

Che cos'è un geotermobarometro?

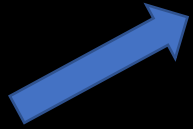
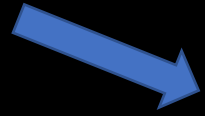
Che cos'è un geotermobarometro?

Composizione
chimica delle fasi
nella roccia

Dati termodinamici
delle fasi (entalpia,
entropia, modelli di
miscibilità, etc)

Geotermobarometro

Pressione e/o
temperatura di
formazione



Che cos'è un geotermobarometro?

Composizione chimica delle fasi nella roccia

Dati termodinamici delle fasi (entalpia, entropia, modelli di miscibilità, etc)

Geotermobarometro

(Sistema di uno o più equazioni non lineari)

Pressione e/o temperatura di formazione

$$\Delta H_e + T \Delta S_e + P \Delta V_e + RT \ln K_e = 0$$

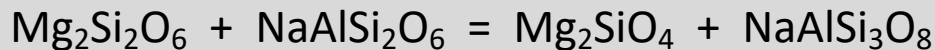
$$K_e = \prod_j (\gamma_j X_j)^{\nu_j}$$

γ_j = coefficiente di attività

X_j = frazione molare
(composizione chimica)

ν_j = coefficiente stechiometrico

Esempio di equilibrio di fase (e) con j end-members:



enstatite

jadeite

forsterite

albite

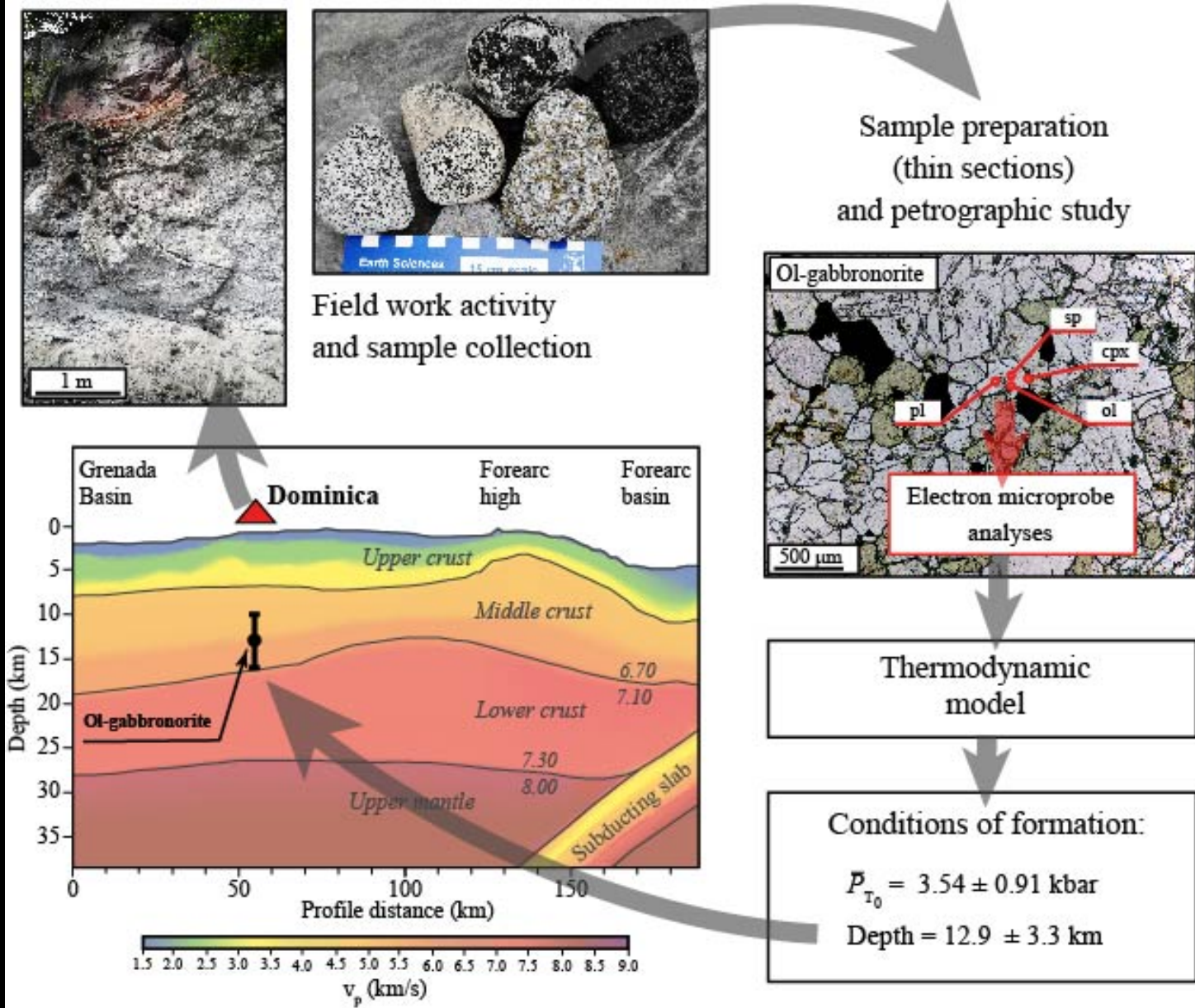
(pirosseno)

(pirosseno)

(olivina)

(plagioclasio)

A cosa serve?



UNA BUONA NOTIZIA:

Alcuni geotermobarometri, sebbene basati sulla termodinamica, sono degli algoritmi più semplificati rispetto alle equazioni che vi ho mostrato finora.

In vari casi, gli algoritmi sono molto semplici, ad esempio:

$$T_{\text{Ca-in-opx}}(\text{K}) = \frac{6425 + 26.4P}{-\ln \text{Ca}^{\text{opx}} + 1.843}$$

Brey & Köhler (1990; J Pet)

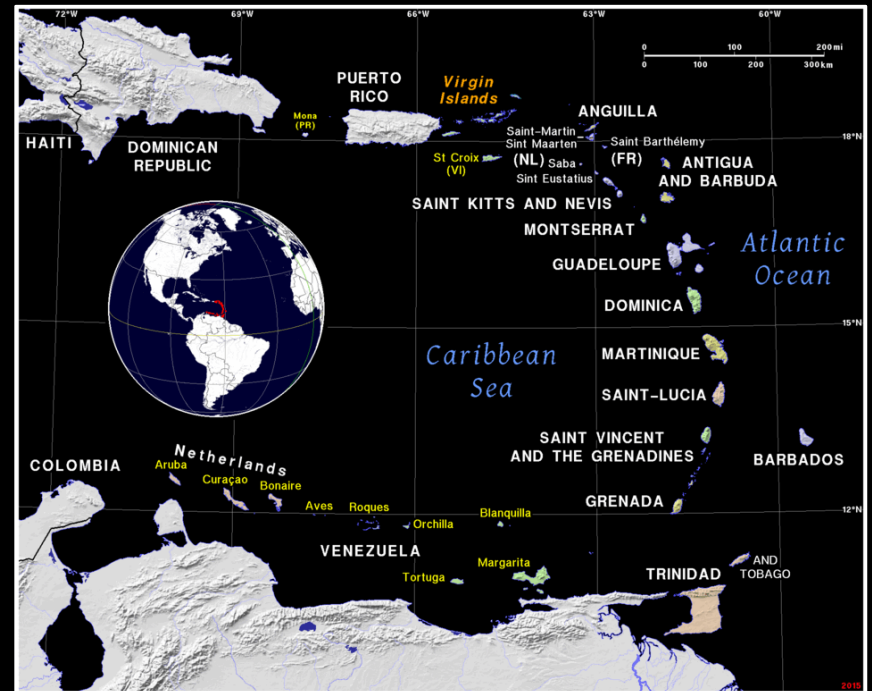
$$T(^{\circ}\text{C}) = \frac{10\,000}{0.512 + 0.873Y_{\text{Cr}} - 0.91\ln(K_{\text{D}})} - 273$$

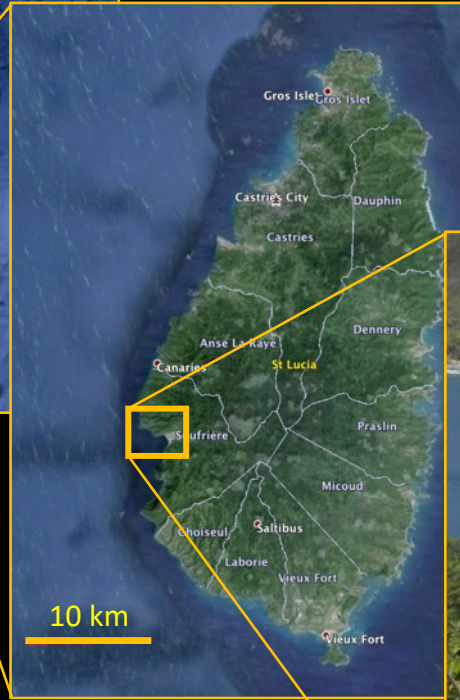
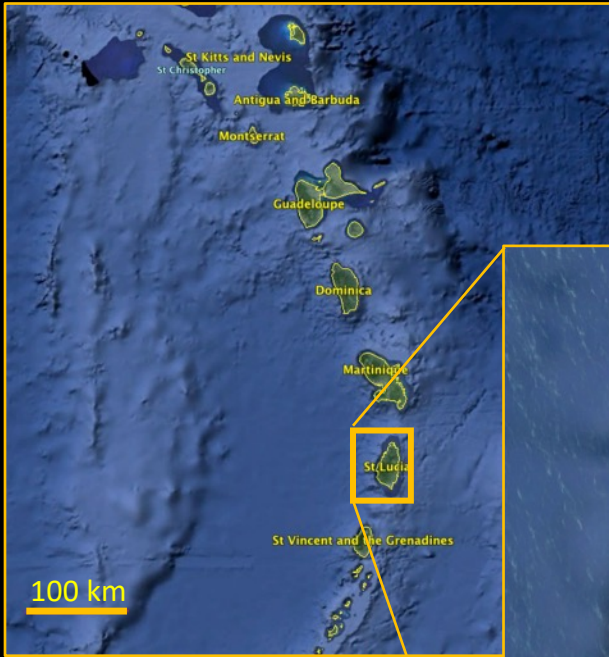
Wan et al. (2008; Am Min)

where $Y_{\text{Cr}} = \text{Cr}/(\text{Cr} + \text{Al})$ in spinel in atomic proportions and $K_{\text{D}} = \text{Al}_2\text{O}_3^{\text{ol}}/\text{Al}_2\text{O}_3^{\text{sp}}$ in wt%

In altri, sono rappresentati da una o più equazioni (relativamente poco complesse) e sono già disponibili e 'pronti all'uso' (tramite software come Excel, Matlab, Python, etc).

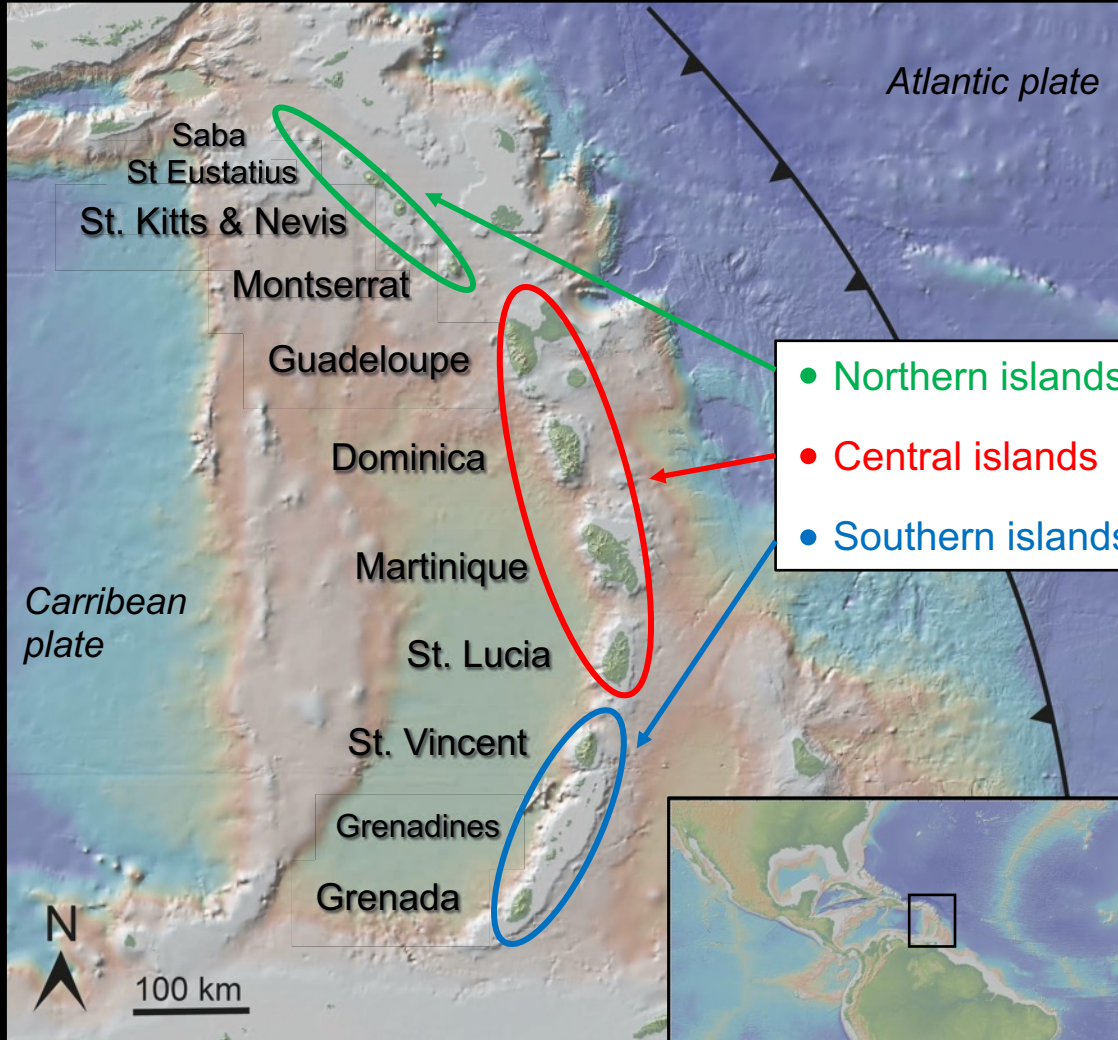
The depth of igneous cumulates in the Lesser Antilles island arc





