The magnetite ore districts of the southern Aosta Valley (Western Alps, Italy): a mineralogical study of metasomatized chromite ore

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ABSTRACT

In the southern Aosta Valley (Italian Western Alps), several massive magnetite bodies occur within serpentinized ultramafic rocks belonging to the Mesozoic meta-ophiolite nappe. The ultramafic rocks consist of lherzolite with minor dunite bodies and show a high pressure metamorphic overprint. The results of a multi-methodological study, based on optical microscopy, electron microprobe analysis and single-crystal X-ray diffraction, are reported here in order to give new insights into (1) the mineralogy and crystal chemistry of spinels and silicates and (2) the genesis of the massive magnetite bodies. Chromium-rich relict cores inside the magnetite grains suggest a derivation from primary chromite concentrations. The major-element behaviour shows the presence of two chromite types: a Cr_2O_3 -rich (Al₂O₃-poor) type and a Cr_2O_3 -poor (Al₂O₃-rich) type. Magnetite ore deposits probably represent the product of transformation from a chromite to magnetite occurred during multiple stages: the premetamorphic setting of the ultramafics and the petrographic evidence suggest that metasomatism started before the onset of the alpine metamorphism and was active during the early alpine, eclogite-facies metamorphic overprint related to a subduction process under high fluid activity.

Keywords: chromite, magnetite, serpentinization, high pressure, ocean floor, metasomatism, Piemonte Zone.

Introduction

In the southern Aosta Valley, a great number of magnetite ore bodies occur in serpentinites derived from lherzolite and minor dunite protoliths. The magnetite bodies were mined for Fe until 1979 and many of them had been exploited since Roman times. The genesis of these massive magnetite ore-bearing serpentinites is not easy to compare with the other magnetite deposits around the world, as magnetite ore in serpentinite represents a very rare type of mineralization

* E-mail: diego.gatta@unimi.it DOI: 10.1180/minmag.2009.073.5.737 (e.g. in Corsica and China, Routhier, 1963). Several genetic models have been suggested for the magnetite ore of the Aosta Valley. A magmatic origin was inferred by Stella (1921), Huttenlocher (1934) and di Colbertaldo et al. (1967), whereas Dal Piaz (1971) related the formation of these mineralizations to the alpine metamorphism and Compagnoni et al. (1979, 1980) suggested that the serpentinization and magnetite concentration are related to an anorogenic oceanic metamorphism. On the basis of the preliminary data on these ore magnetites previously published (Diella et al., 1994), the aim of this study is a reinvestigation of the mineral chemistry of the magnetites from the Aosta Valley, based on a multi-methodological

approach (i.e. optical microscopy, electron microprobe analysis and single-crystal X-ray diffraction), in order to give new insights into the crystal chemistry and genesis of the massive magnetite bodies.

Geological overview of the southern Aosta Valley

The main tectonic unit cropping out in the southern Aosta Valley, which hosts the magnetite deposits, is the Piemonte Zone, a composite nappe, Mesozoic in age, considered as the metamorphic equivalent of a dismembered ophiolite sequence belonging to the alpine Penninic Domain (Fig. 1). The Piemonte Zone is tectonically interbedded between pre-alpine continental units represented by the geometrically underlying Gran Paradiso Massif (to the south) and the overlying Austroalpine nappe system Units (Sesia Lanzo Zone and Austroalpine slices).

The structurally complex Piemonte Zone encompasses two major ophiolitic units, separated by a tectonic contact (Ballèvre and Merle, 1993, and references therein): an upper unit, mainly composed of calcschists interbedded with tabular bodies of tholeiitic metabasalts and tuffs, and a lower unit, made of mafic and ultramafic rocks displaying a close oceanic affinity. These units have been named the 'Combin Zone' and 'Zermatt-Saas Zone' units respectively, in the northwestern Alps; recently, however, this terminology has also been used in the southern Aosta Valley (Ballèvre and Merle, 1993), and is adopted in this paper. While the lower Zermatt-Saas Zone records an early-alpine metamorphic overprint under eclogite-facies conditions, the same event developed lower-P epidote-blueschist facies assemblages in the Combin Zone. In the central Aosta Valley, the Zermatt Saas Zone crops out mostly south of the east-west trending Aosta-Ranzola fault, a normal to transpressive



FIG. 1. Tectonic sketch-map of the southern Aosta Valley. 1 Austroalpine Nappe System Units; 1a = units *with* the Alpine eclogite-facies overprint, Eclogitic Micaschists Complex (EMC) of the Sesia Zone and main tectonic slices (EM: Mt Emilius, GR: Glacier-Rafray); 1b = units *lacking* the Alpine eclogite-facies overprint (GMC: Gneiss Minuti Complex of the Sesia Zone; MM and V: Mt Mary and Verres thrust sheets). 2–4 Penninic Domain: 2 = Upper Penninic units (GP: Gran Paradiso, AB: Arcesa-Brusson); 3 = Faisceau de Cogne; 4 = Piemonte Zone; 4a = eclogite-facies unit (the 'Zermatt-Saas Zone'), with (*u*) the main ultramafic bodies of the Mt Avic Massif and the Cogne serpentinite; 4b = epidote blueschist-facies unit (the 'Combin Zone'). ARF: Aosta Ranzola fault. Bold numbers refer to the studied magnetite mineralizations: 1 Ussel; 2 Torrente Pessey; 3 Val Meriana; 4 Lago Gelato; 5 Tour Ponton; 6 Bella Lana; 7 Alpe Vernouille; 8 Cogne. Modified after Rolfo *et al.* (2004), Beltrando *et al.* (2008) and Dal Piaz *et al.* (2009).

fault, Oligocene–Neogene in age, which lowered the northern block of the nappe pile (Bistacchi *et al.*, 2001, and references therein; Fig. 1).

