GSA DATA REPOSITORY 2012275

"The nature of alkali-carbonate fluids in the lithospheric mantle"

Giuliani A., Kamenetsky V.S., Phillips D., Kendrick M.A., Wyatt B.A., Goemann K.

SUPPLEMENTARY MATERIAL

Figure 1DR

spinel harzburgite wall rock ilmenite-rich domain

Fig.1DR Off-cut of polymict breccia DU-1; note the preferential orientation of the large grains of black ilmenite.

Figure 2DR

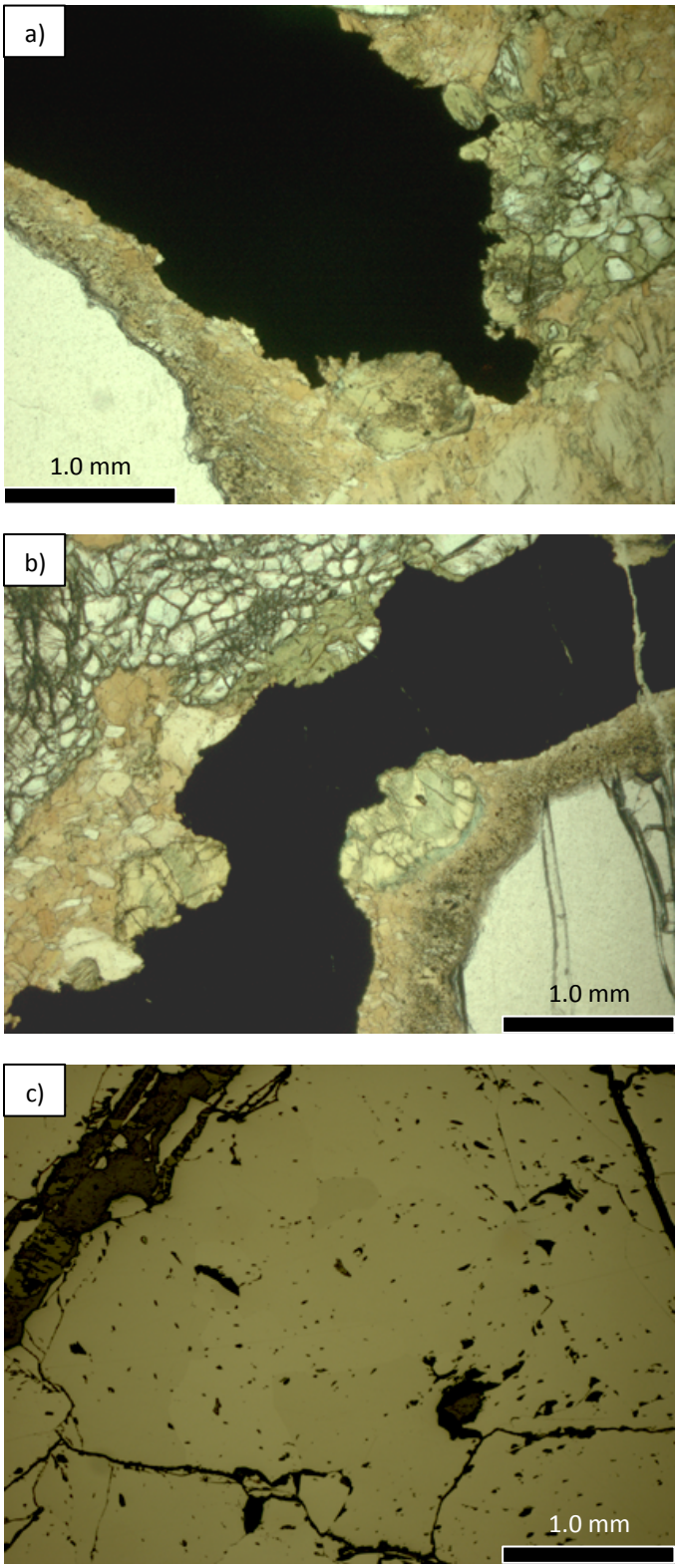

Figure 2DR. Transmitted (a-b) and reflected light (c) micro-photographs of DU-1 ilmenite: a) fragment of ilmenite lens without any evidence of deformation; b) deformed part of ilmenite lens; c) sub-grain texture in deformed crystal of ilmenite.