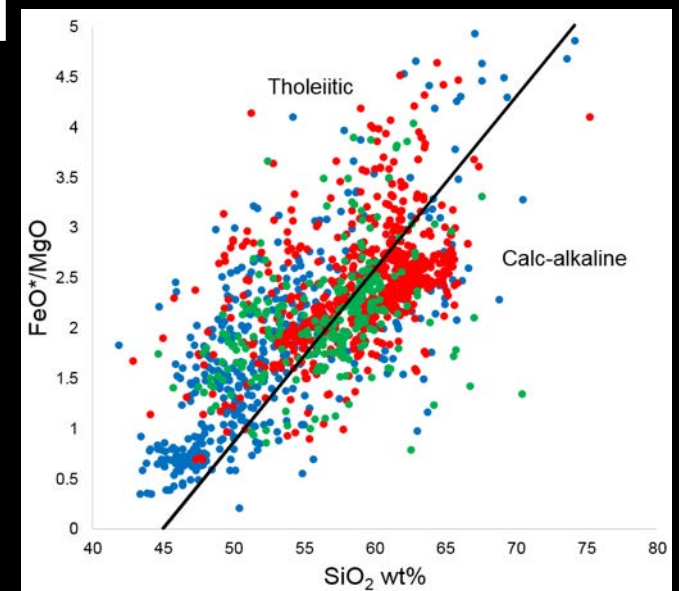
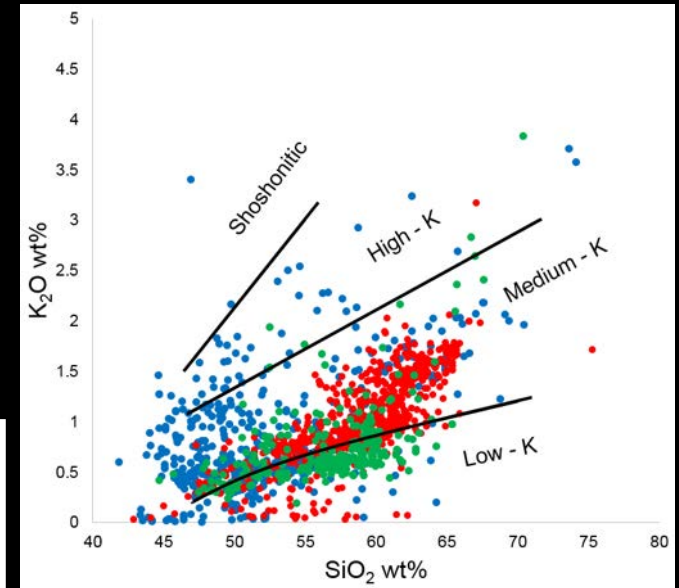


The Lesser Antilles island arc



- Northern islands
- Central islands
- Southern islands

<http://www.geomapp.org/>



Plutonic xenoliths



Courtesy of Richard Arculus

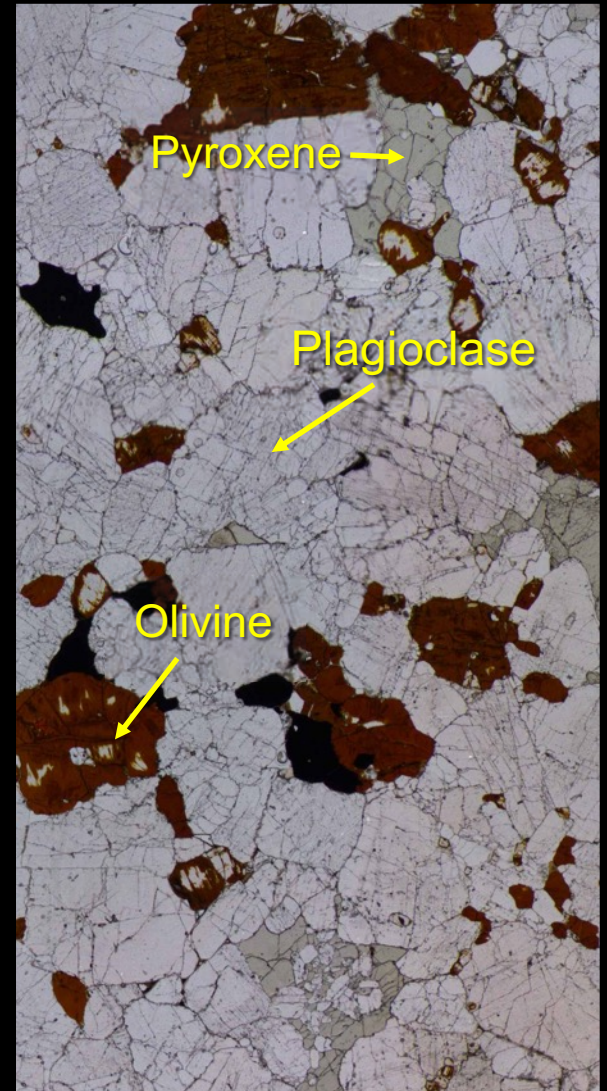
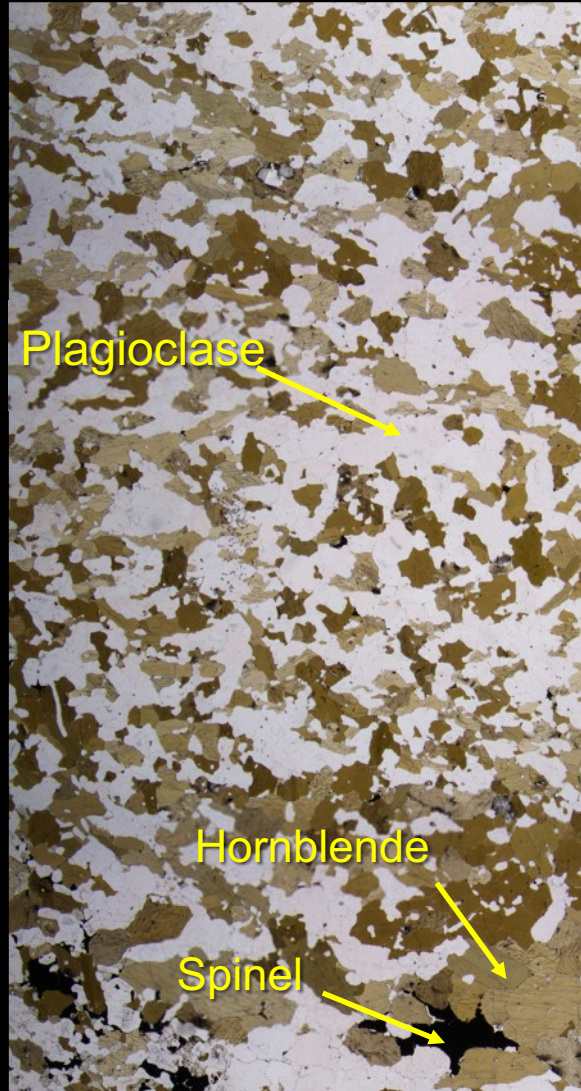
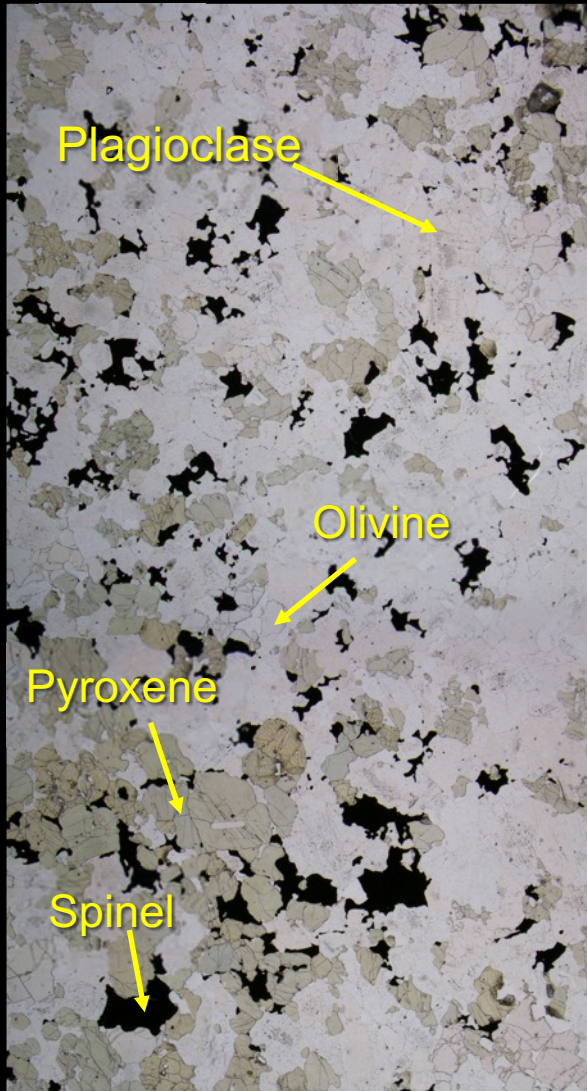


Earth Sciences

15 cm scale

Petrography of the xenoliths

5 mm



Geochemistry and mineral chemistry

Bulk rock chemistry:

- consistent with cumulate origin
- suggest fractional crystallization from magmas related to the erupted volcanics

Plagioclase: $An_{75} - An_{98}$

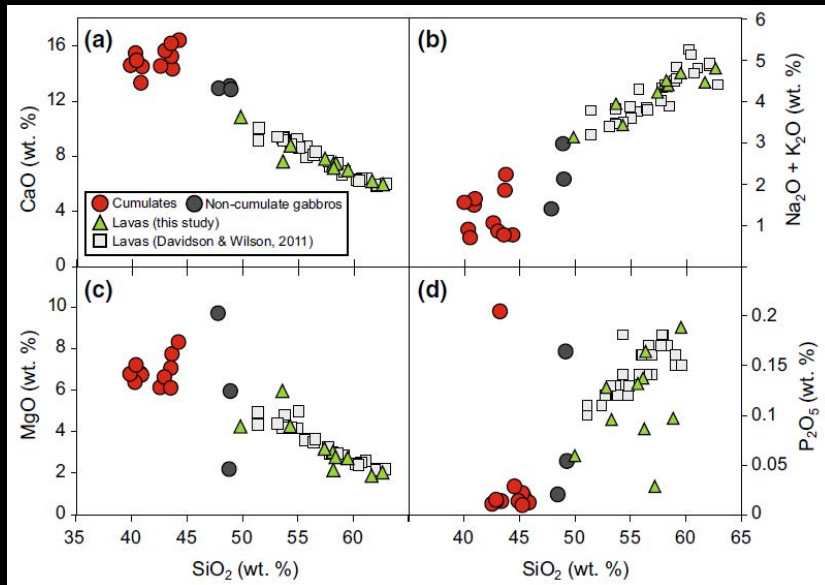
Olivine: $Fo_{60} - Fo_{82}$

Clinopyroxene: augites with $mg\# = 60 - 92$

Spinel: magnetites and minor spinel s.s.

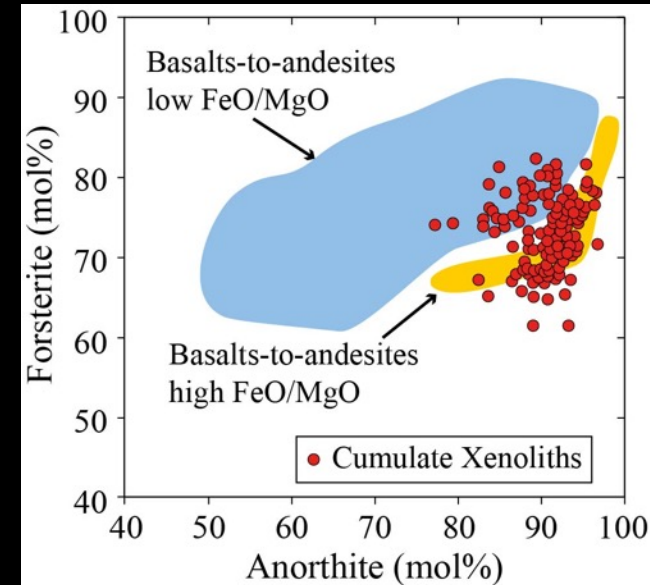
Amphibole: magnesio-hastingsite
magnesio-hornblende

Martinique, bulk rock analyses

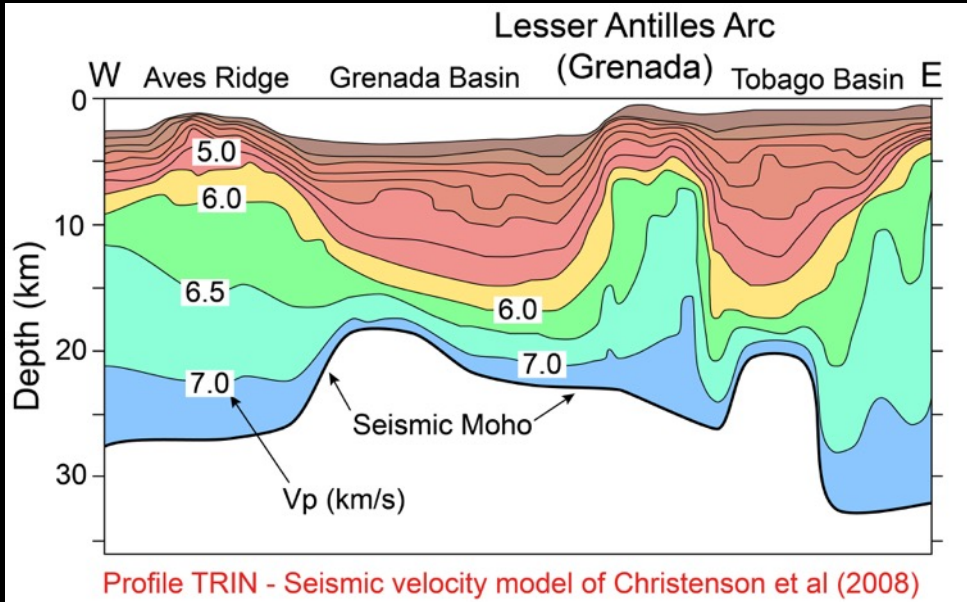


Cooper et al (2016, CMP)

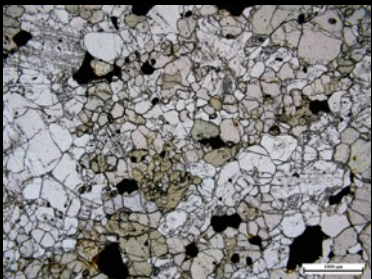
All islands, olivine and plagioclase



Pressure estimates

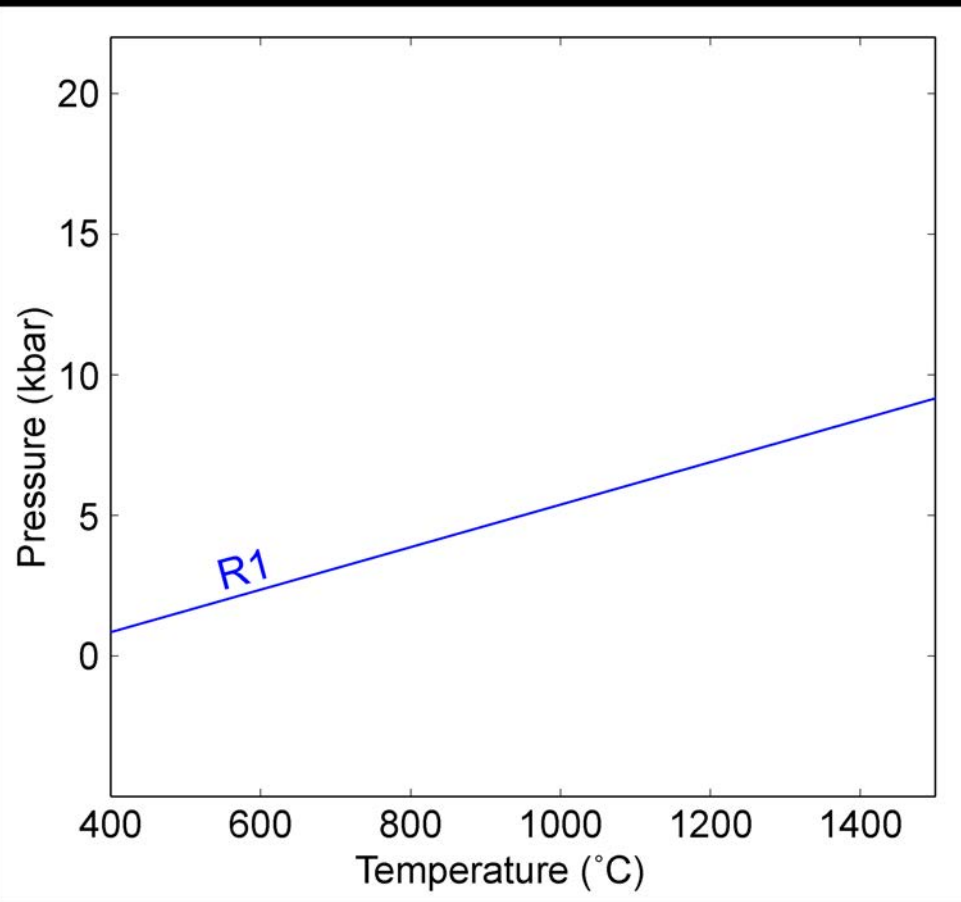
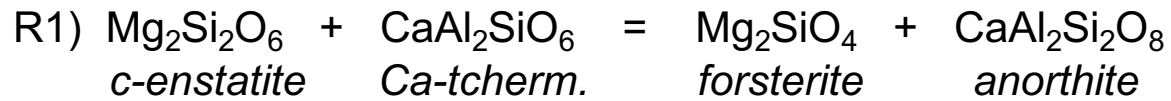


Which methods are suitable for mafic/ultramafic cumulate rocks?



