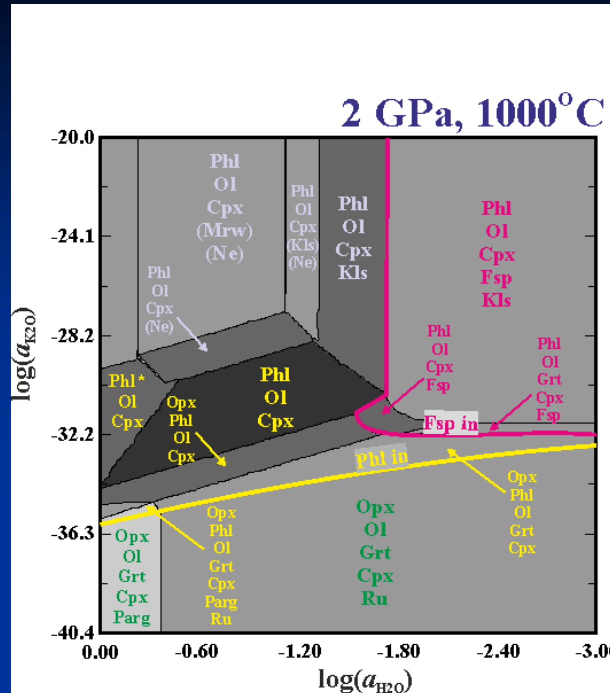
5En + Mg-Ts + {H_2O + 2KCl} = [Cl-Phl + Phl]

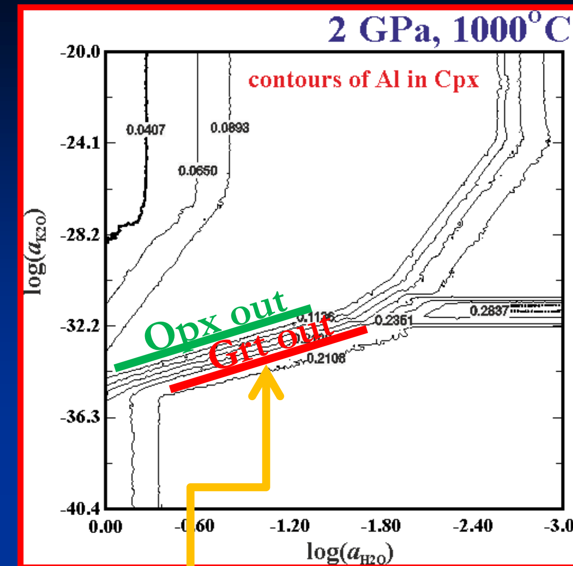
Prg + 7En + {H_2O + 3KCl} = 2Di + [Cl-Phl + 2Phl]+ {NaCl}

- ✓ No Opx, Grt, Amph
- ✓ Leading assemblage Cpx+Fo+Phl
- ✓ Increase of the melt proportion
- ✓ Increase of the Phl content
- ✓ Phl (0.4-0.7 wt. % Cl) is stable above solidus

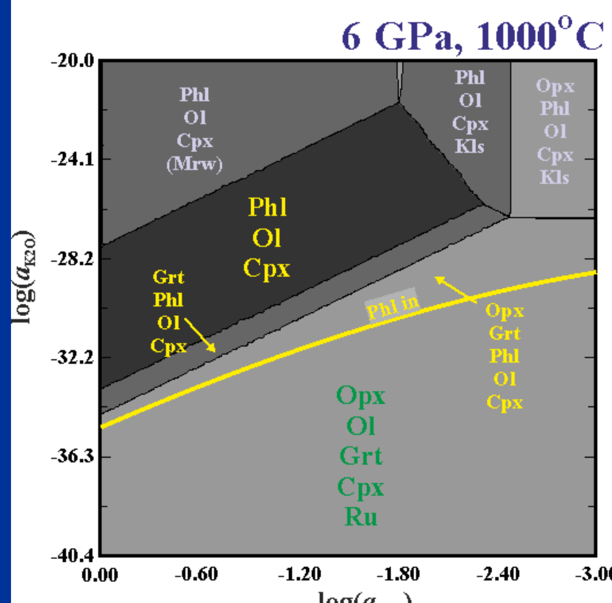
μ_{H2O}-μ_{K2O} relations for lhrezolite







$7/2En+1/2CaTs+1/2K_2O+H_2O=$
$=Phl+1/2Di$



Primitive mantle
(McDonough & Sun, 1995;
Djomani et al., 2001)

