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# Pumpellyite veins in the metadolerite of the Frido Unit (Southern Apennines - Italy)

Maria T. Cristi Sansone<sup>1,\*</sup> and Giovanna Rizzo<sup>2</sup>

<sup>1</sup> Dipartimento di Scienze Geologiche, Università della Basilicata, 85100 Potenza, Italy <sup>2</sup> Dipartimento di Chimica, Università della Basilicata, 85100 Potenza, Italy \* Corresponding author: mariacristisansone@virgilio.it

# Abstract

This study focuses on pumpellyite veins cross-cutting the metadolerites of the Frido Unit Ophiolites (Southern Apennines - Italy). Pumpellyite occurs in the metadolerites as feltradiated aggregates or prism filling veins; metadolerites show mineral assemblages of the prehnite–pumpellyite and lawsonite-glaucophane metamorphic facies. Texture and composition of minerals in these veins are heterogeneous as revealed by SEM and EMPA characterisations, respectively. Either in the host rocks and in the veins, mineral compositions indicate a polyphase metamorphic evolution; these metadolerites recorded both the oceanfloor metamorphism and their emplacement within the Liguride accretionary wedge (HP/LT). In particular, the Fe and Mg amounts in the pumpellyite crystallised in the veins ranges between 0.216 - 0.585 and 0.293 - 0.466 apfu, respectively, whereas Al ranges between 2.518 - 2.802 apfu. These compositional variations reflect a similar metamorphic evolution of the host rock and pumpellyite veins of the Frido Unit.

Key words: Southern Apennines; Frido Unit; ophiolites; metadolerites; veins; pumpellyite.

# Introduction

The ophiolitic sequences outcropping in the Southern Apennines, are remnants of the Ligurian oceanic lithosphere pertaining to the Jurassic western Tethys. The Liguride Units include sequences characterized by high pressure/low temperature (hereafter HP/LT) (Lanzafame et al., 1979; Spadea, 1982) metamorphic overprint in the Frido Unit (Vezzani, 1969; 1970) and sequences lacking orogenic metamorphism in the North-Calabria Unit (Bonardi et al., 1988).

In this study, the veins hosted in the metadolerites of the Frido Unit (San Severino Lucano, Southern Apennines) has been investigated by optical microscopy, SEM, EMPA and XRF methods.

These metadolerites dikes intruded serpentinized peridotites and developed different textures, from intersertal to grano-xenoblastic to mylonitic with increasing metamorphic effects (Sansone et al., 2011). Metadolorites record various degrees of metamorphic re-crystallization: an ocean-floor metamorphism and an orogenic overprint (Sansone et al., 2011); the ocean-floor metamorphism often occured with metasomatic processes of rodingitization (typical of dike-cut serpentinite) and spilitization (Hellman and Henderson, 1977); rodingitization produces Carich basic rocks during serpentinization (Paulick et al., 2006; Sansone et al., 2011).

The different types of veins of the Frido Unit host both non-fibrous and fibrous minerals; their crystal assemblages mainly consist of pumpellyite and subordinately smaller amounts of other minerals, such as chlorite + prehnite + plagioclase + tremolite + actinolite + white mica + quartz + calcite + albite + epidote + glaucophane + lawsonite and + chrysotile. Here, previous results we extended on the metamorphic evolution of the Frido Unit by a careful investigation of the pumpellyite crystalchemical variations, mainly defined by the

Al-Fe<sup>3+</sup> substitution (Ishizuka, 1991), potentially able to constrain the metamorphic evolution in the zeolite, prehnite-pumpellyite, pumpellyite-

In general, Fe-pumpellyite crystallises under lower-grade metamorphic conditions than Alpumpellyite (Ernst et al., 1970; Coombs et al., 1976; Mével, 1981). In the Frido Unit Ophiolites, pumpellyite occurs in the metadolerites affected by ocean-floor rodingitic alteration (Sansone et al., 2011). Our aim is to relate the compositional variation of pumpellyite in metadolerites of the ophiolitic Frido Unit and its relations with respect the host rock composition and metamorphic conditions.

actinolite and blueschist facies.

#### **Ophiolites in the Southern Apennines**

The Southern Apennines fold-and-thrust mountain belt (Figure 1) formed between upper Oligocene and Quaternary (Patacca and Scandone, 2007 and references therein) as the



Figure 1. Geological sketch map of the Southern Apennines, modified after Mazzoli (1998).

result of the convergence between the African and European plates and simultaneous rollback SE-directed by the Ionian subduction (Cello and Mazzoli, 1999; Doglioni et al., 1999; Gueguen et al., 1998).

The Apenninic accretionary prism is issued from a northward subduction of an Alpine Tethys (Stampfli et al., 2002) sea-floor remnant, also known as western Tethys (Bortolotti and Principi, 2005), beneath European plate since Oligocene times.

The Liguride Units include both sequences characterized by HP/LT metamorphic overprint such as the Frido Unit (Vezzani, 1969) and sequences devoid of orogenic metamorphism such as the North Calabria Unit (Bonardi et al., 1988).

Ogniben (1969), Knott (1987; 1994), Monaco et al. (1991) and Tortorici et al. (2009) considered the Liguride Units as suture zones related to the closure of the western Tethys oceanic domain with the European plate (Calabride units) and the African plate. Knott (1987; 1994), Monaco et al. (1991), and Monaco Tortorici (1995)suggested and that metamorphism and deformation of these units took place in an accretionary wedge. In this setting, the Frido Unit has been interpreted as part of an accretionary wedge developed during the NW-oriented subduction of the Ligurian sector of the Tethyan Ocean since the Late Cretaceous age (Knott, 1987; 1994). According to Amodio-Morelli et al. (1976) and Bonardi et al. (1988), the metamorphic Liguride Units are analogous to elements of the eo-alpine chain with a European vergence later included in the Apennines Chain.