The magnetite bodies occur within the Zermatt-Saas Zone, south of the Aosta-Ranzola fault (Fig. 1), in the Mount Avic and Cogne ultramafics.

Geological setting of the Mount Avic and Cogne ultramafics

The Mount Avic massif (Fig. 1) is one of the widest ultramafic bodies of the Western Alps and consists mainly of serpentinized peridotite (lherzolite and minor dunite, Tartarotti and Martin, 1991; Diella *et al.*, 1994) which hosts the magnetite mineralization. Eclogitic Mg- and Fe-Ti metagabbros, metabasalts; locally metasediments also occur in minor amounts. The contact between serpentinite and overlying metasediments is commonly marked by serpentinitic breccias, interpreted as sedimentary breccias deposited on the ultramafic ocean floor (Tartarotti *et al.*, 1998; Fontana *et al.*, 2008).

In the Cogne area (Fig. 1), the magnetite deposits are hosted instead by a relatively small serpentinized ultramafite lens (lherzolite and minor dunite, Compagnoni et al., 1979; Diella et al., 1994) which shows a primary upper contact with Mn-bearing quartzite and metasediments (the calcschists of Elter, 1971). The serpentinite lens is in tectonic contact with the underlying Mesozoic continental shelf deposits of the 'Faisceau de Cogne', a metasedimentary sequence showing strong similarities with the more external continental Briançonnais domain (Elter, 1971). An upper mantle lherzolite protolith, slightly depleted, has been suggested for both the Mount Avic and Cogne ultramafics (Compagnoni et al., 1979; Tartarotti and Martin, 1991).

Both the Mt Avic and Cogne ultramafics record a multiphase alpine evolution, initially dominated by a prograde metamorphism leading to a high pressure event developed under eclogite facies conditions (Compagnoni *et al.*, 1979, 1980; Tartarotti and Martin, 1991), which affected the entire Zermatt-Saas Zone. Temperature estimates of ~450–550°C and a minimum pressure of ~1.0 GPa are suggested by several authors (Baldelli *et al.*, 1985; Benciolini *et al.*, 1988) for this event in the Aosta Valley. The high-pressure event was followed by a retrograde, blueschist to greenschist facies metamorphism (Compagnoni *et al.*, 1979; Tartarotti and Martin, 1991; Fontana *et al.*, 2008). A recent study on the Zermatt-Saas Zone in the Cogne area by Beltrando *et al.* (2007) reports evidence of an even more complex evolution, with two burial–exhumation cycles having taken place during the alpine orogeny.

The magnetite bodies and host serpentinite: geological and petrographic features

All the magnetite bodies from the southern Aosta Valley are hosted by antigorite serpentinites mainly composed of antigorite with highly variable amounts of magnetite, diopside, chlorite, olivine, Ti-clinohumite, tremolite, talc, brucite, chrysotile and very minor Fe-Ni alloys and sulphides; the same minerals also occur along different types of metamorphic veins. These rocks show a variety of textures and mineral assemblages, related to a multistage metamorphic evolution, which started during an early oceanic serpentinization stage, followed by an earlyalpine high pressure overprint (as shown by olivine + Ti-clinohumite-bearing assemblages) and later re-equilibration under blueschist to greenschist facies conditions (Compagnoni et al., 1979; Tartarotti and Martin, 1991). In spite of the metamorphic overprint, the occurrence of primary relics of clino- and orthopyroxene suggests derivation from a lherzolite protolith for both the ultramafics of Mt Avic and Cogne. In both areas, lenses of dunitic composition also occur, characterized by the absence of pyroxene and locally by the occurrence of abundant relics of primary olivine (Diella et al., 1994). At Cogne, the dunitic rocks are associated with strongly serpentinized harzburgite.

The magnetite orebodies occur as strongly deformed lenses of highly variable sizes. In the Mt Avic massif, the lenses vary in length from 10 m to 100 m, and the thickness ranges from a few cm to a few metres. Although not available from the literature, the tonnage of the main orebodies probably ranged from few thousands to tens of thousands tons, at an average grade of $\sim 40-45\%$ Fe. At the Cogne deposit, the main ore body, which occurs close to the lower contact of the host serpentinite slab, is much bigger (at least 10 Mt with 45% Fe; S.A.N.C., 1931), its maximum dimensions being ~250 m along strike and 600 m along dip; the thickness ranges from 60-70 m at the eastern end to only a few metres at the western end (di Colbertaldo et al., 1967; Compagnoni et al., 1980). The mineralized lenses are affected by all the deformation phases recorded by the host serpentinite.

In the Mt Avic area, the lenses are mostly composed of alternating sub-millimetre-to-decimetre thick magnetite- and silicate-rich domains (Fig. 2a); the latter consist mainly of antigorite and/or diopside and/or chlorite, often as monomineralic domains, whereas other phases (particularly metamorphic olivine and Ti-clinohumite) occur only in minor amounts. The average abundance of magnetite in the orebodies is \sim 50-60%, the remainder being composed mostly of antigorite (20-30%), diopside (10-20%) and chlorite (10-20%). Higher grade decimetre-sized pods, containing up to 80-90% magnetite, are also found. Disseminated magnetite mineralization also occurs within the dunitic lenses. The magnetite occurs as fine-grained (100-300 µm) granoblastic intergrowths

showing equilibrium relationships with the metamorphic silicates (Fig. 2*a*). Magnetites containing abundant chromiferous cores (see below) are often embedded by a Cr-bearing chlorite-rich matrix. Chromium-bearing chlorite also occurs, particularly at Ussel (Fig. 1), within antigorite-diopside-olivine-Ti-clinohumite-chlorite high pressure metamorphic veins.