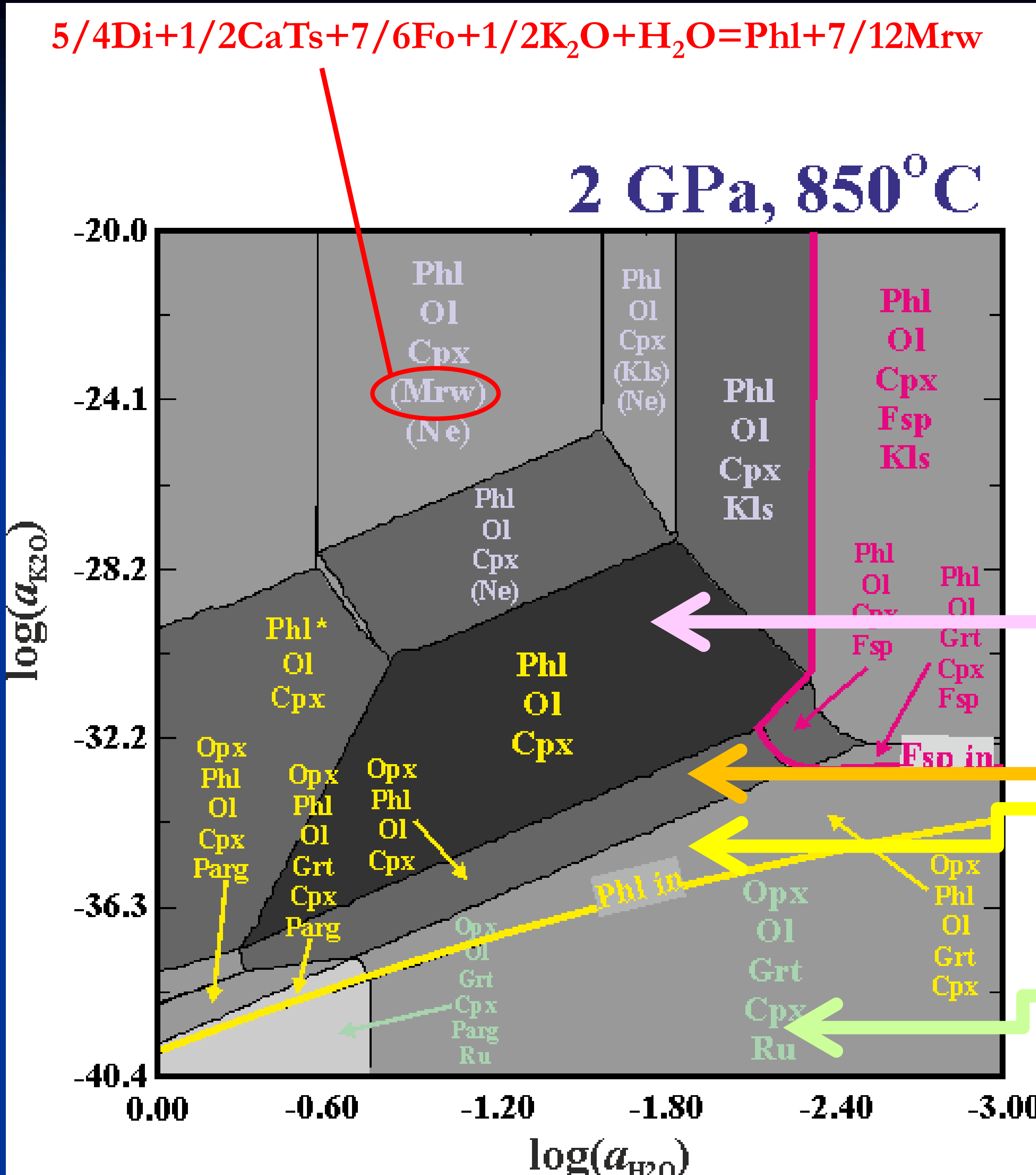
SiO_2	45.0
TiO_2	0.2
Al_2O_3	4.5
Cr_2O_3	0.38
FeO	8.1
MnO	0.14
MgO	37.8
CaO	3.6
Na_2O	0.36

PERPLE_X
(Connolly, 2005)

- Phl, Ol, Opx, Cpx, Grt and feldspar solid solutions from Holland & Powell's database
- K_2O activity is standardized to solid oxide.

Metasomatic stages

(Erlank et al., 1987; Waters & Erlank, 1988; Hawkesworth et al., 1990; van Achterbergh et al., 2001; O'Reilly & Griffin, 2013)



Phl wherlite

Phl peridotite

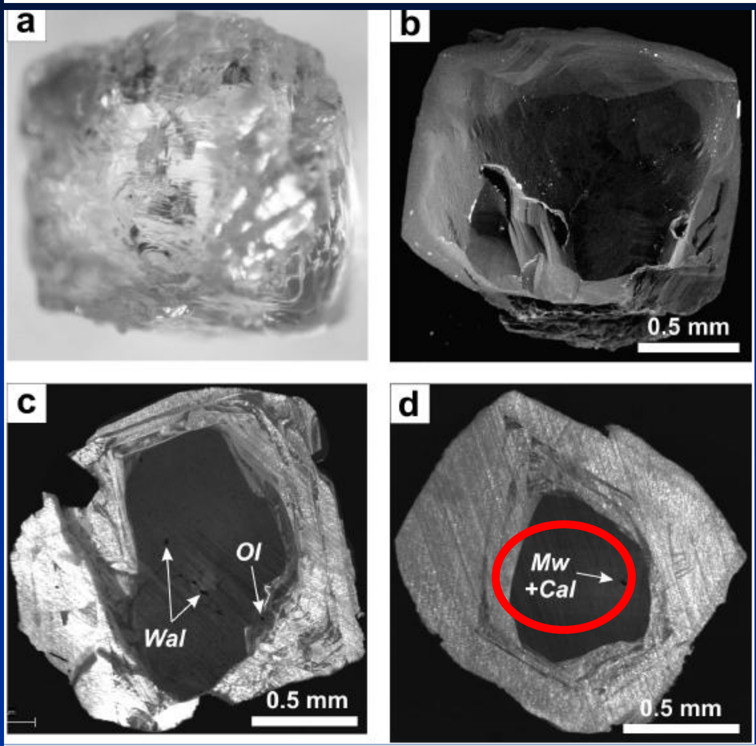
Grt-Phl peridotite

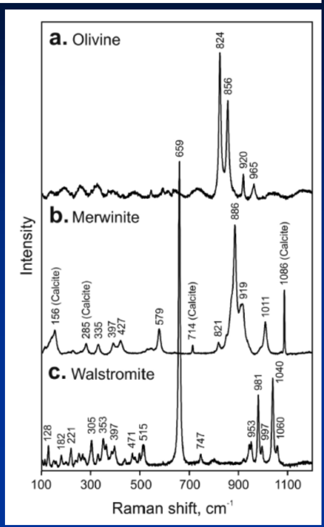
Grt peridotite

Merwinite in diamond from São Luiz, Brazil: A new mineral of the Ca-rich mantle environment

