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The Cogne magnetite deposit (Western Alps, Italy): a Late Jurassic seafloor ultramafic-hosted hydrothermal system?

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ABSTRACT

The Cogne magnetite deposit (Western Alps, Italy) is the largest in a series of apatite and sulphide-free magnetite orebodies that are hosted in serpentinites belonging to western Alpine ophiolitic units. The nearly endmember composition of magnetite, which is unusual for an ultramafic setting, and the relatively high tonnage of the deposit ($18 \cdot 10^6$ tonnes at 45-50 wt% Fe) make Cogne an intriguing case study to explore magnetite-forming processes in ophiolites. The Cogne magnetite shows variable textures, including nodular ores, veins and fine-grained disseminations in serpentinites after tectonitic peridotites and totally serpentinized melt-impregnated peridotites (troctolites). An increase in Co/Ni ratio from magnetite-poor serpentinized peridotites (0.05) to nodular magnetite ores (>1) is observed. Trace element analyses of magnetite from different sites and lithologies by laser-ablation inductively-coupled mass spectrometry indicate that magnetites have typical hydrothermal compositions, characterized by high Mg and Mn (median values up to ~24100 and ~5000 ppm, respectively), and low Cr, Ti and V (median values up to ~30, ~570 and ~60 ppm, respectively). Moreover, the variations in trace element compositions distinguish magnetite that is hydrothermal fluid-controlled [highest (Mg, Mn, Co, Zn)/Ni ratios] from magnetite whose composition is affected by host-rock chemistry (highest Ni ± Ti ± V). U-Th-Pb dating of magnetite-associated uraninite constrains the formation of the deposit to the Late Jurassic (ca. 150 Ma), during an advanced stage of the opening of the Alpine Tethys. Thermodynamic modelling of fluid-rock interactions indicates that fluids produced by seawater–peridotite or seawater–Fe-gabbro are not sufficiently Fe-rich to account for the formation of the Cogne deposit. This suggests that fractionation processes such as phase separation were critical to generate hydrothermal fluids capable to precipitate large amounts of magnetite in various types of ultramafic host-rocks. The oceanic setting and geochemical and mineralogical similarities with some modern ultramafic-hosted volcanogenic massive sulphide deposits on mid-ocean ridges suggest that the exposed mineralized section at Cogne may represent the deep segment of a seafloor, high-temperature (~300–400°C) hydrothermal system. The occurrence of similar magnetite enrichments in present-day oceanic settings could contribute to explain the presence of significant magnetic anomalies centred on active and inactive ultramafic-hosted hydrothermal fields.

1. Introduction

The Cogne mining district (southern Valle d'Aosta region, Western Alps, Italy; Fig. 1) consists of a set of mines, which exploited a magnetite-rich serpentinite unit from the Middle Ages to 1979. The tonnage of the ore deposit was estimated at 18 Mt (Nazionale "Cogne" S.p.a., 1954), and the run-of-mine ore produced in the 1960s had an iron grade of 45-50% (Di Colbertaldo et al., 1967). The Cogne deposit is the largest in a series of apatite and sulphide-free serpentinite-hosted magnetite orebodies that crop out in ophiolitic units along the western Alpine collisional suture in Valle d'Aosta (Castello, 1981; Diella et al., 1994; Rossetti et al., 2009; Stella, 1921) and in its southern extension in Corsica (Farinole mine; Routhier, 1963). In southern Valle d'Aosta, most of these magnetite orebodies occur in the Mt. Avic serpentinite massif (located ca. 15 km ENE of the Cogne serpentinite; Fig. 1) and have been interpreted as former metasomatized podiform chromitites, based on their high Cr concentration and the presence of chromite relicts (Diella et al., 1994; Della Giusta et al., 2011; Rossetti et al., 2009). A similar origin has been proposed for analogous Mesozoic (probably Jurassic), ophiolite-hosted magnetite deposits in Greece (Vermion, Olympus and Edessa regions and Skyros island; Paraskevopoulos and Economou, 1980). The Cogne deposit differs from the above occurrences because its magnetite has a nearly pure endmember composition and contains only trace amounts of compatible elements such as Cr, Ti and V (Carbonin et al., 2014; Compagnoni et al., 1981). This geochemical fingerprint, which is unusual for an ultramafic setting, as well as the relatively high tonnage of the deposit, make Cogne an interesting and still poorly studied example of ophiolite-hosted magnetite deposit. Understanding its genesis may have implications for our interpretation of magnetic anomalies reported from modern ultramafic-hosted hydrothermal sites on slow-spreading mid-ocean ridges (Fujii et al., 2016; Szitkar et al., 2014; Tivey and Dyment, 2010).

Several hypotheses have been put forward to explain the genesis of the Cogne deposit. Di Colbertaldo et al. (1967) proposed a genesis by magmatic segregation from an ultramafic melt. Based on the Cr and Ti-poor composition of the magnetite, Compagnoni et al. (1979, 1981) ascribed the formation of the Cogne magnetite to high-temperature serpentinization of oceanic peridotites and consequent Fe mobilization, but they did not discuss this hypothesis in detail. Recently, Carbonin et al. (2014) investigated some of the magnetite-associated lithologies and suggested their possible hydrothermal origin; however, the ore-forming processes were not explored.

In this paper, we present new petrographic and geochemical data on the Cogne deposit, focusing on the textural relationships and the trace element composition of magnetite. The latter has been a valuable tool in the identification of the petrogenetic environment (e.g., Boutroy et al., 2014; Dare et al., 2014; Dupuis and Beaudoin, 2011; Nadoll et al., 2014; Nadoll et al., 2015). In addition, we determine for the first time the radiometric age of the magnetite orebody by U–Th–Pb dating of uraninite. We will show that the magnetite geochemistry and age support a seafloor oceanic hydrothermal setting for the Cogne deposit, and we will explore the possible formation mechanisms, using constraints from geochemical modelling of seawater-rock reactions.

2. Geology of the Cogne mining area

The Cogne serpentinite is a 2.5 km long sliver, with an average thickness of 100 m (Di Colbertaldo et al. 1967), which is exposed on the S and W slopes of Montzalet (Fig. 1 and 2). The serpentinite is tectonically sandwiched between two different metasedimentary sequences. The foot wall sequence consists of tectonically juxtaposed slivers of calcschists, marbles, dolomitic marbles and quartzites formed in a continental margin and in other paleogeographic domains (Cogne Unit; Polino et al., 2014). The hanging wall sequence is represented by calcschists, marbles and minor, Fe- and Mn-bearing metacherts. The basal contact of the serpentinite is a thrust fault (Elter, 1971), while the upper limit is marked by a few cm- to 3 m-thick boudinaged rodingite, which we tentatively interpret as a tectonically activated, primary serpentinite-sediment interface. According to Elter (1971), the Cogne serpentinite and the hanging wall metasediments form the core of a km-scale isoclinal fold that repeats the Cogne unit in its upper limb (Fig. 2b). The Cogne serpentinite and the hanging wall metasediments are considered to be part of the same greenschist- to blueschist-facies ophiolite-bearing unit (Aouilletta Unit; Polino et al., 2014), which is sandwiched together with the foot wall marbles and quartzites between two eclogite-facies ophiolitic units (Grivola-Urtier Unit and Zermatt-Saas Unit; Dal Piaz et al., 2010). These ophiolitic units are remnants of the Jurassic Piedmont-Liguria ocean (Alpine Tethys; Schmid et al., 2004; Stampfli, 2000). From Late Cretaceous to Eocene, these ophiolitic units followed different P-T paths related to their subduction beneath the Adriatic micro-plate, as a result of Africa-Europe convergence (Schmid et al., 2004). In the Zermatt-Saas Unit (in southern Valle d'Aosta), the high-pressure (eclogitic) metamorphic peak was reached in the Eocene (45-42 Ma; Dal Piaz et al., 2001), contemporaneously with the closure of the ocean (Dal Piaz et al., 2003), and was followed by a greenschist-facies overprint during Late Eocene-Early Oligocene (Dal Piaz et al., 2001, 2003). No P-T-time estimate is available for the Cogne serpentinite and its host Aouilletta Unit.

The Cogne magnetite mineralization is confined to the serpentinite body (Compagnoni et al., 1979; Di Cobertaldo et al., 1967) and it is exposed in three zones, henceforward referred to as Site 1, Site 2 and Site 3 (Fig. 2). At Site 1 (which includes the mines of Liconi, 45.612509 N 7.395377 E, Colonna, 45.609716 N 7.391322 E, and Costa del Pino, 45.610466 N 7.378247 E), the orebody is a 50-70 m-thick, 600 m-long continuous lens that dips and wedges out northward (Di Colbertaldo et al., 1967). This orebody was extensively exploited in the second half of the twentieth century by sublevel caving. At Site 2 (western slope of Montzalet, 45.618124 N 7.386316 E) and Site 3 (Larsinaz mine, 45.619119 N 7.377135 E), the intensely mineralized rock volumes are much smaller, and consist of disseminations and veins at Site 2 and of a less than 10 m-thick lens at Site 3 (Stella, 1916). The mineralized serpentinite was subjected to only low degrees of Alpine deformation and metamorphism (Carbonin et al., 2014), which allowed extensive preservation of the original structures (see below).

3. Materials and methods

3.1. Petrographic and mineralogical analysis

Sixty-eight rock samples from the Cogne mining area were collected from mine dumps and outcrops and studied by means of optical microscopy in thin polished sections. No potential source of lead was present during any stage of the sample preparation, to avoid contamination that could invalidate the subsequent geochronological analyses. Mineral identification was aided by micro-Raman spectroscopy, using a Thermo Scientific™ DXR™ confocal Raman system at the Chemistry Department of the University of Padua (Italy). We chose a 532 nm laser working at a power of 5-10 mW. All of the Raman spectra were collected with a 50x LWD objective lens, reaching a spatial resolution of ~1 μm. Raman spectroscopy was crucial for the identification of serpentine minerals, for which we followed the guidelines by Groppo et al. (2006) and Carbonin et al. (2014). Selected samples were further investigated using a scanning electron microscope (SEM). Back-scattered electron images were obtained using a CamScan MX 2500 SEM at the Department of Geosciences of the University of Padua (Italy) equipped with a LaB_6 crystal, working at 20 kV accelerating voltage and 140 nA current.

Mineral compositions of major minerals were determined by electron microprobe analysis (EPMA) using a CAMECA SX-50 electron microprobe, equipped with four WDS spectrometers and one EDS spectrometer, at IGG-CNR, Padua (Italy). The Kα emission lines of ten elements (Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe) were measured using the following natural and synthetic minerals and oxides as standards: albite (Na), diopside (Si, Ca), orthoclase (K), MgO, Al_2O_3, $MnTiO_3$, Cr_2O_3 and Fe_2O_3. Working conditions were 20 kV, 20 nA, 10 s for peak and 5 s for the background on each side of the peak.

3.2. Bulk rock compositions

Fourteen rock samples, representative of the main lithologies encountered in and around the deposit, were analysed for major, minor and selected trace elements by X-ray fluorescence (XRF). The samples were prepared as fine powder by means of a Retsch M0 agate mortar grinder and a Retsch RS100 vibratory disk mill, equipped with agate disks. The powder samples, fused into beads, were then analysed using a Philips PW2400 XRF wavelength-dispersive sequential spectrometer equipped with a Rh tube at the Department of Geosciences of the University of Padua (Italy). Reference standards were natural geological samples (Govindaraju, 1994). The relative analytical precision is estimated to within ±0.6% for major and minor elements and within ±3% for trace elements. The relative accuracy is within ±0.5% for Si, ±3% for the other major and minor elements, and ±5% for trace elements. Detection limits are better than 0.01 wt% for Al, Mg and Na, 0.2 wt% for Si and 0.005 wt% for Ti, Fe, Mn, Ca, K and P. For trace elements, the detection limits are 3 ppm for Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Th, and U, 5 ppm for Sc, V, Ga, and Pb, 6 ppm for Cr, and 10 ppm for Ba, La, Ce, and Nd.

The geochemistry of seven whole-rock samples was further investigated by inductively coupled plasma mass spectrometry and emission spectroscopy (ICP-MS/ES) analyses, which were performed by Bureau Veritas Mineral Laboratories (Canada). The pulverised rock samples were mixed with $LiBO_2/Li_2B_4O_7$ flux and fused. The cooled beads were then digested with ACS grade nitric acid. The detection limits for trace elements are: 1 ppm for Be, Sc, Sn, and Ba; 8 ppm for V; 14 ppm for Cr; 0.2 ppm for Co and Th; 20 ppm for Ni; 0.5 ppm for Ga, Sr and W; 0.1 ppm for Y, Zr, Nb, Cs, Hf, Ta, U, La, Ce; 0.3 ppm for Nd.