Method	Uncertainties	Main issues
Cpx-Opx (e.g., Putirka 2008)	± 2.8 kbar	<ul style="list-style-type: none"> large uncertainties only few samples have cpx
Amph-plag (e.g., Molina et al 2015)	± 2.3 kbar	<ul style="list-style-type: none"> systematic deviations from experiments
Cpx-melt (e.g., Neave & Putirka 2017)	± 1.4 kbar	<ul style="list-style-type: none"> only few samples with equilibrium melt not reliable when $T < 1100^\circ\text{C}$
Single cpx (e.g., Putirka 2008)	± 3.1 kbar	<ul style="list-style-type: none"> large uncertainties likely dependent on composition
Single amph (e.g., Ridolfi & Renzulli 2012)	± 1.1 kbar? ± 4.3 kbar?	<ul style="list-style-type: none"> likely dependent on composition

Single-reaction geothermobarometry

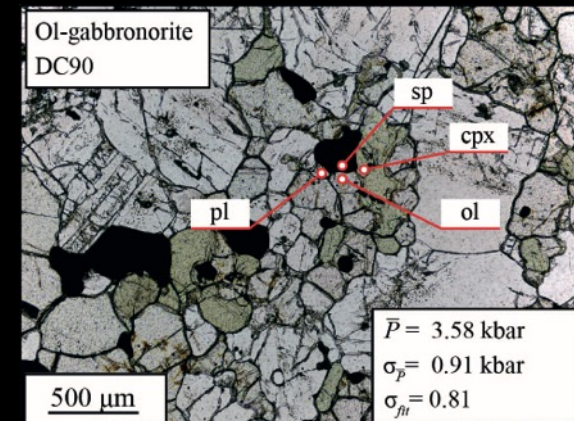


$$\Delta G_1 = \Delta G^0_1 + R T \ln K_1$$

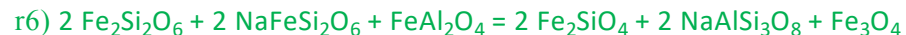
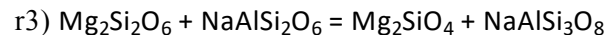
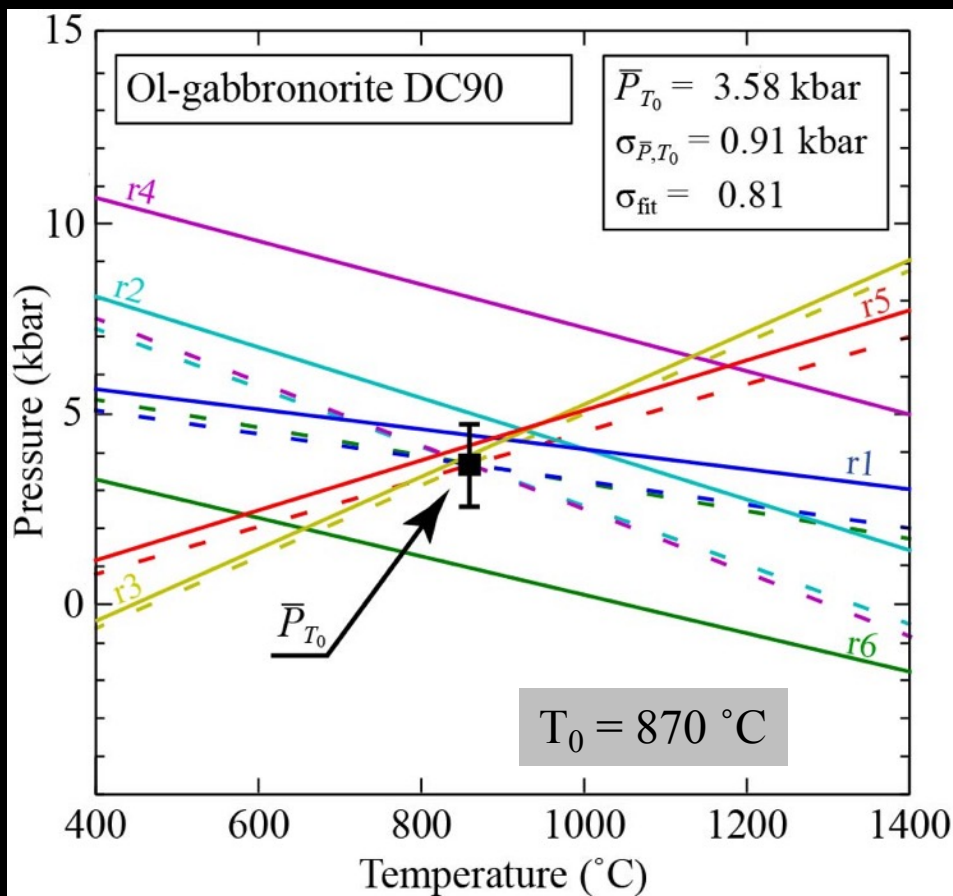
$$\Delta G^0_1 = \Delta H^0_1 - T \Delta S^0_1 + P \Delta V^0_1$$

$$K_1 = \frac{a_{\text{Mg}_2\text{SiO}_4} a_{\text{CaAl}_2\text{Si}_2\text{O}_8}}{a_{\text{Mg}_2\text{Si}_2\text{O}_6} a_{\text{CaAl}_2\text{SiO}_6}}$$

$$\text{R1) } \Delta G^0_1 + R T \ln K_1 = 0$$



Multiple-reaction geothermobarometry (e.g., average P method)



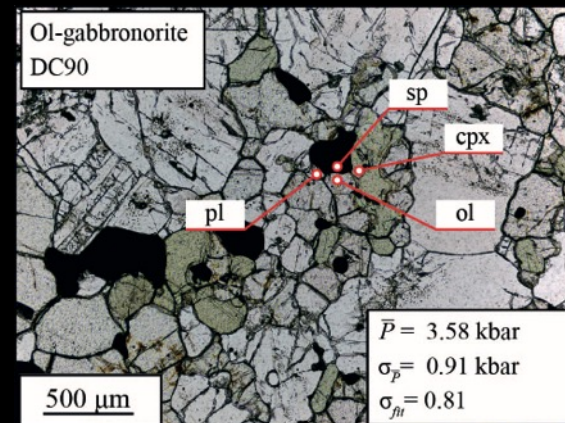
Average P takes into account:

- uncertainties
 - i) analytical errors
 - ii) activity-composition relations
 - iii) thermodynamic properties of pure end-members
- correlations

The positions of the reactions in P-T space are correlated (they share end-members)

The solution is found when:

- The reactions are consistent
- The residuals of the activities and enthalpies are minimized



Application of avP to the experimental samples

Chemical composition of synthetic phases

Thermodynamic data (enthalpy, entropy, interaction parameters)

Temperature

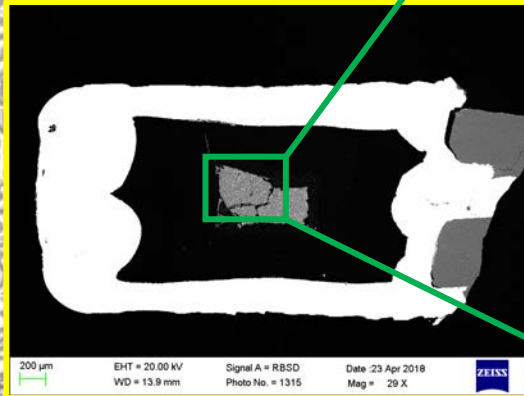
Average P method

Pressure

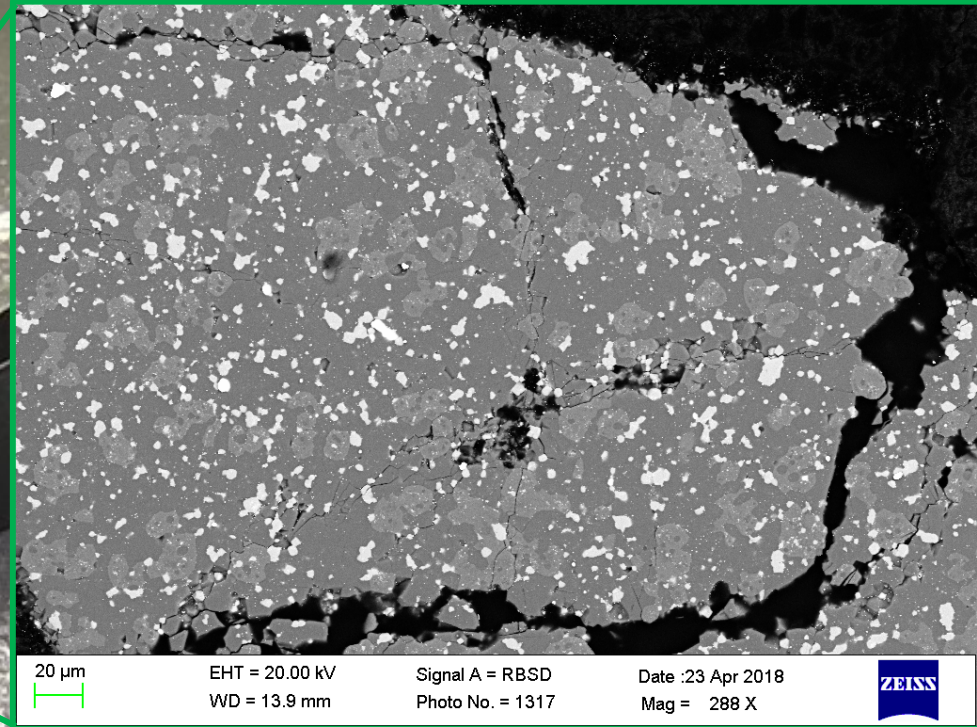


Application of avP to the experimental samples

Chemical composition of synthetic phases



200 μ m EHT = 20.00 kV Signal A = RBSD Date :23 Apr 2018
WD = 13.9 mm Photo No. = 1315 Mag = 29 X ZEISS



20 μ m EHT = 20.00 kV Signal A = RBSD Date :23 Apr 2018
WD = 13.9 mm Photo No. = 1317 Mag = 288 X ZEISS

Application of avP to the experimental samples

Thermodynamic data (enthalpy, entropy, interaction parameters)

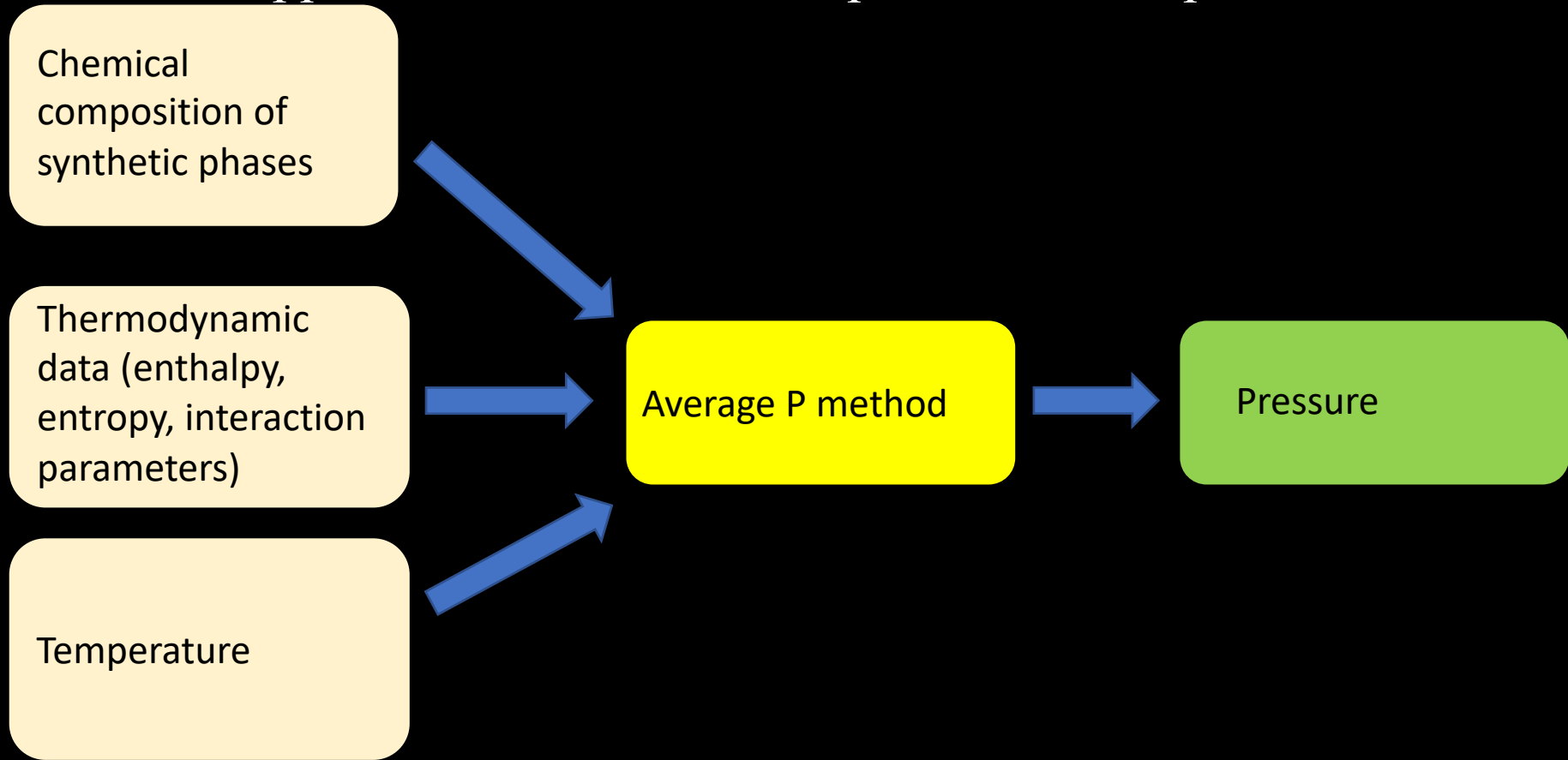
Holland & Powell (2011; J M G)

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Table 2a. Molar thermodynamic properties (units: kJ, K, kbar) of the end-members whose formulae can be found in Table 1.