American Mineralogist, Volume 99, pages 547–550, 2014

Dmitriy A. Zedgenizov[1,2,*], Anton Shatskiy[1,2], Alexey L. Ragozin[1,2], Hiroyuki Kagi[3] and Vladislav S. Shatsky[1,4]





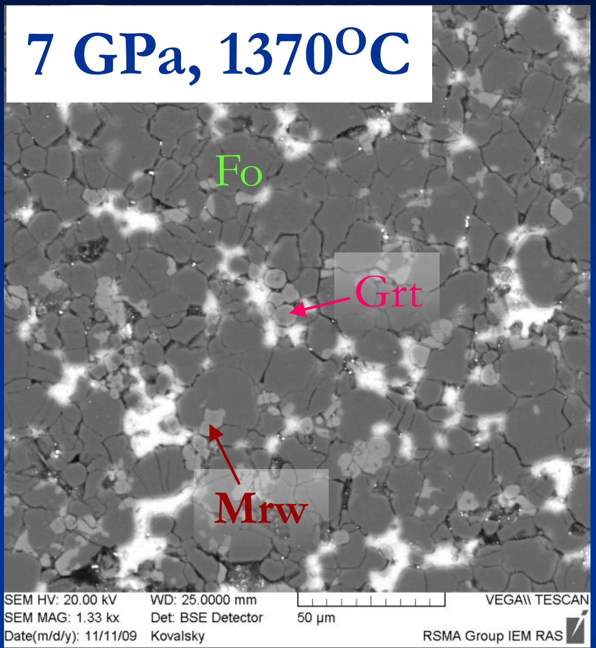
Wal, Ol_{86}, Cal

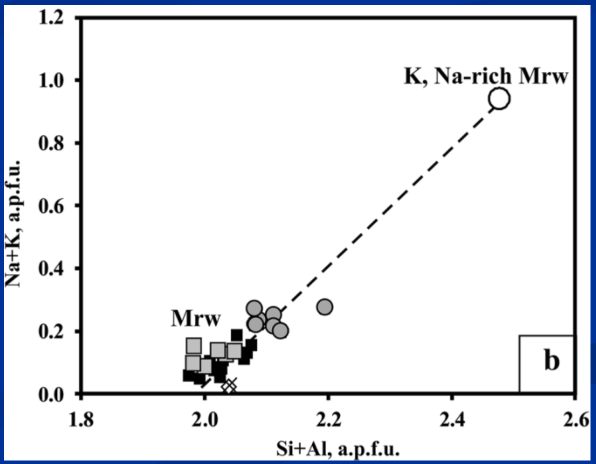
	Walstromite		Merwinite		Olivine	
	wt%	mol%	wt%	mol%	wt%	mol%
SiO_2	51.6	50.3	36.8	34.2	39.8	33.4
TiO_2	0.04	0.03	0.02	0.01	0.0	0.0
Al_2O_3	0.01	0.01	0.10	0.05	0.0	0.0
Cr_2O_3	0.0	0.0	0.02	0.01	0.09	0.03
FeO	0.31	0.26	2.32	1.80	13.6	9.62
MnO	0.00	0.00	0.04	0.03	0.04	0.03
MgO	0.00	0.00	11.7	16.1	45.4	56.8
CaO	47.3	49.4	47.9	47.6	0.12	0.10
Na_2O	0.03	0.03	0.24	0.22	0.0	0.0
K_2O	0.00	0.00	0.01	0.00	0.0	0.0
NiO	n.d.	n.d.	n.d.	n.d.	0.25	0.17
Total	99.3	100.0	99.1	100.0	99.3	100.0

Merwinite-structured phases as a potential host of alkalis in the upper mantle

Contrib Mineral Petrol (2015) 170:14

Luca Bindi[1,2] · Oleg G. Safonov[3,4,5] · Dmitriy A. Zedgenizov[6,7]