3.3. U-Th-Pb dating

Thirteen thin sections of magnetite ore were scanned for uraninite crystals by back-scattered electron imaging with a Scanning Electron Microscope (SEM). Four of these samples showed uraninite grains of sufficient size to allow their chemical analysis by EPMA and successive dating by the U-Th-Pb method. Uraninite compositions were measured at the Department of Earth Sciences of the University of Milan (Italy), using a JEOL JXA-8200 electron microprobe equipped with five WDS and one EDS spectrometers. An accelerating voltage of 15 kV and a beam current intensity of 20 nA were used. Nine elements were measured by WDS spectrometry using the following X-ray lines: Mg$K\alpha$, Si$K\alpha$, Ti$K\alpha$, Ca$K\alpha$, Cr$K\alpha$, Fe$K\alpha$, U$M\beta$, Th$M\alpha$ and Pb$M\alpha$. The counting time was 60 s for the peak and 30 s for the background for all analysed elements. The standards were olivine (Mg), grossular (Si and Ca), ilmenite (Ti), fayalite (Fe), pure Cr and synthetic UO_2, ThO_2 and PbO. Detection limits for elements relevant to geochronology are 290 ppm for U, and 170 ppm for Th and Pb. Relative errors (relative standard errors) of 0.1%, 0.5% and 0.7% for U, Th and Pb concentrations, respectively, were calculated on the basis of 5 repetitions of the same measurement. However, a more realistic minimum relative error for U, Th and Pb concentrations >7500 ppm is 2% (Cocherie and Albarede, 2001).

Chemical maps were preliminarily acquired on the uraninite grains to assess the presence of chemical zoning. In order to collect a significant amount of data, we performed both single spot analyses and automated traverses. The latter method allowed us to obtain a large number of data points, although the proportion of mixed or poor-quality analyses increased. Thus, prior to calculating ages, we excluded the analyses which showed obvious contaminations, low totals or anomalously low Pb contents, if compared to adjacent points in the same traverse.

The possibility of dating uraninite with EPMA was discussed by Bowles (1990) and calculated ages were demonstrated to be accurate and consistent with independent isotopic measurements (Bowles, 2015; Cross et al., 2011). According to Bowles (2015), the best accuracy is obtained for ages from ~2 Ma to 700-1000 Ma: the lower limit is imposed by the EPMA detection limit of Pb and the upper limit is linked to metamictization of the uraninite crystal lattice, which may lead to Pb loss. Meaningful ages are obtained if the initial concentration of non-radiogenic Pb is negligible and the U-Th-Pb system remained closed after uraninite crystallization. The former assumption is considered to hold true because Pb^{2+} is incompatible in the uraninite crystal structure (Alexandre and Kyser, 2005), whereas the latter assumption needs to be assessed by careful sample examination.

The formula used to calculate the age *t* (in years) is (Montel et al., 1996):

$$\mathrm{Pb} = 208(\mathrm{Th}/232) \cdot [\exp(\lambda^{232} \cdot t) - 1] + 206(\mathrm{U}/238.04) \cdot [1 - ({}^{235}\mathrm{U}/{}^{238}\mathrm{U})] \cdot [\exp(\lambda^{238} \cdot t)] +$$

$$+ 207(\mathrm{U}/238.04) \cdot ({}^{235}\mathrm{U}/{}^{238}\mathrm{U})] \cdot [\exp(\lambda^{235} \cdot t)],$$

where Th and U are the measured concentrations in ppm, λ^{232}, λ^{238}, λ^{235} are the decay constants of ^{232}Th, ^{238}U and ^{235}U, respectively, and $^{235}U/^{238}U$ is the bulk Earth's uranium isotopic ratio. The values used in the calculations are: $\lambda^{232} = 4.9475 \cdot 10^{-11}$ a^{-1} (LeRoux and Glendenin, 1963); $\lambda^{238} = 1.55125 \cdot 10^{-10}$ a^{-1} and $\lambda^{235} = 9.8485 \cdot 10^{-10}$ a^{-1} (Jaffey et al., 1971); $^{235}U/^{238}U = 0.0072559$ (Hiess et al., 2012). To obtain an initial guess of *t* we used the formula (modified from Bowles, 2015):

$$t = (1/\lambda^{238}) \cdot \ln (1 + \mathrm{Pb}/\{[1 - ({}^{235}\mathrm{U}/{}^{238}\mathrm{U})] \cdot 206(\mathrm{U}/238.04)\}).$$

Then the difference between the calculated and the measured values of Pb is minimized by least-squares method, varying *t*. Whenever possible, ages were obtained as weighted averages of several analyses, after outlier rejection based on a modified 2σ set of criteria (Ludwig, 2012).

3.4. Trace elements in magnetite

Trace elements in magnetite were measured by laser-ablation inductively-coupled plasma mass spectrometry (LA-ICP-MS) at the Petrology of the Ocean Crust Laboratory, University of Bremen (Germany), using a high-resolution double-focussing ThermoFinnigan Element2, equipped with a solid-state laser with a wavelength of 193 nm (New Wave UP193). Magnetite grains were analysed on standard thin polished sections using a 35 μm laser spot size, a pulse frequency of 5 Hz, an irradiance at the sample of ~1.3 GW/cm^2 and an acquisition time of 60 s, comprehensive of 25 s for background measurement. To avoid any risk of contamination on the surface of the rock section, the zone to be investigated was pre-ablated using two laser pulses with 50 μm spot size. The analysed elements (^{25}Mg, ^{29}Si, ^{43}Ca, ^{47}Ti, ^{51}V, ^{53}Cr, ^{55}Mn, ^{57}Fe, ^{59}Co, ^{60}Ni, ^{66}Zn, ^{90}Zr, ^{98}Mo) were measured in low-resolution mode in order to shorten the acquisition time, although preserving high counts per second (cps). We opted for this configuration to avoid deep ablation pits, thus reducing the probability of hitting inclusions or adjacent minerals. The Fe concentration of magnetite as determined by EPMA was used as an internal standard. External standards (reference materials NIST61, BCR-2G and BHVO) were analysed under the same conditions as the samples every 5 to 9 analyses during the same session, in order to check for possible drift. Signal files, reporting intensities (cps) vs. time, were inspected for possible heterogeneities related to the presence of inclusions and chemical zoning. Integration of the signal and calculation of concentrations were performed with the GeoPro™ software (CETAC Technologies). Detection limits (DL) were calculated on reference materials using the formula:

$DL_i = [3\sqrt{2}s_{bkgd}/(\bar{X}_{sgl} - \bar{X}_{bkgd})] \cdot C_i,$

where i is the ith element, s_{bkgd} is the sample standard deviation of the background (in cps), $\bar{X}_{sgl}$ and $\bar{X}_{bkgd}$ are the average signal and the background (in cps) respectively, and C_i is the concentration (in ppm) of the ith element in the reference materials.

The statistical relationships between chemical elements in magnetite were explored by robust principal component analysis (PCA), using the function "pcaCoDa" in the "robCompositions" library for R software (Templ et al., 2011). Robust PCA was preferred to "classical" PCA because it is less sensible to outliers (Filzmoser et al., 2009; Filzmoser and Hron, 2011). Four analyses (out of ninety-four) with V contents below the detection limit were excluded from calculations.

3.5. Geochemical modelling

In an attempt to simulate the genesis of the Cogne deposit in a seafloor hydrothermal model system, fluid-rock interactions were modelled with the EQ3/6 (Version 8.0a) software package (Wolery, 2013), using the database compiled by Klein et al. (2009), which contains thermodynamic properties of minerals and solutes in the 0-400°C range at the fixed pressure of 500 bar. The database was modified to include revised data for $HCl_{(aq)}$ (Ho et al., 2001), $NaCl_{(aq)}$ (Ho et al., 1994), $KCl_{(aq)}$ (Ho et al., 2000), $FeCl_{2(aq)}$ and $FeCl^{+}_{(aq)}$ (Ding and Seyfried, 1992). The modelling procedure, which in the first steps follows that of Klein et al. (2009), is described below.

First, 1 kg of modern seawater (Table 1; composition from Klein et al., 2009) is speciated at 25°C and 1 bar. Then, seawater is heated and reacted with 1 g of fresh harzburgite (Table 2) in a closed system to the desired temperature (at P = 500 bar), to simulate a downward fluid path towards the reaction zone (Klein et al., 2009). The chosen pressure of 500 bar simulates conditions at ~2000 m below seafloor, which do not exceed the reported depth of magma chambers fuelling hydrothermal fields on slow-spreading ridges (~3 km; Singh et al., 2006), assuming a 3000-m water column, which is a typical value for modern slow-spreading ridge hydrothermal systems (Edmonds, 2010). All the produced minerals are removed at the end of the run, because in a real fluid pathway they would be left behind by downwelling seawater. A positive effect of this step is to narrow down the f_{O_2} range in following calculations, thus improving the code stability (Wolery and Jarek, 2003). In the successive step, which simulates a reaction zone, 1 kg of the resulting hydrothermal fluid is reacted at 400°C with an increasing amount of either fresh harzburgite or Fe-gabbro (Table 2) in a closed system (Wolery and Jarek, 2003). We chose the temperature of 400°C because it maximizes Fe solubility, which is strongly temperature-dependent (Seyfried et al., 2004), and is also compatible with estimates of fluid temperatures in modern subseafloor reaction zones (T >375°C, Berndt et al., 1989; T ~ 400°C based on the maximum amount of heat that water can carry by buoyancy-driven advection, Jupp and Schultz, 2004 and references therein) and with measured temperatures of modern seafloor vent fluids (e.g., Edmonds, 2010). The reaction path is terminated after the maximum value of dissolved Fe is reached. Finally, the Fe-rich hydrothermal fluid is titrated in a closed system with selected lithologies (Table 2) at 300°C or 400°C, in accordance with the temperature range estimated for hydrothermal mineral assemblages by Carbonin et al. (2014). The equilibrium mineral assemblages and the relative abundances of the phases obtained for different water/rock (W/R) ratios are then compared to those observed in the natural rocks. The model does not account for solid solutions, hence, by suppressing Fe-Mg exchange in secondary phases, it maximises the extent of magnetite production.

4. Results

4.1. Petrographic features of the magnetite ores and mineral compositions

The Cogne magnetite ore is heterogeneous in terms of texture and gangue mineral assemblage. Three main textural types of magnetite ore are distinguished, which are termed here *nodular, fine-grained disseminated* and *vein*.

The nodular ores (Fig. 3a, b) are characterized by mm to cm-sized magnetite crystals in a silicate matrix, giving the rock a macroscopic appearance similar to that of nodular chromitites. The nodular textures show a continuum between three major subtypes, which are termed here *leopard*, *harrisitic* and *massive* subtype, respectively. In the leopard subtype, the magnetite crystals, which mostly consist of aggregates of subgrains, are subrounded and constitute up to 50 vol% of the rock. In the harrisitic subtype, the magnetite crystals form up to 10 cm-long rods, mimicking the texture shown by dendritic olivine in harrisite. In the massive subtype, the magnetite content is as high as 80-90 vol%, but subrounded crystals similar to those of the nodular ores are still recognizable.

The fine-grained disseminated ores consist of bands in the host-rock, which contain variable proportions of sub-millimetric magnetite grains (up to ~70 vol). The vein ores (Fig. 3c) are cm-thick, dismembered veins composed of magnetite, chalcopyrite and antigorite; the proportion of opaque minerals over the associated silicates is ~50 vol%.

Since the distribution of the different ore types is not uniform across the deposit, we will treat each sampling site separately.

4.1.1. Site 1

The magnetite orebody lies below magnetite-poor (3-6 vol% Mag) serpentinized tectonitic harzburgites. The harzburgites show a more or less developed foliation, and are characterized by the presence of lizardite + antigorite + magnetite ± talc pseudomorphs after former olivine and orthopyroxene (distinguished based on the presence of mesh and bastite textures, respectively) and relicts of accessory Mg-Al-rich chromite (Table 3). Magnetite is fine-grained (<20 μm) and Cr-bearing (Carbonin et al., 2014). A detailed description of the mineralogy and conditions of subseafloor serpentinization of these rocks was given in Carbonin et al. (2014; T = 200-300°C, log f_{O_2} = –36 to –30, log ΣS = –2 to –1).

Only nodular ores can be found at this site (Fig. 3a, b). Independently of the ore texture, the gangue mineral assemblage is fairly uniform and comprises, in the order of decreasing abundance, antigorite, lizardite, forsterite, brucite, clinochlore, carbonates, and Ti-rich chondrodite (Table 3). Antigorite composes more than 90 vol% of the matrix between the magnetite crystals. It usually shows an interlocking texture (average grains size = 150 μm), but it can form euhedral, randomly oriented blades when in contact with lizardite or magnetite, forming indented crystal boundaries with the latter mineral (Fig. 4a). This feature was already described in rocks from the western Alps by Debret et al. (2014), who interpreted it as a prograde dissolution texture produced during Alpine subduction metamorphism; however, the antigorite studied by Debret et al. (2014) generally has higher Fe content (up to 8 wt% FeO) than antigorite at Cogne (mostly <3 wt% FeO). Lizardite forms yellowish aggregates of submicron-sized crystals, which are interstitial between euhedral antigorite and magnetite. The Al_2O_3 content of lizardite (~5 wt%) is systematically higher than that in antigorite (<1 wt%). Forsterite (Fo_{99}) forms up to 50 μm anhedral crystals, usually arranged into elongated aggregates, which replace and seldom form pseudomorphs after antigorite. The forsterite crystals are often altered to fine-grained antigorite along the rim and the fractures. Brucite is of nearly pure Mg-endmember composition and forms subhedral, tabular crystals up to 200 μm in size. Clinochlore forms tabular crystals and intergrowths with antigorite. These intergrowths probably result from the breakdown of Al-rich lizardite. The carbonates (calcite, magnesite, dolomite) form anhedral patches which include antigorite, brucite and fine-grained (<50 µm) anhedral magnetite. Calcite is the most common carbonate and is also present as late veins. Ti-rich chondrodite forms up to 500 µm, colourless to pale yellow, anhedral crystals, which are sometimes surrounded by a corona of olivine. Rare accessory minerals are xenotime, sphalerite, Ni-bearing linnaeite, pyrrhotite and uraninite.