The ophiolitic rocks occurring in the very lowgrade Frido Unit (Vezzani, 1970) consist of serpentinites derived from a lherzolite mantle and subordinately harzburgites. The serpentinites are frequently associated to tectonic slices made of diabase and medium- to high-grade metamorphic rocks such as amphibolites, gneiss, granofels as well as meta- Fe-gabbros and metabasalts with relic pillow structures (Lanzafame et al., 1979; Spadea, 1979; 1982; 1994). Ophiolite sequences show a NE vergence in the Southern Apennines (Knott, 1987; 1994; Monaco, 1993).

# Sampling and analytical methods

Thirty-five samples of metadolerites from the Frido Unit were collected near the village of San Severino Lucano (Basilicata region, Southern Italy) (Figure 2).

Preliminary petrographic characterisation of all the thirty-five samples was carried out with an optical microscopy on oriented rock samples as a function of their foliations and lineations (Table 1).

Then, major element bulk composition was carried out on nineteen selected samples of metadolerites (Table 2), using a PHILIPS PW-1480 XRF spectrometer installed at the Department of Earth Sciences, University of Calabria; XRF data were corrected according to the protocols of Franzini et al. (1972; 1975) and Leoni and Saitta (1976).

The micro-chemical composition of minerals was obtained with a CAMECA SX-50 equipped with four WDS spectrometers (Tables 3, 6) and one EDS electron microprobe at the Istituto di Geoscienze e Georisorse (IGG) of the CNR (Padua, Italy); the analytical conditions were: 15 kV accelerating voltage and 15 nA beam current, count time 10 s at peak and 5 s at background. Natural and synthetic oxides and silicate minerals were used as standards. Data were treated using the classical PAP analytical procedure.

SEM-EDS analyses were performed at the Department of Earth Sciences, University of Calabria (Arcavacata di Rende, Cosenza, Italy), using a FEI/Philips scanning microscope with GENESIS-4000 EDAX X-ray system based on a Si/Li crystal detector.



Figure 2. Geological map of the Liguride Unit cropping out near Pollino Ridge (Sansone et al., 2011, modified after Monaco et al., 1995). (1) Alluvial deposits; (2) Pleistocene deposits; (3) Frido Unit; (4) Ophiolites; (5) Amphibolites, gneiss, and granofels; (6) North-Calabrian Unit; (7) Faults; (8) Stratigraphic limit.

We adopted the symbols for minerals recommended by Siivola and Schmid (2007), excepting for the following symbols: bl Am\*(blue amphibole), gr Am\*(green amphibole), br Am\*(brown amphibole), Olg\*(oligoclase), wht Mca\*(white mica) (see Table 1).

### **Results and Discussion**

# Petrography of the host rocks

The mineral assemblage in each metadolorite are reported in Table 1, the bulk chemical compositions of the 19 selected samples are reported in Table 2, whereas the composition of pyroxene, amphibole, plagioclase and pumpellyite phases are shown in Tables 3, 4, 5 and 6, respectively.

Metadolerites present different kinds of texture: intersertal, blastophitic, and a mylonitic fabric (Figure 3a, b). Opaque minerals, Fehydroxides, zircon, and spinel occur as accessory phases. Metadolerites are cut by veins (Figure 3c) filled with pumpellyite and  $\pm$  chlorite  $\pm$  prehnite  $\pm$  plagioclase  $\pm$  tremolite  $\pm$  actinolite  $\pm$  white mica  $\pm$  quartz  $\pm$  calcite  $\pm$  albite  $\pm$  epidote  $\pm$  lawsonite  $\pm$  glaucophane and  $\pm$  chrysotile.

The petrographical features allowed us to subdivide the metadolerites into three different types depending on oceanic and/or orogenic metamorphic mineral assemblages (Table 1):

1) Rocks with Pl and Cpx have an intersertal, blastophitic texture or a mylonitic fabric and at times a seriate texture (Type A). Some samples (Type A\*) have a high content of prehnite whose crystals occur in cataclastic-mylonitic bands (Sansone et al., 2011).

2) Rocks with Pl, Cpx, and brown Hbl show an intersertal or a blastophitic texture (Type B) (Sansone et al., 2011).

3) Rocks with Pl, Cpx, brown Hbl, and blue Amph have an intersertal or a blastophitic texture (Type C) (Sansone et al., 2011).

Original magmatic plagioclase (PL1) (Table 5) in the matrix is completely sericitized and