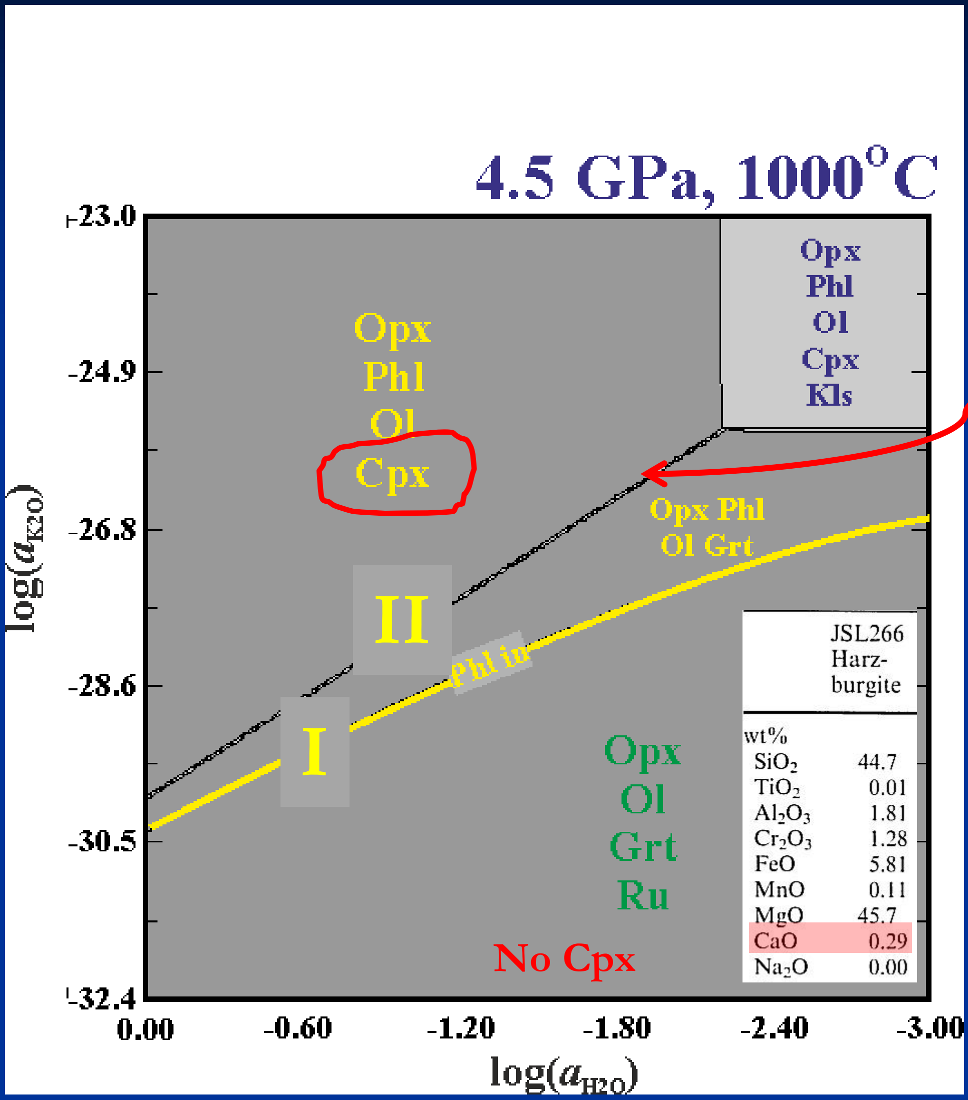


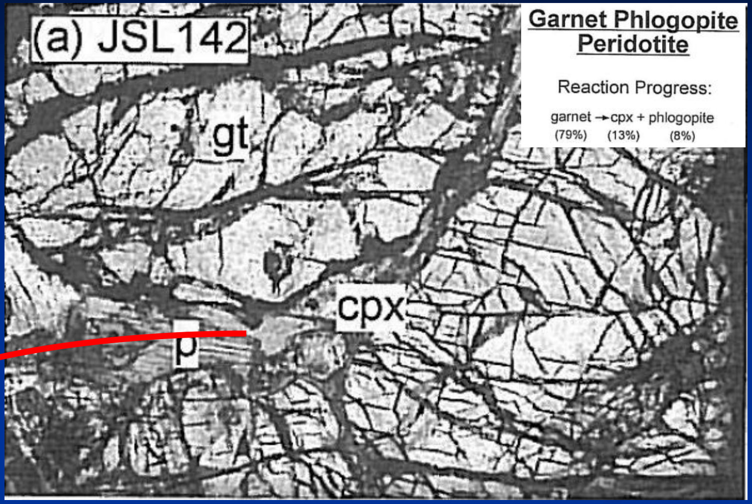


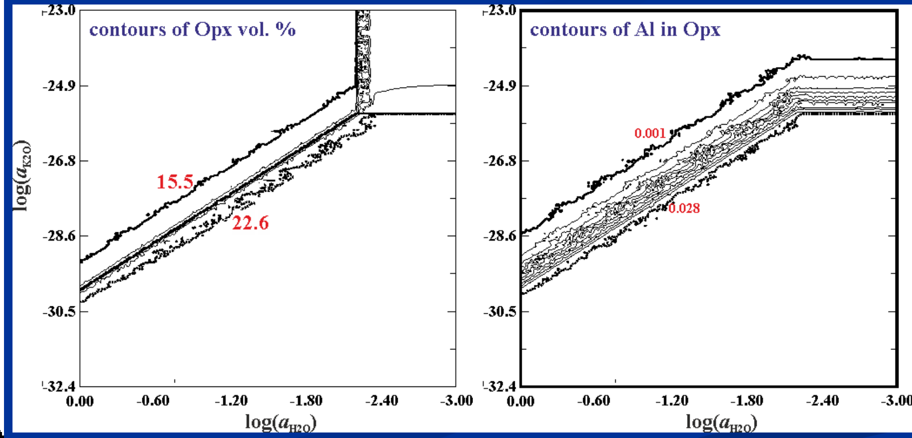
$$2Ca^X + Mg^M \leftrightarrow 2(Na, K)^X + Si^M$$