Figure 3DR

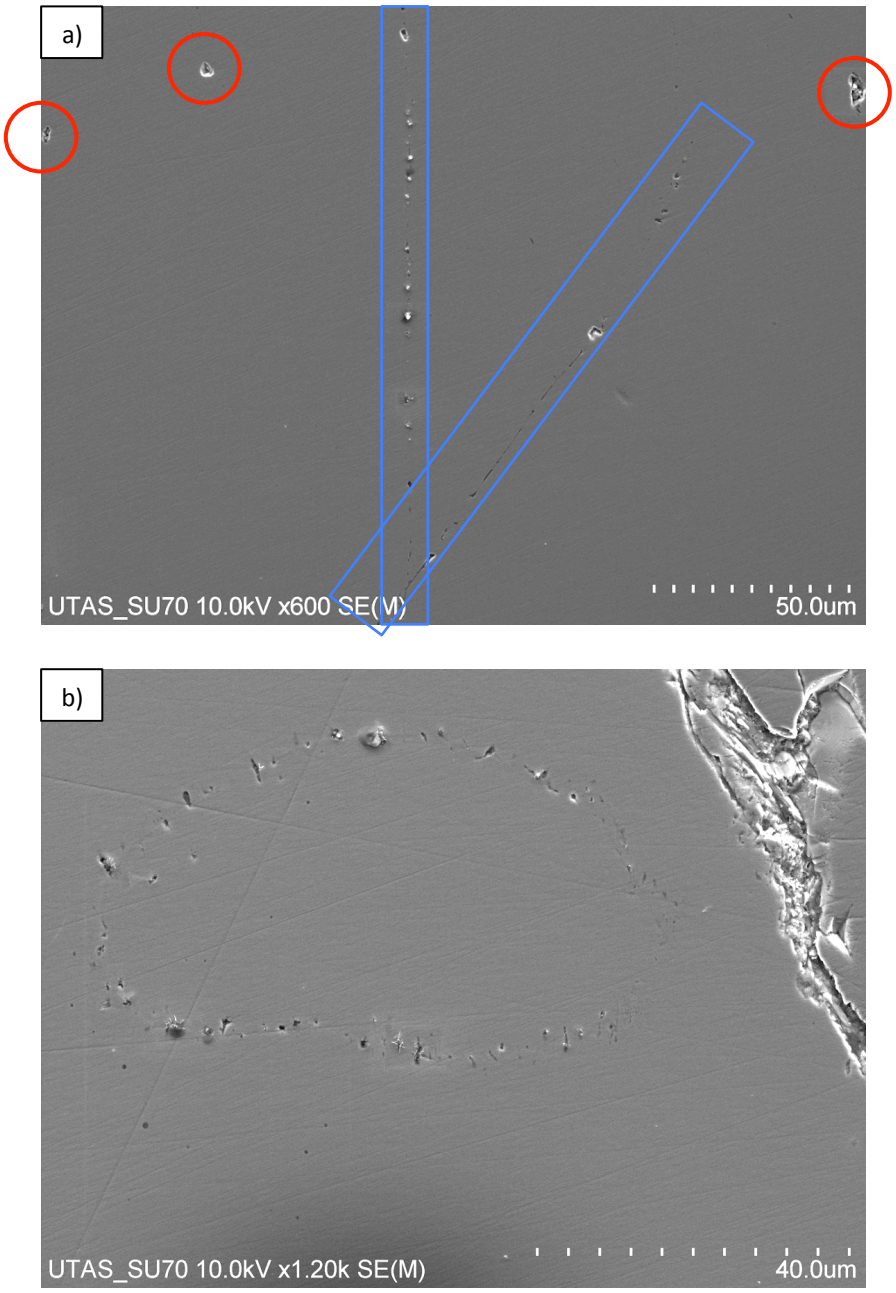

Figure 3DR. FESEM secondary electron images showing the distribution of primary and secondary inclusions in DU-1 ilmenite grains. a) Linear trails of secondary inclusions (blue boxes) and isolated primary inclusions (red circle); b) trail of secondary inclusions located along a sub-grain.

Figure 4DR

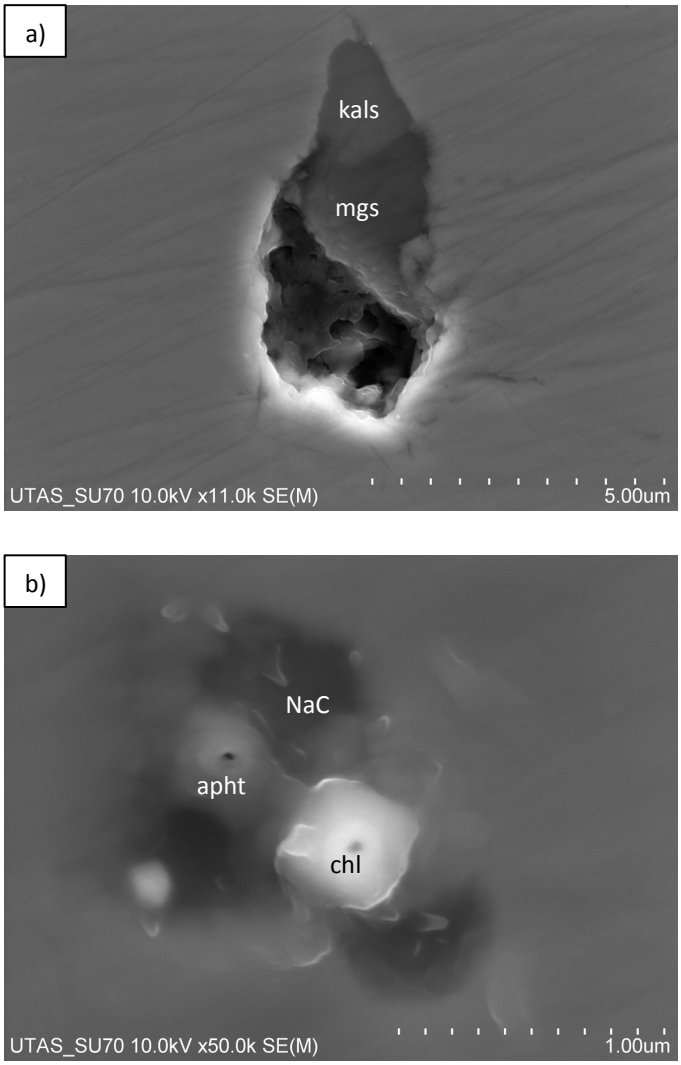

Figure 4DR. FESEM secondary electron images of primary (a) and secondary (b) inclusions in DU-1 ilmenite grains. a) Multiphase inclusion enriched in magnesite (mgs) and kalsilite (kals); the void is only partially filled with magnesite; b) decrepitated fluid inclusions with distinct crystals of chloride (solid solution of KCl, NaCl and $CaCl_2$), aphthitalite (apht) and less evident Na-rich carbonate.