At Cogne, both massive and disseminated mineralizations occur. The massive mineralization is composed of fine-grained magnetite (average grain size 200 μ m) intergrown with very minor antigorite (10–20%, Fig. 2b). The disseminated mineralization consists of coarser-grained magnetite porphyroblasts (up to 1–2 cm in size) which, in the serpentinized lherzolite, are associated with a variable amount of antigorite,



FIG. 2. Microstructural features of the magnetite ores. (a) Strongly deformed alternating domains composed of magnetite (black), antigorite (white to blue-grey) and diopside (bright colours). Ussel mineralization, transmitted light, crossed polars. Scale bar = 0.5 mm. (b) Massive mineralization from the Cogne deposit under plane polarized reflected light. Fine-grained magnetite (whitish-grey) is intergrown with antigorite (grey). Black portions are pits on the surface of the polished section. Scale bar = 0.5 mm. (c) and (d) Disseminated mineralization in dunitic rocks from the Cogne deposit under different magnifications. Magnetite porphyroblasts (black) are embedded by antigorite (Atg, blue-grey to whitish); olivine porphyroclasts (Ol, bright colours) are partially transformed to antigorite. Magnetite also occurs as very fine-grained disseminations contouring the serpentinized olivine grains. Transmitted light, crossed polars. Scale bars: c = 2.0 mm, d: 0.5 mm.

diopside, Ti-clinohumite or, more rarely, brucite. In the dunite lenses, two magnetite generations occur. The first generation is represented by coarse-grained (from a few mm to 1-2 cm), rounded to sub-euhedral crystals embedded in fine-grained antigorite, locally in apparent equilibrium relationships with up to few millimetresized olivine porphyroclasts (relics of the primary olivine, possibly recrystallized during the highpressure stage; Fig. 2c,d). These magnetite crystals are often crosscut by chrysotile veinlets which are sealed by (and therefore predate) the host antigorite matrix. As chrysotile predating antigorite must be related to an early (possibly oceanic: Compagnoni et al., 1979, 1980) low-T serpentinization stage, this coarse-grained magnetite probably formed before the onset of the alpine metamorphism. In the same rocks, a second magnetite generation also occurs as very finegrained (50-100 µm) disseminations associated with very fine-grained antigorite around the olivine grains (Fig. 2c,d), clearly related to the alpine-age serpentinization. In the Larcinaz mine (located at the western end of the Cogne orebody), centimetre-sized granoblastic magnetite occurs associated with coarse-grained diopside related to rodingitic transformations. Late carbonate veining is common.

As reported by Diella et al. (1994), a peculiar feature of the mineralization is the frequent occurrence of magnetite crystals showing structural relics. The crystals may contain a dusty cloudy core (up to tens of microns in size) composed of a spinel with variable amounts of Cr_2O_3 (up to 50 wt.%). The cloudy, porous appearance of the relict cores is due to the presence of tiny inclusions of silicates; very finegrained inclusions of Ni-Fe alloys and sulphides also occur in the cores. The chromiferous cores have previously been reported from the Ussel, Valmeriana and Lago Gelato mineralizations (Diella et al., 1994); the new data reported here also highlight the ubiquitous occurrence of chromiferous cores in the other mineralizations of the Mt Avic Massif (at Torrente Pessey, Tour Ponton, Alpe Vernouille, Bella Lana). Conversely, chromiferous relics have not been found in the Cogne orebody.

Experimental methods: crystal-chemistry of spinels and silicates

An initial series of quantitative chemical analyses of spinels and silicates were performed on selected polished samples using an ARL electron microprobe fitted with six wavelength-dispersive spectrometers and a Tracor Northern Energy Dispersive Spectrometer located at the laboratory of the CNR- Istituto per la Dinamica dei Processi Ambientali, Milan. The system was operated using an accelerating voltage of 15 kV, a sample current on brass of 15 nA and a counting time of 20 s on the peaks and 10 s on the backgrounds. A series of natural minerals kaersutite for Si, Mg, Na, Ti, K, Fe, Al, chromite for Cr, niccolite for Ni and rodonite for Mn were employed as standards. The results were processed for matrix effects using a conventional ZAF routine in the Tracor Northern TASK series of programs.

A second series of quantitative chemical analyses were performed using a JEOL JXA-8200 electron microprobe at the laboratory of the Department of Earth Sciences, University of Milan. The system was operated using an accelerating voltage of 15 kV, a probe current of 15 nA and a counting time of 30 s on the peaks and 10 s on the backgrounds. Natural minerals – omphacite for Na, olivine for Mg, anorthite for Al, wollastonite for Si and Ca, K-feldspar for K, ilmenite for Ti, chromite for Cr, rodonite for Mn, fayalite for Fe and niccolite for Ni – were employed as standards. The results were processed for matrix effects using a conventional ZAF routine in the JEOL series of programs.

Representative chemical analyses of spinels and silicates of samples from different localities of the Aosta Valley are reported in Tables 1 and 2 respectively. In addition, detailed X-ray maps have been collected on selected samples in order to highlight Cr, Al, and Fe distribution. The operating conditions for X-ray mapping were: 15 kV accelerating voltage, 15 nA probe current, 1 μ m pixel size and 40–50 ms dwell time.

Eight magnetite crystals, free of defects on the optical scale, were selected for X-ray diffraction experiments – four from Cogne (LG22; LG45; LG47; LG49), three from Ussel (LG10; LG12; LG61) and one from Val Meriana (LG52). The chemical composition of some of the selected samples, representative of the three different localities, is given in Table 3. One further small crystal of Cr-Al-Fe-Mg spinel (CROM1, Table 4), found as relict core of a magnetite crystal from Ussel, was selected for the diffraction experiment.

Diffraction data were collected with a STOE AED4 four-circle diffractometer, using a graphite

TABLE 1. Representative analyses of spinels from the Aosta Valley.