μ_{H2O}-μ_{K2O} relations for harzburgite

Esmé van Achterbergh · William L. Griffin · Johann Stiefenhofer
Contrib Mineral Petrol (2001) 141: 397–414
Metasomatism in mantle xenoliths from the Letlhakane kimberlites: estimation of element fluxes



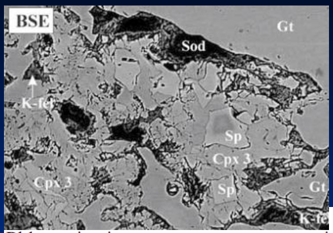


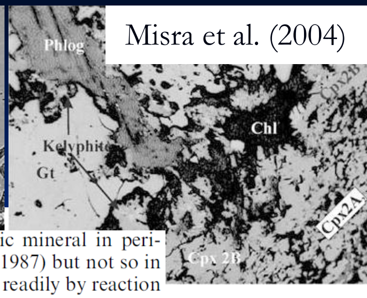


I $1/2Prp + 3/2En + 1/2K_2O + H_2O = 2Phl$

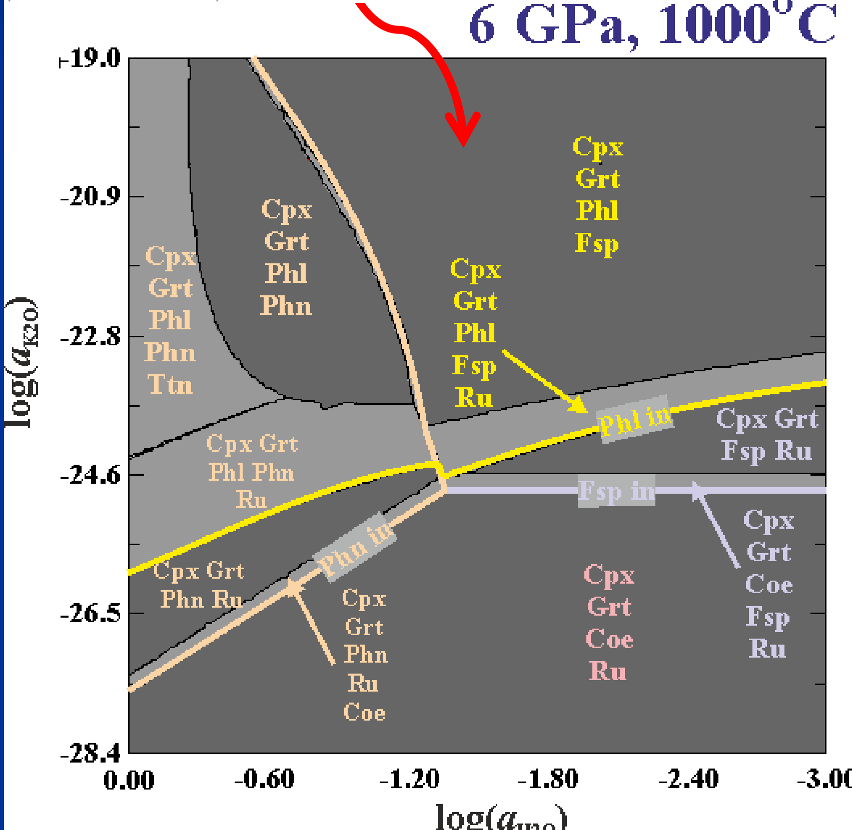
II $1/2Grs + 1/2Prp + 6En + K_2O + 2H_2O = 2Phl + 3/2Di$