Magnetite-rich (~25 vol%) diopsidites have also rarely been found. In these peculiar rocks, magnetite is interstitial between mm- to cm-sized diopside crystals and coexists with antigorite, andradite and clinochlore. The assemblage antigorite + andradite appears to replace diopside. Samples of this kind were thoroughly described by Carbonin et al. (2014).

4.1.2. Site 2

At this site, the serpentinized tectonitic peridotite can be either replaced by fine-grained disseminated magnetite or crosscut by cm-thick magnetite + chalcopyrite + antigorite veins. The disseminated and vein ores are deformed and dismembered into lenses by Alpine deformation, which at small scale results in an anastomosing pattern of mm- to cm-spaced cleavage planes. This deformation is associated with dynamic recrystallization of antigorite and magnetite, the latter forming elongated porphyroclasts.

The disseminations occur as cm-sized magnetite-enriched bands in antigorite serpentinite and typically show relict features of the former serpentinized peridotite, i.e., bastites (Fig. 4b) and Mg-Al-rich chromite grains (Fig. 4c, d; Table 3). The Mg-Al-rich chromite grains (Fig. 4d) are anhedral and fractured. They are irregularly altered along the rims and fractures into Fe-rich (~41 wt% FeO) chromite + fine-grained Cr-rich (~4–6 wt% Cr_2O_3, determined by SEM-EDS) chlorite and are mantled by a continuous rim of Cr-bearing magnetite intergrown with antigorite and minor secondary diopside.

In the vein ores, magnetite forms elongated, millimetric patches with a chalcopyrite core in an antigorite matrix (Fig. 4e). Magnetite shows well developed crystal boundaries towards chalcopyrite, while the contacts to the surrounding antigorite are irregular. The limit between the vein and the host serpentinite is sharp.

In both disseminations and veins, antigorite shows an interlocking texture. When it is in contact to magnetite or lizardite it forms up to 100 μm-long euhedral lamellar crystals, producing typical indented boundaries. A generation of nearly pure diopside (Table 3) always accompanies magnetite mineralization. In magnetite disseminations, diopside forms up to 400 μm-long isolated needles, intergrown with antigorite (Fig. 4c, d), while in the vein ore, it forms rare aggregates of 10-60 μm long crystals disseminated in the vein selvages. From textural relationships, diopside appears to postdate the formation of bastite pseudomorphs after orthopyroxene in the host serpentinite.

4.1.3 Site 3

At this site, the magnetite ores exhibit nodular textures, but only the leopard and massive subtypes are found. Antigorite is commonly the sole gangue mineral, but the leopard subtype can be characteristically enriched in diopside ± chlorite (Fig. 3d, 4f; Table 3). Antigorite shows an interlocking texture or forms euhedral crystals when in contact to magnetite or diopside. Antigorite veins crosscutting diopside crystals have been observed. Diopside has a nearly pure endmember composition. In the leopard ores, it forms a granofels composed of mm- to cm-sized subhedral crystals, which include subhedral millimetric magnetite. A late generation of smaller subhedral crystals (<50 μm) fills the interstices between larger grains. The diopside crystals may show patchy or concentric oscillatory zoning, determined by slight variations in Fe content. Textural relationships indicate that diopside formed during a late stage of magnetite growth (Fig. 4f), which was then locally overprinted by antigorite. Veins made up of euhedral diopside in a matrix of lizardite ± chlorite are commonly observed. Clinochlore is found in diopside-rich leopard ores and has variable Mg# ratios and Al contents (Table 3): the Al-rich variety is found as large (up to 1 mm) subhedral tabular crystals associated with diopside and magnetite; the Al-poor clinochlore is fine-grained and fills the interstices between larger clinochlore and diopside crystals. Calcite is found as interstitial material between diopside crystals and as late veins. Rare accessory minerals are andradite, uraninite, talc and apatite.

4.1.4. Inclusions in magnetite

The magnetite crystals can be rich in mineral inclusions, which, in the largest poikiloblats, are typically concentrated in their cores (Fig. 4a).

At Site 1, the most common inclusions are clinochlore and brucite lamellae (Table 3, often oriented along magnetite (111), anhedral calcite, anhedral sphalerite, rare anhedral pyrite, rare lizardite and forsterite, and very rare euhedral uraninite and apatite. Antigorite inclusions are often present in the outermost zones of the magnetite crystals. Composite inclusions made up of clinochlore + brucite or, rarely, clinochlore + calcite are also observed.

At Site 2, the most abundant inclusions are euhedral antigorite and anhedral sulphides. The sulphides consist of fine lamellar chalcopyrite–cubanite intergrowths and unmixed "bornite solid solution" grains, composed of lamellar intergrowths of bornite and chalcocite. Also present are pyrrhotite, which shows exsolution of Co-rich pentlandite, and sphalerite. Other minor included minerals are lamellar clinochlore and anhedral andradite.

At Site 3, the inclusions are mainly composed of clinochlore, which can be associated with rare andradite (Table 3) and very rare diopside and uraninite; antigorite inclusions are only present near the rims of the magnetite crystals.

4.2. Petrography of peculiar host rocks at sites 1 and 3

At sites 1 and 3, serpentinites showing a pegmatoid texture are associated with the magnetite ore and can be variably enriched in magnetite. In the barren rocks (Fig. 3e), cm-sized amoeboid domains made of dominant euhedral coarse-grained (50-300 μm) antigorite that replaces yellow, fine-grained (sub-micron sized) lizardite are interweaved with domains composed of mesh textured antigorite + lizardite and very fine-grained magnetite (magnetite I) lining the rims of the mesh. Lizardite is Al-rich in both domains (Raman peak at 382-385 cm^{-1}, indicating Al substitution for Si in the tetrahedral sites; Groppo et al., 2006). Coronae of interlocking antigorite line the boundaries between the two domains. In magnetite-enriched rocks, the early fine-grained (<30 μm), usually euhedral magnetite (I) associated with Al-rich lizardite (Table 3) is overgrown by a new generation of coarser-grained, subhedral to anhedral disseminated magnetite (magnetite II) + euhedral antigorite + lamellar clinochlore. Clinochlore probably forms as consequence of the transformation of Al-rich lizardite to Al-poor antigorite, since its content is proportional to the amount of antigorite that replaces lizardite. The two magnetite generations have similar major element compositions (Table 3). Possible variations in trace element compositions could not be determined because of the small crystal size of magnetite I. Magnetite II can completely replace the lizardite-rich domains, but the amoeboid shape of the domains and the antigorite coronae are usually preserved (Fig. 3f, Fig. 4g, h). On the contrary, the antigorite domains and coronae show only scarce anhedral magnetite (Fig. 4g, h). A magnetite-rich diopsidite, composed of dominant fine-grained diopside (<50 μm), subordinate magnetite and minor euhedral antigorite (<150 μm; Fig. 3f; Tables 3 and 4), has been observed in contact with the magnetite-rich pegmatoid serpentinite.

4.3. Bulk rock geochemistry

Bulk rock compositions are reported in Table 4. The magnetite-poor (Fe_2O_3 <8.5 wt%) serpentinized peridotites have major and trace element concentrations typical for refractory peridotites (cf. Andreani et al., 2014; Bodinier and Godard, 2003; Niu, 2004; Paulick et al., 2006), such as low Al_2O_3 (~1-3 wt%) and TiO_2 (0.02-0.1 wt%), high Ni (~1400-2800 ppm) and Cr (~1900-2600 ppm) and low

Co/Ni ratio (~0.05-0.07). The Cu and Zn contents (~20 and ~40-50 ppm, respectively) are also typical for upper mantle peridotites (cf. O'Neill and Palme, 1998; Niu 2004; Fouquet et al. 2010). The pegmatoid serpentinites have variable Al_2O_3 (~0.8-2.6 wt%), Fe_2O_3 (~4.5-10 wt%), Ni (~500-2000 ppm), and Cr (~10-2700 ppm) contents and Co/Ni ratios (~0.05-0.2). However, Cu and Zn show very little variation (~20 and ~30-40 ppm, respectively).

The magnetite-enriched (Fe_2O_3 >28 wt%) serpentinites have different compositions reflecting their distinct host rocks. The magnetite-rich pegmatoid serpentinite has a high Al_2O_3 content (~2 wt%) and a high Co/Ni ratio (~0.4), but low Ni, Cr, Cu and Zn contents (~280, ~10, ~70, ~60 ppm, respectively). The fine-grained disseminated ore has Al_2O_3, Cr and Ni contents (~1 wt%, ~2200, ~1200 ppm, respectively) in the same range as the magnetite-poor serpentinized peridotites, but has higher Cu and Zn contents (~200 and ~120 ppm, respectively) and a higher Co/Ni ratio (~0.1). With further increase in magnetite content, the concentrations of Cr (~1300 ppm) and Ni (~240 ppm) decrease, but the Co/Ni ratio increases (~0.6). The magnetite vein ore (Fe_2O_3 ~44 wt%) has low Ni (~500 ppm) and Cr (~70 ppm) contents and an intermediate Co/Ni ratio (~0.3). Moreover, it exhibits moderately high Zn (130 ppm) and the highest Cu content (~14000 ppm), which reflects the presence of chalcopyrite. The magnetite-rich diopsidite (Fe_2O_3 ~21 wt%) has a trace element composition similar to that of the pegmatoid serpentinite it is in contact with, but it has a higher Co/Ni ratio (~0.9).

In the nodular ores, the SiO_2 and MgO contents are inversely proportional to the amount of magnetite present. The Al_2O_3 and CaO concentrations are variable and reflect the different relative abundances of clinochlore and diopside (or carbonates), respectively. The TiO_2 content is generally low (0.02 wt%), but in the ore from Site 1 it can be slightly higher (~ 0.06 wt%), consistently with the presence of Ti-rich chondrodite. The nodular ores are virtually Cr-free (~10 ppm), have low Ni (~10-110 ppm) and relatively high Co (~320-440 ppm) contents, which translate into the highest observed Co/Ni ratios (~3-30). Moreover, compared to serpentinized peridotites and pegmatoid serpentinites, they show somewhat higher Cu and Zn (~30-50 ppm and ~80-100 ppm, respectively). The nodular ores, the magnetite-rich pegmatoid serpentinite and the magnetite-rich diopsidite share significant U and Th contents, which reach the maximum values at Site 1 (U = 2.9 ppm; Th = 0.9 ppm). In both magnetite-poor and magnetite-enriched serpentinized tectonitic peridotites, U and Th contents are below the detection limits of ICP-MS analysis (<0.01 and <0.02 ppm, respectively).

The relationships between magnetite enrichment, Co/Ni ratio and Cr content are shown in Figure 5. Magnetite enrichment is generally accompanied by an increase in the Co/Ni ratio, but shows no correlation with the Cr content. In particular, the Cr content is very low (<30 ppm) in the nodular ores, in the diopsidites and in most pegmatoid serpentinites (both magnetite-poor and magnetite-enriched) and is higher (Cr >1200 ppm) in both barren and magnetite-enriched serpentinites after peridotites.

4.4. Age of the deposit

The high U (+ Th) contents in nodular ores from Site 1 and Site 3 can be attributed to the presence of uraninite inclusions in magnetite. Uraninite forms anhedral to euhedral cuboctahedral crystals, ranging in size from ~1 to 40 μm (Fig. 6a-c, e, g). Textural evidence suggests that uraninite and magnetite (+clinochlore) were contemporaneous (Fig. 6b, g). The compositions of the uraninite crystals are reported in Table 5. The U/Th ratios are variable (3 to 21), especially at Site 1, where both the highest and the lowest Th contents were measured. The FeO and CaO concentrations are relatively high (FeO = 0.8-4.9 wt%; CaO = 0.06-1.2 wt%), but they are unrelated to PbO contents, which excludes late-stage alteration (Alexandre and Kyser, 2005). Excitation of the host magnetite within the microprobe interaction volume could explain the presence of Fe in the analyses. On the contrary, the Ca content is considered to be primary and ascribed to lattice-bound substitutions of Ca for U. A less than 1 μm-thick, U-rich rim is sometimes observed in uraninite crystals (Fig. 6e), and is ascribed to partial alteration.