	LG58		rim	0.08	0.13	I	2.64	66.29	29.02	0.40	1.16	Ι	99.72		0.003	0.004	I	0.080	1.907	0.928	0.013	0.066	I	3.001
feriana –	LG58		inter	0.07	0.20	I	7.82	60.83	28.17	0.76	1.49	Ι	99.34		0.003	0.006	I	0.236	1.747	0.899	0.025	0.085	I	3.001
- Val M	LG58		inter	1.16	0.54	0.22	24.32	41.35	24.13	2.92	3.88	I	98.52		0.043	0.015	0.010	0.716	1.158	0.751	0.092	0.215	Ι	3.000
	LG58		core	1.00	0.48	0.22	26.81	39.46	24.46	2.96	3.58	I	98.97		0.037	0.013	0.010	0.787	1.102	0.759	0.093	0.198	I	2.999
Gelato	LG2			1.73	0.26	0.72	11.52	53.46	29.12	0.80	2.41	0.40	100.42		0.064	0.007	0.031	0.337	1.489	0.901	0.025	0.133	0.012	2.999
1.300	LG2			1.50	0.29	0.64	13.16	52.74	29.32	0.86	2.25	0.32	101.08		0.055	0.008	0.028	0.383	1.462	0.903	0.027	0.124	0.010	3.000
	ΓG	12-8	rim	0.08	0.17	0.03	7.98	62.06	30.27	0.28	0.88	0.09	101.84		0.003	0.005	0.001	0.236	1.747	0.947	0.009	0.049	0.003	3.000
	LG	12-3	inter	0.02	0.28	0.08	15.46	54.12	29.70	0.65	1.01	0.11	101.43		0.001	0.008	0.004	0.457	1.522	0.929	0.021	0.056	0.003	3.001
sel	LG	12-9	inter	I	0.33	0.79	42.81	25.33	27.79	1.78	1.75	0.07	100.65		0.000	0.009	0.034	1.246	0.702	0.856	0.056	0.096	0.002	3.001
sil	ΓG	12-7	inter	0.03	0.25	0.69	45.31	22.22	27.16	1.91	1.85	0.03	99.45		0.001	0.007	0.030	1.332	0.622	0.845	0.060	0.103	0.001	3.001
	ΓG	12-6	inter	0.04	0.22	0.81	47.28	20.12	27.34	1.86	1.82	I	99.49		0.002	0.006	0.035	1.387	0.562	0.849	0.059	0.101	I	3.001
	ΓG	12-1	core	0.01	0.11	4.37	51.41	12.72	27.46	1.67	2.34	I	100.09		I	0.003	0.185	1.463	0.345	0.827	0.051	0.126	I	3.000
ne –	LG24			0.02	0.05	0.02	0.01	70.06	26.18	0.32	2.88	0.04	99.58		0.001	0.001	0.001	0.000	1.995	0.828	0.010	0.162	0.001	2.999
- Coc	LG24			0.05	0.02	0.00	0.01	70.23	26.87	0.27	2.58	0.02	100.05		0.002	0.001	0.000	0.000	1.995	0.848	0.009	0.145	0.001	3.001
	BL22			0.40	0.55	1.94	24.14	42.26	26.80	2.32	2.51	0.12	101.04		0.015	0.015	0.083	0.697	1.161	0.818	0.072	0.137	0.004	3.002
ella Lans	BL15			0.08	0.30	31.75	33.45	4.14	17.35	0.81	12.59	0.17	100.64		0.002	0.007	1.107	0.783	0.092	0.429	0.020	0.555	0.004	2.999
E H	BL10			0.36	0.51	1.42	29.01	36.80	25.58	2.71	2.60	0.09	90.08		0.013	0.014	0.062	0.853	1.030	0.796	0.085	0.144	0.003	3.000
	TP7 A		rim	0.14	0.06	0.45	0.68	67.75	30.48	0.14	0.41	0.22	100.33		0.005	0.002	0.020	0.021	1.945	0.973	0.005	0.023	0.007	3.001
	TP7 A		rim	0.04	0.06	0.04	1.02	68.30	30.56	0.09	0.38	0.12	100.61		0.002	0.002	0.002	0.031	1.961	0.975	0.003	0.022	0.004	3.002
Sev	TP7 A		inter	0.02	0.24	0.27	13.20	55.74	29.53	0.83	0.79	0.22	100.84		0.001	0.007	0.012	0.393	1.580	0.930	0.027	0.044	0.007	3.001
ente Pes	TP7 A		inter	0.02	0.33	0.83	28.00	39.94	28.73	1.53	1.13	0.14	100.65	IS	0.001	0.009	0.036	0.824	1.119	0.895	0.048	0.063	0.004	2.999
- Torre	TP7 A		core	0.04	0.30	1.84	31.03	35.76	28.77	1.64	1.22	0.08	100.68	gen aton	0.002	0.008	0.080	0.906	0.994	0.889	0.051	0.067	0.002	2.999
	TP7 A		inter	0.07	0.25	0.53	15.38	53.63	29.90	0.88	0.80	0.18	101.62	n 4 oxy	0.003	0.007	0.023	0.453	1.504	0.932	0.028	0.044	0.005	2.999
	TP7 A		rim	0.02	0.12	0.07	5.75	63.63	30.39	0.22	0.47	0.22	100.89 1	based o	0.001	0.003	0.003	0.172	1.816	0.964	0.007	0.027	0.007	3.000
Oxide	(wt.%)			SiO_2	TiO_2	Al_2O_3	Cr_2O_3	Fe_2O_3	FeO	MnO	MgO	NiO	Total	Formulae	Si	Ti	Al	C	Fe^{3+}	Fe^{2+}	Mn	Mg	ï	Cation sum

Cations calculated assuming stoichiometry and charge balance.