Sample	Magmatic assemblage	Metamorphic minerals	Туре
MC2	Pl1 + Cpx	$Chl \pm gr Am^{*} \pm Pmp \pm Qtz \pm Prh \pm wht Mca^{*}$	А
MC3	Pl1 + Cpx	Br Am* +Chl $\pm$ Pmp $\pm$ wht Mca* $\pm$ Qtz $\pm$ Prh $\pm$ gr Am*	В
MC6	Pl1 + Cpx	Br Am* +Chl $\pm$ Pmp $\pm$ wht Mc* $\pm$ Qtz $\pm$ Prh $\pm$ gr Am*	В
MC14	Pl1 + Cpx	$Chl \pm gr Am^{*} \pm Pmp \pm Qtz \pm Prh \pm wht Mca^{*}$	А
MC18	P11 + Cpx	$Chl \pm gr \ Am^{*} \pm Pmp \pm Qtz \pm Prh \pm wht \ Mca^{*}$	А
MC20	Pl1 + Cpx	$Chl \pm gr Am^{*} \pm Pmp \pm Qtz \pm Prh \pm wht Mca^{*}$	А
MC23	Pl1 + Cpx	Br Am* + Chl $\pm$ Pmp $\pm$ wht Mca* $\pm$ Qtz $\pm$ Prh $\pm$ gr Am*	В
MC25	Pl1 + Cpx	$Prh + Chl \pm Qtz \pm wht \ Mca^* \pm Pmp \pm Srp^*$	A*
MC29	P11 + Cpx	Br Am* + Chl $\pm$ Pmp $\pm$ wht Mca* $\pm$ Qtz $\pm$ Prh $\pm$ gr Am*	В
MC31	Pl1 + Cpx	$Br Am^{*} + Chl \pm Pmp \pm wht Mca^{*} \pm Qtz \pm Prh \pm gr Am^{*}$	В
MC32a	Pl1 + Cpx	Br Am* + Chl $\pm$ Pmp $\pm$ wht Mca* $\pm$ Qtz $\pm$ Prh $\pm$ gr Am*	В
MC33	Pl1 + Cpx	$Prh + Chl \pm Qtz \pm wht \ Mca^* \pm Pmp \pm Srp^*$	A*
MC35	Pl1 + Cpx	$Chl \pm gr Am^{*} \pm Pmp \pm Qtz \pm Prh \pm wht Mca^{*}$	
MC38	Pl1 + Cpx	$Chl \pm gr Am^{*} \pm Pmp \pm Qtz \pm Prh \pm wht Mca^{*}$	А
MC40	Pl1 + Cpx	Ab (Pl3) +Olg* (Pl2) +br Am* + Qtz + Chl + bl Am* $\pm$ Lws $\pm$ wht Mca* $\pm$ Prh	С
MC42	Pl1 + Cpx	Br Am* + Chl $\pm$ Pmp $\pm$ wht Mca* $\pm$ Qtz $\pm$ Prh $\pm$ gr Am*	В
MC45	P11 + Cpx	Br Am* +Chl $\pm$ Pmp $\pm$ wht Mca* $\pm$ Qtz $\pm$ Prh $\pm$ gr Am*	В
MC49	P11 + Cpx	$Chl \pm gr \ Am^{*} \pm Pmp \pm Qtz \pm Prh \pm wht \ Mca^{*}$	А
MC51	P11 + Cpx	Br Am* + Chl $\pm$ Pmp $\pm$ wht Mca* $\pm$ Qtz $\pm$ Prh $\pm$ gr Am*	В
MC59	P11 + Cpx	$Chl \pm gr Am^* \pm Pmp \pm Qtz \pm Prh \pm wht Mca^*$	А
MC60	P11 + Cpx	$Br Am^{*} + Chl \pm Pmp \pm wht Mca^{*} \pm Qtz \pm Prh \pm gr Am^{*}$	В
MC61	P11 + Cpx	Br Am* +Chl $\pm$ Pmp $\pm$ wht Mca* $\pm$ Qtz $\pm$ Prh $\pm$ gr Am*	В
MC62	P11 + Cpx	Br Am* +Chl $\pm$ Pmp $\pm$ wht Mc* $\pm$ Qtz $\pm$ Prh $\pm$ gr Am*	В
MC65	P11 + Cpx	$Br Am^{*} + Chl \pm Pmp \pm wht Mca^{*} \pm Qtz \pm Prh \pm gr Am^{*}$	В
MC68	Pl1 + Cpx	$Br Am^* + Chl \pm Pmp \pm wht Mca^* \pm Qtz \pm Prh \pm gr Am^*$	В
MC69	Pl1 + Cpx	Ab (Pl3) +Olg* (Pl2) +br Am* +Qtz +Chl +bl Am* $\pm$ Lws $\pm$ wht Mca* $\pm$ Prh	С
MC70	Pl1 + Cpx	Ab (Pl3) +Olg* (Pl2) +br Am* +Qtz +Chl +bl Am* ±Lws ±wht Mc* ±Prh	С
MC71	Pl1 + Cpx	$BrAm^{*}+Chl\pm Pmp\pm whtMca^{*}\pm Qtz\pm Prh\pm grAm^{*}$	В
MC72	Pl1 + Cpx	$BrAm^{*}+Chl\pm Pmp\pm whtMca^{*}\pm Qtz\pm Prh\pm grAm^{*}$	В
MC73	Pl1 + Cpx	$BrAm^{*}+Chl\pm Pmp\pm whtMca^{*}\pm Qtz\pm Prh\pm grAm^{*}$	В
MC74	Pl1 + Cpx	$Chl \pm gr \ Am^{*} \pm Pmp \pm Qtz \pm Prh \pm wht \ Mca^{*}$	А
MC75	Pl1 + Cpx	$BrAm^{*}+Chl\pm Pmp\pm whtMca^{*}\pm Qtz\pm Prh\pm grAm^{*}$	В
MC76	Pl1 + Cpx	$Br Am^{\boldsymbol{*}} + Chl \pm Pmp \pm wht Mca^{\boldsymbol{*}} \pm Qtz \pm Prh \pm gr Am^{\boldsymbol{*}}$	В
MC77	Pl1 + Cpx	Ab (Pl3) + Olg* (Pl2) + br Am* + Qtz + Chl + bl Am* ± Lws ± wht Mca* ± Prh	С
MC78	P11 + Cpx	$Prh + Chl \pm Qtz \pm wht \ Mca^* \pm Pmp \pm Srp^*$	A*

Table 1. Magmatic and metamorphic assemblages of the metadolerites.

bl Am\*(blue amphibole), gr Am\*(green amphibole), br Am\*(brown amphibole), Olg\*(oligoclase), wht Mca\*(white mica)

of metadolerites.
chemistry
Bulk rock
Table 2.