The U-Th-Pb ages calculated for a group of three small (<10 μm) uraninite grains from Site 1 (Fig. 6a-c) are plotted in Fig. 6d. Due to the small grain size, only single-spot analyses were acquired. The weighted average age is 161.8 ± 3.5 Ma (MSWD = 0.51). Figure 6f shows the ages obtained for an aggregate of zoned grains from Site 1 (Fig. 6e). The crystals have a U-rich rim, which testifies for partial alteration. Therefore, we only considered sixteen analyses that form a plateau for PbO, UO_2 and ThO_2 concentrations (Fig. 7). The weighted average age for the plateau, after rejecting two outliers, is 150.8 ± 2.0 Ma (MSWD = 1.03). The weighted average age calculated for a big (~ 40 μm), unzoned uraninite crystal from Site 3 (Fig. 6g), which is intergrown with magnetite and contains chlorite, is 151.9 ± 1.4 Ma (MSWD = 0.91) (Fig. 6h). Also in this case only plateau PbO values were considered (Fig. 7). The two age determinations that yield the lowest uncertainties and best MSWD values (i.e., close to unity) are within errors of each other and are considered to be the most reliable. However, considering the limited age scatter, it is reasonable to combine all the data into a single age determination, which yields a value of 152.8 ± 1.3 Ma (MSWD = 1.3; Fig 6i).

4.5. Geochemistry of Cogne magnetite

The compositions of the Cogne magnetites are reported in Tables 3 and 6. The magnetites show significant substitutions of Fe by Mg and Mn (Fig. 8). The concentrations of these metals are the highest at Site 1 (median = ~24100 ppm and ~5000 ppm, respectively). Concentrations of Ca, Si, Mo, Zr and Cr are generally below or close to the ICP-MS detection limits; only magnetite forming the disseminated ore from Site 2 has significant Cr contents, which can be as high as ~150 ppm. Among the other trace elements, the concentrations of Ni, Co, Ti, and Zn are generally an order of magnitude higher than those of V (Fig. 8). The highest concentrations of Co are found at Site 1 (median = ~570 ppm), whereas the lowest concentrations are in magnetite in disseminated ore from Site 2 (median = ~80 ppm). In spite of across-site variations, the Co content is fairly constant in magnetite from the same sample. The Ti content is the highest in magnetite from disseminated ore from Site 2 (median = ~570 ppm) and the lowest in magnetite from diopside-rich rocks from Site 1 and Site 3 (median = ~60 ppm). The Ni and V contents are highest in magnetite from the magnetite-rich pegmatoid serpentinite (median = ~670 ppm and ~60 ppm, respectively). The lowest Ni and V contents are observed in Site 1 ore (median = ~80 ppm) and in vein magnetite (median = ~6 ppm), although in the latter both elements are highly variable. The Zn contents show minor variability: the highest values are found in the vein magnetite (median: ~160 ppm) and the minimum values are found in magnetite from Site 3 (median: ~80 ppm).

Robust PCA indicates that the two first principal components (PC1 and PC2) can explain 97% of the variability of the magnetite compositional data and thus can adequately be used to describe the various magnetite populations. As shown by the loading plot (Fig. 9), Mg, Mn, Co and Zn are highly correlated, while Ni is anti-correlated and V and Ti vary independently from the other elements. In the PC1 vs. PC2 plot, one cluster of samples, which encompasses the magnetites in the nodular ores from Site 1 and Site 3 and the magnetite-rich diopsidite, is characterized by the highest (Mg, Mn, Co, Zn)/Ni ratios. High Ni contents are instead distinctive of disseminated magnetite in serpentinized peridotite and in the magnetite-rich pegmatoid serpentinite from Site 3 (Fig. 8). These high-Ni magnetites form two distinct groups, in which high Ni is associated with high Ti (and Cr) and high V, respectively. Vein magnetites, having a very variable Ni and low overall V, plot in an intermediate position between high-Ni and low-Ni magnetites. When plotted on the Zn vs. Co plane (Fig. 10), most of the magnetites show a nearly constant Zn/Co ratio of ~0.28. Magnetites in the veins and in the fine-grained disseminated ore have higher Zn/Co ratios (~1).

4.6. Thermodynamic modelling

We attempted to reproduce the mineral assemblages observed at Cogne in a model seafloor hydrothermal system. The fluids produced by interaction at 400°C of modified seawater with harzburgite and Fe-gabbro (Table 2), respectively, provide two potential endmember compositions for fluids circulating in and reacting with the original oceanic substrate rocks. Harzburgite composes the uppermost part of the Cogne deposit and is the most common type of abyssal peridotite (Mével, 2003). Fe-gabbro is the most Fe-rich rock that can be found in the ophiolitic units of southern Valle d'Aosta (Benciolini et al., 1988; Bocchio et al., 2000; Dal Piaz et al., 2010; Polino et al., 2014) and it can be an efficient source of iron if altered at high temperature. Based on our calculations, dissolved Fe in the harzburgite-reacted fluid (Fig. 11a) increases from W/R ~1 to W/R ~7 where it reaches a maximum value of ~11 mmol/kg (604 ppm). The increase in Fe concentration follows the pH decrease that is in turn controlled by hydrolysis of mantle orthopyroxene, which is much more reactive than olivine at 400°C (Charlou et al. 2002). In general, the Fe-gabbro-reacted fluids are more acidic and more Fe-rich. The Fe concentration is up to one order of magnitude higher (Fig. 11b), reaching a maximum value of ~26 mmol/kg (1439 ppm) at W/R ~80. Such a high dissolved Fe content again reflects a pH minimum, which immediately follows the total breakdown of plagioclase. This is consistent with experimental evidence that plagioclase alteration to Mg-silicates (chlorite, epidote, talc) by seawater at 400°C and high W/R buffers pH to low values (Seyfried, 1987; Seyfried et al., 2010). Other major differences between the two fluid types at their Fe peak concern the concentrations of Mg and Si, which are about one order of magnitude lower and two order of magnitude higher, respectively, in the Fe-gabbro-reacted fluid. The high W/R ratios required to maximize the Fe contents could potentially be achieved in a highly fractured substrate, such as at the foot wall of a detachment fault in an oceanic core complex (e.g., McCaig et al., 2007).

The harzburgite-reacted and Fe-gabbro-reacted fluids carrying the maximum dissolved Fe were further reacted at either 300°C or 400°C with the different lithologies listed in Table 2. We considered temperatures ≥300°C to account for the ubiquitous presence of antigorite (predominant at T >300°C; Evans, 2004, 2010) in all ore assemblages at Cogne and because these high temperatures disfavour substitution of Fe for Mg in minerals (especially in brucite; Klein et al., 2009), thus accounting for the very high 100 · $Mg/(Mg+Fe)_{mol}$ ratios (Mg# >90) of gangue minerals in the Cogne deposit (Table 3). Moreover, at the high temperatures considered, and especially at high W/R ratios, the thermodynamic properties of the very Mg-rich gangue minerals are well approximated by their Mg endmembers, hence neglecting solid solutions can be considered to be a minor problem. The only mineral phase that significantly deviates from the ideal composition is lizardite, which is always Al-rich (Table 3). However, textural evidence indicates that lizardite is a minor relict phase that was formed during an early serpentinization event and rarely survived the successive higher temperature ore-forming process (cf. section 4.1). Accounting for the presence of Al-rich lizardite would not have significantly influenced the modelling of the fluid-rock system at high temperature.

The mineral assemblages produced by hydrothermal fluid-rock interactions are shown in Figure 12. Magnetite is stable for both fluids over the whole considered W/R range at both 300°C and 400°C (with the exception of fresh troctolites reacting with harzburgite-reacted fluid at 300°C). Under *rock-dominated conditions* (W/R <1), the final alteration mineral assemblages are similar for both fluids: forsterite and brucite are generally formed in addition to magnetite, but their stability is dependent on temperature, with forsterite being stable at higher temperature (Fig. 12b, d) than brucite (Fig. 12a, c). Fayalite is predicted to form at both 300°C and 400°C in fresh troctolites and pegmatoid serpentinites. The presence of pure fayalite may be an artefact induced by neglecting solid solutions in olivine. Clinochlore is present in all mineral assemblages at 400°C (with the exception of the model of a fresh dunite reacting with harzburgite-reacted fluid), but at 300°C it forms in abundant quantities only in troctolites (both fresh and serpentinized) and pegmatoid serpentinites. Diopside is abundant only in Ca-rich rocks, i.e. harzburgites and troctolites (Table 2), and in troctolites it is associated with tremolite. In these rocks also minor anhydrite forms. At 300°C in fresh harzburgites and serpentinized dunites the diopside is soon destabilized and the liberated Mg and Si combine with dissolved Al to form clinochlore. At higher temperatures this reaction is limited to higher W/R ratios. Some phlogopite is produced during alteration of fresh troctolites. At *intermediate W/R ratios*, diopside disappears at both 300°C and 400°C. In troctolites, diopside breakdown is accompanied by an increase in the modal amount of tremolite (and fayalite at 300°C). In serpentinized harzburgites, diopside reacts at 300°C with brucite and magnetite to form andradite and antigorite (cf. reaction n. 44 in Frost and Beard, 2007; Fig. 12a, c). Talc becomes abundant in pegmatoid serpentinites at 400°C, but at 300°C it only forms when the rocks react with Fe-gabbro derived fluid. Formation of talc is enhanced by the low pH, high Si and low Ca activities of the Fe-gabbro-reacted hydrothermal fluid. At *high W/R ratios*, in both fresh and serpentinized dunites and harzburgites, brucite reacts with either the harzburgite-reacted fluid or the Fe-gabbro reacted fluid to form antigorite or clinochlore, respectively. Talc is formed in Si-rich systems, i.e. those involving Si-rich lithologies (troctolites, pegmatoid serpentinite) or fluids (Fe-gabbro-reacted fluids). In the systems dominated by Fe-gabbro-reacted fluids, talc replaces forsterite and antigorite, thus forming talc + magnetite + clinochlore assemblages.

5. Discussion

5.1. Cogne as an ultramafic-hosted subseafloor hydrothermal deposit

5.1.1. Constraints from magnetite geochemistry and ocean seafloor studies

Important clues about the origin of the Cogne magnetite can be derived from the comparison with existing published datasets for magnetite from various genetic environments. The Cogne magnetite is poor in Ti and Cr (<640 ppm and <150 ppm, respectively), which is a typical feature for hydrothermal magnetite (Fig. 13). In fact, based on the data compiled by Dare et al. (2014), hydrothermal magnetite can be distinguished from magmatic magnetite, because the former has generally low Ti contents (<10000 ppm) and high Ni/Cr ratios (≥1), in virtue of the higher mobility of Ni in aqueous fluids. Cogne magnetite is also poor in V (<140 ppm) and rich in Mn (>2500 ppm), similar to hydrothermal magnetite from skarn deposits (Fig. 14). However, the Cogne magnetite ore was not emplaced in carbonate rocks but in mantle serpentinites, as testified by the geochemical and textural features of the host rocks.

Serpentinization of peridotites can produce magnetite that is depleted in Cr, Ti, V and Ni compared to the primary magmatic magnetite (Boutroy et al., 2014). However, serpentinization alone cannot account for the amount of magnetite observed in most of Cogne rocks. In fact, magnetite production during serpentinization is limited by the amount of FeO available in the peridotite, which is commonly less than 10 wt% (Bodinier and Godard, 2003). Therefore, an efficient mechanism of mobilization and concentration of Fe is needed to explain the formation of the Cogne deposit.

Low-T (100-300°C) hydrothermal fluids causing peridotite serpentinization at high W/R can leach Fe from the peridotite and precipitate it as magnetite in veins (up to a few cm-thick), as reported for the Bou Azzer ophiolite, Morocco (Gahlan et al., 2006). However, the compositions of Bou Azzer vein magnetites, although considerably depleted in trace elements as a consequence of their low formation temperatures (Nadoll and Koenig, 2011), are very different from those of Cogne magnetites. The latter have higher Co/Ni ratios (0.2-67 vs. 0.004-0.12) and are richer in Mn (2600-5000 vs. 400-470 ppm), Zn (80-160 vs. 3-20 ppm) and Mg (5600-24000 vs. 97-1000 ppm). These differences suggest that the formation of Cogne magnetite took place under substantially dissimilar physicochemical conditions.