Figure 5DR

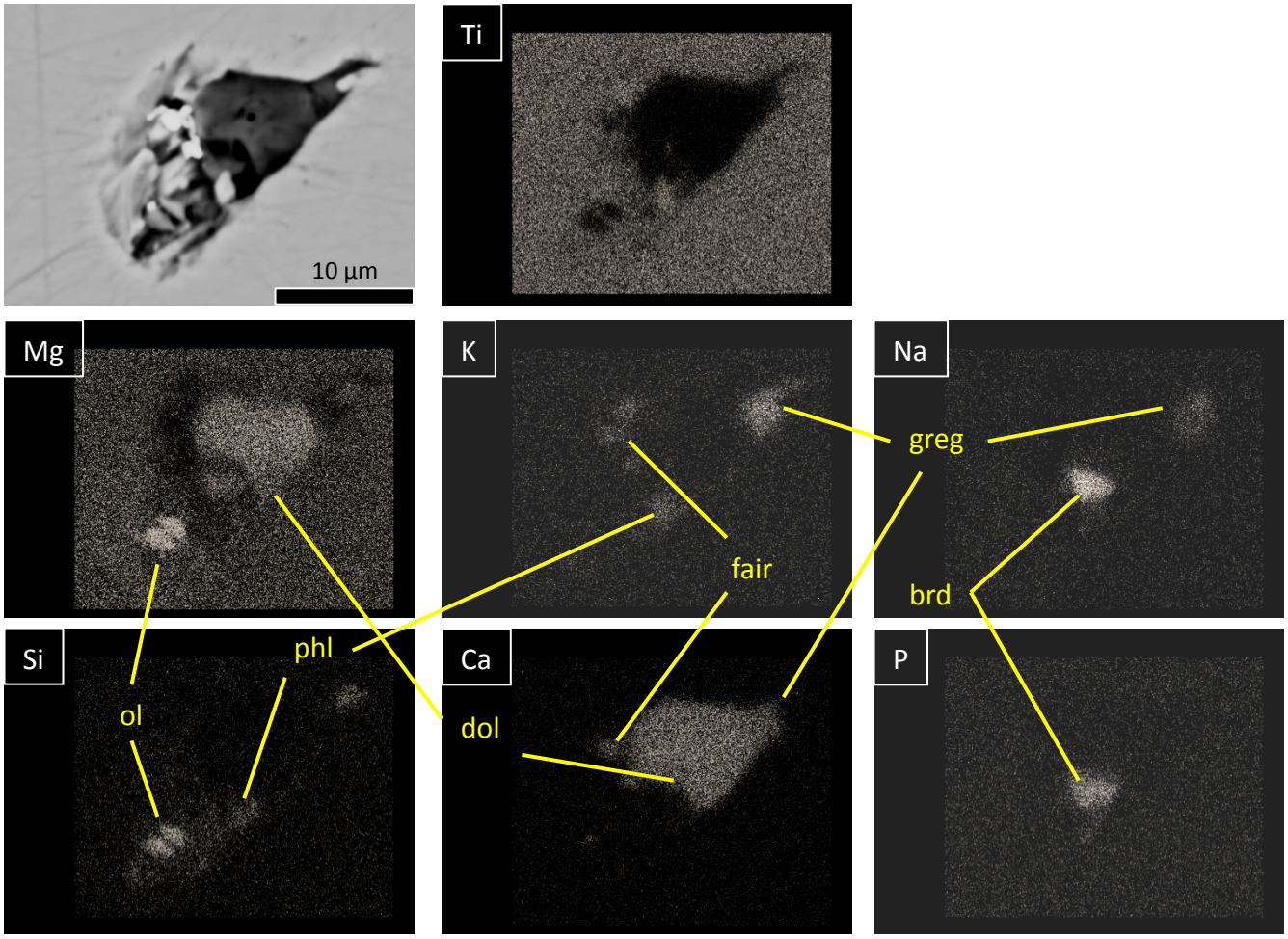

Figure 5DR. X-ray elemental map of carbonate-rich inclusion 2A-in1 in DU-1 ilmenite; the inclusion hosts abundant dolomite (dol) and subordinate bradleyite (brd), gregoryite (greg), fairchildite (fair), phlogopite (phl) and olivine (ol).