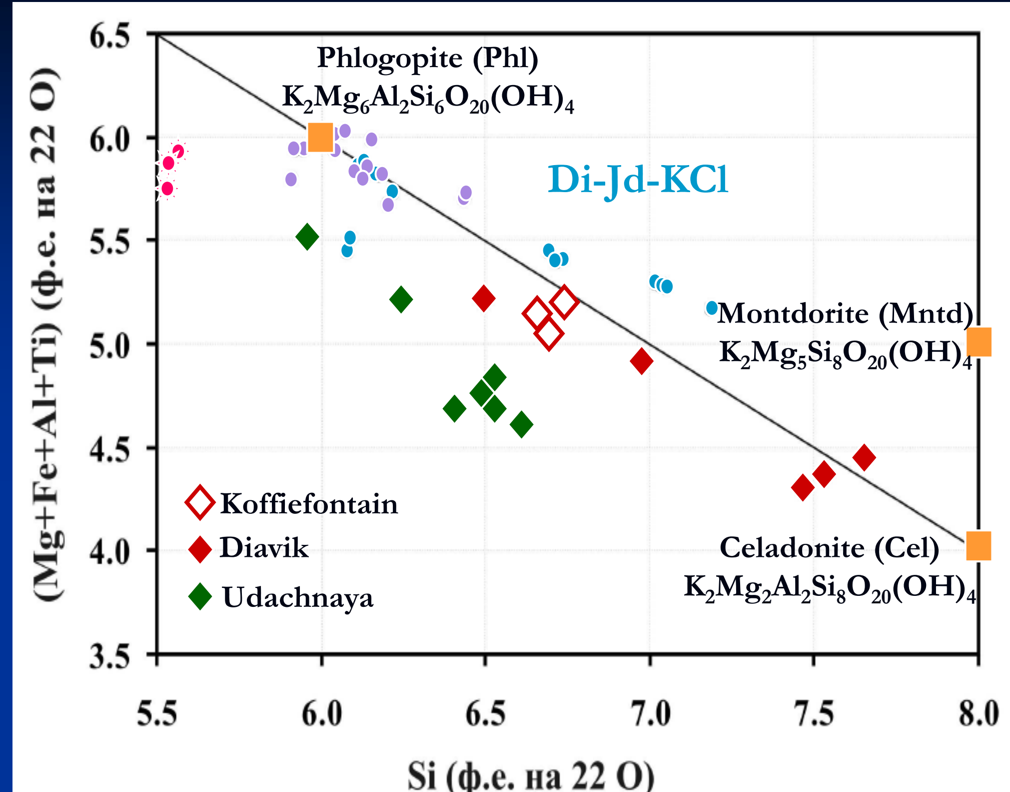
μ_{H2O}-μ_{K2O} relations for eclogite

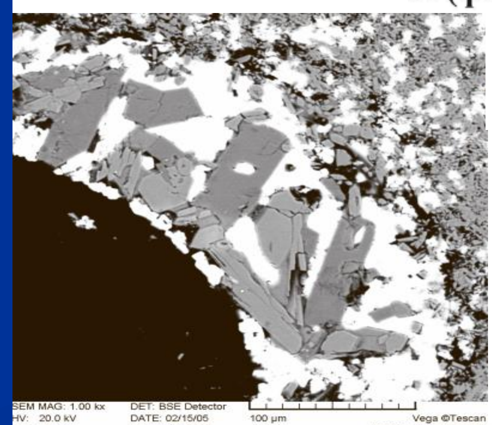


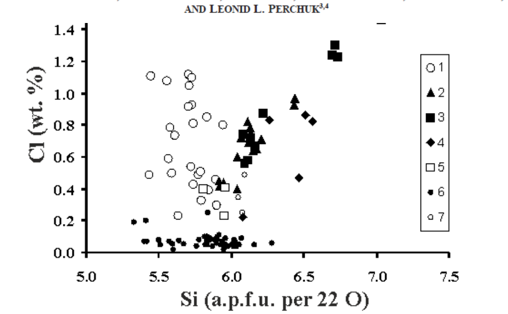


Phlogopite is a common metasomatic mineral in peridotite mantle xenoliths (Erlank et al. 1987) but not so in eclogite xenoliths, as it does not form readily by reaction of metasomatizing fluids with clinopyroxene or garnet (Kushiro and Aoki 1968)