Some indications on the various factors that controlled the composition of Cogne magnetite can be derived from the PCA (Fig. 9). The PC1 clearly discriminates high-(Mg, Mn, Co, Zn) magnetites in nodular ores and diopsidites from high-(Ni, V, Ti) magnetites in fine-grained disseminated ore and in magnetite-rich pegmatoid serpentinite. The relatively low Mn, Co and Zn contents in the host rocks and the fluid-compatible nature of these metals suggests that the composition of the high-(Mg, Mn, Co, Zn) magnetites was controlled by an externally-buffered fluid (cf. Dare et al., 2014; Nadoll et al., 2014). The high Co/Ni ratios these magnetites (Table 6) also support this hypothesis, because it would suggest a mafic metal source (cf. Melekestseva et al., 2013), which is in contrast with the ultramafic nature of most of the Cogne host rocks. On the contrary, the high-(Ni, V, Ti) magnetites are more enriched in elements that are weakly mobile and/or relatively abundant in the host rocks, suggesting formation under rock-buffered conditions (cf. Nadoll et al., 2014). The PC1 may thus be interpreted as reflecting magnetite formation under different W/R ratios from possibly similar parent fluids. The PC2 further discriminates between the different host rocks (i.e. high-V magnetite in pegmatoid serpentinite and high-Ti magnetite in serpentinized tectonitic peridotites). Magnetite in veins shows intermediate geochemical features between hydrothermal fluid-buffered and host rock-affected compositions.

Hydrothermal fluids carrying a significant load of transition metals (high Fe, Mn, Cu, Zn ± Co ± Ni) issue from ultramafic substrates in high-T (>350°C) hydrothermal systems associated with oceanic core complexes in slow-spreading mid-oceanic ridges, such as at Rainbow and Logatchev on the Mid-Atlantic Ridge (Douville et al. 2002; Andreani et al., 2014). In particular, the hydrothermal vent fluids at Rainbow are the richest in Co (Douville et al., 2002), have the highest Co/Ni ratios (~4) and are probably saturated in magnetite + chlorite + talc (Seyfried et al., 2011). The surveyed portion of the Rainbow hydrothermal deposit is almost entirely made up of sulphides (Fouquet et al., 2010; Marques et al., 2006, 2007), as expected for the upper part of a seafloor hydrothermal system, where the hot hydrothermal fluid mixes with seawater (Janecky and Seyfried, 1984). Notwithstanding this, at Rainbow, hydrothermal magnetite is locally abundant in serpentinites hosting sulphide stockworks and in semi-massive sulphides, where magnetite sometimes replaces pyrite (Marques, 2005). Magnetite forming coarse-grained disseminations in the serpentinites that host stockworks at Rainbow precipitated later than the sulphides during a distinct hydrothermal stage (Marques et al., 2006) and, notably, has a similar geochemical fingerprint as magnetite in fine-grained disseminations in serpentinized peridotites at Cogne (the concentrations of the trace elements, with the exception of Si, are in the same order of magnitude). Recently, Yıldırım et al. (2016) described a hydrothermal magnetite mineralization in a non-metamorphic volcanogenic massive-sulphide (VMS) deposit from the Upper Triassic-Upper Cretaceous Koçali complex, a Tethyan ophiolite in Turkey. These findings and the above observations support the possibility that Cogne magnetite has directly formed in a seafloor hydrothermal system. The presence of a positive magnetic anomaly at Rainbow has been ascribed to a ~$2 \cdot 10^6$ m^3 magnetite-rich stockwork zone (Szitkar et al., 2014). If this volume was entirely composed of magnetite, it would correspond to 10 Mt of mineral, which is on the same order of magnitude as the estimated amount of magnetite at Cogne (~12 Mt). It is worth noting that the Rainbow hydrothermal system is still highly active (Fouquet et al. 2010) and its vent fluids are magnetite-saturated (Seyfried et al., 2011). It can thus be inferred that the Rainbow hydrothermal system may eventually produce at depth a magnetite deposit of comparable size as Cogne.

In such a scenario, the general scarcity of sulphides at Cogne, along with their presence in the veins above the main magnetite bodies, suggest that the exposed mineralized section represents the deep segment of a seafloor, ultramafic-hosted, high-temperature hydrothermal system, which was possibly associated with shallower, now eroded, sulphide-rich bodies. According to this interpretation, the magnetite + sulphide veins and fine-grained disseminations in the hanging wall serpentinite (Site 2) may mark the transition between the magnetite-rich and the sulphide-rich portions of the hydrothermal system (Fig. 15).

5.1.2. Geological, geochronological and textural constraints

The Cogne mantle peridotites underwent complete serpentinization at 200-300°C beneath the seafloor of the Jurassic Piedmont-Liguria ocean (Carbonin et al., 2014). Our radiometric data on magnetite-associated uraninite (152.8 ± 1.3 Ma) places the ore-forming event in proximity of the Kimmeridgian-Tithonian boundary (152.1 ± 0.9 Ma). This age overlaps with that of the spreading of the Piedmont-Liguria ocean, as inferred by biochronological dating of supra-ophiolitic deep-sea sediments (radiolarites), whose oldest ages span from Late Bajocian to Middle Bathonian (~ 168 Ma; Cordey et al., 2012), and by radiometric dating of magmatic rocks, which places the latest magma pulses (mainly plagiogranites) in the Western Alps and Liguria in the Kimmeridgian-Tithonian (~157.3 ± 1.0 - ~145.5 Ma; Lombardo et al., 2002; Manatschal and Müntener, 2009 and references therein).

Very little information can be obtained about the original lithological and thermal structure of the oceanic lithosphere at Cogne, because of the limited exposure. Some indirect information can be obtained from the nearby Mt. Avic serpentinite massif (Fig. 1). Although located in a different structural position in the orogen (see Dal Piaz et al., 2010), the Mt. Avic massif provides the most complete section of the oceanic lithosphere of the Alpine Tethys in the southern Valle d'Aosta region. In the Mt. Avic massif, dominant serpentinized mantle peridotites, associated with gabbroic intrusions (Mg-metagabbros), rodingitic dykes, minor Fe-Ti-oxide metagabbros and other metabasites (Dal Piaz et al., 2010; Fontana et al. 2008, 2015; Panseri et., al 2008), are thought to have been exposed on the seafloor in an oceanic core complex (Tartarotti et al., 2015). This is consistent with the proposed slow- to ultra-slow nature of the Piedmont-Liguria ocean (Manatschal et al., 2011; Manatschal and Müntener, 2009; Piccardo et al., 2008). Jurassic magmatic activity in the Mt. Avic massif was sufficient to sustain high-temperature hydrothermal convection cells, as testified by widespread, small, massive sulphide (Cu-Fe-Zn) deposits, which are mostly associated with metabasites (Castello et al., 1980; Castello, 1981; Martin et al., 2008; Dal Piaz et al., 2010; Fantone et al., 2014) and are thought to have formed in the seafloor (Martin et al., 2008). The distinctive enrichment in Co and Cu observed in Cogne nodular and vein magnetite ores, respectively, as well as the low Ni content in all magnetite ore types, suggests a contribution from mafic sources or a combined contribution from ultramafic and mafic sources, as observed in some ultramafic-hosted, mid-ocean ridge, hydrothermal deposits (e.g. Rainbow, Fouquet el al., 2010; Marques et al., 2006; Semenov, Melekestseva et al., 2014) and in other ultramafic-hosted VMS deposits in ophiolitic belts (Melekestseva et al., 2013). In analogy with these modern and ancient examples, also at Cogne the presence of deep magmatic intrusions (gabbro) would be required to provide heat and suitable chemical conditions (low pH) to produce metal-rich fluids (e.g., Marques et al., 2006; Seyfried et al., 2011). Gabbroic intrusions, mainly represented by gabbros and Fe-Ti gabbros, are not observed in the small Cogne unit, but are common in the wider Mt. Avic area (see above) and in the other ophiolitic units in southern Valle d'Aosta (Grivola-Urtier and Zermatt-Saas units; Benciolini et al., 1988; Bocchio et al., 2000; Dal Piaz et al., 2010; Polino et al., 2014). Therefore, we infer that similar rock types could have occurred also at Cogne in the original oceanic lithosphere section.

The texture, geochemistry (low Co/Ni, high Cr) and relict mineralogy (bastites, Mg-Al-rich chromite) of Site 2 magnetite-enriched serpentinites suggest that the host rock was a harzburgitic mantle tectonite, with composition comparable with that of modern abyssal peridotites. However, chemical and textural evidence from both Site 1 and Site 3 indicates that part of the hydrothermal ore was emplaced in more atypical serpentinites, which exhibit a ghost pegmatoid texture marked by interlobate domains separated by coronae structures (Fig. 3f). Similar textures have been described in some troctolites from modern oceanic and ancient ophiolitic settings (Blackman et al., 2006; Renna and Tribuzio, 2011). These rocks are interpreted to have formed from melt-impregnation and melt-peridotite reactions, which dissolved orthopyroxene and partially dissolved olivine producing rounded or embayed grain boundaries (Drouin et al., 2009; Renna and Tribuzio, 2011; Suhr et al., 2008). In particular, olivine-rich troctolites originating from melt-peridotite reactions are usually coarse-grained and can show a harrisitic texture (Renna and Tribuzio, 2011), which is reminiscent of the “harrisitic” texture of some nodular ores at Cogne. This suggests that many, if not most, nodular ores at Cogne formed by hydrothermal alteration of original serpentinized troctolites, with magnetite preferentially replacing the original olivine domains.

5.1.3. Insights from thermodynamic modelling

From a qualitative point of view, interaction of various types of fresh or serpentinized mantle rocks with either a harzburgite-reacted fluid at intermediate to high W/R or a Fe-gabbro-reacted hydrothermal fluid at intermediate W/R (Fig. 12) can produce mineral assemblages made of magnetite + antigorite + clinochlore ± brucite (at 300°C) ± forsterite (at 400°C), which resemble the most common mineral assemblages in the Cogne magnetite ores. However, even when the natural mineral assemblage is qualitatively reproduced, the calculated modal magnetite content invariably remains too low to produce a magnetite ore. This indicates that our model fluids are not sufficiently

Fe-rich to account for the formation of the Cogne deposit. Note that a Rainbow-type fluid (Table 7) would produce broadly similar mineral assemblages as our model fluids, since its Na, Mg, Si, Fe, Cl concentrations are fairly similar. We could not envisage any other reasonable substrate lithology which could have released significantly higher Fe to the hydrothermal fluids under reasonable conditions. This suggests that additional processes other than simple seawater/rock reactions have played a role in the formation of the magnetite parent fluids.

One such process could be phase separation in the hydrothermal fluid, which could have produced brines enriched in weakly volatile Fe. Phase separation is commonly invoked to explain the wide chlorinity range observed in modern seafloor hydrothermal vent fluids (e.g., Bischoff and Rosenbauer, 1987; Charlou et al., 2002; Douville et al., 2002; Foustoukos and Seyfried, 2007; Pester et al., 2014; Seyfried et al., 2011). A higher chlorinity would enhance solubility of metals as chloride complexes. At the same time, H_2S partitioning into the vapour phase would cause sulphide undersaturation in the brine (Bischoff and Rosenbauer, 1987; Fouquet et al., 2010; Seyfried et al., 2004; Seyfried at al., 2010; Von Damm, 2004), thus delaying sulphide precipitation. This is in agreement with the general scarcity of sulphides in the Cogne magnetite ores. The presence of chalcophile metals in the fluid is still testified by Cu sulphides in magnetite veins from Site 2. In this case, the transition from bornite + magnetite to chalcopyrite + magnetite assemblages suggests a progressive variation in the parent fluids towards higher H_2S activity or lower Cu/Fe ratios (cf. Seyfried et al., 2004, 2010).

Another process which could potentially lead to enhanced Fe concentrations in the fluid is the incorporation of a magmatic gaseous component, which could promote acidification and thus increase Fe solubility (cf. Berkenbosch et al., 2012; de Ronde et al., 2011). However, assuming a gas composition similar to that of gases emitted from mafic lavas (Erta 'Ale volcano, Ethiopia; Sawyer et al., 2008), it can be calculated that a relatively high condensed gas/fluid mass ratio of 1:10 would increase the Fe concentrations only by a factor of ~2.3. This increase is too small to allow a significant increase in the final amount of precipitated magnetite. Therefore, phase separation remains the most likely hypothesis.

Another feature that is not explained by our models is the diopside-rich gangue observed at Site 3. Textural relationships suggest that diopside formed during a late stage of magnetite mineralization, most likely from a fluid with higher pH and/or higher Ca^{2+} activity (see Fig. 9 in Bach and Klein, 2009). This fluid could have derived from serpentinization of country peridotites and troctolites, and may thus have some affinity with rodingite-forming fluids. Alternatively, a higher Ca content could result from more extensive interaction with gabbroic rocks. The possible role of gabbroic rocks in producing Ca-Si-(Al)-rich fluids has been suggested, for instance, for fluids responsible for strong calcic metasomatism in fault zones in modern oceanic core complexes (Boschi et al., 2006).