Group	End-member	$\Delta_f H$	$\sigma(\Delta_f H)$	S	V	C_P				$\alpha\kappa$				ℓ
						a	b	c	d	α_0	κ_0	κ'_0	κ''_0	
Garnet and olivine	Almandine (alm)	-5260.65	1.31	342.00	11.525	0.6773	0	-3772.7	-5.0440	2.12	1900.0	2.98	-0.0016	
	Andradite (andr)	-5769.08	1.56	316.40	13.204	0.6386	0	-4955.1	-3.9892	2.86	1588.0	5.68	-0.0036	
	grossular (gr)	-6642.95	1.46	255.00	12.535	0.6260	0	-5779.2	-4.0029	2.20	1720.0	5.53	-0.0032	
	Knorringite (knor)	-5687.75	3.88	317.00	11.738	0.6130	0.3606	-4178.0	-3.7294	2.37	1743.0	4.05	-0.0023	
	Majorite (maj)	-6050.33	9.62	255.20	11.457	0.7136	-0.0997	-1158.2	-6.6223	1.83	1600.0	4.56	-0.0028	
	Pyrope (py)	-6282.13	1.06	269.50	11.313	0.6335	0	-5196.1	-4.3152	2.37	1743.0	4.05	-0.0023	
	Spessartine (spss)	-5693.65	3.14	335.30	11.792	0.6469	0	-4525.8	-4.4528	2.27	1740.0	6.68	-0.0038	
	Clinohumite (chum)	-9609.82	2.49	443.00	19.785	1.0700	-1.6533	-7899.6	-7.3739	2.91	1194.0	4.79	-0.0040	
	Fayalite (fa)	-1477.74	0.68	151.00	4.631	0.2011	1.7330	-1960.6	-0.9009	2.82	1256.0	4.68	-0.0037	
	Forsterite (fo)	-2172.57	0.57	95.10	4.366	0.2333	0.1494	-603.8	-1.8697	2.85	1285.0	3.84	-0.0030	
	Larnite (lrn)	-2307.04	0.90	127.60	5.160	0.2475	-0.3206	0	-2.0519	2.90	985.0	4.07	-0.0041	1
	Monticellite (mont)	-2251.31	0.52	109.50	5.148	0.2507	-1.0433	-797.2	-1.9961	2.87	1134.0	3.87	-0.0034	
	Tephroite (teph)	-1733.95	1.05	155.90	4.899	0.2196	0	-1292.7	-1.3083	2.86	1256.0	4.68	-0.0037	
	Aluminosilicates	Andalusite (and)	-2588.72	0.68	92.70	5.153	0.2773	-0.6588	-1914.1	-2.2656	1.81	1442.0	6.89	-0.0048
Kyanite (ky)		-2593.02	0.67	83.50	4.414	0.2794	-0.7124	-2055.6	-2.2894	1.92	1601.0	4.05	-0.0025	
Sillimanite (sill)		-2585.85	0.68	95.40	4.986	0.2802	-0.6900	-1375.7	-2.3994	1.12	1640.0	5.06	-0.0031	2
Mullite (amul)		-2485.51	0.91	113.00	5.083	0.2448	0.0968	-2533.3	-1.6416	1.36	1740.0	4.00	-0.0023	
Mullite (smul)		-2569.28	0.69	101.50	4.987	0.2802	-0.6900	-1375.7	-2.3994	1.36	1740.0	4.00	-0.0023	
Chloritoid (fctd)		-3208.31	0.80	167.00	6.980	0.4161	-0.3477	-2835.9	-3.3603	2.80	1456.0	4.06	-0.0028	
Chloritoid (mctd)		-3549.31	0.75	146.00	6.875	0.4174	-0.3771	-2920.6	-3.4178	2.63	1456.0	4.06	-0.0028	
Chloritoid (mnctd)		-3336.20	1.68	166.00	7.175	0.4644	-1.2654	-1147.2	-4.3410	2.60	1456.0	4.06	-0.0028	
Staurolite (fst)		-23 755.04	6.34	1010.00	44.880	2.8800	-5.6595	-10642.0	-25.3730	1.83	1800.0	4.76	-0.0026	
Staurolite (mnst)		-24 246.42	8.60	1034.00	45.460	2.8733	-8.9064	-12688.0	-24.7490	2.09	1800.0	4.76	-0.0026	
Staurolite (mst)		-25 124.32	6.28	910.00	44.260	2.8205	-5.9366	-13774.0	-24.1260	1.81	1684.0	4.05	-0.0024	
Topaz (tpz)		-2900.76	0.96	100.50	5.339	0.3877	-0.7120	-857.2	-3.7442	1.57	1315.0	4.06	-0.0031	

Application of avP to the experimental samples

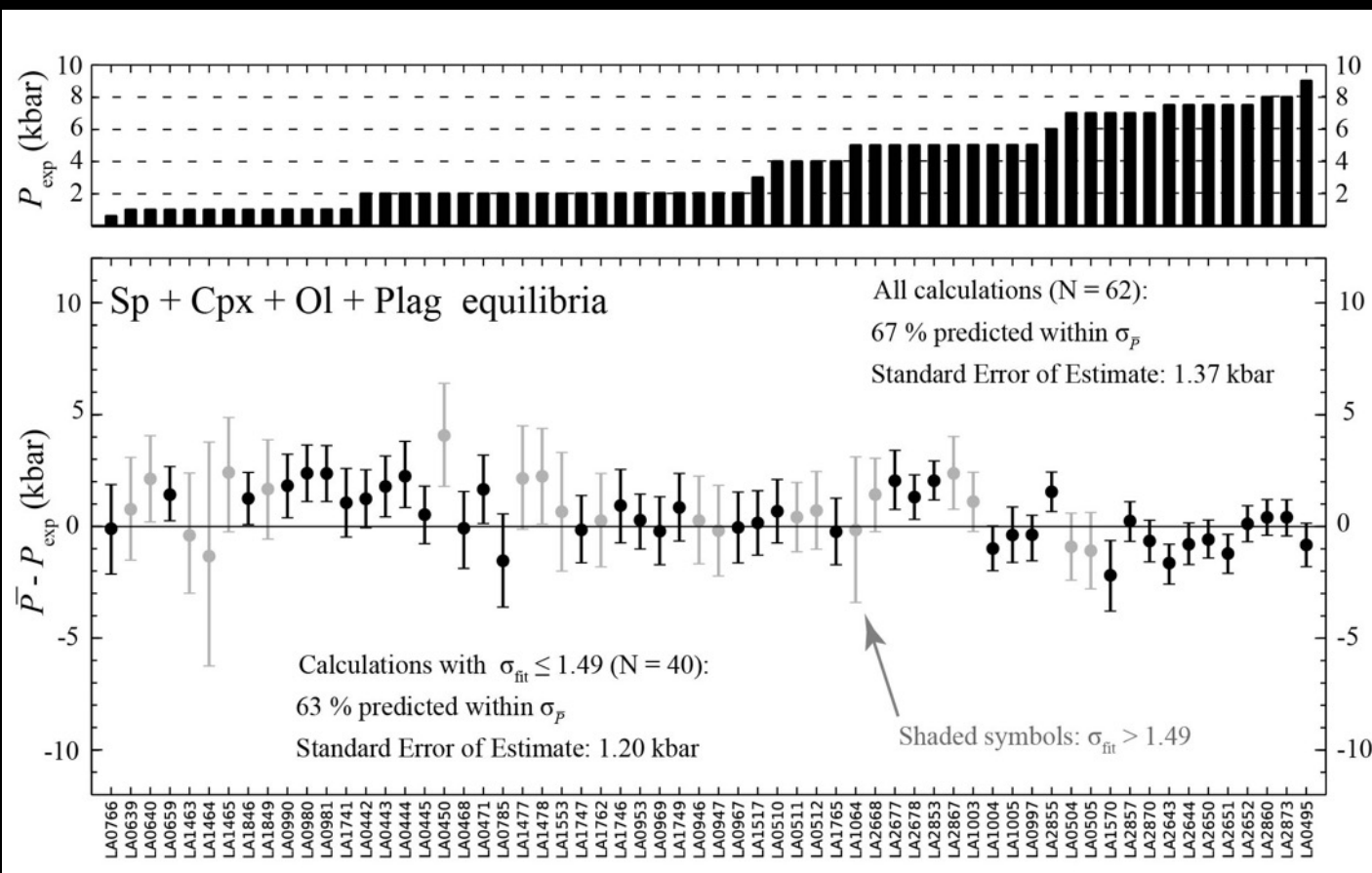


Application of avP to the experimental samples

Tested on: phase equilibrium experiments in andesitic, basaltic and peridotitic systems

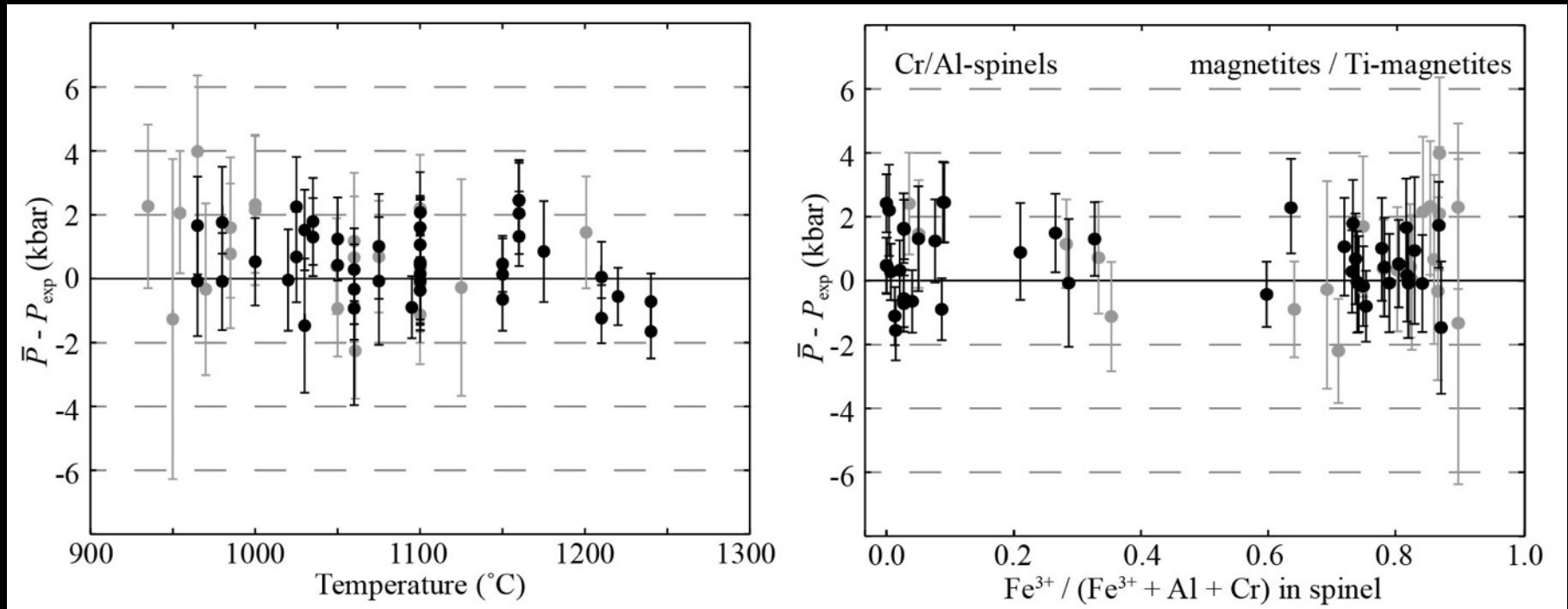
P-T range: P = 0.5 – 9.5 kbar; T = 950 – 1250 °C