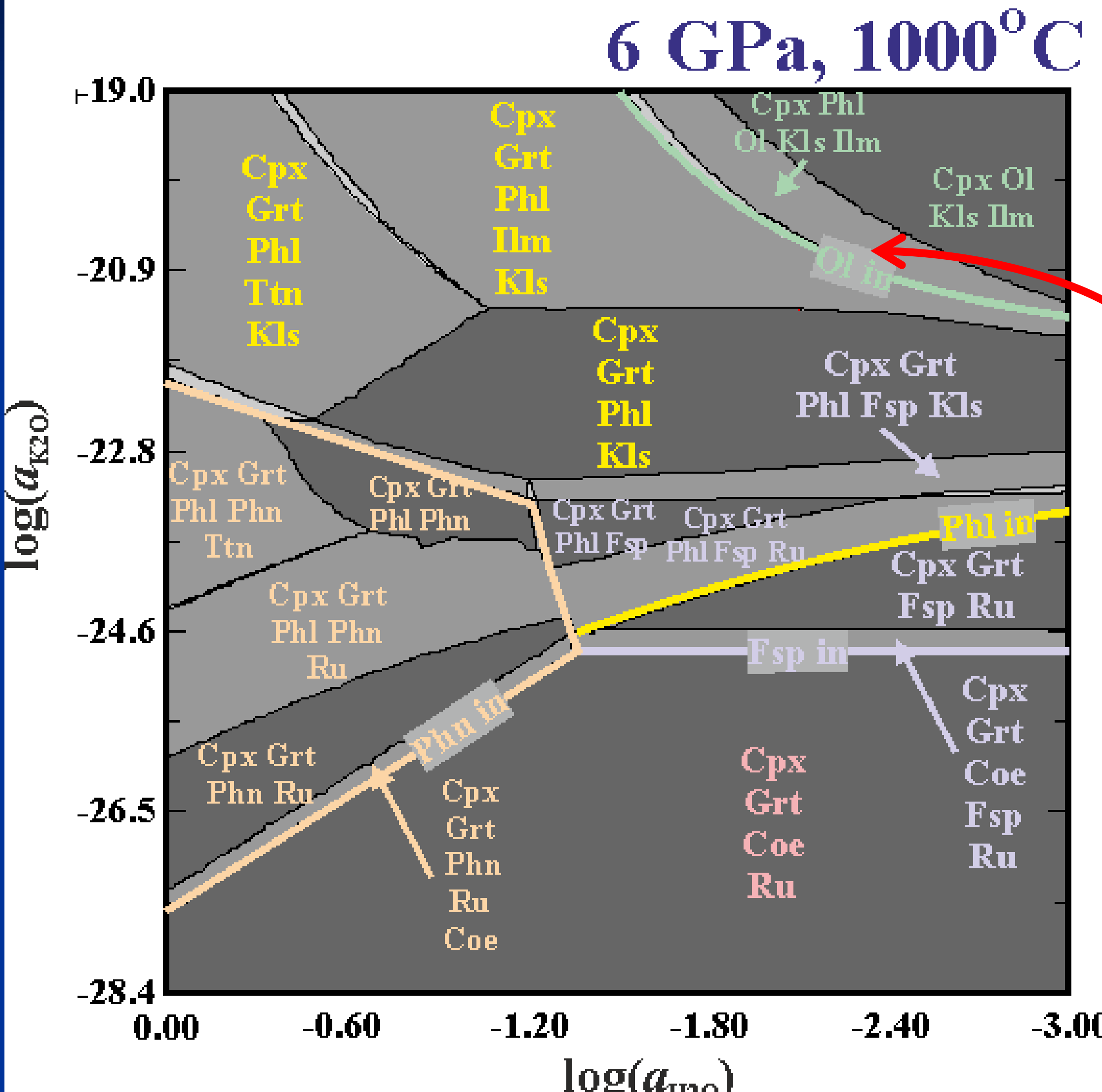


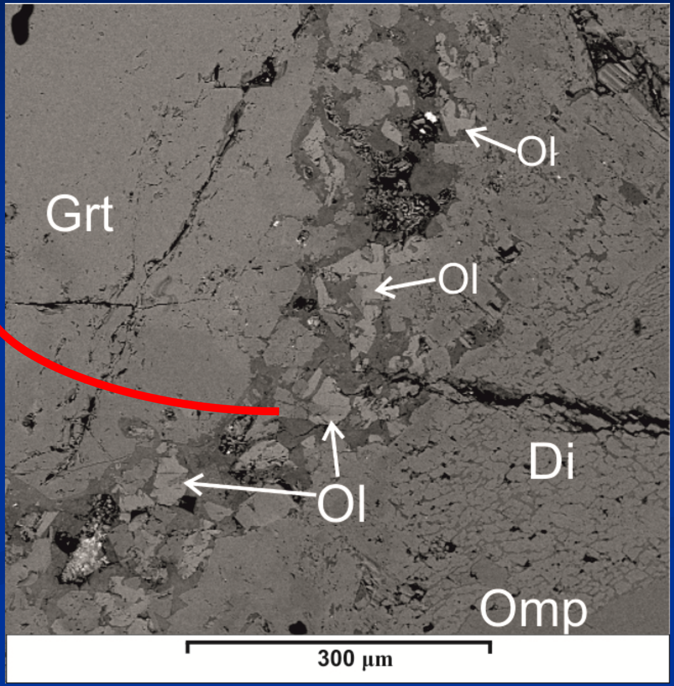
American Mineralogist, Volume 93, pages 1429–1436, 2008

Synthetic hypersilicic Cl-bearing mica in the phlogopite-celadonite join: A multimethodical characterization of the missing link between di- and tri-octahedral micas at high pressures

SABRINA NAZZARENI,[1,*] PAOLA COMODI,[1] LUCA BINDI,[2] OLEG G. SAFONOV,[3] YURIY A. LITVIN,[3] AND LEONID L. PERCHUK[3,4]

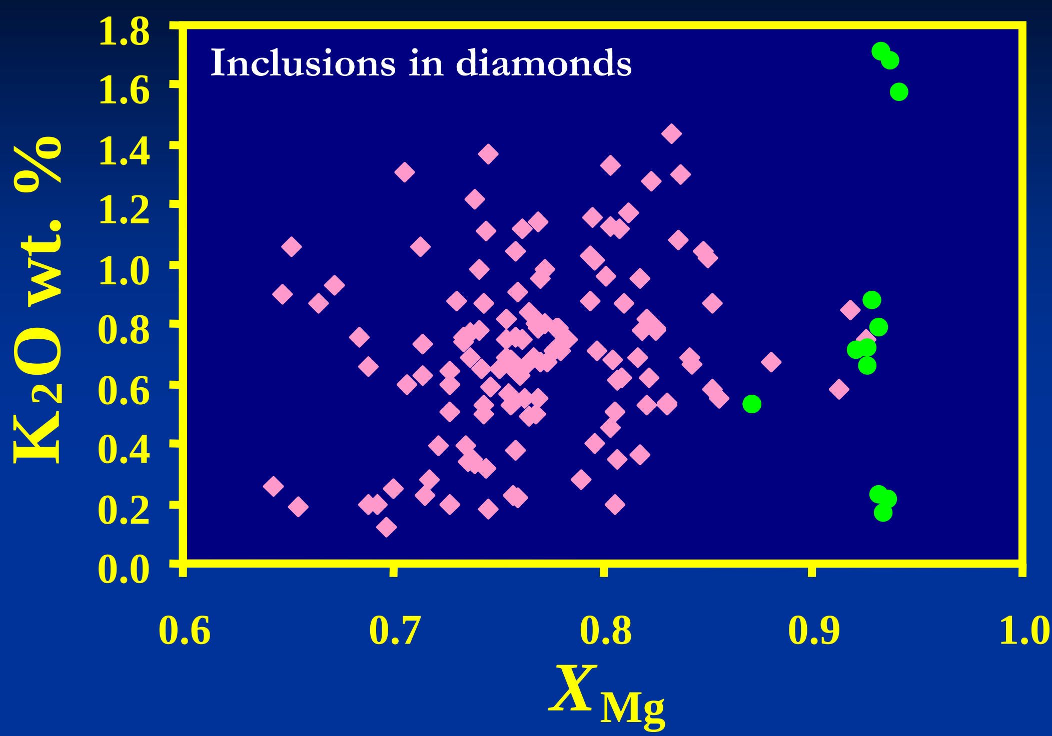
Phl + [21/5SiO_2 + 2/5K_2O + 4/5H_2O] = Cel + 4/5Mntd





Eclogite xenolith, Udachnaya pipe (photo by D. Mikhailenko and A. Korsakov)

K-bearing clinopyroxene as indicator of potassium activity



- common and stable both in peridotite and eclogite assemblages

- within a wide P-T range

- compatible with silicate and carbonate-silicate melts.