METASOMATIZED CHROMITE ORE FROM THE WESTERN ALPS

Phase	— C	рх —	— Oli	vine —		– Chlorite –		Ti-hum
Locality	Lago	Gelato	Cogne	Ussel		Ussel		Ussel
Sample	LG 6	LG 6	LG 22	LG 11	LG 11	LG 11	LG 12	LG 11
	relict	met.	relict	met.				
Oxide (wt.	%)							
SiO ₂	51.81	54.77	41.88	40.65	33.82	33.88	34.89	36.80
TiO ₂	0.18	0.03	_	0.01	_	—	0.02	3.74
Al_2O_3	4.58	0.16	0.01	0.01	12.07	12.67	12.48	0.02
Cr_2O_3	0.91	0.05	_	_	1.56	0.16	2.66	0.03
Fe ₂ O ₃	_	_	_	_	_	_	_	_
FeO	2.41	1.10	1.85	11.31	4.30	4.48	4.35	11.12
MnO	0.10	0.06	0.24	0.42	0.10	0.06	0.05	0.41
MgO	16.03	17.73	55.27	48.59	35.62	35.65	35.50	47.24
NiO	_	_	0.08	_	_	_	_	_
CaO	23.46	25.35	_	0.01	0.04	0.03	_	_
Na ₂ O	0.19	0.01	_	_	0.04	0.01	_	0.03
K ₂ O	—	—	0.06	—	0.04	0.03	—	_
Total	99.67	99.26	99.39	101.00	87.59	86.97	89.95	99.39
Si	1.892	1.999	0.996	0.992	6.411	6.438	6.443	3.925
Ti	0.005	0.001	_	_	_	_	0.003	0.300
Al	0.197	0.007	_	_	2.697	2.838	2.716	0.003
Cr	0.026	0.001	_	_	0.234	0.024	0.388	0.003
Fe ³⁺	_	_	_	_	_	_	_	_
Fe ²⁺	0.074	0.034	0.037	0.231	0.682	0.712	0.672	0.992
Mn	0.003	0.002	0.005	0.009	0.016	0.010	0.008	0.037
Mg	0.872	0.965	1.959	1.768	10.064	10.098	9.772	7.510
Ni	_	_	0.002	_	_	—	—	_
Ca	0.918	0.991	_	_	0.008	0.006	_	_
Na	0.013	0.001	_	_	0.015	0.004	—	0.006
K	_	—	0.002	—	0.010	0.007	—	—
Σ_{cations}	4.000	4.001	3.001	3.000	20.137	20.137	20.002	12.776

TABLE 2. Representative analyses of silicates from the Aosta Valley.

Cations calculated assuming stoichiometry and charge balance: cpx 6 ox, ol 4 ox, chl 28 ox, Ti-hum 17 ox.

monochromator for Mo-K α -radiation, operated at 50 kV and 40 mA. The unit-cell constants were measured on the basis of 22 Bragg reflections

accurately centred in the range 8 < θ <20°, and reported in Table 5. Intensity data for the structural refinements were collected using ω -2 θ

TABLE 3. Chemical c	composition (given	as cations per	formula unit,	calculated	on the basi	is of 4 oxyg	ens) of the
single-crystals of	magnetite used for	the structure r	efinements fro	om Cogne ((LG22), Us	sel (LG10	and LG12)
and Val Meriana	(LG52).						

	Ti	Cr	Fe ³⁺	Fe ²⁺	Mn	Mg	Ni	Σ_{cations}
LG22	0	0	1.999(15)	0.892(4)	0.011(1)	0.097(2)	0	2.999
LG10	0.006(1)	0.018(1)	1.968(6)	0.956(5)	0.005(1)	0.042(1)	0.004(1)	2.999
LG12	0.006(1)	0.032(1)	1.958(6)	0.959(5)	0.004(1)	0.038(1)	0.005(1)	3.000
LG52	0.001(1)	0.002(1)	1.996(12)	0.933(5)	0.011(1)	0.055(1)	0.002(1)	3.000

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TABLE 4. (Chemical	composition	(given as	s cations j	per formula	ι unit) of the	e CROM1	crystal (44	point-analysis),
showing	g an inho	mogeneous	distributio	on of cati	ons within	the crystal.			

			- 3+	- 2+		
Ti	Al	Cr	Fe	Fe ²	Mg	Σ_{cations}
0.012	0.001	0.391	1.584	0.958	0.053	2.999
0.007	0.131	1.383	0.471	0.902	0.105	2.999
0.005	0.229	1.317	0.443	0.889	0.117	3.000
0.005	0.279	1.191	0.520	0.880	0.125	3.000
0.008	0.248	1.105	0.631	0.893	0.114	2.999
0.002	0.400	1.339	0.257	0.859	0.144	3.001
0.004	0.398	1.200	0.394	0.855	0.149	3.000
0.003	0.487	1.417	0.090	0.832	0.171	3.000
0.018	0.007	0.851	1.106	0.937	0.081	3.000
0.004	0.001	0.137	1.853	0.974	0.030	2.999
0.005	0.000	0.148	1.841	0.971	0.034	2.999
0.004	0.000	0.135	1.857	0.971	0.033	3.000
0.007	0.000	0.190	1.796	0.972	0.035	3.000
0.017	0.003	0.507	1.456	0.962	0.055	3.000
0.017	0.010	1.095	0.861	0.930	0.087	3.000
0.007	0.003	0.234	1.749	0.975	0.032	3.000
0.007	0.118	1.363	0.504	0.907	0.100	2.999
0.016	0.009	0.877	1.083	0.940	0.076	3.001
0.006	0.122	1.354	0.514	0.903	0.102	3.001
0.017	0.015	1.139	0.812	0.932	0.085	3.000
0.010	0.001	0.283	1.696	0.964	0.046	3.000
0.005	0.174	1.373	0.442	0.893	0.113	3.000
0.001	0.473	1.397	0.127	0.833	0.168	2.999
0.006	0.177	1.398	0.414	0.895	0.110	3.000
0.014	0.003	0.436	1.533	0.961	0.053	3.000
0.007	0.059	1.389	0.537	0.913	0.094	2.999
0.009	0.000	0.287	1.696	0.969	0.040	3.001
0.006	0.171	1.390	0.427	0.897	0.109	3.000
0.019	0.009	0.907	1.046	0.935	0.084	3.000
0.011	0.000	0.323	1.656	0.965	0.046	3.001
0.004	0.473	1.392	0.127	0.834	0.170	3.000
0.000	0.441	1.411	0.147	0.838	0.162	2.999
0.002	0.407	1.344	0.246	0.851	0.151	3.001
0.002	0.422	1.381	0.192	0.841	0.161	2.999
0.006	0.339	1.190	0.459	0.876	0.130	3.000
0.002	0.345	1.314	0.338	0.865	0.136	3.000
0.007	0.132	1.379	0.475	0.903	0.105	3.001
0.008	0.076	1.396	0.512	0.915	0.093	3.000
0.014	0.004	0.495	1.474	0.958	0.055	3.000
0.008	0.055	1.358	0.570	0.919	0.090	3.000
0.006	0.002	0.173	1.814	0.974	0.032	3.001
0.008	0.114	1.281	0.588	0.910	0.098	2.999
0.012	0.003	0.402	1.571	0.965	0.047	3.000
0.016	0.014	1.115	0.840	0.930	0.086	3.001
0.006	0.000	0.133	1.856	0.973	0.033	3.001