Sample	MC51	MC49	MC45	MC42	MC40 ]	MC38 ]	MC35	MC33 M	IC32A ]	MC31	MC29 ]	MC25	MC23	MC20 ]	MC18	MC14	MC6	MC3	MC2
Oxides (wt %)																			
SiO <sub>2</sub>	39.59	39.03	43.41	37.87	44.98	37.70	38.95	30.96	40.95	39.74	39.63	31.80	38.32	37.66	41.31	37.65	46.97	38.25	37.75
$TiO_2$	1.81	1.67	1.45	1.62	1.4	1.01	0.83	0.80	1.08	1.05	1.07	0.66	1.73	1.74	0.97	1.00	1.48	2.27	1.61
$Al_2O_3$	14.38	14.42	15.7	16.43	16.98	15.4	18.4	17.78	14.91	14.88	14.06	13.97	14.2	13.19	15.81	15.93	16.81	14.46	13.18
$\mathrm{Fe_2O_3}$	11.05	11.18	9.53	9.77	9.30	10.27	7.00	8.44	9.82	9.28	9.29	9.33	10.85	10.42	9.66	10.49	9.36	11.24	10.01
MnO	0.17	0.17	0.15	0.22	0.14	0.20	0.15	0.21	0.17	0.20	0.19	0.31	0.15	0.15	0.14	0.18	0.13	0.19	0.18
MgO	11.08	11.87	10.25	10.57	9.26	13.69	10.23	26.83	13.52	13.97	15.1	30.95	10.73	15.26	14.87	13.45	9.08	11.56	16.00
CaO	16.81	16.19	12.83	17.65	9.90	16.36	18.5	5.80	13.61	15.30	15.55	2.86	19.26	15.97	8.88	15.33	7.58	16.46	15.65
Na <sub>2</sub> O	0.46	0.44	1.85	0.48	2.45	0.10	0.19	n.d.	1.03	0.39	0.19	n.d.	0.16	0.16	2.11	0.32	3.47	0.40	0.14
$K_2O$	0.03	0.02	0.75	0.02	1.48	n.d.	n.d.	n.d.	0.23	0.12	n.d.	n.d.	n.d.	n.d.	0.40	n.d.	1.36	0.03	n.d.
$P_2O_5$	0.24	0.19	0.17	0.21	0.18	0.08	0.09	0.08	0.11	0.11	0.12	0.05	0.22	0.24	0.08	0.09	0.17	0.35	0.23
IOI	4.38	4.82	3.91	5.15	3.94	5.19	5.66	9.11	4.57	4.97	4.79	10.07	4.38	5.22	5.78	5.57	3.59	4.79	5.24
n.d. not-d	etected																		

Sample	MC40	MC40	MC40	MC40
N. Analysis	11	12	13	14
Oxides (wt%)	rim	core	core	rim
SiO <sub>2</sub>	51.89	48.74	51.30	50.96
TiO <sub>2</sub>	1.21	1.67	1.03	1.20
$Al_2O_3$	4.27	6.70	4.76	4.77
Cr <sub>2</sub> O <sub>3</sub>	0.04	0.18	0.75	0.68
FeO tot	6.55	7.31	5.31	5.36
MnO	0.13	0.16	0.13	0.22
MgO	15.51	14.72	15.35	15.77
CaO	21.34	18.83	21.24	21.42
Na <sub>2</sub> O	0.83	1.11	0.71	0.86
K <sub>2</sub> O	0.03	0.01	n.d.	0.02
Sum	101.79	99.41	100.58	101.26
Si	1.880	1.811	1.873	1.854
Al <sup>IV</sup>	0.120	0.189	0.127	0.146
Al <sup>VI</sup>	0.062	0.104	0.078	0.058
Fe <sup>3+</sup>	0.074	0.099	0.031	0.096
Cr	0.001	0.005	0.022	0.019
Ti	0.033	0.047	0.028	0.033
Fe <sup>2+</sup>	0.123	0.126	0.131	0.065
Mn	0.004	0.005	0.004	0.007
Mg	0.838	0.815	0.835	0.855
Ca	0.829	0.750	0.831	0.835
Na	0.058	0.080	0.050	0.061
K	0.001	0.001	0.000	0.001
Sum	4.024	4.031	4.010	4.031
Mol %				
Wo	43.025	39.984	44.145	43.494
En	43.502	43.485	44.395	44.565
Fs	10.451	12.275	8.799	8.771
Aeg	3.022	4.255	2.661	3.171
Species	Aug-Di	Aug	Aug	Aug-Di

Table 3. Representative analyses of clinopyroxene.