Equilibria: **Spinel + Clinopyroxene + Olivine + Plagioclase**

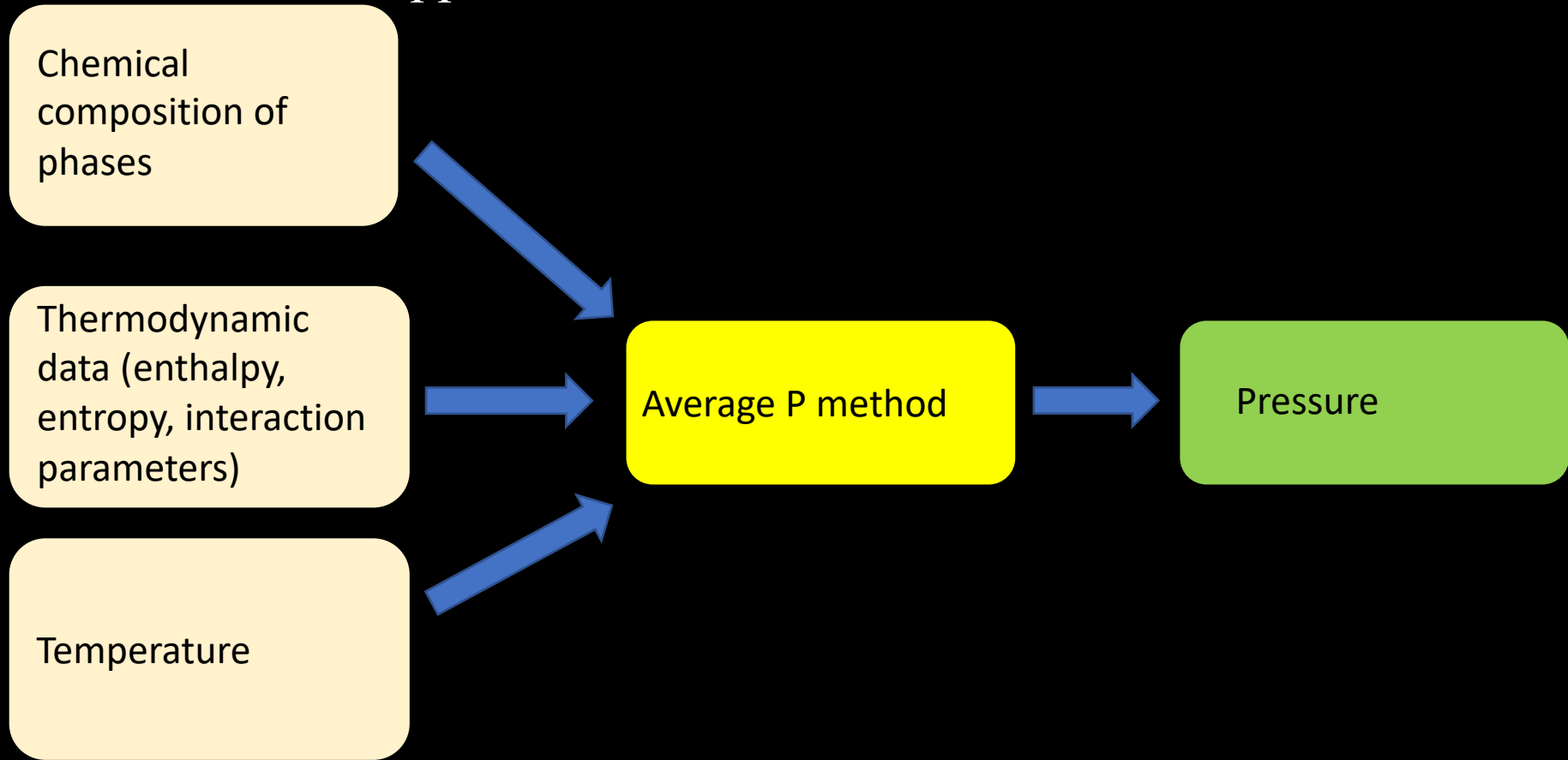


Application of avP to the experimental samples

No deviations with temperature and composition

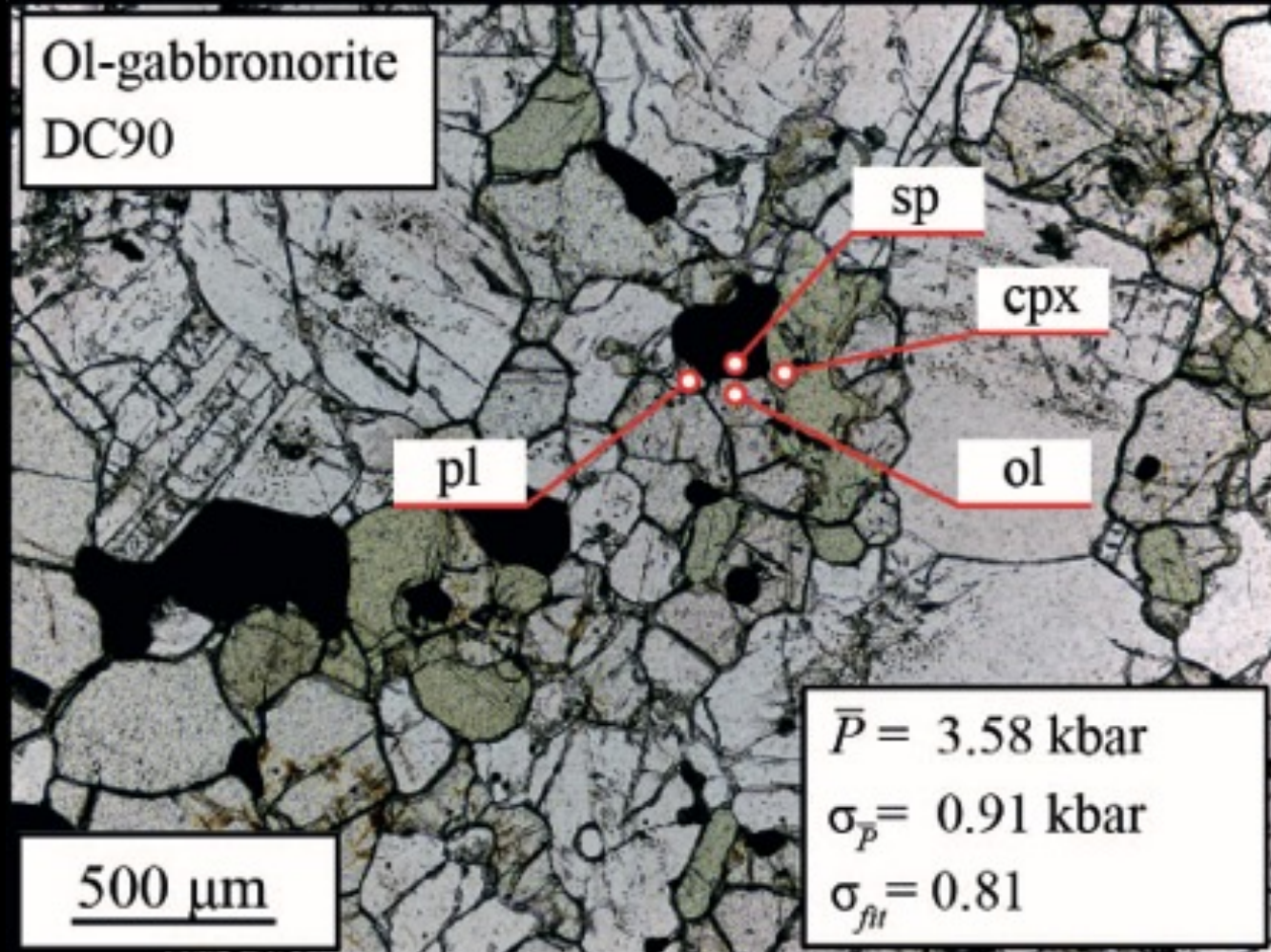


Application of avP to the xenoliths



Application of avP to the xenoliths

Chemical
composition of
phases



Application of avP to the xenoliths

Thermodynamic data (enthalpy, entropy, interaction parameters)

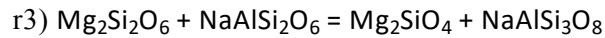
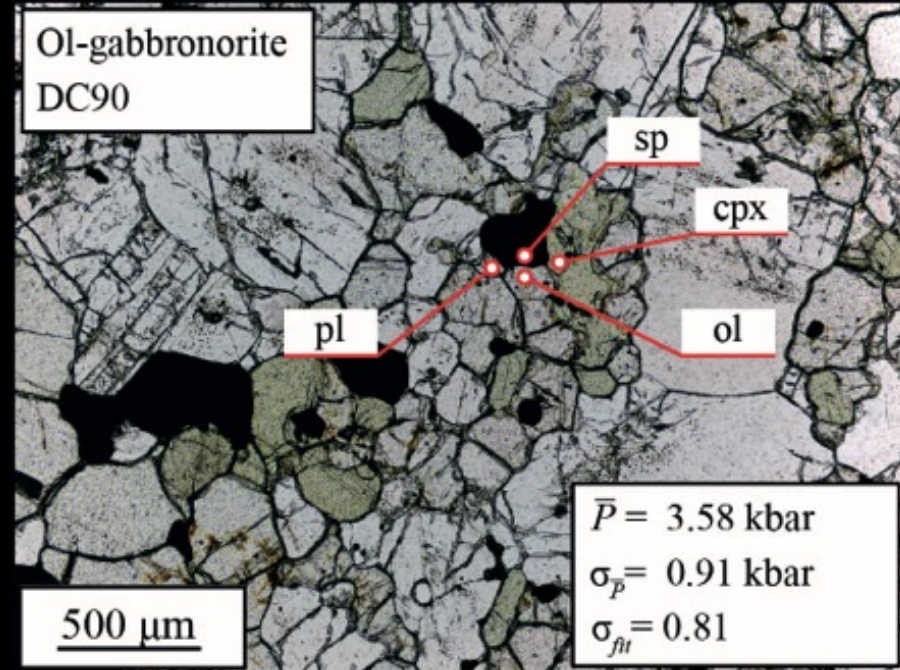
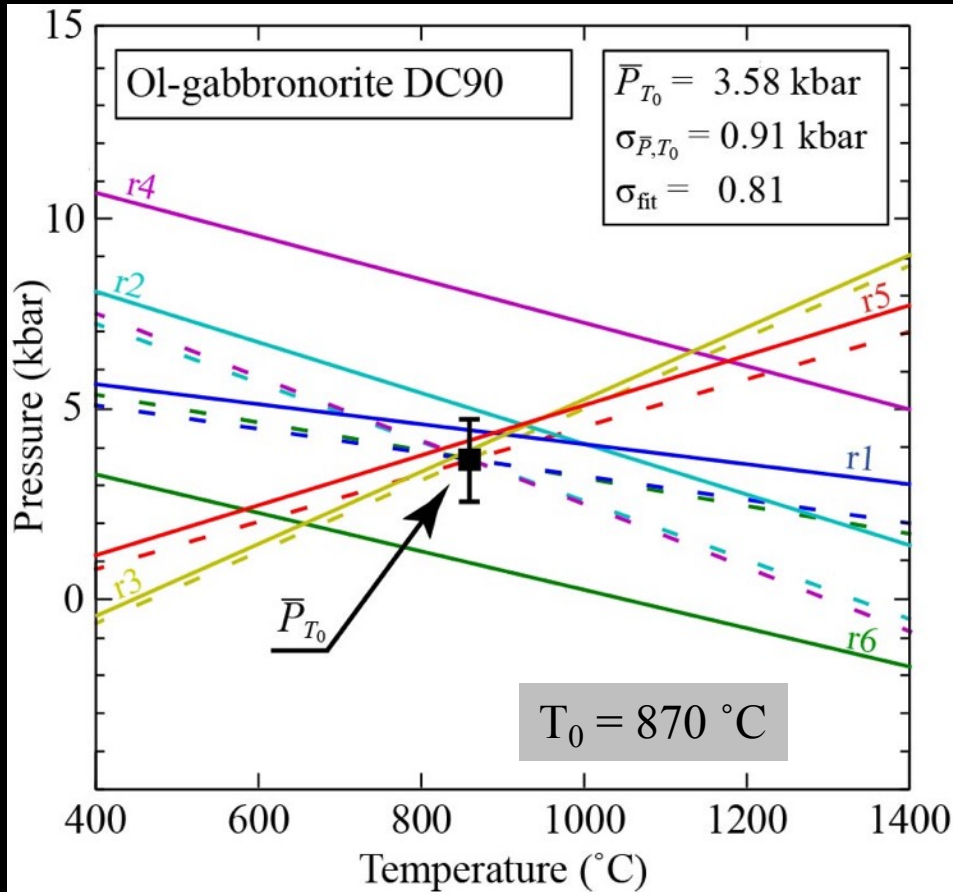
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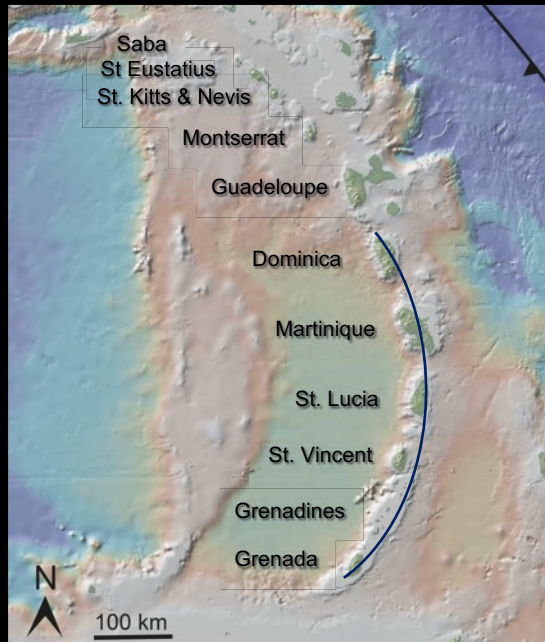
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Mullite (amul)		-2485.51	0.91	113.00	5.083	0.2448	0.0968	-2533.3	-1.6416	1.36	1740.0	4.00	-0.0023	
Mullite (smul)		-2569.28	0.69	101.50	4.987	0.2802	-0.6900	-1375.7	-2.3994	1.36	1740.0	4.00	-0.0023	
Chloritoid (fctd)		-3208.31	0.80	167.00	6.980	0.4161	-0.3477	-2835.9	-3.3603	2.80	1456.0	4.06	-0.0028	
Chloritoid (mctd)		-3549.31	0.75	146.00	6.875	0.4174	-0.3771	-2920.6	-3.4178	2.63	1456.0	4.06	-0.0028	
Chloritoid (mnctd)		-3336.20	1.68	166.00	7.175	0.4644	-1.2654	-1147.2	-4.3410	2.60	1456.0	4.06	-0.0028	
Staurolite (fst)		-23 755.04	6.34	1010.00	44.880	2.8800	-5.6595	-10642.0	-25.3730	1.83	1800.0	4.76	-0.0026	
Staurolite (mnst)		-24 246.42	8.60	1034.00	45.460	2.8733	-8.9064	-12688.0	-24.7490	2.09	1800.0	4.76	-0.0026	
Staurolite (mst)		-25 124.32	6.28	910.00	44.260	2.8205	-5.9366	-13774.0	-24.1260	1.81	1684.0	4.05	-0.0024	
Topaz (tpz)		-2900.76	0.96	100.50	5.339	0.3877	-0.7120	-857.2	-3.7442	1.57	1315.0	4.06	-0.0031	