scan mode, with peak-base widths of $2\theta = 2^{\circ}$, 45step integration, 0.6 s per step counting time. The reflection conditions were consistent with the space group $Fd\bar{3}m$. Intensity data were then corrected for Lorentz-polarization and absorption effects, following the empirical method of North *et al.* (1968). The structural refinement was performed using the *SHELX-97* software (Sheldrick, 1997). The first cycles of refinement of magnetites were performed using neutral

nt of magnetites from: Cogne (LG22, LG45, LG47 and LG49); Ussel (LG10, LG61,	
TABLE 5. Details pertaining to the X-ray single-crystal structu	LG12); CROM1; Val Meriana (LG52).

Sample	LG22	LG45	LG47	LG49	LG10	LG61	LG12	CROMI	LG52
<i>a</i> (Å)	8.3949(9)	8.3964(9)	8.3988(16)	8.3990(6)	8.3957(8)	8.3963(6)	8.3943(6)	8.3809(16)	8.3969(9)
T (8a) x $U_{iso} (Å^2)$ Occupancy	1/8 0.0096(2) 0.995(17)	1/8 0.0086(2) 0.990(17)	1/8 0.0084(2) 1.002(15)	1/8 0.0060(1) 1.021(10)	1/8 0.0082(3) 0.970(18)	1/8 0.0086(2) 1.013(20)	1/8 0.0068(2) 1.009(15)	1/8 0.0113(4) 0.947(25)	1/8 0.0095(2) 0.997(18)
M (16 d) $V_{\rm liso}$ (Å ²) Occupancy	1/2 0.0112(2) 0.951(16)	1/2 0.0102(2) 0.950(16)	1/2 0.0100(1) 0.977(15)	1/2 0.0079(9) 0.993(10)	1/2 0.0094(2) 0.944(16)	1/2 0.0104(2) 1.001(19)	1/2 0.0085(1) 1.001(14)	1/2 0.0106(2) 0.960(21)	$1/2 \\ 0.0111(2) \\ 0.983(17)$
O (32 e) x (u) U_{1so} (Å ²) T_{-O} (Å) M-O (Å) No. unique reflections No. unique refl. with	0.2554(2) 0.0113(4) 1.896(3) 2.054(1) 216	0.2552(2) 0.0106(4) 1.894(3) 2.056(2) 216 140	0.2553(2) 0.0100(4) 1.895(2) 2.056(1) 216 147	0.2554(1) 0.0071(3) 1.897(2) 2.056(1) 2.16 136	0.2552(3) 0.0108(6) 1.893(4) 2.057(2) 216 121	0.2551(2) 0.0105(5) 1.893(3) 2.057(2) 216 138	0.2553(2) 0.0082(4) 1.894(2) 2.055(1) 216 140	0.2601(3) 0.0122(5) 1.961(4) 2.014(2) 216 135	0.2552(2) 0.0112(4) 1.894(2) 2.057(1) 216 147
$F_{o} > 4\sigma(F_{o})$ No. refined parameters R int R_{1} (F) R_{1} (F) with $F_{o} > 4\sigma$ (F_{o})	8 0.0361 0.0519 0.0297	8 0.0347 0.0568 0.0297	8 0.0434 0.0560 0.0272	8 0.0468 0.0498 0.0147	8 0.0766 0.0729 0.0326	8 0.0577 0.0555 0.0292	8 0.0387 0.0442 0.0193	8 0.1015 0.1212 0.0589	8 0.0324 0.0462 0.0271
Origin fixed at $\bar{3}m$. $R_{\text{int}} = N$. Radiation used Mo- $K\alpha$.	$\Sigma F_{ m obs.}^2 - F_{ m obs.i}^2$	$\sum_{n=an}^{2} \langle \Sigma[F_{obs.}^{2}]; \rangle$	$R_1(F) = \Sigma(F_{\rm obs.} $	$ - F_{\mathrm{calc.}})/\Sigma F$	obs. -				

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atomic scattering factors of Fe and O from the International Tables for Crystallography (Wilson and Prince, 1999). As the mean atomic number of tetrahedral (T) and octahedral (M) sites determined by least squares refinement is sensitive to the ionization level of scattering curves (Della Giusta et al., 1986, 1987; Andreozzi et al., 2000). further refinement cycles were performed using ionized scattering curves for Fe and O. The best values of the agreement parameters (e.g. $R_1(F)$) were obtained with a partially ionized curve for the O site ($\sim O^{-1.6}$) and neutral curves for Fe at the T and M sites. The final agreement indexes $R_1(F)$ for eight refined parameters and 216 unique reflections were all less than 0.06. The variancecovariance matrix of the final refinement cycles showed no significant correlation between the refined parameters. At the end of the refinements, the shifts in all the parameters were less than their estimated standard deviations (esd). Refined atomic positions, displacement parameters and bond distances are reported in Table 5. For the Cr-Al-Mg-Fe spinel (CROM1), the neutral scattering curve of Fe at the T-site and (Cr+Fe) at the M-site, and a partially ionized curve for the oxygen site ($\sim O^{-1.6}$), were used. In this case, the quality of the refinement is poorer then those of magnetites (Table 5), as expected for a chemically inhomogeneous crystal (Table 4).