n.d. not-detected

mple · · ·	MC40	MC40	MC40	MC40 _	MC40	MC40	MC40	MC40	MC40	MC40	MC40	MC40	MC40
alysis	c	S	9	2	27	28	29	43	44	45	46	4	6
es ()	rim	core	core	rim	rim	core	rim	rim	core	core	rim	rim/br Am*	rim/br Am*
	44.02	45.93	45.70	52.99	49.98	51.03	50.42	41.63	45.43	46.42	44.42	56.24	54.27
	3.38	2.90	2.79	0.62	0.43	0.34	0.35	0.58	0.69	0.29	0.42	0.08	0.12
$\mathbf{D}_3$	9.54	8.43	8.60	2.96	69.9	5.36	6.64	13.08	10.30	9.07	12.01	6.37	6.30
J <sub>3</sub>	n.d.	n.d.	0.08	n.d.	0.06	n.d.	0.01	n.d.	0.02	n.d.	n.d.	n.d.	0.05
tot	13.76	13.79	13.91	12.30	12.37	12.87	10.23	14.22	14.01	14.42	12.61	15.60	15.87
0	0.15	0.32	0.38	0.21	0.34	0.36	0.28	0.14	0.14	0.19	0.27	n.d.	0.19
0	12.82	13.81	13.92	15.30	17.38	17.52	17.55	12.76	12.96	14.75	13.72	9.95	11.08
	10.25	10.14	10.19	12.15	9.84	8.98	10.97	10.76	11.49	10.20	11.16	2.50	4.97
0	2.90	2.55	2.61	0.96	1.87	1.53	1.78	2.62	2.51	1.60	2.71	5.62	4.74
~	0.38	0.51	0.56	0.16	0.33	0.36	0.25	0.48	0.42	0.28	0.42	0.06	0.11
-	97.19	98.37	98.74	97.65	99.27	98.35	98.47	96.27	97.96	97.22	97.73	96.42	69.76
	6.464	6.602	6.550	7.636	6.857	66.9	7.013	6.115	6.617	6.593	6.408	7.975	7.688
	1.536	1.398	1.450	0.364	1.081	0.866	0.987	1.885	1.383	1.407	1.592	0.025	0.312
	0.114	0.029	0.002	0.138	0.000	0.000	0.100	0.379	0.385	0.110	0.450	1.039	0.739
	0.554	0.816	0.883	0.041	1.418	1.476	1.019	1.158	0.473	1.638	0.766	0.654	0.711
	0.373	0.314	0.301	0.067	0.044	0.035	0.036	0.064	0.076	0.031	0.046	0.009	0.013
	0.000	0.000	0.009	0.000	0.006	0.000	0.001	0.000	0.002	0.000	0.000	0.000	0.005
	1.135	0.841	0.785	1.440	0.000	0.000	0.171	0.588	1.234	0.075	0.755	1.195	1.169
	0.019	0.039	0.046	0.026	0.040	0.042	0.033	0.017	0.017	0.022	0.033	0.000	0.023
	2.806	2.960	2.974	3.287	3.554	3.582	3.640	2.793	2.815	3.123	2.950	2.104	2.340
	1.612	1.561	1.564	1.876	1.447	1.319	1.635	1.693	1.793	1.552	1.725	0.380	0.755
	0.827	0.710	0.724	0.269	0.496	0.407	0.481	0.745	0.708	0.441	0.757	1.544	1.302
	0.071	0.094	0.102	0.029	0.057	0.062	0.045	0.089	0.079	0.050	0.078	0.011	0.020
_	15.510	15.364	15.391	15.174	15.000	14.788	15.160	15.527	15.579	15.044	15.560	14.935	15.077
cies	$\mathrm{T}_{\mathrm{S}}$	Mg-Hbl	Mg-Hbl	Act	Mg-Hbl	Mg-Hbl	Mg-Hbl	$\mathrm{T}_{\mathrm{S}}$	Ed	Mg-Hbl	$\mathrm{T}_{\mathrm{S}}$	Glf	Win

Table 4. Representative analyses of amphibole.

n.d. not-detected

Sample	MC40	MC40	MC40
N. Analysis	40	41	42
Oxides (wt%)	rim	core	rim
SiO <sub>2</sub>	69.50	68.67	69.05
TiO <sub>2</sub>	n.d.	n.d.	0.04
Al <sub>2</sub> O3	19.88	19.76	19.70
Cr <sub>2</sub> O3	0.01	n.d.	n.d.
FeO Tot	0.26	0.96	0.19
MnO	n.d.	0.03	n.d.
MgO	0.03	0.66	0.08
CaO	0.41	0.07	0.61
Na <sub>2</sub> O	9.96	10.70	11.52
K <sub>2</sub> O	0.04	0.03	0.04
Sum	100.07	100.88	101.24
Si	12.057	11.973	11.948
Al	4.063	4.06	4.017
Fe <sup>2+</sup>	0.037	0.14	0.028
Ca	0.076	0.013	0.113
Na	3.349	3.616	3.863
К	0.008	0.007	0.009
Sum	19.59	19.809	19.979
An	2.218	0.353	2.844
Ab	97.546	99.451	96.927
Or	0.235	0.196	0.23

Table 5. Representative analyses of plagioclase.

n.d. not-detected

saussuritized. Crystals display an intersertal texture and are pseudomorphosed by pumpellyite, prehnite, chlorite, and epidote.

Clinopyroxene (augite) (Table 3) is often twinned and shows wavy extinction. Chlorite, white mica, and green amphibole replace clinopyroxene. Minerals such as titanite, green and brown amphibole form coronas around clinopyroxene, indicative of ocean-floor metamorphism. Brown amphibole ( $c/\gamma$  36°), sometimes twinned, also occurs in the metadolerites as isolated idioblasts; these minerals have rims of green amphiboles, opaque minerals, titanite, and orogenic blue amphibole.

Two types of green amphibole with different compositions are recognized: 1) a green hornblende occurs as single crystals and/or rims and coronas around brown hornblende or pyroxenes; 2) a pale green amphibole occurs in the veins or replaces clinopyroxene and has an actinolite composition (Table 4).

Blue amphibole forms rims and coronas after brown and/or green hornblende, and locally after clinopyroxene.

Chlorite occurs as fan-felt-radiated aggregates, sometimes overgrowing clinopyroxene or replacing amphibole.

Quartz occurs subordinately in these rocks and is found on the border of the clinopyroxene crystals in agreement with Cortesogno et al. (1994). Quartz shows dynamic recrystallization, deformation bands and sub-grain boundaries.

Pumpellyite aggregates are pseudomorph after plagioclase. Prehnite occurs as ovoid-fan-radiated aggregates, and shows a ductile deformation. White mica replaces clinopyroxene crystals.