Figure 6DR

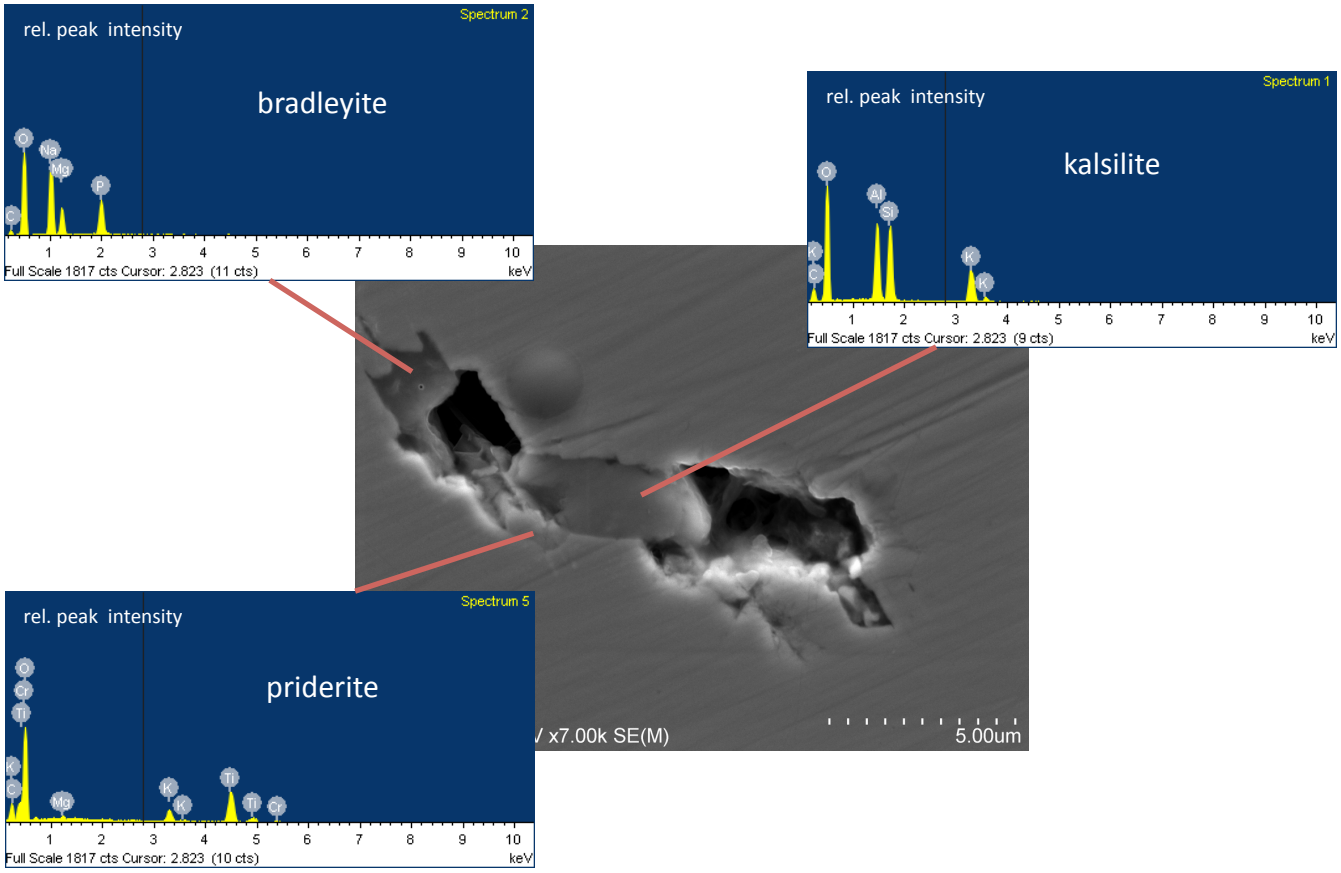

Figure 6DR. Secondary-electron image (from Fig.2c) and BSE spectra of primary inclusion 3F-m5 in DU-1 ilmenite. The other phases reported in Fig.1b (eitelite and Na-rich carbonate) have been identified through x-ray elemental maps.