Results: crystal-chemistry of spinels and silicates

Silicates: chemical composition

Among the silicates (Table 2), primary olivine from Cogne shows a composition close to pure forsterite (up to Fo_{97}), as commonly found in dunite associated with chromitite bodies (Jan and Windley, 1990), whereas metamorphic olivine in serpentinized lherzolite shows an average composition (Fo_{88}) similar to that reported from other metamorphic ultramafics from the Western Alps (Cimmino *et al.*, 1979, 1981; Scambelluri *et al.*, 1991).

Relics of primary clinopyroxene from Lago Gelato are characterized by small Al_2O_3 (~4 wt.%), Na_2O (~0.2 wt.%) and TiO₂ (~0.2 wt.%) contents, and are relatively Cr_2O_3 -rich (~0.9 wt.%), as is usually found in mantle ultramafics depleted by partial melting processes (Kornprobst *et al.*, 1981; Piccardo, 1984).

Metamorphic clinopyroxene displays a composition close to pure diopside (maximum FeO_{tot} content \sim 1.5 wt.%). Chlorite is Cr-free when intergrown with antigorite; when in the form of coronas surrounding spinel grains, both Cr-free and Cr-bearing chlorite (up to $\sim 2 \text{ wt.}\% \text{ Cr}_2\text{O}_3$) occur, the Cr-rich chlorite surrounding highly chromiferous cores (e.g. in the Ussel mineralization).

Antigorites show a small Cr_2O_3 content (up to ~0.25 wt.%). Ti-clinohumite shows an average composition comparable with that described from other Alpine ultramafic rocks which have undergone a high-pressure metamorphic overprint (Scambelluri *et al.*, 1991).

Spinels: chemical composition

The heterogeneities observed in the spinel grains from Mt Avic correspond to different compositional domains. The relict cores are always composed of a Cr-rich spinel (chromite relic), surrounded by a more-or-less developed magnetite portion. The boundary between core and the magnetite portion is generally sharp.

On the basis of the most preserved relict cores, it is possible to distinguish between two groups of chromite relics: the first one (Type I: Ussel, Lago Gelato, Valmeriana) with a large Cr_2O_3 content (up to 54 wt.%) and small Al_2O_3 content (up to 12 wt.% but generally <5 wt.%) and the second one (Type II: Torrente Pessey and Bella Lana) with a smaller Cr_2O_3 content (up to 37 wt.%) and a larger Al_2O_3 content (up to 32 wt.%) (Fig. 3).

The large Cr_2O_3 content of the most preserved relict cores shows strong analogies with chromite from podiform chromitite, though affected by major modifications (strong depletion in MgO, Al_2O_3 and Cr_2O_3) with respect to the primary composition. The composition of chromite of the second group seems to be better preserved, at least in the concentration of the major elements.

Magnetite surrounding the chromite relics shows compositions close to the pure end member, containing variable, but always present, Cr_2O_3 , small amounts of NiO (up to 0.5 wt.%) and MnO (up to 3 wt.%) but no trace of TiO₂.

Analyses of spinel from Cogne always show a pure magnetite composition. The large MgO (up to 11 wt.%) and SiO_2 (up to 4 wt.%) contents, sometimes detected, are related to the presence of submicroscopic inclusions of gangue minerals (e.g. serpentine, chlorite, brucite).

Aluminium, Cr and Fe X-ray maps of a chromite relic from Torrente Pessey and a second one from Cogne, along with backscattered electron images, are shown in Fig. 4. For the



FIG. 3. Cr_2O_3 vs. Al_2O_3 and FeO_{tot} diagram based on the spinel chemistry from different localities of the Aosta Valley.

Torrente Pessey sample, a diagram of compositional zonation of Al and Fe is also reported.

Spinels: single-crystal X-ray diffraction data

The unit-cell constants of the eight samples of magnetites from Cogne, Ussel and Val Meriana, selected for single-crystal X-ray diffraction investigation, show similar values to other natural and synthetic magnetites (Gatta *et al.*, 2007), ranging between 8.3943-8.3990 Å. The structural refinements give tetrahedral bond distances within the range 1.893-1.987 Å, slightly longer than that observed in synthetic magnetite (e.g. T-O = 1.885(1) Å, Gatta *et al.*, 2007). In contrast, the octahedral bond distances refined in this study (2.054 <M-O <2.057 Å, Table 5) are significantly shorter than that

observed in synthetic magnetite (e.g. M-O = 2.0607(8) Å, Gatta *et al.*, 2007). The longer T-O bond in the natural material can be ascribed to the presence of cations larger than Fe³⁺ at the T-site, e.g. Mg²⁺ or Fe²⁺. Similarly, a multi-element distribution at the octahedral site (i.e. with Mg²⁺, Fe²⁺ and Fe³⁺) might explain the unexpectedly short M-O bond distances refined in this study.

Discussion

The similar pre-metamorphic features of the ultramafite bodies investigated here, their premetamorphic setting (on the ocean floor), the common metamorphic evolution and the mineralization features suggest a common origin for the Mt Avic and Cogne magnetite bodies. In the Mt Avic ultramafics, the derivation from strongly metasomatized chromitite ore is proved by the ubiquitous occurrence of chromite relics in magnetite, often surrounded by Cr-bearing chlorite.