# Petrography of the veins

Veins are heterogeneous in texture and mineralogical composition, and show brittle (Figure 4) to ductile deformation (Figure 5). They are generally a few millimetres thick, and can be isolated or organised in closely spaced sets. Vein morphology ranges from planar, sinuous to irregular, with orientation that is slightly discordant to the metadolerite foliation, while minerals in the veins lack a preferred orientation. This indicates a syn- to postkinematic vein formation with respect to the main foliation.

Veins are principally made of pumpellyite and other minerals such as  $\pm$  chlorite  $\pm$  prehnite  $\pm$ plagioclase  $\pm$  tremolite-actinolite  $\pm$  white mica  $\pm$ quartz  $\pm$  calcite  $\pm$  albite  $\pm$  epidote  $\pm$  lawsonite  $\pm$ glaucophane and  $\pm$  chrysotile.

Sample	MC40	MC81	MC77	MC77	MC77	MC77	MC70	MC70						
N. Analysis	51	54	55	56	57	58	59	220	49	52	56	57	168	170
Oxides (wt%)	Veins													
SiO <sub>2</sub>	37.76	38.27	37.21	38.18	38.55	37.70	38.08	37.51	37.51	37.25	37.31	37.33	38.22	37.70
$TiO_2$	0.13	0.07	0.05	n.d.	0.03	0.01	0.05	0.07	0.13	0.05	0.04	0.07	0.07	0.06
$Al_2O_3$	25.12	24.51	23.67	26.08	24.22	23.97	25.21	24.41	23.18	22.68	24.96	24.07	25.74	26.04
$Cr_2O_3$	n.d.	0.04	0.01	n.d.	n.d.	0.08	0.05	n.d.	0.02	0.01	0.03	0.06	0.02	n.d.
FeO tot	4.47	4.39	5.14	3.95	4.36	5.05	2.92	4.27	6.04	7.43	3.38	5.49	2.83	3.18
MnO	0.07	0.11	0.18	0.07	0.08	0.18	0.04	0.08	0.10	0.10	0.23	0.11	0.21	0.24
MgO	2.64	2.92	2.80	2.16	3.15	2.68	3.17	2.89	2.45	2.54	2.98	2.31	3.43	3.17
CaO	23.31	23.03	23.49	23.26	23.10	23.15	23.53	22.46	22.06	22.22	22.22	22.35	22.20	22.52
$Na_2O$	0.04	0.06	0.08	0.01	0.05	0.05	0.06	0.06	0.03	0.04	0.07	0.03	0.09	0.08
$K_2O$	0.02	0.04	n.d.	n.d.	0.01	0.01	0.02	n.d.	n.d.	0.01	n.d.	n.d.	n.d.	n.d.
Sum	93.54	93.44	92.63	93.72	93.54	92.88	93.13	91.76	91.52	92.33	91.22	91.82	92.81	92.98
Si	3.459	3.504	3.468	3.472	3.524	3.493	3.477	3.493	3.532	3.509	3.478	3.496	3.484	3.443
Ti	0.009	0.005	0.003	0.000	0.002	0.001	0.003	0.005	0.009	0.004	0.003	0.005	0.005	0.004
Al	2.711	2.644	2.600	2.795	2.608	2.617	2.713	2.679	2.573	2.518	2.742	2.657	2.765	2.802
Cr	0.000	0.004	0.001	0.000	0.000	0.008	0.005	0.000	0.002	0.002	0.003	0.006	0.002	0.000
$\mathrm{Fe}^{2+}$	0.342	0.336	0.401	0.301	0.333	0.391	0.223	0.332	0.476	0.585	0.263	0.430	0.216	0.243
Mn	0.005	0.009	0.014	0.005	0.006	0.014	0.003	0.007	0.008	0.008	0.018	0.009	0.016	0.018
Mg	0.361	0.399	0.389	0.293	0.430	0.370	0.431	0.401	0.344	0.357	0.414	0.323	0.466	0.432
Са	2.287	2.259	2.345	2.265	2.262	2.298	2.302	2.241	2.226	2.242	2.219	2.243	2.168	2.203
Na	0.006	0.011	0.014	0.002	0.008	0.010	0.011	0.011	0.006	0.007	0.013	0.005	0.016	0.014
K	0.002	0.005	0.000	0.000	0.001	0.002	0.003	0.000	0.000	0.001	0.000	0.000	0.000	0.000
Sum	9.181	9.176	9.236	9.132	9.174	9.204	9.170	9.168	9.176	9.233	9.154	9.173	9.137	9.159
n.d. not-detec	sted													

Table 6. Representative analyses of pumpellyite.