Figure 7DR

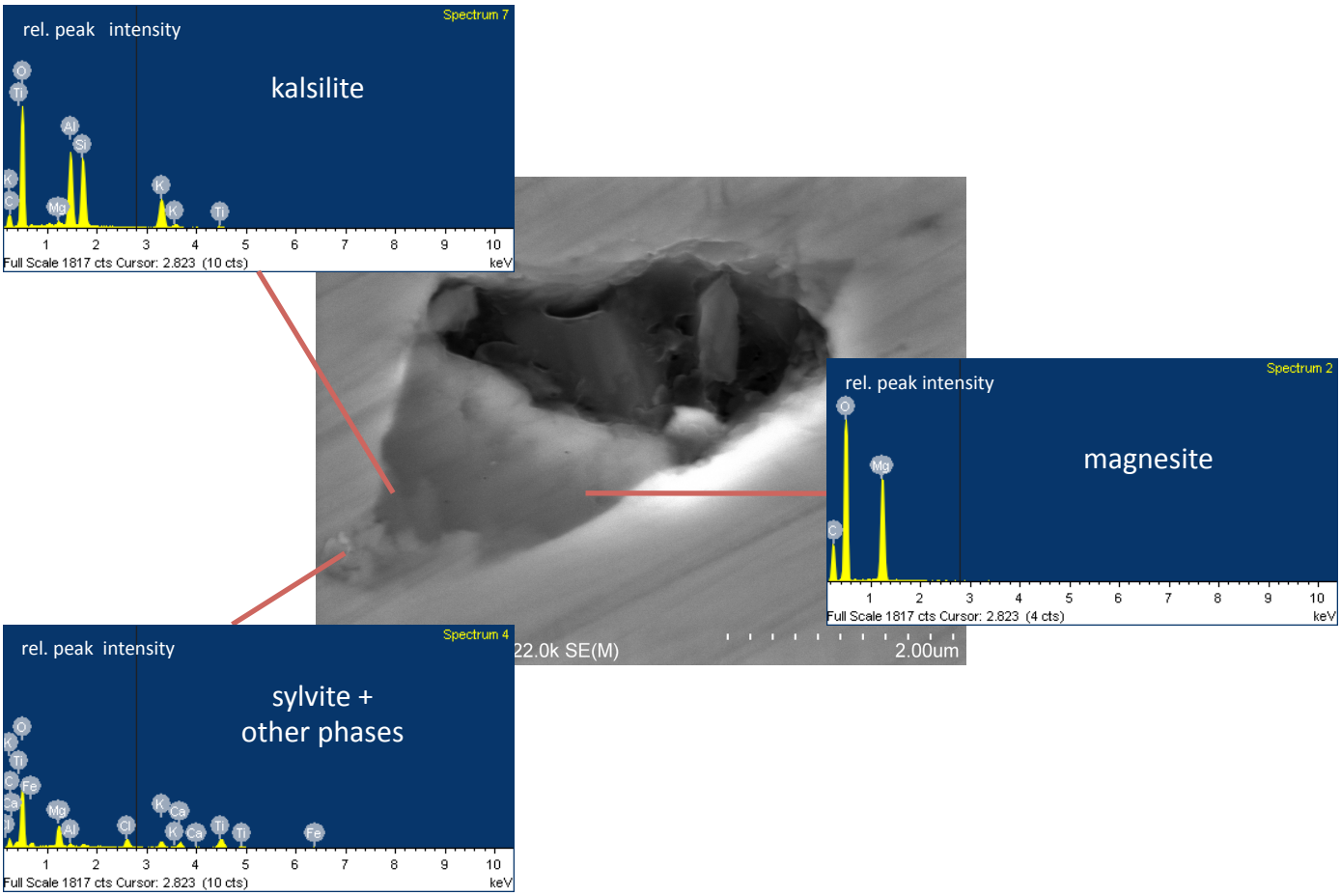

Figure 7DR. Secondary-electron image and BSE spectra of primary inclusion 3F-m3 in DU-1 ilmenite.

Figure 8DR

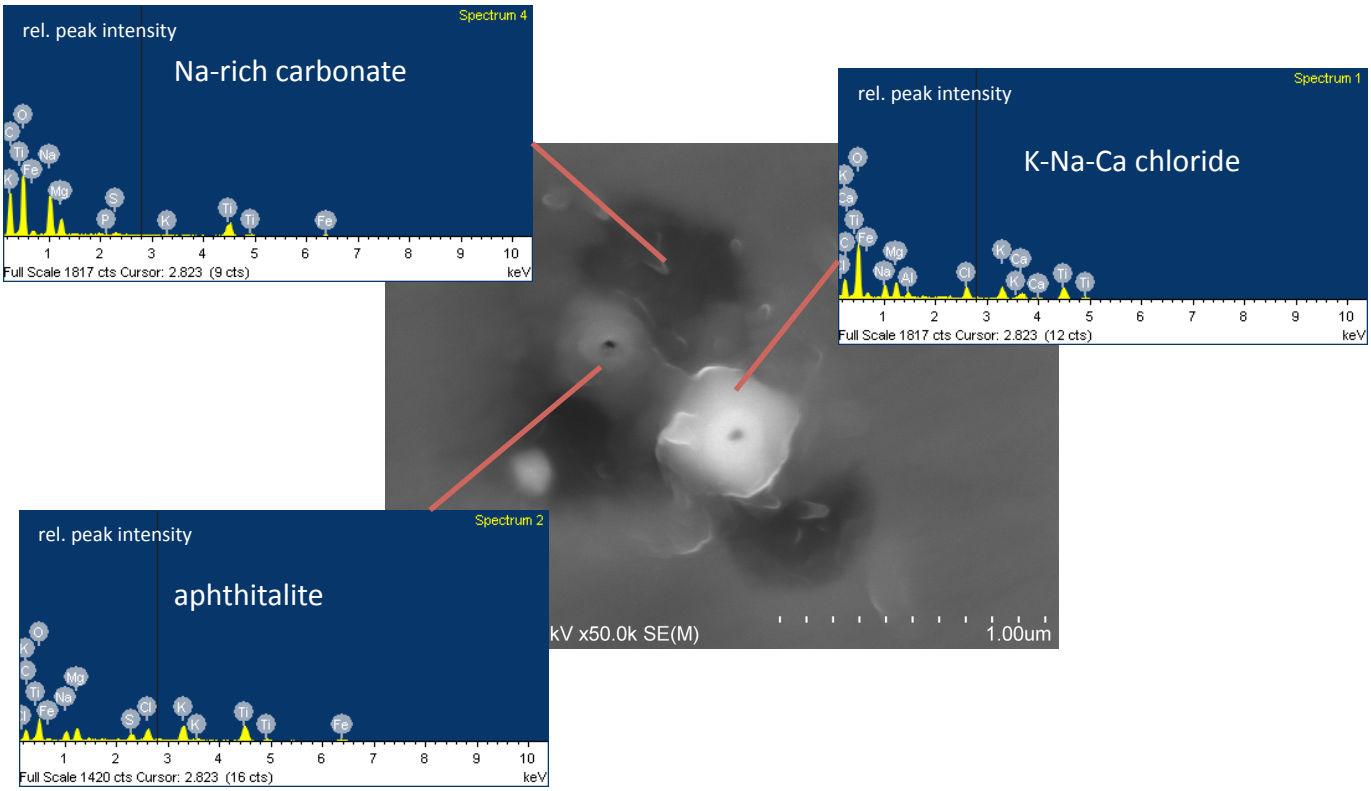

Figure 8DR. Secondary-electron image (from Fig.3bDR) and BSE spectra of secondary inclusion in DU-1 ilmenite. Note the small holes in chloride and aphthitalite due to electron beam spot. Each spectrum shows contribution by the surrounding phases because the x-ray excitation volume exceed the size of targeted grains.