- with a potassium content regularly changing with P, T, potassium activity in a mineral forming media.

Atomistic Model of Diopside–K-jadeite ($CaMgSi_2O_6$–$KAlSi_2O_6$) Solid Solution

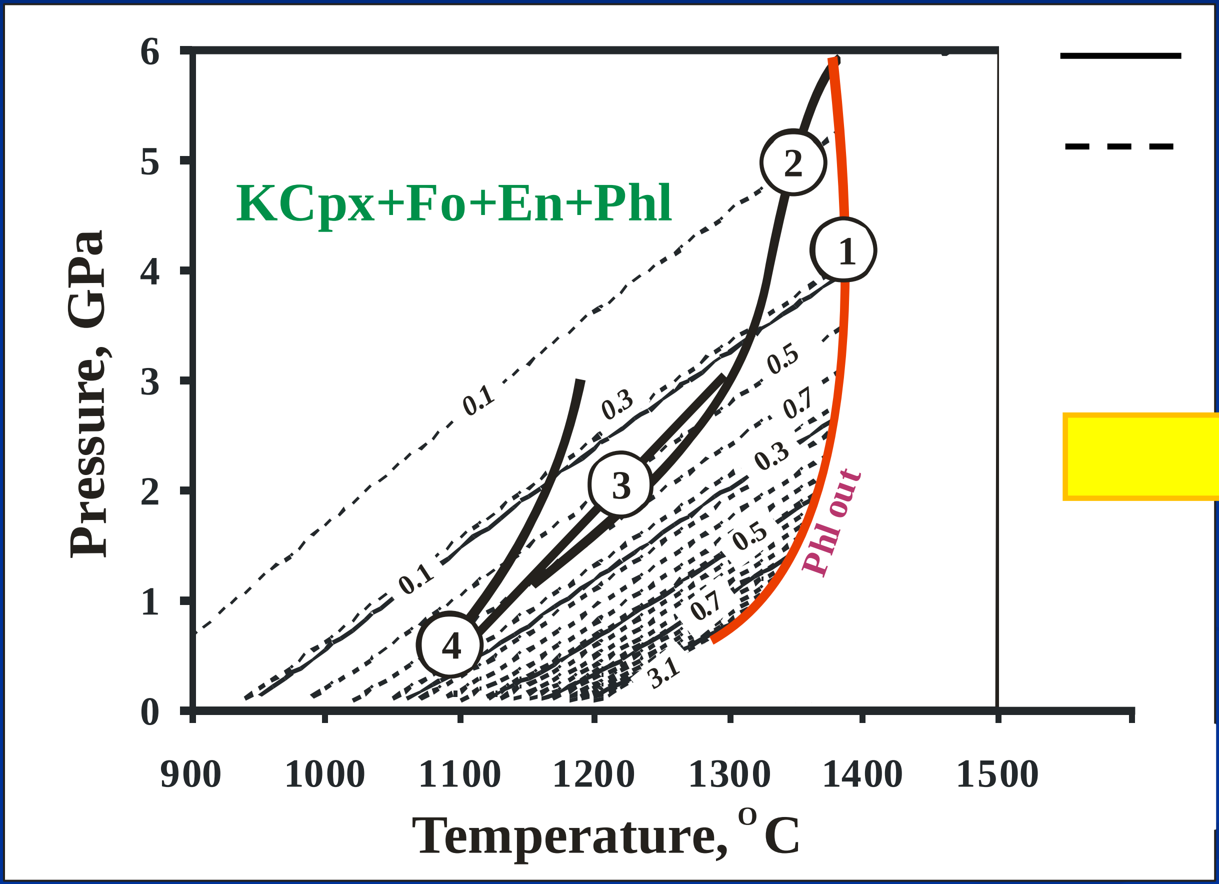
Petrology, 2010, Vol. 18, No. 4, pp. 447–459.

V. L. Vinograd[a], O. G. Safonov[b], D. J. Wilson[a], L. L. Perchuk[b†], L. Bindi[c], J. D. Gale[d], and B. Winkler[a]

	$\Delta_f H$ kJ/mol	S J/K/mol	V J/bar/mol	K (GPa^{-1})	α 10^{-5} (K^{-1})
$KAlSi_2O_6$ (KJd)	-2932.7	141.24	6.479	145	3.3 (298–1298 K)

The isopleths of KJd in the Di-KJd s.s. in the assemblage Phl+Fo+En

Reaction	$\Delta H_{298,1}$ (kJ/mol)	$\Delta S_{298,1}$ (J/mol/K)	$\Delta V_{298,1}$ (J/mol/bar)
KJd + 2Fo + H_2O = En + Phl	-246.36	-125.99	2.884



——— a_{H2O} = 1.0

– – – a_{H2O} = 0.1

→ a_{K2O}

1 – stability curve of pure Phl (Trønnes, 2002)

2, 3 – Di+Phl solidi (Luth, 1997; Modreski & Boettcher, 1973)

4 – Phl+Di+H_2O solidus (Modreski & Boettcher, 1973)

Thank you for attention