5.2. Alternative hypotheses

As ultramafic rocks in ophiolitic massifs often contain accumulations of chromite (e.g., Bédard and Hébert, 1998), a potential origin of magnetite in Sites 1 and 3 could be by leaching of Cr from former chromitite bodies. Indeed, Cr appears to be mobile during high-temperature (>500-550°C) peridotite-water interactions, as shown by Arai and Akizawa (2014) for the Oman ophiolite. Also, in the Mt. Avic massif, some small-scale magnetite ores were apparently formed after former chromitites (Diella et al., 1994; Rossetti et al., 2009). There are two lines of evidence against this hypothesis for the Cogne magnetite. First, in the Mt. Avic ores, chromite is still preserved in the cores of the magnetite grains (Diella et al., 1994; Fontana et al., 2008; Rossetti et al., 2009), whereas neither chromite relicts nor Cr-rich magnetite cores are found in nodular and vein ores at Cogne. Second, there is no evidence for a high-temperature alteration at Cogne such as that described in the Oman ophiolite by Arai and Akizawa (2014). At the temperatures under which serpentinization and successive hydrothermal metasomatism at Cogne took place (200-300°C and 300°-400°C, respectively; Carbonin et al., 2014), Cr is essentially immobile and any Cr dissolved at higher temperatures deeper in the system should be precipitated (Arai and Akizawa, 2014). The immobility of Cr during magnetite mineralization is testified by the mantle tectonites containing the fine-grained disseminated magnetite from Site 2, which have similar bulk-rock Cr content as their magnetite-poor counterparts (Fig 5). In these rocks, the original Mg-Al-rich chromite (the main Cr carrier) was replaced *with no Cr loss* by Fe-rich chromite + Cr-rich chlorite, according to reactions of the type

$$\underset{\text{Mg-Al-rich chromite}}{24\,(Mg,Fe)(Al,Cr)_2O_4} + \underset{\text{serpentine}}{18\,(Mg,Fe,Al)_3Si_2O_5(OH)_4} + 12H_2O + O_2 \rightarrow$$

$$\underset{\text{Cr-rich chlorite}}{12(Mg,Fe,Al,Cr)_5(Si_3Al)O_{10}(OH)_8} + \underset{\text{Fe-rich chromite}}{14\,(Mg,Fe)(Cr,Fe,Al)_2O_4}$$

(cf. Mellini et al., 2005; Merlini et al., 2009), and then overgrown by Cr-poor magnetite (Fig. 4d). The P-T conditions for the subsequent Alpine metamorphism at Cogne are not precisely known. However, assuming a typical subduction geothermal gradient (<10°C/km), the coexistence of lizardite and antigorite in both serpentinized peridotites and pegmatoid serpentinites suggests temperatures not exceeding 390°C (Schwartz et al., 2013), which are too low to determine significant mobilization of Cr.

Iron (Mn) oxyhydroxides and Fe sulphide deposits are the most common forms of Fe accumulation in modern seafloor hydrothermal settings (e.g., Rona, 1988). In principle, magnetite may form by reduction and dehydration of Fe-oxyhydroxides or by desulphurization of Fe-sulphides during metamorphism. However, our geochronological data demonstrate that the magnetite-forming event was coeval with the spreading of the Piedmont-Liguria ocean and thus predates Alpine metamorphism. Also the geochemistry of Cogne magnetite ores and associated rocks contradicts the metamorphic hypothesis. In fact, in Fe-oxyhydroxide accumulations, an enrichment in trace elements such as P and Sr is typically observed (e.g., Hekinian et al., 1993; Puteanus et al., 1991). A similar enrichment is indeed preserved in seafloor hydrothermal Mn-(Fe) deposits in southern Valle d'Aosta ophiolites (median P_2O_5 = 0.06 wt%, median Sr = 1650 ppm; Tumiati et al., 2010), which were metamorphosed up to eclogite-facies conditions (T = 550 ± 60°C, P = 2.1 ± 0.3 GPa; Martin et al., 2008; Tumiati et al., 2015), but it is not observed in Cogne ores (P_2O_5 ≤0.01 wt%, median Sr = 1.6 ppm). In the same ophiolites, sulphide (pyrite + chalcopyrite) deposits show no evidence of S mobilization and depletion linked to subduction metamorphism (Giacometti et al., 2014). Consistently, serpentinized mantle tectonites overlying the Cogne magnetite orebody are not depleted in S (Table 4).

5.3. The role of the Alpine event

The present structural position of the Cogne serpentinite, the lithological associations and the shape of the orebodies are in part the result of the tectonic activity that accompanied the Alpine orogenesis. The main magnetite orebodies at Site 1 and Site 3 behaved as rigid masses during the early ductile deformation events and they were affected by only low degrees of shear deformation, thus preserving the original textures and the proportions between magnetite and gangue minerals. The Alpine deformation was more intense at Site 2, which was probably located in a peripheral position with respect to the main orebody, where the fine-grained disseminated ores and the associated veins were dismembered into lenses. The Alpine metamorphism did not promote significant magnetite remobilization, as testified by the lack of isotopic resetting in uraninite inclusions in magnetite. The Alpine metamorphism is possibly responsible for the transformation of lizardite into antigorite, which is observed also in rocks that do not contain hydrothermal mineralization (i.e. magnetite-poor serpentinized peridotites and pegmatoid serpentinites). In any case the metamorphic temperatures were not sufficient to cause significant serpentine dehydration, since neoblastic forsterite is not widespread and is only found within the nodular ore at Site 1. The restriction of neoblastic forsterite to this specific site suggests that its formation could be related to higher temperature conditions (~400°C) being attained locally during the magnetite hydrothermal event, rather than to the subsequent metamorphism. Based on the above considerations, we conclude that Alpine metamorphism did not play a significant role in concentrating magnetite, although Alpine deformation may have pulled away portions of the deposit (now exposed at sites 1, 2 and 3) that could have been much closer to one another in their original oceanic setting.

5.4 Stages of formation of the Cogne deposit

Considering all available data, we propose the following sequence of events for the formation of the Cogne deposit (Fig. 15):

1) Formation of an oceanic core complex made of tectonitic peridotites, containing bodies of gabbros and Cr-poor melt-impregnated peridotites (troctolites).

2) Extensive low-temperature serpentinization, producing lizardite serpentinites containing a first generation of disseminated magnetite (Cr-bearing in mantle tectonites and Cr-free in melt impregnated peridotites). This process probably occurred at high water/rock ratios and determined the complete serpentinization of the primary silicates and an extensive loss of Ca.

3) Production of a high-temperature, Fe-rich hydrothermal fluid by reaction of downwelling seawater with substrate rocks. The involvement of Fe-gabbros in the reaction zone is likely, as this would enhance the content of Fe in the fluid.

4) Phase separation in the upwelling hydrothermal fluid, producing a more Fe-rich brine.

5) Reaction of the upwelling hot brine (~300–400°C) with various lithologies (serpentinites after mantle tectonites and troctolites) at various fluid/rock ratios, producing the dissolution of lizardite and the precipitation of abundant magnetite along with antigorite and clinochlore (± brucite and forsterite), forming fine-grained disseminated, nodular and massive replacive ores. Further upwelling of the magnetite-buffered fluid produced magnetite + Cu-sulphide + antigorite veins and fine-grained disseminations in shallower serpentinites.

6) Circulation of late fluids with higher pH and/or higher Ca^{2+} activity, producing diopside-rich, magnetite-bearing metasomatic rocks.

6. Conclusions

The Cogne magnetite deposit was formed at ~150 Ma by hydrothermal processes during an advanced stage of the opening of the Piedmont–Liguria ocean. Based on geological and petrographic features and on geochemical and mineralogical similarities with some modern ultramafic-hosted VMS deposits on mid-ocean ridges, the exposed mineralized section at Cogne may represent the deep segment of a seafloor, high-temperature (~300–400°C) hydrothermal system, which was possibly associated with shallower, now eroded, sulphide-rich bodies (Fig. 15). As suggested by thermodynamic modelling, simple seawater-rock interactions cannot produce the Fe endowment observed at Cogne. Fractionation processes such as phase separation were probably critical to generate sufficiently Fe-rich hydrothermal fluids capable to precipitate large amounts of magnetite in various types of mantle host-rocks. The possible occurrence of similar ultramafic-hosted magnetite deposits in present-day oceanic settings could contribute to explain the presence of significant magnetic anomalies centred on active and inactive ultramafic-hosted hydrothermal fields (Fujii et al., 2016; Szitkar et al., 2014; Tivey and Dyment, 2010).

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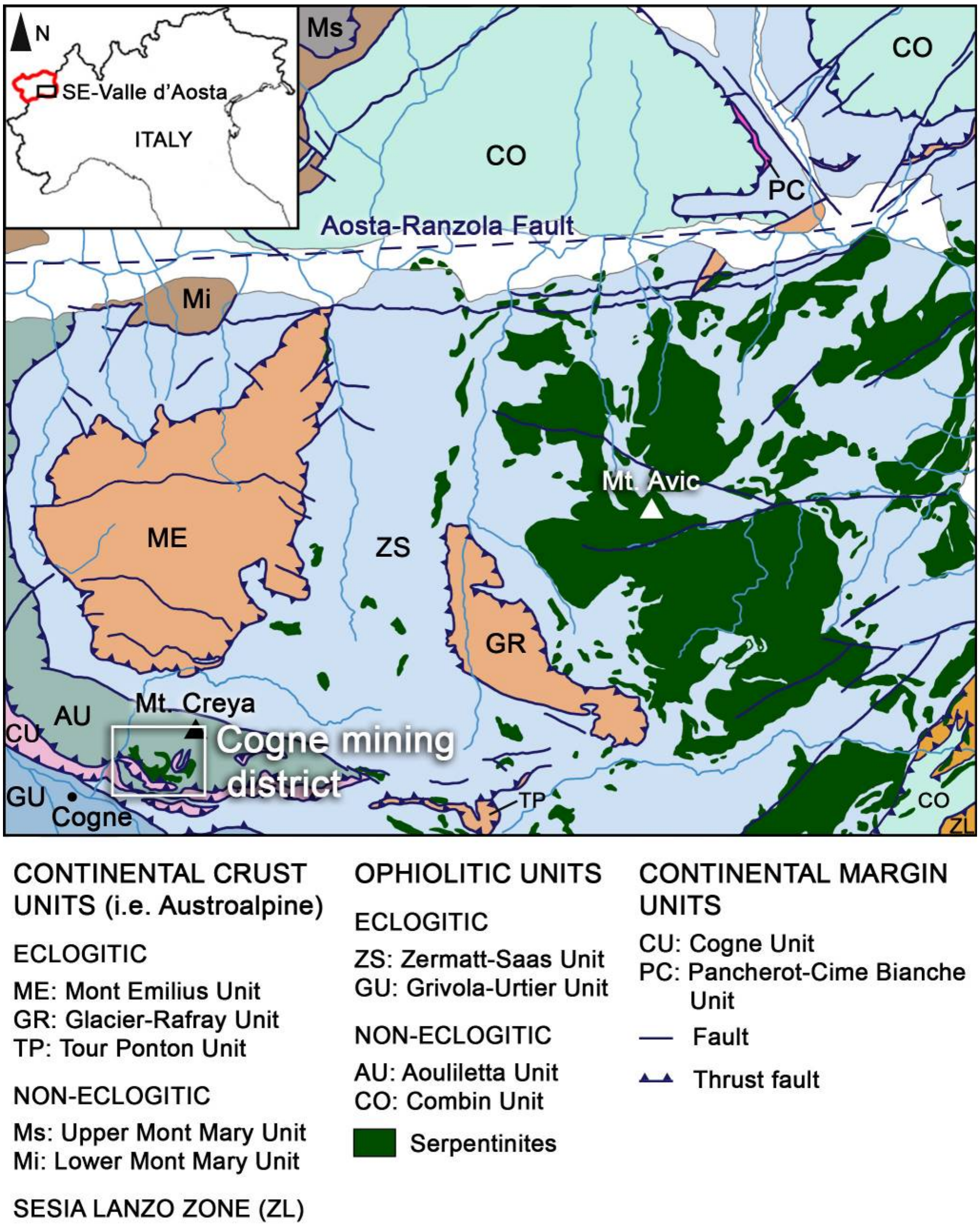


Fig. 1 Geological map of the southern Valle d'Aosta region. Redrawn and modified after Dal Piaz et al. (2010).