Table 1DR. Geothermometry of the spinel harzburgite domains in polymict breccia DU-1

olivine	1C-Ol-11	1C-Ol-c27	1C-Ol-36	1F-Ol-c8	2D-Ol-c15	1C-Ol-11	1C-Ol-c27
orthopyroxene	1C-Opx-6	1C-Opx-13	1C-Opx-7	1C-Opx-8	1C-Opx-r26	1C-Opx-c29	1C-Opx-c30
spinel	1C-Spl-3	1C-Spl-4	1C-Spl-20	1C-Spl-1	1C-Spl-9	1C-Spl-1	1C-Spl-7
T (°C)	887	818	832	898	829	895	879

olivine	1C-Ol-36	1F-Ol-c8	2C-Ol	2D-Ol-c15			
orthopyroxene	1C-Opx-r35	2C-Opx-19	1C-Opx2-6	1C-Opx2-6	MIN	MAX	**MEDIAN**
spinel	1C-Spl-9	1C-Spl-3	1C-Spl-4	1C-Spl-20			
T (°C)	850	891	863	811	811	898	**863**

Thermometer based on Fe-Mg exchange between olivine and spinel (Ballhaus, C., Berry, R.F. and Green, D.H. (1991). Contr Mineral Petrol 107: 27-40)

Chemical composition of minerals used for thermometric calculations

Olivine

Label	1C-Ol-11	1C-Ol-c27	1C-Ol-36	1F-Ol-c8	2C-Ol	2D-Ol-c15
SiO_2	40.41	40.64	40.12	40.42	40.41	39.48
TiO_2	0.04	0.02	0.01	0.01	bdl	bdl
Al_2O_3	0.01	bdl	bdl	bdl	bdl	0.01
Cr_2O_3	0.04	bdl	0.04	0.06	0.02	0.03
FeO	7.79	7.79	7.82	7.73	8.69	7.46
MnO	0.14	0.15	0.10	0.15	0.13	0.09
MgO	51.60	51.29	51.45	50.75	49.88	52.38
NiO	0.33	0.37	0.50	0.40	0.40	0.42
CaO	0.02	0.02	0.01	0.01	0.01	0.03
Total	100.39	100.29	100.05	99.52	99.54	99.90

Orthopyroxene

Label	1C-Opx-6	1C-Opx-7	1C-Opx-8	1C-Opx-13	1C-Opx-r26	1C-Opx-c29	1C-Opx-c30	1C-Opx-r35	1C-Opx2-6	2C-Opx-19
SiO_2	57.63	58.18	58.26	57.85	57.15	57.41	57.10	57.58	56.76	57.84
TiO_2	0.05	0.07	0.06	0.06	0.08	0.07	0.07	0.06	0.08	0.07
Al_2O_3	0.41	0.41	0.40	0.40	0.38	0.43	0.42	0.41	0.41	0.36
Cr_2O_3	0.18	0.31	0.28	0.23	0.19	0.20	0.22	0.25	0.22	0.21
FeO	4.88	4.81	4.56	4.89	4.86	4.91	4.71	4.88	4.81	4.69
MnO	0.13	0.11	0.11	0.14	0.12	0.14	0.12	0.11	0.14	0.14
MgO	36.62	36.86	36.25	36.78	36.49	36.37	36.24	36.11	36.31	35.92
NiO	0.10	0.11	0.07	0.07	0.09	0.10	0.07	0.05	0.11	0.11
CaO	0.28	0.33	0.27	0.23	0.25	0.24	0.24	0.25	0.33	0.25
Na_2O	0.09	0.13	0.19	0.06	0.08	0.07	0.07	0.08	0.07	0.06
Total	100.37	101.32	100.45	100.70	99.68	99.93	99.27	99.78	99.24	99.64

Spinel

Label	1C-Spl-1	1C-Spl-3	1C-Spl-4	1C-Spl-7	1C-Spl-9	1C-Spl-20
SiO_2	0.01	0.02	0.02	bdl	0.02	0.01
TiO_2	1.66	1.57	1.67	1.66	1.71	1.77
Al_2O_3	6.79	6.84	6.68	6.33	6.53	6.62
Cr_2O_3	54.63	55.60	54.74	55.15	54.29	56.51
V_2O_3	0.32	0.26	0.26	0.28	0.30	0.32
Fe_2O_3*	8.06	7.96	7.97	7.73	8.29	6.17
FeO	16.54	16.85	18.69	16.98	17.83	18.26
MnO	0.13	0.15	0.14	0.12	0.14	0.13
MgO	11.42	11.46	10.22	11.00	10.64	10.63
NiO	0.17	0.14	0.14	0.17	0.16	0.12
ZnO	0.06	0.14	0.18	0.13	0.06	0.06
Total	99.79	101.01	100.72	99.56	99.96	100.61

bdl = below detection limit; *=calculated by stoichiometry

Table 2DR. Chemical composition of ilmenite lenses in polymict breccia DU-1 (major oxides and trace element)

	ilmenite core		**ilmenite rim**	
	33 analyses		13 analyses	
	average	st dev	average	st dev
TiO_2	55.31	0.40	54.98	0.57
Al_2O_3	0.33	0.05	0.22	0.10
Cr_2O_3	1.63	0.33	2.28	0.28
FeO	28.79	0.52	28.18	0.64
MnO	0.27	0.03	0.27	0.04
MgO	13.27	0.24	13.42	0.42
NiO	0.16	0.03	0.18	0.03
CaO	0.02	0.01	0.03	0.02
V_2O_3	0.25	0.08	0.23	0.07
Nb_2O_5	0.11	0.04	0.08	0.04
Total	100.14	0.49	99.90	0.51
Fe_2O_3 rec.	3.50	0.57	3.39	0.66
FeO rec.	25.56	0.64	25.05	0.78
Tot. rec.	99.85	0.45	99.62	0.45
Fe_2O_3 mol%	2.05	0.35	2.01	0.40
Mg#	45.1	0.8	45.9	1.3
	13 analyses		9 analyses	
	average	st dev	average	st dev
Si	1388	288	1227	274
V	1270	48	1321	127
Ni	1297	261	1496	195
Sr	0.41	0.02	0.49	0.11
Zr	563	88	633	106
Nb	729	137	548	104
Hf	20	4	24	4
Ta	117	27	101	17