The chromiferous cores and, more generally, the mineralization composition (e.g. relict Crbearing cores in pure magnetite; the frequent association with both Cr-bearing and Cr-free chlorite), suggest metasomatic exchanges, under high fluid activity, during the transformation of chromite into magnetite. Such exchanges led to an increase of FeO_{tot} and a strong depletion of Cr₂O₃ and Al₂O₃ (the latter especially affecting Type-I chromite, Fig. 3); the Al₂O₃ content is, however, not directly related to the Cr₂O₃ content.

Metasomatism probably developed through different stages associated with multiple, preorogenic to orogenic, serpentinization episodes. In fact, the microscopic observations show the occurrence of multiple magnetite generations. At Cogne, an early pre-metamorphic magnetite generation is suggested for part of the coarsegrained mineralization within the dunitic bodies. The following metamorphic P-T path surely played an important role in the chromite-tomagnetite transformation. In particular, in the Mt Avic ultramafics, the occurrence of Cr-bearing chlorite in early-alpine, eclogite-facies metamorphic veins proves that metasomatic processes affecting chromite were active during the high pressure event. The behaviour of chromiferous spinel at high-pressure and high fluid activity is poorly known; however, studies on other ultramafics affected by high-pressure metamorphism, from the Western Alps and in other localities, provide evidence of destabilization of chromi-

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ferous spinel, often associated with Cr mobility (e.g. the Lanzo Massif in the Western Alps: Rossetti and Zucchetti, 1988; Cabo Ortegal in the Iberian Massif: Gil Ibarguchi *et al.*, 1991). In general, mobility of Cr seems to be favoured by the presence of large amounts of reducing fluid during metamorphic processes (Treloar, 1987; Tracy, 1991; Ottaway *et al.*, 1994).

The apparent lack of chromite relics at Cogne may be due to a sampling bias or, more likely, to a higher degree of metasomatic transformation(s). As already shown by Compagnoni *et al.* (1979, 1980), the Cogne ultramafic slice records a complex evolution which started before the metamorphic process, under high fluid activity ('oceanic serpentinization'); such evolution may have completely transformed the chromite relics (which are, instead, preserved in the Mt Avic ultramafics). However, recently, Cr has been detected qualitatively in the core of small magnetite crystals found in the Cogne serpentinites (Silvana Martin, pers.comm.).

In this respect, the structural refinements performed on magnetites from different localities (including Cogne) do not provide clear and unambiguous evidence of transformation of Cr-rich spinels to magnetites. However, the M-Obond distances observed in this study (2.054 <M-O < 2.057 Å, Table 5), range between that of a synthetic pure magnetite (M-O = 2.0607(8) Å, Gatta et al. 2007) and that of the Cr-Al-Fe-Mg spinel (M-O = 2.014(2) Å, CROM1). Similarly, the refined T-O distances (1.893–1.897 Å) range between that of a synthetic magnetite (T-O) = 1.885(1) Å, Gatta et al., 2007) and that of the spinel CROM1 (T-O = 1.961(4) Å, Table 5). In other words, if the magnetites investigated here were actually the transformation product from primary Cr-rich spinels, then a weak 'memory effect' occurs, at least in the octahedral bond distances. However, such an effect is not clearly shown by unit-cell constants and oxygen coordinates.

Conclusions

This study shows that the Aosta Valley mineralizations derive from strongly metasomatized ophiolitic chromitite bodies, which were part of a depleted upper mantle section mostly consisting of lherzolite with minor dunite and harzburgite. The composition of relict chromite cores preserved in magnetite, although modified by the metasomatic transformations, shows two different types: a Cr_2O_3 -rich (Al₂O₃-poor) and a Cr_2O_3 -poor (Al₂O₃-rich) type, which probably correspond to different primary types of chromitite in the mantle slab.

The metasomatic processes that drive the (almost complete) transformation from chromite to magnetite ore lead to a strong depletion of Cr₂O₃, Al₂O₃ and MgO and an increase in FeO_{tot} in an environment of high fluid activity, as is typical of serpentinization processes.. The microstructural observations suggest that these transformations occurred during multiple stages. The pre-metamorphic setting of both the Mt Avic and Cogne ultramafics (on the ocean floor) and the petrographic evidence suggest that metasomatism started before the onset of the Alpine metamorphism (particularly at Cogne, during an oceanic serpentinization stage) and was surely active during the early Alpine, eclogite-facies metamorphic overprint.

The paucity, on a world scale, of magnetite deposits associated with serpentinized ultramafics (Routhier, 1963) implies that although magnetite is a typical product of serpentinization, such a process alone cannot produce significant magnetite concentrations. Their formation requires the occurrence of former Cr-spinel concentrations and later metasomatic transformations. Apart from the Aosta Valley deposits, similar deposits in the Mediterranean area derived from metasomatized chromitite occur in Greece (Paraskevopoulos and Economou, 1980) and Corsica (authors unpubl. data). This study suggests that the Cogne-type mineralizations can be considered as being derived from depleted upper mantle sequences containing dunitic lenses which were exposed on the ocean floor and experienced high-pressure metamorphism; as a consequence, the occurrence - in the same sequences - of preserved chromitite is highly unlikely.

The single-crystal X-ray structural refinements do not provide clear and unambiguous evidence of the transformation of Cr-rich spinel to

FIG. 4 (*facing page*). Aluminium, Cr and Fe X-ray and BSE images of two chromite samples from: (*a*) Torrente Pessey and (*b*) Cogne. The composition variation diagram refers to the line superimposed on BSE image of the Torrente Pessey sample.

magnetite. However, the intra-octahedral M-O bond distances observed in this study, significantly shorter than that expected in synthetic magnetite, leave an open question about the reason for such values, which might be ascribed to some kind of 'memory effect' of the primary Cr-rich spinel structure.

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