Sample N. Analysis	MC77 64 Pseudo- mombais	MC77 78 Pseudo-	MC77 79 Pseudo-	MC77 83 Pseudo-	MC77 49 Pseudo-	MC77 101 Pseudo-	MC77 102 Pseudo-	MC77 115 Pseudo-	MC70 161 Pseudo-
Oxides (wt%)	after Pl	after Pl	after Pl	after Pl	after PI	after Pl	after Pl	after Pl	after PI
SiO <sub>2</sub>	37.64	38.33	37.72	41.00	37.85	37.82	37.98	38.40	38.05
$TiO_2$	0.08	0.06	0.06	0.04	0.06	0.02	0.03	0.03	0.10
$Al_2O_3$	25.04	25.12	25.40	24.37	25.02	25.58	25.63	25.31	25.36
$Cr_2O_3$	n.d.	n.d.	n.d.	n.d.	0.02	0.04	n.d.	n.d.	0.01
FeO tot	4.11	4.09	3.24	4.16	3.43	3.57	3.57	3.42	2.95
MnO	0.23	0.20	0.25	0.29	0.23	0.21	0.20	0.26	0.27
MgO	2.77	2.70	2.86	2.82	2.89	2.89	2.82	2.76	3.23
CaO	22.29	22.03	22.31	21.03	22.01	22.46	22.51	22.20	21.79
$Na_2O$	0.08	0.13	0.07	0.91	0.14	0.08	0.08	0.19	0.06
$K_2O$	n.d.	0.02	0.02	0.26	n.d.	n.d.	0.01	0.01	n.d.
Sum	92.24	92.68	91.94	94.89	91.64	92.68	92.82	92.58	91.83
Si	3.481	3.519	3.483	3.664	3.506	3.471	3.478	3.519	3.504
Ti	0.005	0.004	0.004	0.002	0.004	0.002	0.002	0.002	0.007
Al	2.729	2.718	2.764	2.567	2.732	2.766	2.766	2.734	2.753
Cr	0.000	0.000	0.000	0.000	0.002	0.004	0.000	0.000	0.001
$\mathrm{F}\mathrm{e}^{2+}$	0.318	0.314	0.250	0.311	0.266	0.274	0.273	0.262	0.227
Mn	0.018	0.016	0.020	0.022	0.018	0.017	0.015	0.020	0.021
Mg	0.382	0.370	0.394	0.376	0.399	0.395	0.385	0.377	0.443
Са	2.208	2.167	2.207	2.014	2.184	2.208	2.209	2.180	2.150
Na	0.015	0.023	0.013	0.158	0.024	0.014	0.014	0.033	0.010
K	0.000	0.003	0.002	0.030	0.000	0.000	0.001	0.001	0.001
Sum	9.157	9.132	9.138	9.144	9.136	9.152	9.144	9.129	9.118
n.d. not-detected									

Table 6. Continued ...

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Figure 3. Textural features of metadolerites. (a) Intersertal texture; (b) blastophitic and mylonitic fabric; (c) veinscutting metadolerites. Plane-polarized light.

Pumpellyite occurs as felt-radiated aggregates and single isolated prismatic to acicular crystals, either in monomineralic veins (Figure 4) or in association with other minerals. The crystals show an undulose extinction and a ductile deformation. Pumpellyite is generally colourless, or shows a pale green-to-pale yellow grey and brown colour. In other cases they show a marked pleochroism from green to bluish green, displaying a typical birefringence colour in cross-polarized light, sometimes they show an anomalous interference colour. Chlorite flakes show an undulose extinction and occur as fanfelt-radiating aggregates (Figure 5).

Prehnite shows a ductile deformation and is usually found in association with chrysotile (Figure 6).

Plagioclase crystals have a granoblastic texture and show deformation twins as well as an undulose extinction. Plagioclase crystals have oligoclase (PL2) and albite (PL3) compositions.

Amphibole of actinolite composition occurs as nematoblasts and shows a ductile deformation. Isolated tiny crystals of blue amphibole may also occur in the veins. White mica occurs only as tiny flakes in the veins. Quartz shows undulose extinction and sometimes deformation bands, subgrain boundaries or evidence of new grain



Figure 4. Pumpellyite vein displaced by microfault. Plane-polarized light.

crystallization and deformation recovery.

Calcite shows deformation twinning. Epidote mainly occurs as subidiomorphic crystals in plagioclase, chlorite, and actinolite crystals; they show both pale green and brown colours, and textures resulting from ductile deformation. Lawsonite occurs as small colourless crystals (Figure 7) and is associated to chlorite and pumpellyite. As already observed by Sansone et al. (2011), glaucophane forms rims developed at the expense of brown amphibole or as single tiny crystals. Chrysotile has a fibrous stretched subidiomorphic habit; it is colourless and associated to prehnite. Zircon, phosphates and sulphides are also enclosed in veins with



Figure 5. Vein with chlorite and amphibole. Plane-polarized light.



Figure 6. Prehnite vein. Crossed polars.

pumpellyite and chlorite.

Small idiomorphic crystals of zircon, and xenomorphs of apatite and chalcopyrite may also be associated to pumpellyite and chlorite in the veins.

# Composition of rocks and minerals

The metadolerite samples show N-MORB patterns (Sansone, 2010a; Sansone et al., 2011). The general inverse correlation between CaO and Na<sub>2</sub>O (Table 2) suggests that the Ca-rich metadolerites were affected by rodingitic alteration, whereas Na-rich metadolerites suffered spilitic alteration, in agreement with ocean-floor and metasomatic metamorphic processes (Hart, 1970; Rollinson, 1993) and with previous results (Sansone et al., 2011).

In the metadolerites, the microstructures of clinopyroxenes are indicative of a relict magmatic phase, whereas those of amphibole and plagioclase phases of metamorphic and metasomatic processes (Sansone et al., 2011).

The structural formulas of clinopyroxenes (Table 3), calculated on the basis of 6 oxygens according to Morimoto (1988; 1989), show a progressive decreasing of augite from cores to rims; the diopsidic component follows an inverse trend.

The structural formulas of amphiboles (Table 4), based on 23 oxygens, encompasses different



Figure 7. Lawsonite into vein. Plane-polarized light.

amphibole sub-groups, i.e. calcic, sodic and sodic–calcic (Leake et al., 1997; 2004). Green amphiboles ranges among edenite, actinolite, magnesiohornblende and tschermakite, whereas brown amphiboles among pargasite, magnesiohornblende and tschermakite; glaucophane and winchite systematically grow at the rims of brown amphiboles.

Plagioclases were recalculated on the basis of 32 oxygens as reported in Table 5; the magmatic plagioclase crystals are completely altered in the metadolerites, whereas the metamorphic plagioclases are albite-rich in composition.