Table 3DR. Mineralogy of carbonate-rich inclusions in DU-1 ilmenite

	phase	chemical formula	comment
carbonates	magnesite	$MgCO_3$	
	dolomite	$CaMg(CO_3)_2$	
	gregoryite/zemkorite	$(Na_{2,}K_{2,}Ca)CO_3$	
	fairchildite	$K_2Ca(CO_3)_2$	
	nahcolite/natrite	$NaHCO_3$ / $Na_2(CO_3)_3$	
	shortite/nyerereite	$Na_2Ca_2(CO_3)_3$ / $Na_2Ca(CO_3)_2$	
	eitelite	$Na_2Mg(CO_3)_2$	
silicates	olivine	$(Mg,Fe)_2SiO_4$	
	kalsilite	$KAlSiO_4$	
	phlogopite	$KMg_3(Si_3Al)O_{10}(F,OH)_2$	often F-rich
Fe-Ti oxides	priderite	$(K,Ba)(Ti,Fe^{3+})_8O_{16}$	Ba is very low
	freudenbergite	$Na_2Fe^{3+}{}_2Ti_6O_{16}$	
	rutile	TiO_2	
	pleonaste	$MgAl_2O_4$	
	magnetite-magnesioferrite	$(Fe,Mg)Fe^{3+}{}_2O_4$	
phosphates	apatite	$Ca_5(PO_4)_3(OH,F,Cl)$	often F-rich
	strontian apatite	$(Ca,Sr)_5(PO_4)_3F$	
	bradleyite	$Na_3Mg(PO_4)(CO_3)$	
chlorides	halite	$NaCl$	
	sylvite	KCl	
sulfides and sulfates	pentlandite	$(Fe, Ni)_9S_8$	
	pyrrhotite	$Fe_{(1-x)}S$ with x=0-0.17	
	djerfisherite	$K_6Na(Fe,Cu,Ni)_{25}S_{26}Cl$	Cu is very low
	celestine	$SrSO_4$	
	kogarkoite	$Na_3(SO_4)F$	
	aphthitalite	$(K,Na)_3Na(SO_4)_2$	

Table 4DR. Mineral assemblages of representative primary inclusions in DU-1 ilmenite

	label	size[1]	mineral phases (vol%[2])	void vol%[3]	comment
1)	DU1-2A-in1	18×9	magnesite(35), dolomite(35), pyrrhotite(5)	20	
2)	DU1-2D-dk	15×7	dolomite(60), priderite(30), phlogopite(10)	0	
3)	DU1-2D-in1	20×8	dolomite(50), bradleyite(10), olivine(10), gregoryite(10), phlogopite(10), fairchildite(5)	5	Fig.5DR
4)	DU1-2D-in5	9×6	magnesite(50), apatite(15), dolomite(15), olivine(5)	15	
5)	DU1-3C-in1	15×10	magnesite(25), dolomite(20), kalsilite(15), nahcolite/natrite (10)	30	
6)	DU1-3C-in4	15×12	dolomite(40), magnesite(20), kalsilite(10), bradleyite(5), Al-Mg-Fe spinel(5), priderite(5)	15	Fig.3
7)	DU1-3C-in9	12×5	magnesite(60), kalsilite(20), apatite(5)	15	
8)	DU1-3F-m1	15×7	magnesite(30), kalsilite(25), dolomite(10), apatite(<5)	30	Fig.2b
9)	DU1-3F-m3	15×8	magnesite(30), kalsilite(10), priderite(5), sylvite(<5)	50	Fig.7DR
10)	DU1-3F-m4	6×4	priderite(40),phlogopite (15), halite±sylvite(10), celestine(5), apatite(<5)	30	Fig.2d
11)	DU1-3F-m5	17×5	kalsilite(25), bradleyite(10), priderite(10), eitelite(5), nahcolite/natrite(5), djerfisherite(<5)	40	Fig.2c

[1]=maximum length × maximum width
[2]=based on visual estimate of x-ray elemental maps
[3]=based on visual estimate of secondary electron images

Table 5DR. Representative standardless chemical analyses (as 100 wt%) of minerals in the inclusions hosted by DU-1 ilmenite lenses

inclusion type	primary carbonate-rich	primary carbonate-rich	primary carbonate-rich	primary carbonate-rich	primary carbonate-rich	primary carbonate-rich
label	3F-mgs-6	3F-mgs-13	3F-dol-6	3F-kals-6	3F-kals-1	3C-Phl-1
phase	magnesite	magnesite	dol-mgs	kalsilite	kalsilite	phlogopite[1]
beam voltage	10 kV	10 kV	10 kV	10 kV	10 kV	15 kV
O	56.1	57.3	53.7	41.9	41.6	41.5
C	13.6	14.6	12.8			
Si				20.2	20.0	19.2
Ti						3.3
Al				16.3	16.0	6.8
Cr						
Mg	30.4	28.1	24.3			13.9
Fe						4.0
Ni						
Cu						
Ca			9.3			
Sr						
Na						
K				21.6	22.5	8.6
P						
S						
F						2.7
Cl						
SiO_2				43.2	42.8	40.8
TiO_2						5.4
Al_2O_3				30.8	30.2	12.8
Cr_2O_3						
MgO	50.3	46.6	40.2			22.8
FeO						5.2
CaO			13.0			
SrO						
Na_2O						
K_2O				26.0	27.0	10.3
P_2O_5						
CO_2	49.7	53.4	46.8			
SO_3						
F						2.7

[1]= contamination by the ilmenite host (i.e. anomalously high concentration of Ti and, secondarily Fe and Mg)

Note that the C amount of numerous analyses (i.e. phlogopite, freudenbergite, priderite, apatite, and partly bradleyite) is due to the graphite coating.