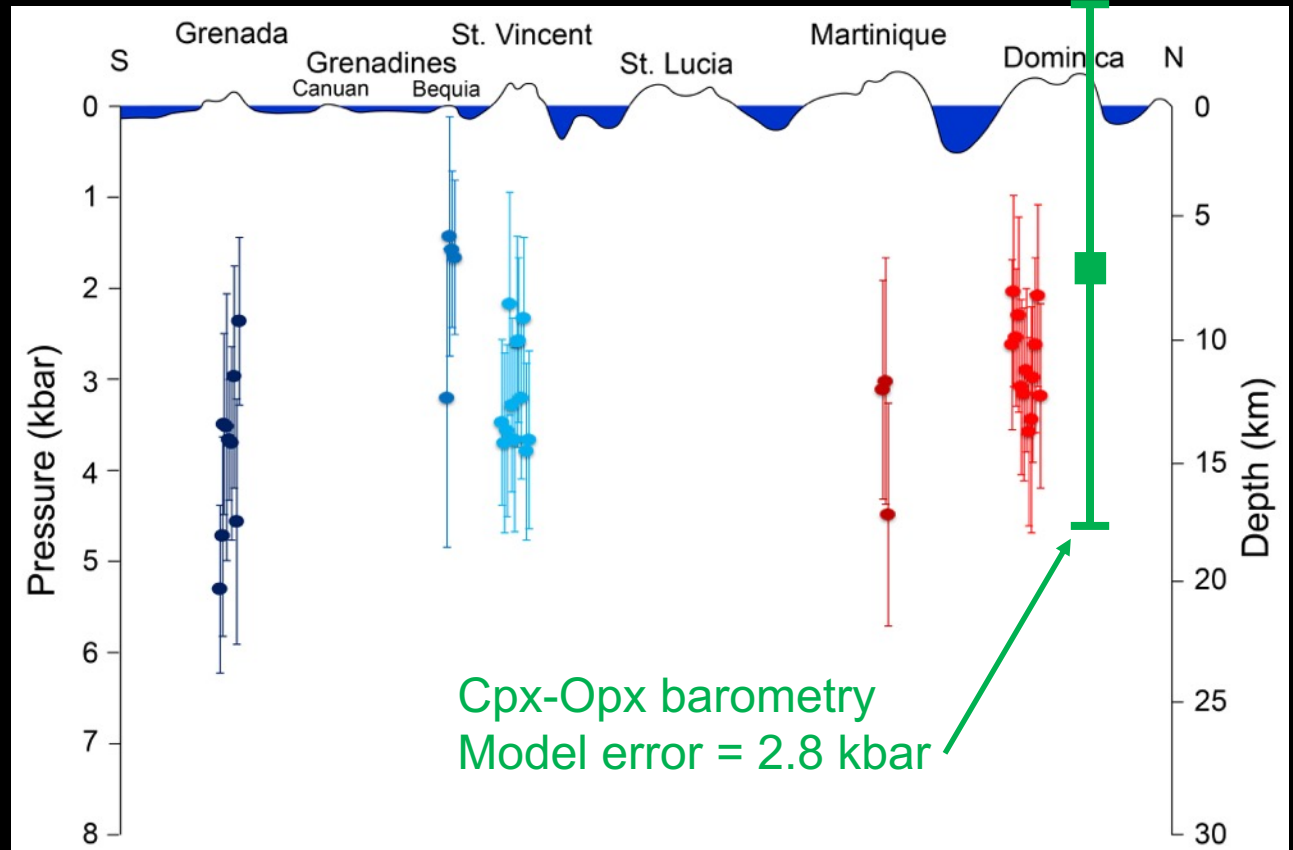
Application of avP to the xenoliths



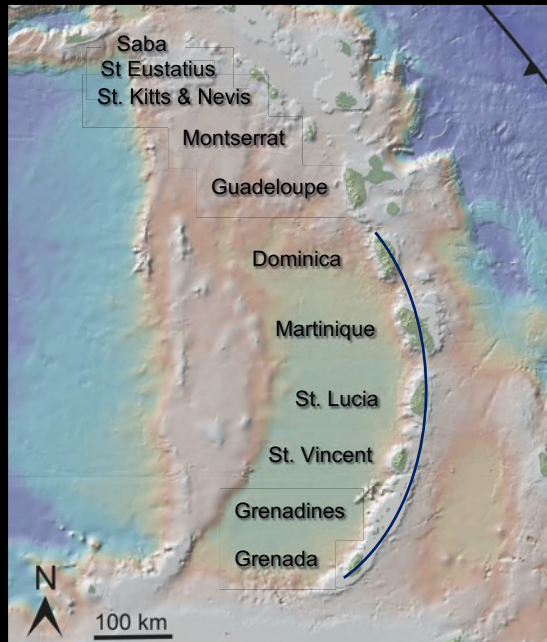
Application of avP to the xenoliths



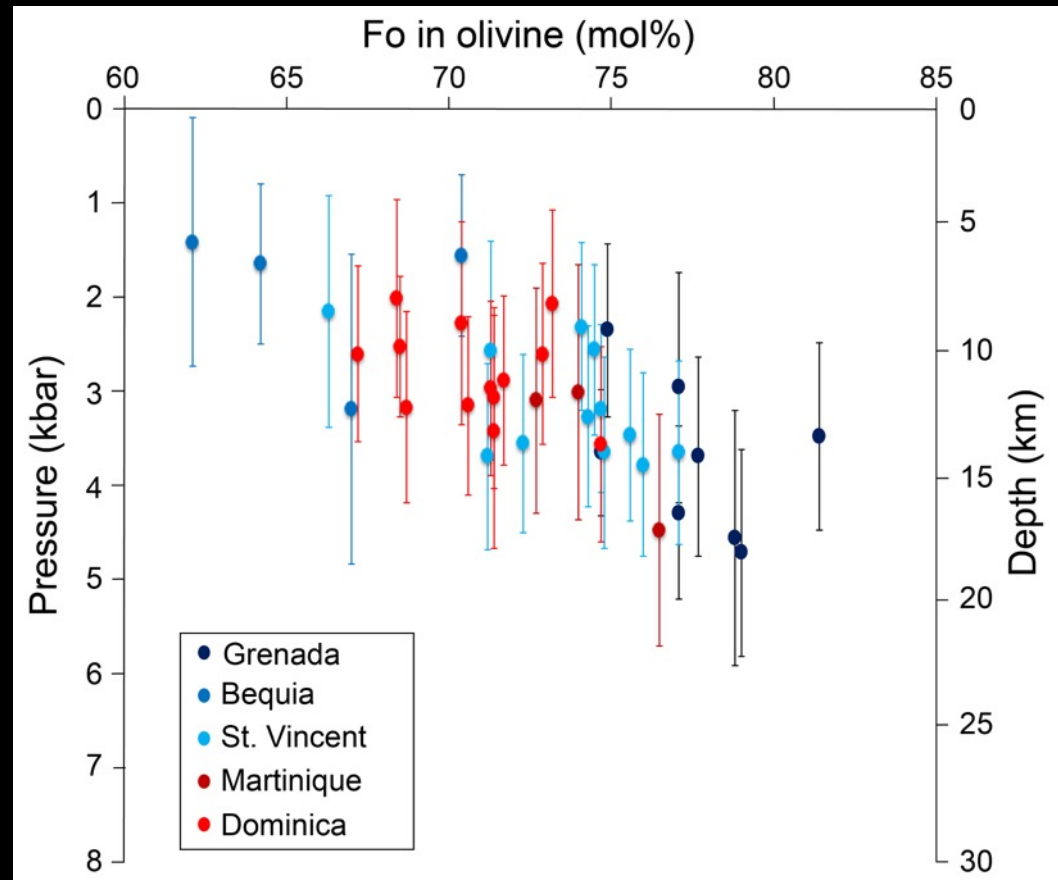
Along-arc variations



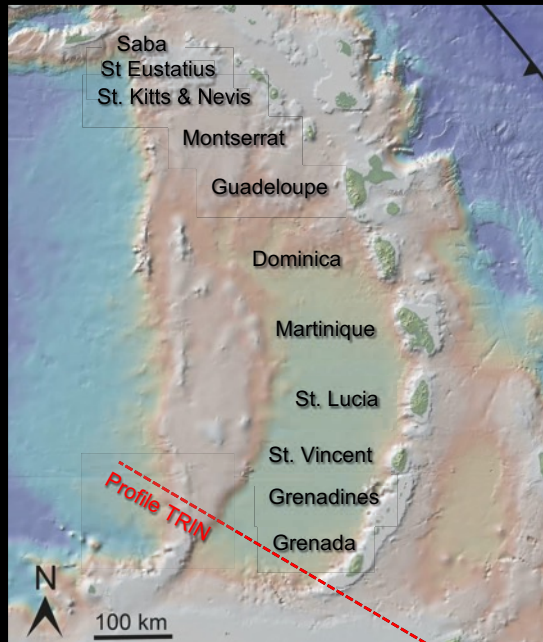
Application of avP to the xenoliths



Variations of petrological variables with depth



Integration with seismic models

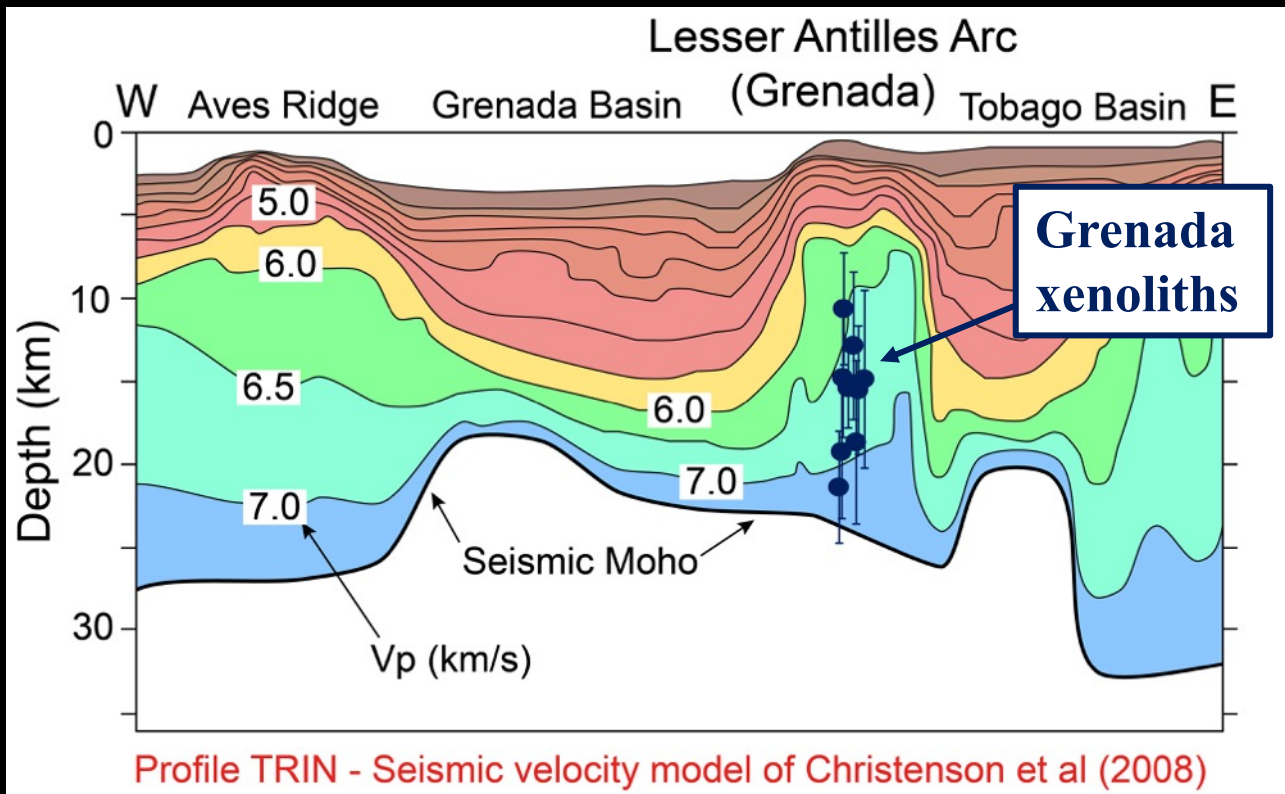


Calculated seismic properties (using Hacker & Abers, 2004)

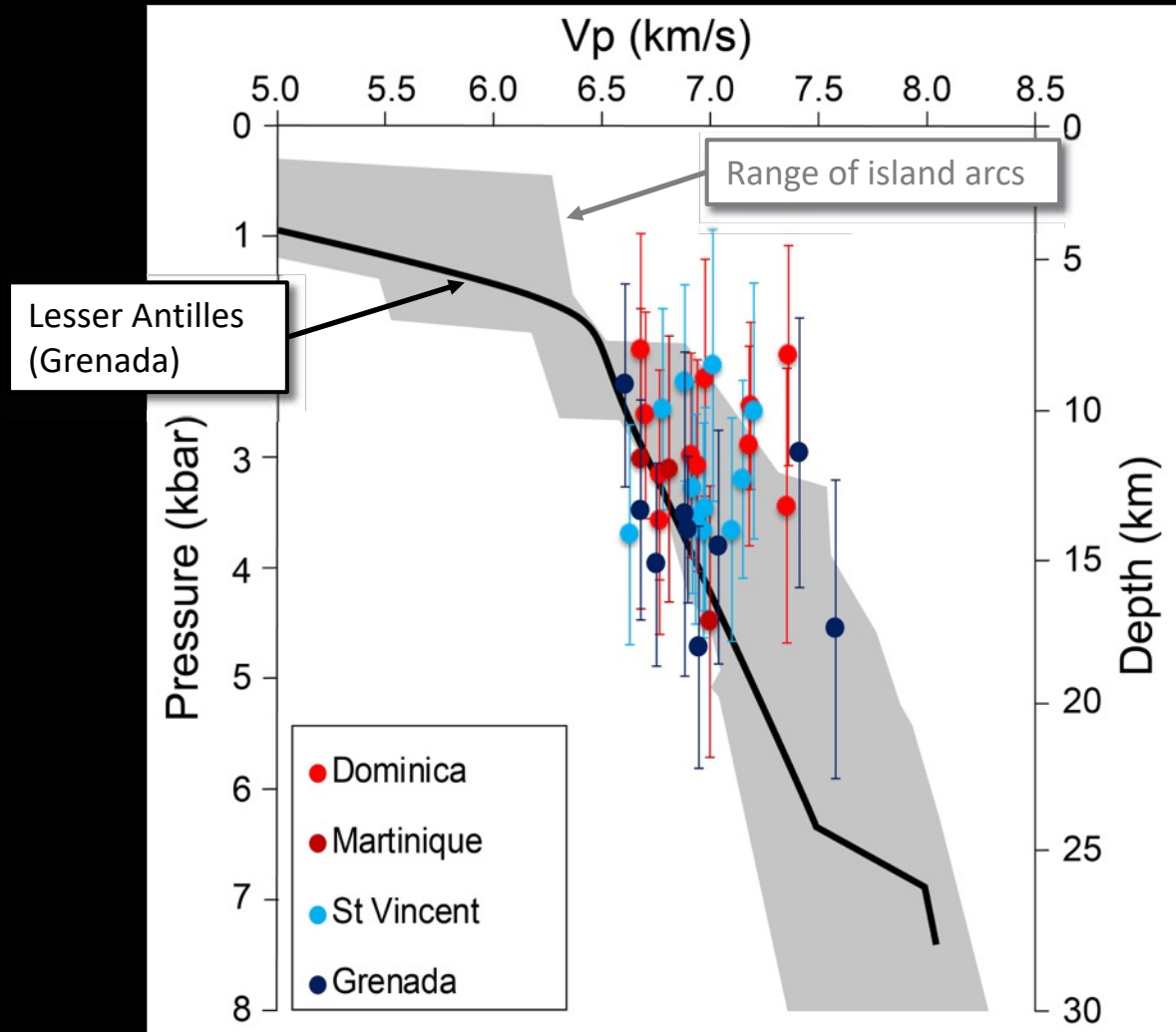
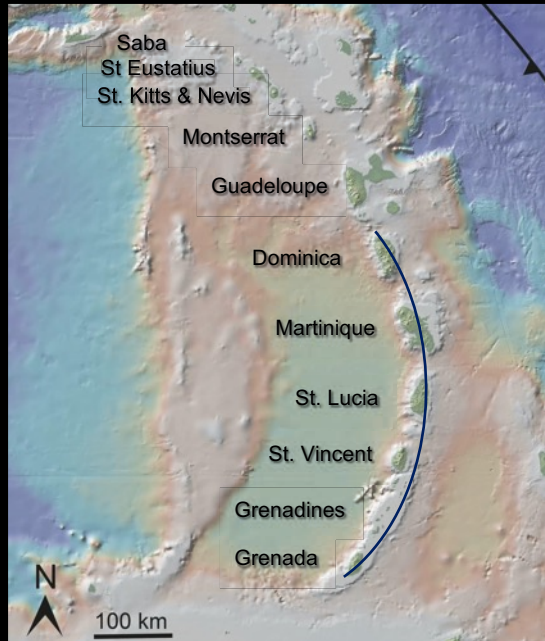
Grenada xenoliths:

$$\rho \text{ (density)} = 2.84 - 3.20 \text{ g/cm}^3$$

$$V_p \text{ (P wave velocity)} = 6.63 - 7.58 \text{ km/s}$$



Integration with seismic models



Modelli termodinamici diretti

La modellizzazione termodinamica diretta viene utilizzata per predire come la mineralogia e le proprietà chimico-fisiche delle rocce e dei magmi variano in funzione delle condizioni (P, T, fO_2 , etc).

I principi su cui si basa sono gli stessi della termobarometria classica.