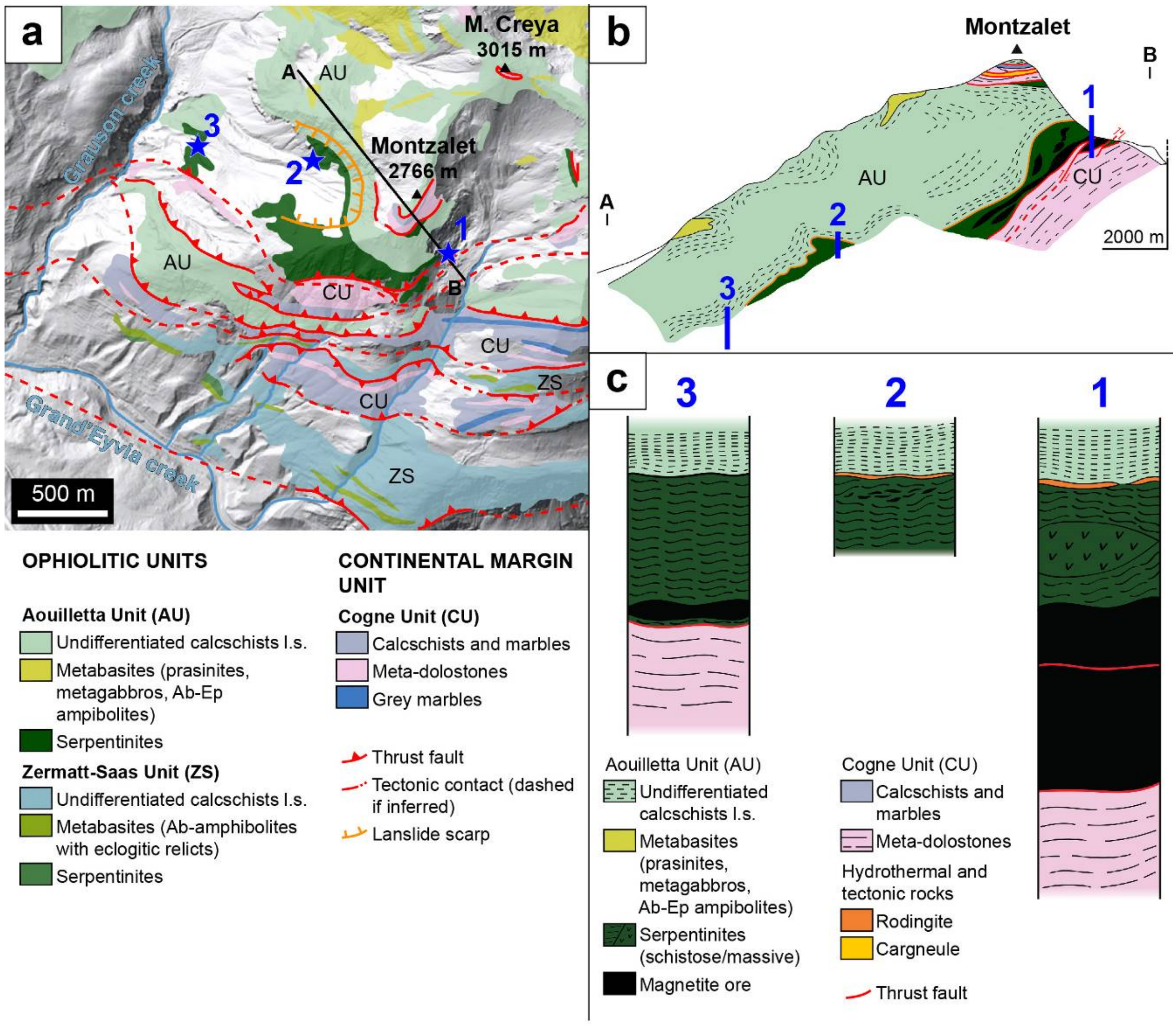


Fig. 2 3D model of the Cogne mining district depicting the structural relationships between the Cogne serpentinite and the associated units. Numbers indicate the sampling sites (see text for details). Units after Dal Piaz et al. (2010).

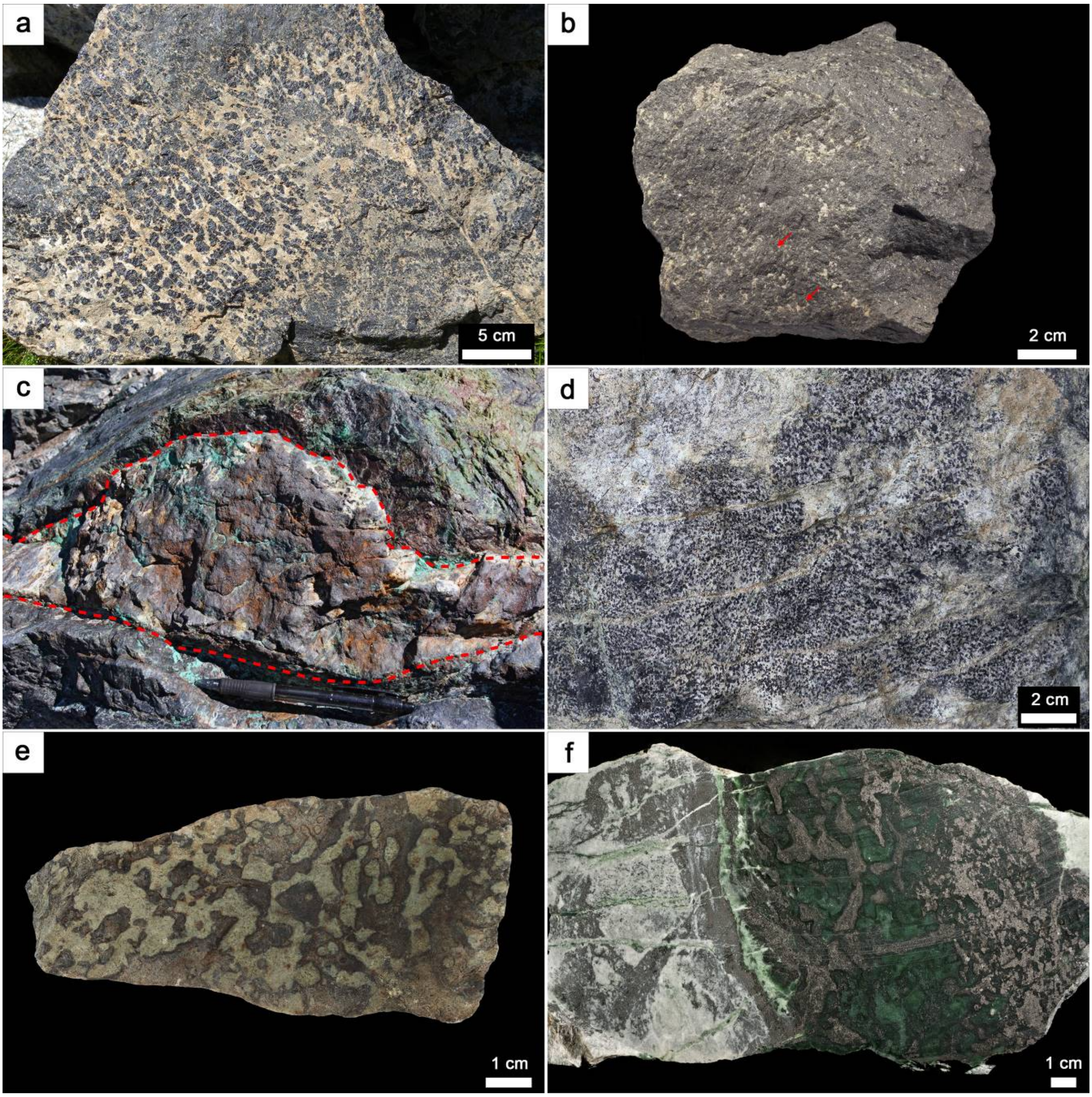
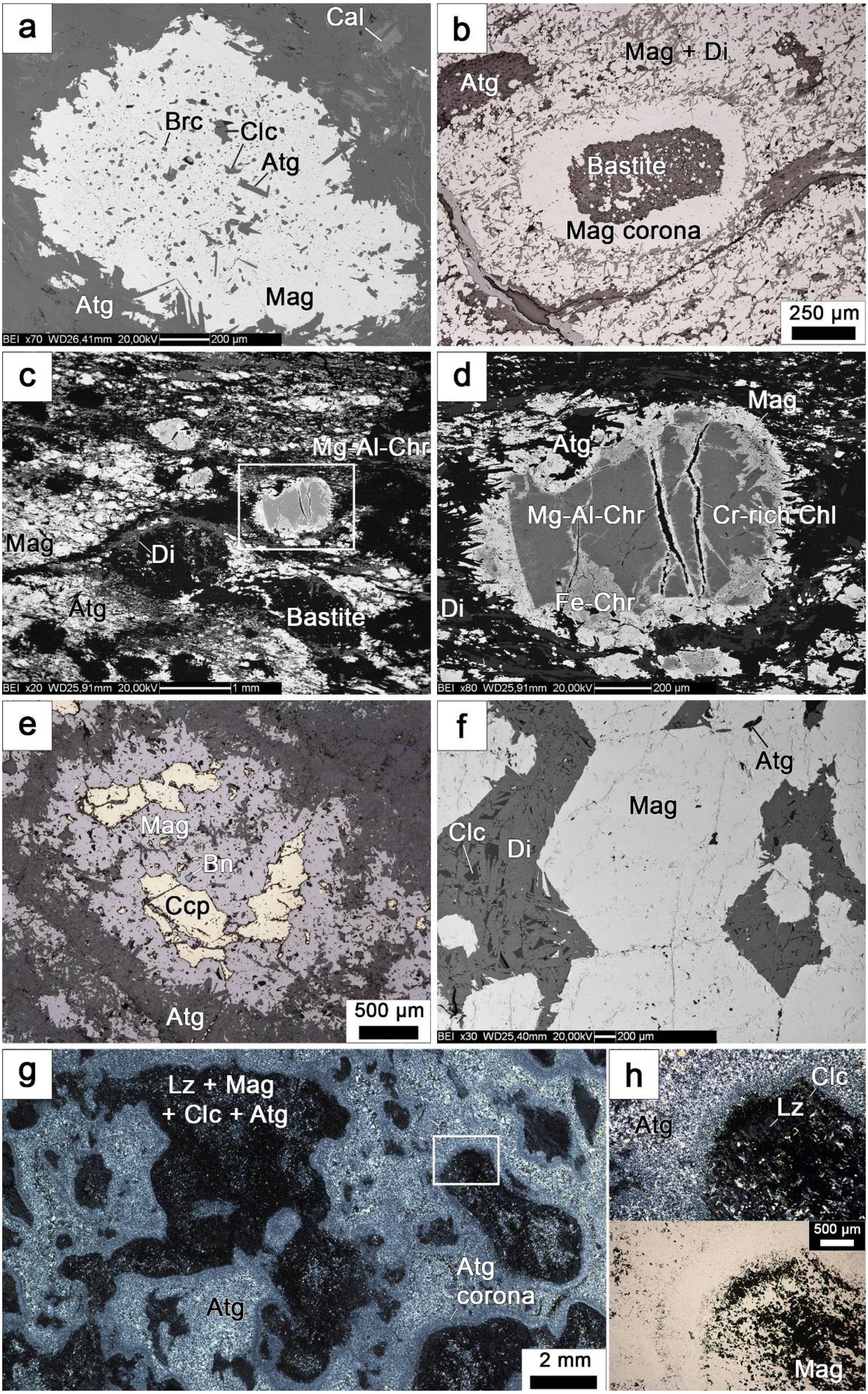


Fig. 3 Typical ore and rock samples from Site 1 (a, b, c), Site 2 (d) and Site 3 (e, f). a) "Leopard" ore showing variation of texture at the sample scale. Dark areas are magnetite aggregates, the light portion is composed of serpentine and minor brucite and olivine. b) "Harrisitic" ore, characterized by elongated magnetite aggregates (dark areas) in serpentine (+ minor bucite and olivine) matrix. c) Massive magnetite ore, with minor serpentine gangue. d) Dismembered stockwork zone (outlined by dashed lines) in serpentinite after tectonitic peridotite. Chalcopyrite is completely altered into Fe-oxyhydroxides and secondary copper minerals. The pen is 14 cm long. e) "Leopard" ore (right) grading to almost barren serpentinite. The rock is impregnated by diopside (whitish areas), which form patches and veinlets. The pen cap is 3 cm long. f) Serpentinized pegmatoid ultramafic rock variably enriched in magnetite (cut and polished sample). The left portion is a magnetite-rich diopsidite with relict brecciated texture.



a
Cal
Brc
Clc
Atg
Atg
Mag
BEI x70 WD26,41mm 20,00kV 200 µm
b
Mag + Di
Atg
Bastite
Mag corona
250 µm
c
Mg-Al-Chr
Mag
Di
Atg
Bastite
BEI x20 WD25,91mm 20,00kV 1 mm
d
Mag
Atg
Mg-Al-Chr
Cr-rich Chl
Di
Fe-Chr
BEI x80 WD25,91mm 20,00kV 200 µm
e
Mag
Bn
Ccp
Atg
500 µm
f
Atg
Mag
Clc
Di
BEI x30 WD25,40mm 20,00kV 200 µm
g
Lz + Mag
+ Clc + Atg
Atg
Atg
corona
2 mm
h
Clc
Lz
Atg
500 µm
Mag

1380

Fig. 4 Microstructural features in Cogne rocks. a) Magnetite poikiloblast in "leopard" ore from Site 1, showing indented boundaries with antigorite. Inclusions in magnetite are clinochlore (usually anhedral), brucite (small and euhedral) and antigorite (large euhedral crystals). Gangue is antigorite. Calcite forms late impregnations and veins. Back-scattered electron (BSE) image. b) Bastite with a magnetite corona in massive magnetite (white) with acicular diopside (grey). Magnetite-impregnated serpentinized peridotite from Site 2. Reflected plane-polarized light. c) Magnetite-impregnated serpentinized peridotite from Site 2. Magnetite (white), antigorite (black) and diopside (medium grey) replace former silicates, however bastite sites (round black areas) are still preserved. Mg-Al-chromite (medium grey) is partly altered into ferrian chromite (light gray) + chlorite (black veins crosscutting the crystal) and shows a rim of magnetite. BSE image. d) Magnetite + chalcopyrite dismembered vein associated with antigorite from Site 2. Bluish inclusions in magnetite are bornite. Antigorite is both included in magnetite or surrounds it forming indented boundaries. Reflected plane-polarized light. e) External portion of a magnetite stockwork zone (located further to the left, not visible) from Site 2, in which an antigorite front replaces lizardite. White veins are Fe-oxyhydroxides produced by weathering of chalcopyrite in the vein. BSE image. f) Euhedral magnetite crystals in a diopside-rich portion of a "leopard" ore sample from Site 3. Diopside forms randomly-oriented subhedral prismatic crystals (medium gray) with interstitial antigorite (dark grey). Black mineral included in magnetite or interstitial between diopside crystals (right) is clinochlore. BSE image. g) Serpentinized pegmatoid ultramafic rock from Site 3 (see Fig. 3f), showing an eutectic-like texture. Transmitted light, crossed polars. h) Enlargement of framed area in c). Light-coloured domain (upper left) is composed of coarse-grained interlocking antigorite; dark domain (right) is made up of isotropic lizardite, clinochlore (anomalous brown interference colour), antigorite (white-light grey) and magnetite (opaque). Fine-grained interlocking antigorite lines the boundary between the two domains. Transmitted light, crossed polars (upper) and plane polarized light (lower). Mineral abbreviations (after Whitney and Evans, 2010): Mag, magnetite; Atg, antigorite; Clc, clinochlore; Brc, brucite; Cal, calcite; Di, diopside; Lz, lizardite; Ccp, chalcopyrite; Bn, bornite; Mg-Al-Chr, Mg-Al-chromite.