Some analyses suffered contribution by surrounding minerals (mainly the ilmenite host) because for grains smaller than ca. 2-3 μm x-rays generates back-scattered electrons in a volume larger than the targeted grain.

Table 4DR. continue

inclusion type	primary carbonate-rich	primary carbonate-rich	primary carbonate-rich	primary carbonate-rich	primary carbonate-rich	primary carbonate-rich
label	3F-phl-vol	3C-NaT-1	3F-freud-fr3	3C-KT-1	3F-prid-10	3F-prid-12
phase	phlogopite	freudenbergite	freudenbergite	priderite[2]	priderite[2]	priderite[2]
beam voltage	10 kV	15 kV	10 kV	15 kV	10 kV	10 kV
O	45.2	40.0	37.0	48.3	41.6	38.0
C	2.5				4.4	2.7
Si	17.7					
Ti	1.8	48.9	45.9	40.0	37.8	36.6
Al	6.1		0.6			
Cr				1.5		
Mg	12.9	1.6	1.7	1.4	1.2	1.0
Fe	6.7	3.8	7.6	3.5	6.5	14.8
Ni						
Cu						
Ca						
Sr						
Na		5.7	7.3		1.8	
K	6.8			5.3	6.8	7.0
P						
S						
F	0.3					
Cl						
SiO_2	37.8					
TiO_2	3.0	84.2	76.6	81.3	63.0	61.1
Al_2O_3	11.5		1.0			
Cr_2O_3				2.7		
MgO	21.4	2.7	2.8	2.8	1.9	1.6
FeO	8.6	5.1	9.8	5.4	8.4	19.0
CaO						
SrO						
Na_2O			9.8		2.4	
K_2O	8.2	8.0			8.2	8.4
P_2O_5				7.8		
CO_2	9.2				16.1	10.0
SO_3						
F	0.3					

[2]= Ba not estimated

Table 4DR. continue

inclusion type	primary carbonate-rich	primary carbonate-rich	primary carbonate-rich	primary carbonate-rich	primary carbonate-rich	primary carbonate-rich
label	3F-spl-4	3F-bradl-5	3F-Ap-13	3C-dj-1	3C-dj-2	3F-kog
phase	spinel[3]	bradleyite[4]	apatite[1]	djerfisherite	djerfisherite	kogarkoite[1]
beam voltage	10 kV	10 kV	10 kV	15 kV	15 kV	10 kV
O	25.8	43.0	44.9			36.8
C			6.1			
Si						
Ti	2.1		3.2			17.3
Al	0.6					
Cr						
Mg	8.7	10.3	1.9			4.3
Fe	61.7			39.0	41.0	
Ni				19.4	18.9	
Cu						
Ca			22.5			
Sr			3.2			
Na	1.1	25.4				17.5
K				8.7	8.8	
P		21.2	12.2			
S				31.6	29.8	10.9
F			6.0			13.2
Cl				1.2	1.6	
SiO_2						
TiO_2	3.5		5.3			28.8
Al_2O_3	1.2					
Cr_2O_3						
MgO	14.4	17.1	3.2			7.2
FeO	79.4					
CaO			31.5			
SrO			3.8			
Na_2O	1.5	34.3				23.6
K_2O						
P_2O_5		48.6	27.9			
CO_2			22.3			
SO_3						27.3
F			6.0			13.2

[1]= contamination by the ilmenite host (i.e. anomalously high concentration of Ti and, secondarily Fe and Mg)
[3]= Na due to contamination; [4]= C not measured

Table 4DR. continue

inclusion type	primary olivine-rich	primary olivine-rich	secondary	secondary	secondary
label	2D-Ol-1a	2D-Ol-3	3F-hal-expl2	3F-NaC-expl3	3F-bradl-expl4
phase	olivine	olivine	halite[1]	Na-rich carb.[1]	bradleyite[1]
beam voltage	15 kV	15 kV	10 kV	10 kV	10 kV
O	43.3	43.3	48.0	59.3	56.5
C			14.9	18.4	15.7
Si	19.4	19.5			
Ti			1.8	5.7	5.0
Al					
Cr					
Mg	28.0	28.1	0.8	1.1	3.5
Fe	9.3	9.0	3.8	6.9	
Ni					
Cu					
Ca					
Sr					
Na			14.2	7.2	8.8
K			0.9	0.5	1.0
P				0.3	4.4
S			0.3	0.4	
F					5.0
Cl			15.4		
SiO_2	41.6	41.8			
TiO_2				9.5	8.3
Al_2O_3					
Cr_2O_3					
MgO	46.5	46.6		1.8	5.8
FeO	11.9	11.6		8.9	
CaO					
SrO					
Na_2O				9.7	11.9
K_2O				0.7	1.1
P_2O_5				0.7	10.1
CO_2				67.6	57.7
SO_3				1.0	
F					5.0

[1]= contamination by the ilmenite host (i.e. anomalously high concentration of Ti and, secondarily Fe and Mg)