I software di modellizzazione termodinamica più utilizzati in petrologia sono:

- MELTS (<http://melts.ofm-research.org/index.html>)
- PERPLE_X (<http://perplex.ethz.ch>)
- THERMOCALC (<http://www.metamorph.geo.uni-mainz.de/thermocalc/>)

Esempio di studio

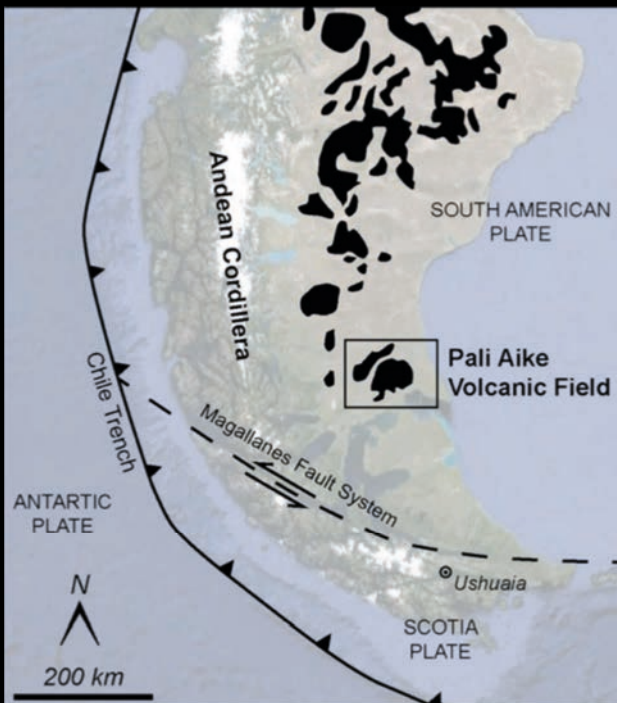
Contrib Mineral Petrol (2016) 171:16
DOI 10.1007/s00410-016-1229-9



ORIGINAL PAPER

Application of thermodynamic modelling to natural mantle xenoliths: examples of density variations and pressure–temperature evolution of the lithospheric mantle

L. Ziberna¹ · S. Klemme²



Esempio di studio

Table 1 Bulk compositions for which phase relations were calculated in this study

	LS1		PA3		LS2		TM16	
	Spinel harzburgite		Spinel harzburgite		Spinel harzburgite		Spinel-garnet harzburgite	
	Whole-rock ^a	Model ^b	Whole-rock ^a	Model	Whole-rock ^c	Model	Whole-rock ^a	Model
SiO ₂	43.31	43.74	43.95	44.53	42.11	42.66	47.34	47.52
TiO ₂	0.04	–	0.05	–	0.03	–	0.23	–
Al ₂ O ₃	0.52	0.53	1.03	1.04	3.55	3.60	3.27	3.28
Cr ₂ O ₃	0.34	0.34	0.46	0.47	0.82	0.83	0.37	0.37
FeO _{tot}	6.80	6.87	7.58	7.68	9.03	9.15	8.73	8.76
MnO	0.10	–	0.12	–	0.11	–	0.13	–
MgO	47.64	48.12	44.86	45.46	41.94	42.48	39.06	39.21
CaO	0.40	0.40	0.79	0.80	1.23	1.25	0.81	0.81
Na ₂ O	0.00	0.00	0.02	0.02	0.04	0.04	0.05	0.05
K ₂ O	0.00	–	0.02	–	n.a.	–	0.09	–
NiO	0.33	–	0.32	–	0.24	–	0.24	–
Mg#	0.93	0.93	0.91	0.91	0.89	0.89	0.89	0.89
Cr#	0.30	0.30	0.23	0.23	0.13	0.13	0.07	0.07
Ca#	0.01	0.01	0.01	0.01	0.02	0.02	0.01	0.01

	LS1	
	Spinel harzburgite	
	Whole-rock ^a	Model ^b
SiO ₂	43.31	43.74
TiO ₂	0.04	–
Al ₂ O ₃	0.52	0.53
Cr ₂ O ₃	0.34	0.34
FeO _{tot}	6.80	6.87
MnO	0.10	–
MgO	47.64	48.12
CaO	0.40	0.40
Na ₂ O	0.00	0.00
K ₂ O	0.00	–
NiO	0.33	–
Mg#	0.93	0.93
Cr#	0.30	0.30
Ca#	0.01	0.01

Composizione chimica
utilizzata come input
per il modello

Esempio di studio

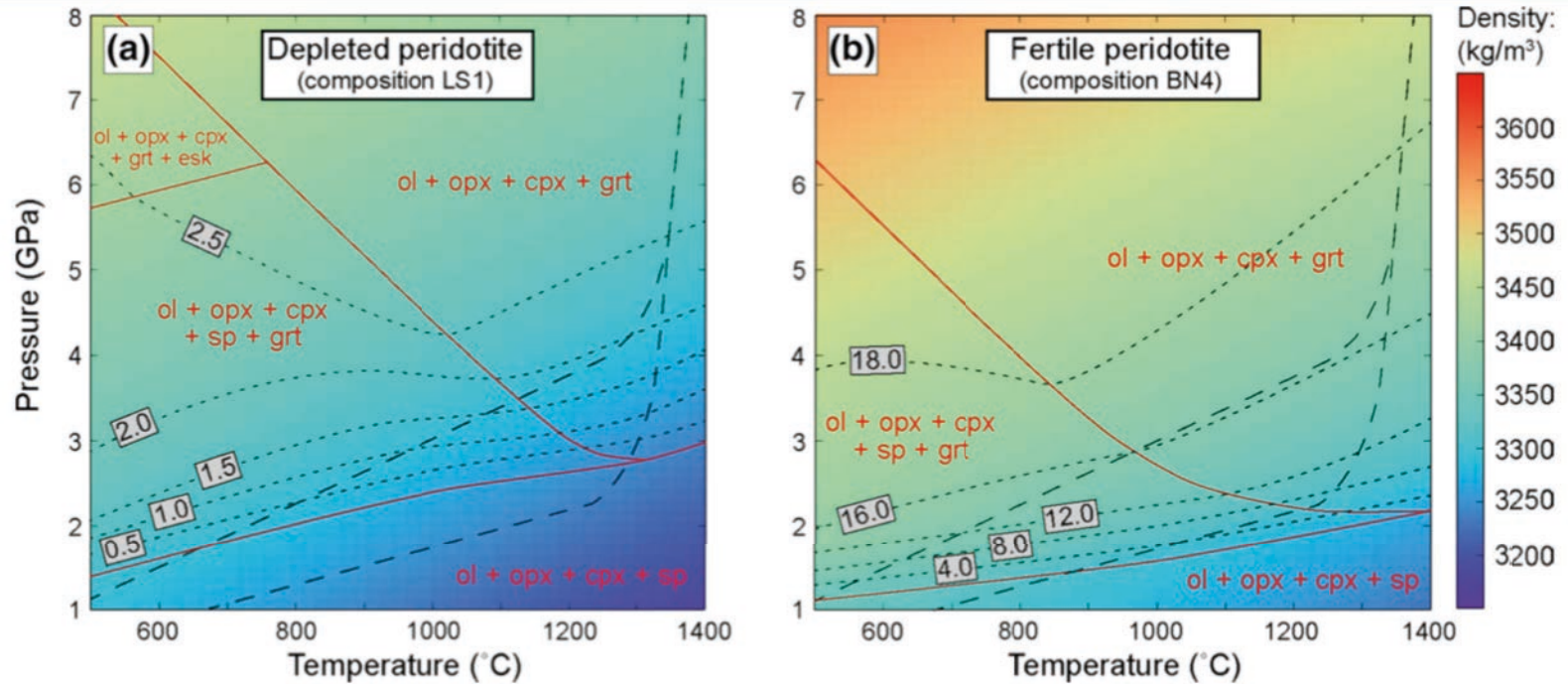
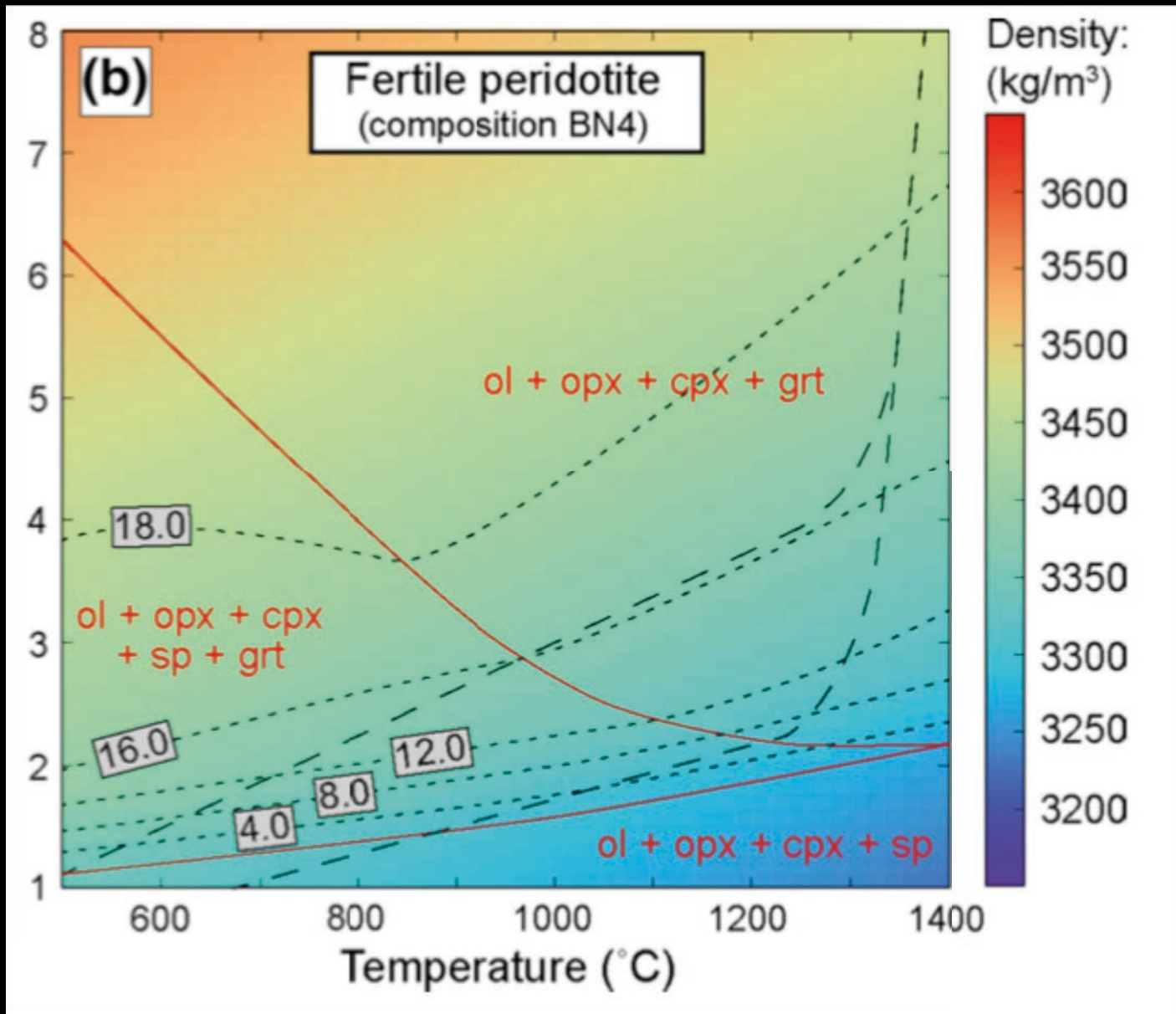


Fig. 3 Pressure–temperature diagram showing a colour map of the calculated density for the compositions **a** LS1 and **b** BN4 (mantle xenoliths from Pali-Aike, Stern et al. 1999). The two dashed curves represent a 50 (*higher curve*) and a 70 mW/m² (*lower curve*) conductive geotherms both joining the 1300 °C adiabat (Hasterok and Chapman 2011). The solid red curves delimit the stability fields predicted by the thermodynamic model (*ol* olivine, *opx* orthopyroxene, *cpx*

clinopyroxene, *grt* garnet, *sp* spinel, *esk* eskolaite). It is worth noting that garnet modes (*isopleths marked by grey squares*) have the major control on density variations across the spinel–garnet transition. The smoother density variation at the spinel–garnet transition in (a) is indeed related to the very low modes of garnet (<3.0 wt%) for composition BN4 (see text)

Esempio di studio



Esempio di studio

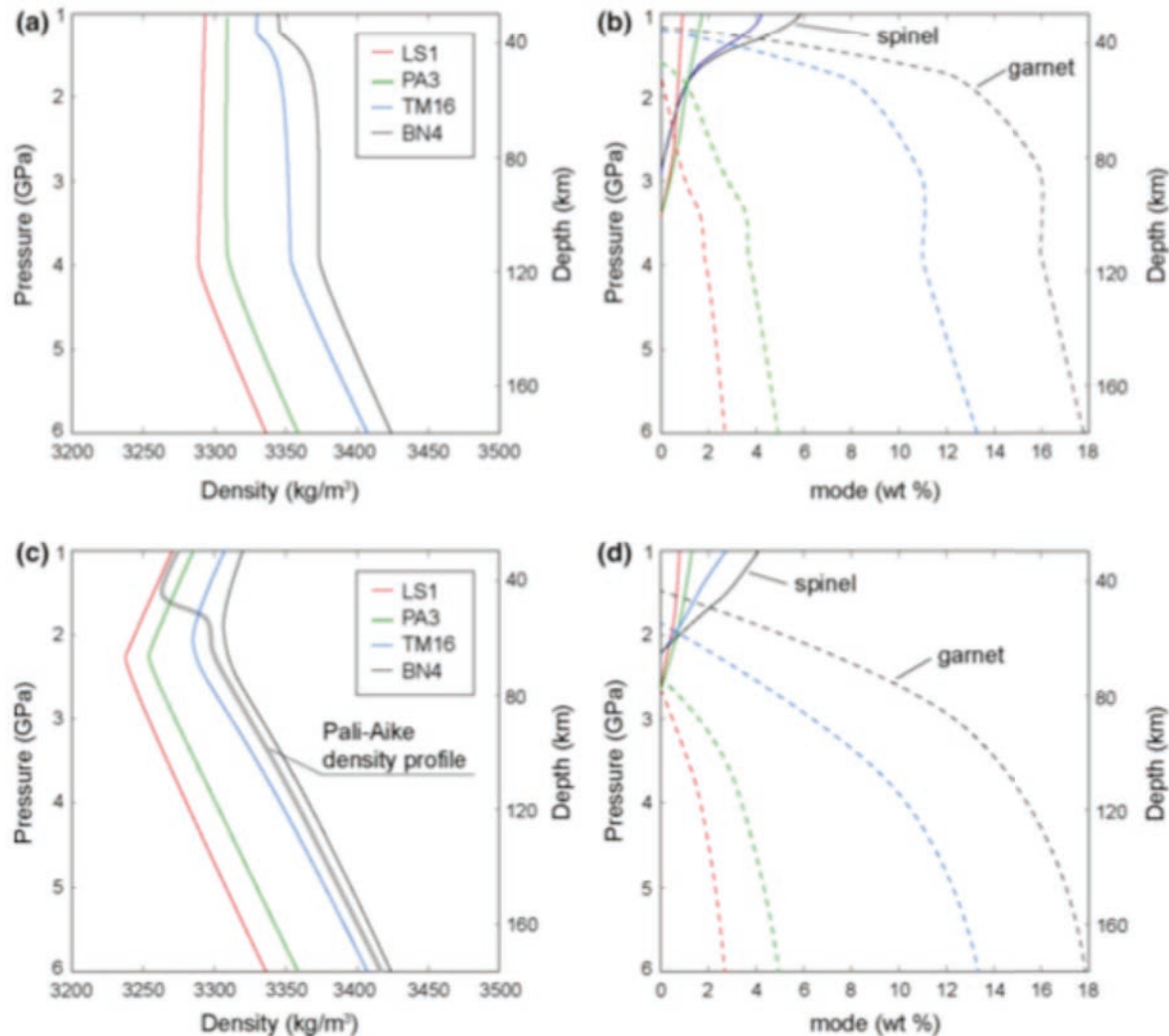


Fig. 4 Calculated density profiles and garnet (*dashed lines*) and spinel (*solid lines*) modes for some representative Pali-Aike peridotite compositions (Table 1) along a 50 mW/m^2 steady state geotherm (**a, b**) and a 70 mW/m^2 geotherm (**c, d**). The *solid grey curve* in (**c**)

represents a possible density profile beneath Pali-Aike based on the compositional layering observed by (Stern et al. 1999). For sake of simplicity, the depth values shown on the right axes were calculated assuming constant density (i.e. $\text{depth} = P(\text{GPa}) \cdot 9.8 \text{ m/s}^2 \cdot 3.0 \text{ kg/cm}^3$)