The general formula of pumpellyite can be expressed in the form W<sub>2</sub>XY<sub>2</sub>Z<sub>3</sub>(O, OH)<sub>14</sub> (Deer et al., 1994). The W site is occupied by Ca, Na and K whereas the Z site is occupied by Si. The X and Y are octahedral sites, where the X site is larger than the Y site. The X site is occupied by divalent and trivalent cations (Mg<sup>2+</sup> Al<sup>3+</sup>, Mn<sup>2+</sup>, Mn<sup>3+</sup>,  $Fe^{2+}$ ,  $Fe^{3+}$ ,  $Cr^{3+}$ ) whereas the Y site is occupied by trivalent cations (Al<sup>3+</sup>, Fe<sup>3+</sup>). The classification and nomenclature of pumpellyite have been largely based on the occupancy of the Y site (Passaglia and Gottardi, 1973): if the most abundant cation at the Y-site is Al, Fe<sup>3+</sup>, Cr<sup>3+</sup> and Mn<sup>3+</sup> the corresponding pumpellyite endmemebers are pumpelliyte (Palache and Vassar, 1925), julgoldite (Moore, 1971), shuiskite (Ivanov et al., 1981) and okhotskite (Togari and Akasaka, 1987), respectively.

The crystal-chemical formulas of pumpellyites analysed in this study indicate that the Al endmember is by far the most abundant, the  $Fe^{3+}$  amount is small, whereas the Cr and Mn contents are negligible (Table 6). Moreover, the pumpelleyite are invariably Al-rich (Figure 8) and very close in composition irrespectively of their occurrence.

The linear and negative Fe and Al cotent correlation (Figure 9), evidences that in the veins the Fe content ranges between 0.216-0.585 and Al between 2.518-2.802 apfu, whereas pumpellyite pseudomorph shows Fe content up to 0.318.

SEM-BSE image shows that pumpellyite crystals are zoned with rims enriched in Al, Mg and depleted in Fe and Ca (Figure 10).

The core of pumpellyite crystals in the veins display a pale green pleochroism, while the rim is colourless; this variability could be correlated with the chemical composition and metamorphic conditions (Cortesogno et al., 1984 and reference therein). Pumpellyite pseudomorph after plagioclase is colourless.

#### Metamorphic evolution of the metadolerites

The metadolerites (Type A, B and C) from the Frido Unit Ophiolites (Southern Apennines -Italy) have been affected by an ocean-floor metamorphism under greenschist to amphibolite facies conditions and subsequent orogenic metamorphism under relatively HP/LT conditions (Sansone, 2010a; b; Sansone et al., 2011). Oceanfloor metamorphism often produced metasomatic reactions of rodingitization (Sansone et al., 2011).

Microscopic observations allow us to state that pumpellyite crystallised under high P and low T conditions in the veins, often in equilibrium with



O EMPA Composition Pmp pseudomorph after Pl

Figure 8. Composition of pumpellyite projected in the chemographic diagram Al, Fe<sup>tot</sup>, Mg (atomic proportion).



Figure 9. Fe vs Al (apfu) plot of pumpellyite. Cross for pumpellyite into veins; circle for pumpellyite pseudomorph after plagioclase.

lawsonite and glaucophane. The occurrence of prehnite in assemblage with pumpellyite indicates a retrograde metamorphic evolution. Pumpellyite in the veins is Fe-poor (0.216-0.585 apfu) and Al-rich (2.518-2.802 apfu). Pumpellyite pseudomorph after plagioclase shows Fe contents in the range 0.227-0.318 apfu and is Al-rich (2.567-2.766 apfu).

Al-pumpellyite in the veins cross-cutting metadolerites crystallised under conditions of the blueschist facies. It is known that temperature and pressure control the Al and Fe contents of pumpellyite: pumpellyite with Fe > 0.800 apfu crystallises in conditions of zeolite and prehnitepumpellyite facies (Schiffman and Liou, 1980), while Al-pumpellyite crystallises under blueschist and pumpellyite-actinolite facies (AlDahan, 1986; Evans, 1990; Yuasa et al., 1992; Rahn et al., 1994; 1995). In the veins, pumpellyites associated with epidote contain less Fe and give information on the metamorphic conditions (Nakajima et al., 1977), suggesting that the rocks were altered at temperatures above the Fe pumpellyite stability curve (Liou, 1979).

BSE-SEM image in Figure 10 shows a zoned crystal of pumpellyite, with a Fe-rich core, and a Al-rich and Fe-poor rim, suggesting that the rim

of these pumpellyite crystal formed during oceanfloor metamorphism, although Fe-content in pumpellyite is lower than that found in pumpellyite from other low-grade metamorphic rocks (Cortesogno et al., 1984). Al-rich rim suggests different metamorphic conditions typical of the pumpellyite-actinolite and blueschist facies condition. Therefore, the HP/LT orogenic



Figure 10. BSE image showing a zoned crystal of pumpellyite.

metamorphic event correlated to the underplating of the ophiolitic rocks situated at the base of the Liguride accretionary wedge, crystallised mineral assemblages typical of the lawsonite-glaucophane facies as also corroborated by the zoning of pumpellyite crystals. According to Knott (1994) and Sansone et al. (2011) this metamorphic facies developed at 6 - 8 kbar and 200-300 °C.

Pumpellyite compositions record the metamorphic evolution of the metadolerites (Type C), suggesting that both host rocks (pumpellyite pseudomorph after plagioclase) and pumpellyite filled veins shared the same metamorphic evolution. The occurrence of pumpellyite in assemblage with glaucophane, Mg-riebekite, lawsonite, phengite, pumpellyite and aegirine-augite (Sansone, 2010a; b) indicates that it crystallises under blueschist facies conditions.

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