Esempio di studio

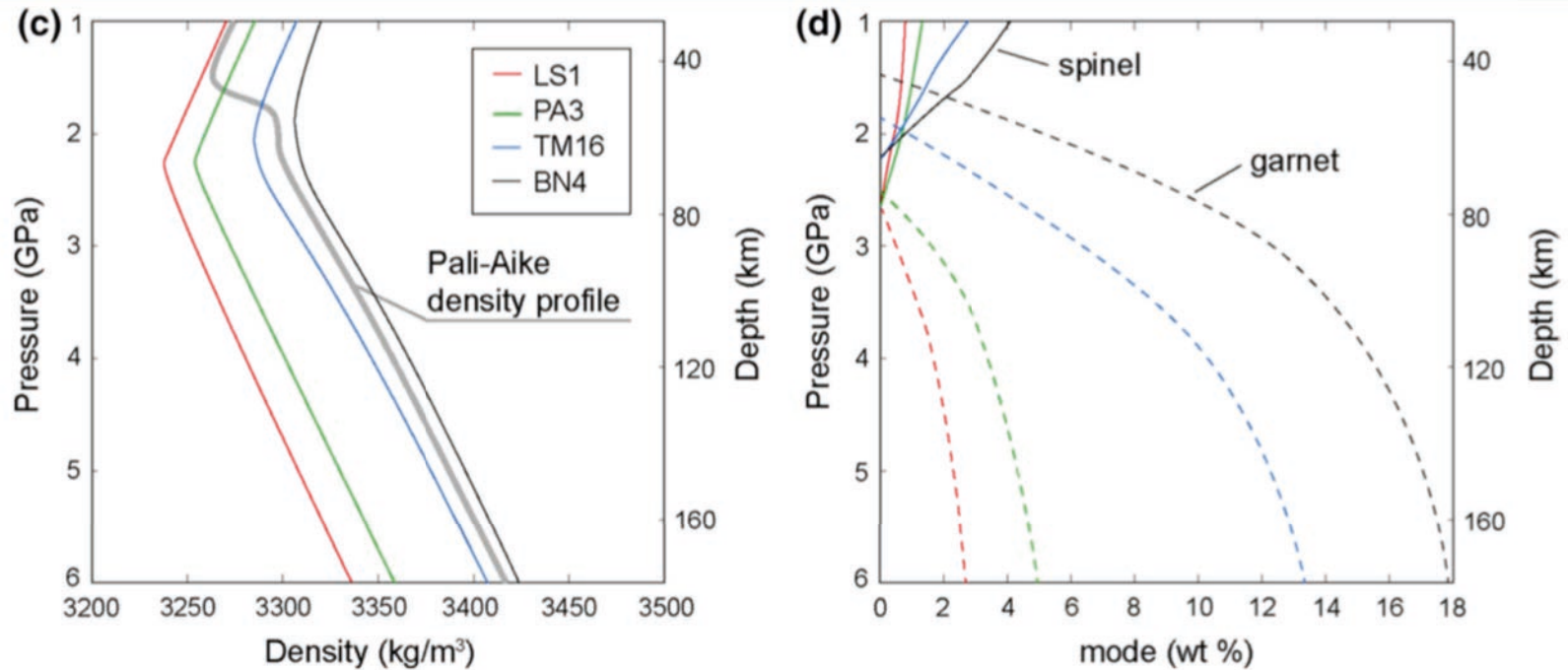


Fig. 4 Calculated density profiles and garnet (*dashed lines*) and spinel (*solid lines*) modes for some representative Pali-Aike peridotite compositions (Table 1) along a 50 mW/m² steady state geotherm (a, b) and a 70 mW/m² geotherm (c, d). The *solid grey curve* in (c)

represents a possible density profile beneath Pali-Aike based on the compositional layering observed by (Stern et al. 1999). For sake of simplicity, the depth values shown on the right axes were calculated assuming constant density (i.e. $\text{depth} = P(\text{GPa}) \cdot 9.8 \text{ m/s}^2 \cdot 3.0 \text{ kg/cm}^3$)

Esempio di studio con MELTS

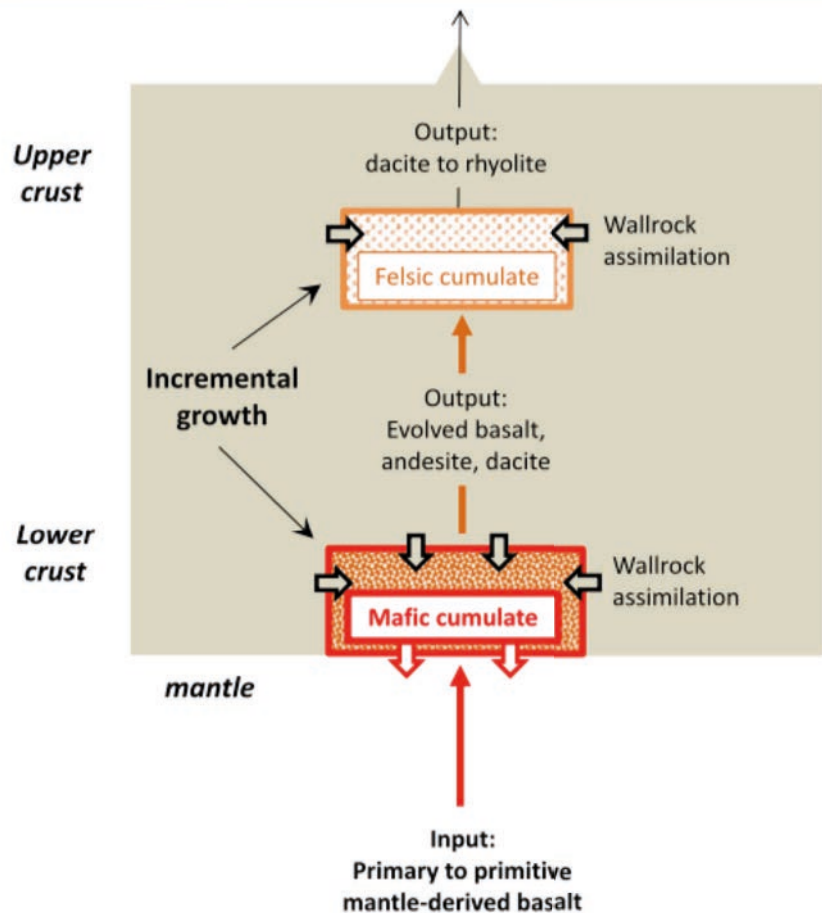


Fig. 7. Cartoon showing polybaric multi-stage differentiation history of magmas. Primary, mantle derived basalts rise from the mantle and stall in or below the deep crust, resulting in cooling, crustal assimilation and crystal fractionation. This generates a range of compositions from evolved basalts to dacites, depending on conditions, such as water content. Andesites dominate in continental arc settings. Such melts then rise into the middle and upper crust, where they differentiate by crystal-liquid segregation to form rhyolitic liquids. Mixing can occur anywhere along this path due to the incremental growth of reservoirs, but is not crucial to the generation of intermediate magmas.

Esempio di studio con MELTS

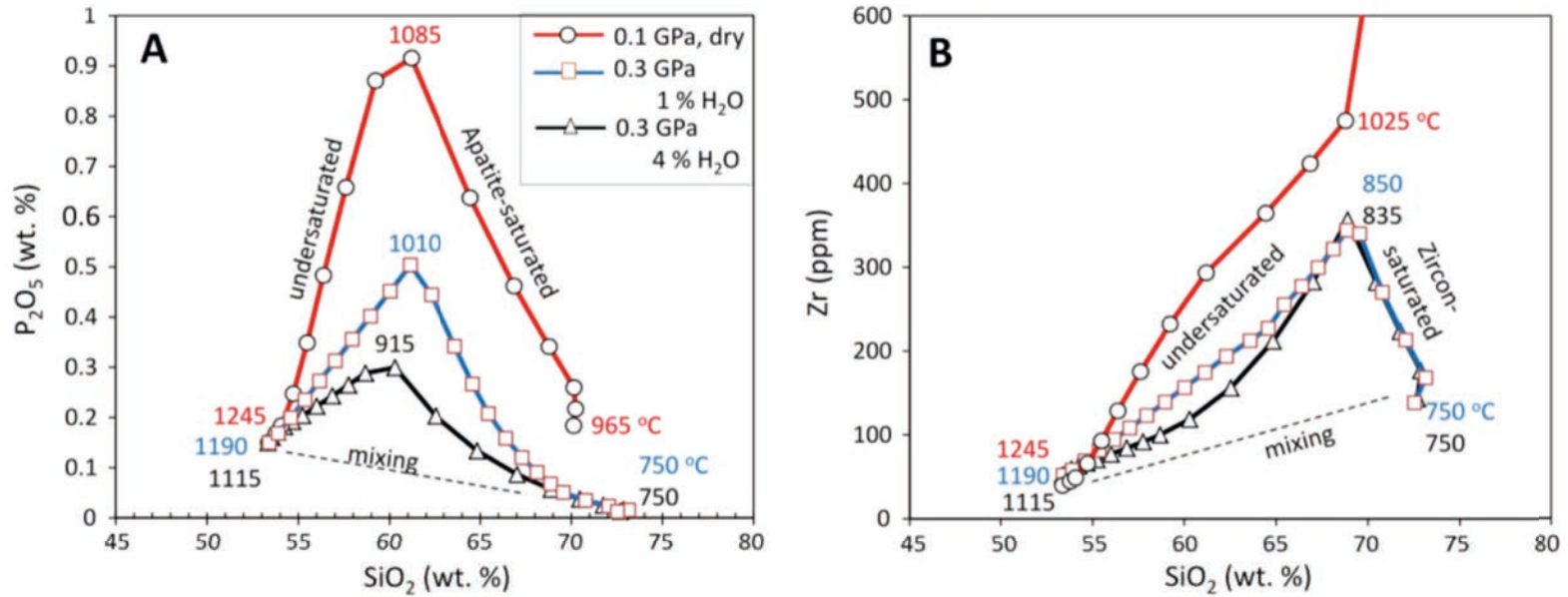
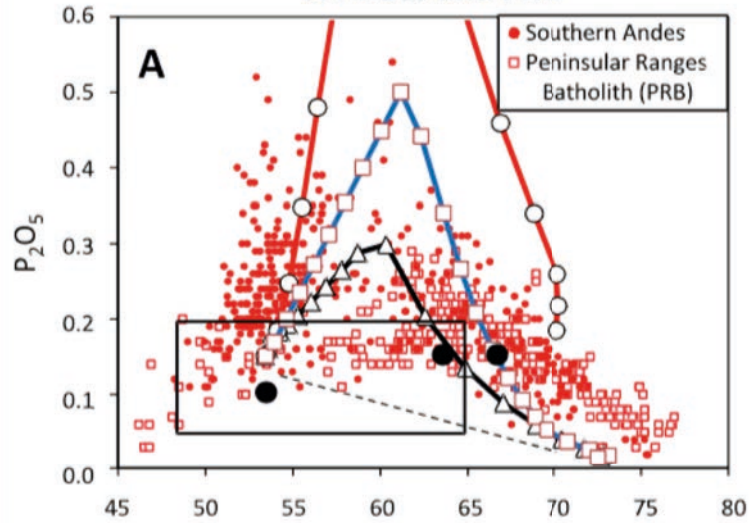


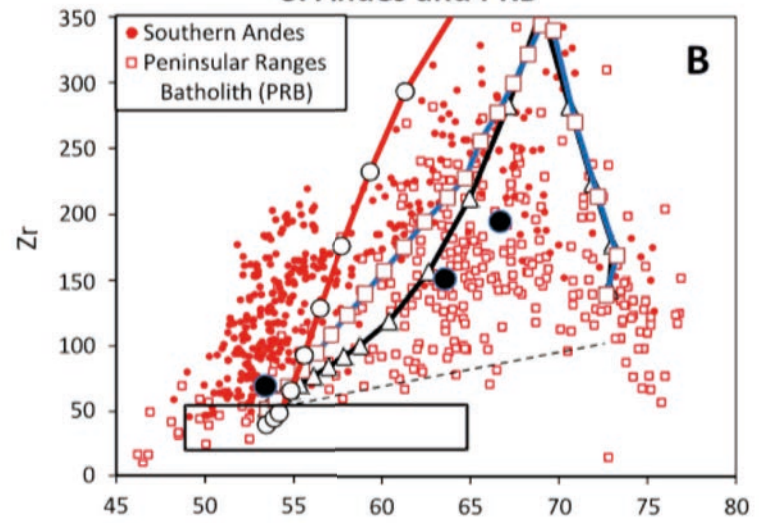
Fig. 2. Modeled residual liquids formed by equilibrium crystallization of dry and hydrous parental basalts using Rhyolite-Melts (Gualda et al., 2012). P₂O₅ (wt.%) and Zr (ppm) are plotted against SiO₂ (wt.%) in (a) and (b), respectively. Elemental concentrations have been normalized to a volatile-free system. Temperatures at the liquidus, point of saturation in apatite or zircon, and the solidus are shown for reference. Dashed straight line in (a) and (b) are hypothetical mixing lines.

Esempio di studio con MELTS

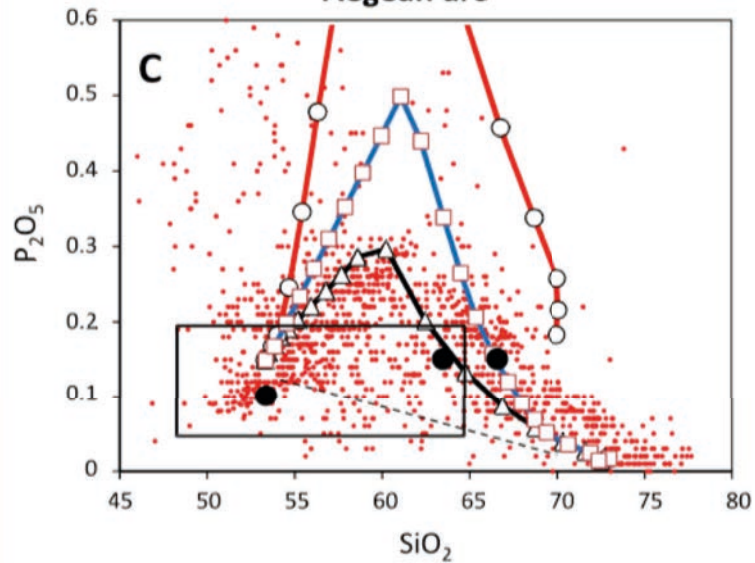
Continental Arc Magma
S. Andes and PRB



Continental Arc Magma
S. Andes and PRB



Aegean arc



Aegean arc