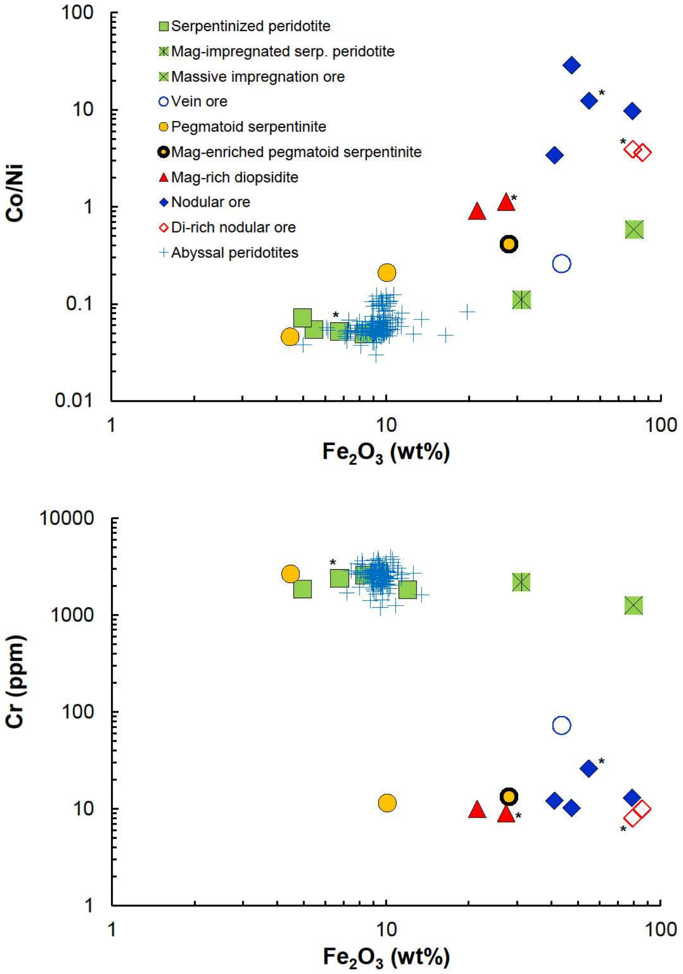


Fig. 5 Cogne rocks plotted in a Co vs Ni plane and compared to abyssal ultramafic and mafic rocks and Fe-Ti gabbros from Valle d'Aosta ophiolites. Data for Cogne include compositions by Carbonin et al. (2014; marked with an asterisk). Data for abyssal peridotites after Niu (2004), Paulick et al. (2006), Andreani et al. (2014). Data for oceanic mafic intrusives after Casey (1997), Werner (1997), Holm (2002), Boschi et al. (2006), Paulick et al. (2006). Data for Fe-Ti gabbros after Bocchio et al. (2000).

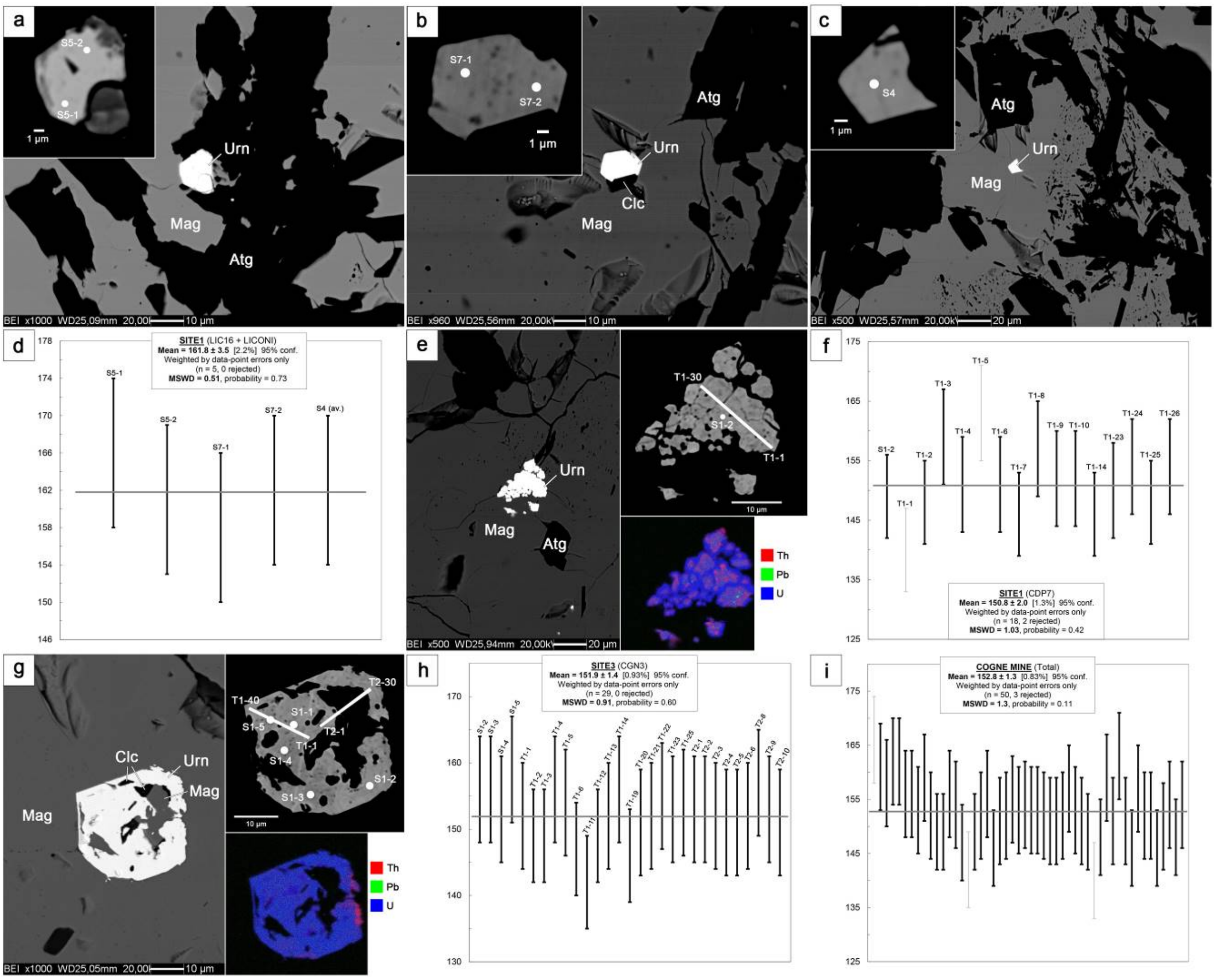


Fig. 6 Uraninite microstructural features and U-Th-Pb dating. a-d) Uraninite in Site 1 “leopard” ore and related dating [b) and c) from the same ore sample]. e-f) Aggregate of uraninite crystals in Site 1 “leopard” ore and related dating. Chemical map shows a U-rich rim. g-h) Inclusion-rich (magnetite, dark grey; clinochlore, black) uraninite crystal in Site 3 “leopard” ore and related dating. The chemical map reveals a homogeneous composition. i) Combination of all single-spot datings. Images and maps were obtained by SEM-BSE and EPMA, respectively. Geochronological data plotted using ISOPLOT (v. 3.75) Visual Basic add-in for Excel® (Ludwig 2012).

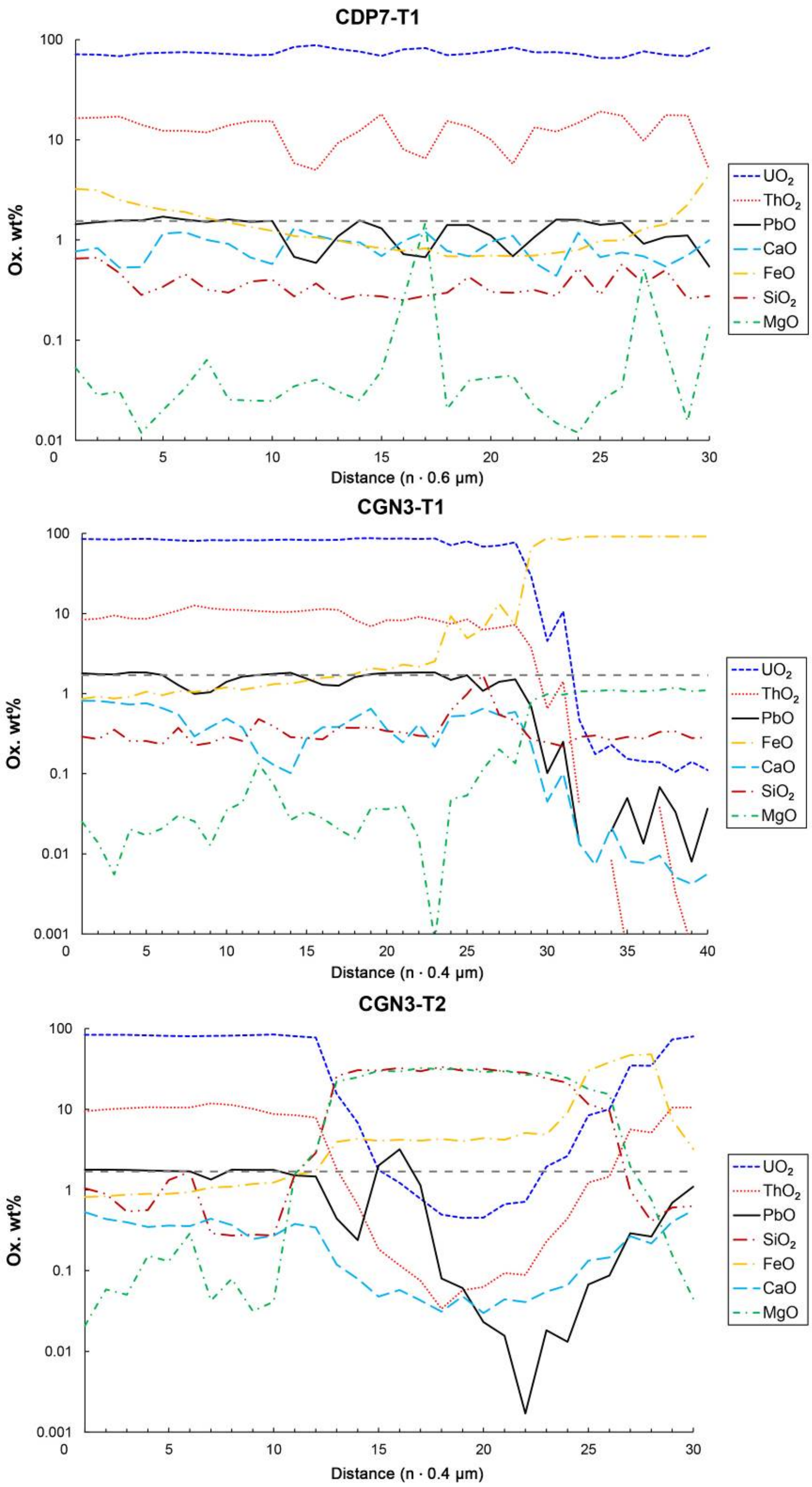


Fig. 7 Electron microprobe traverses across uraninite crystals (see Fig. 6). Horizontal dashed lines indicate PbO plateau.

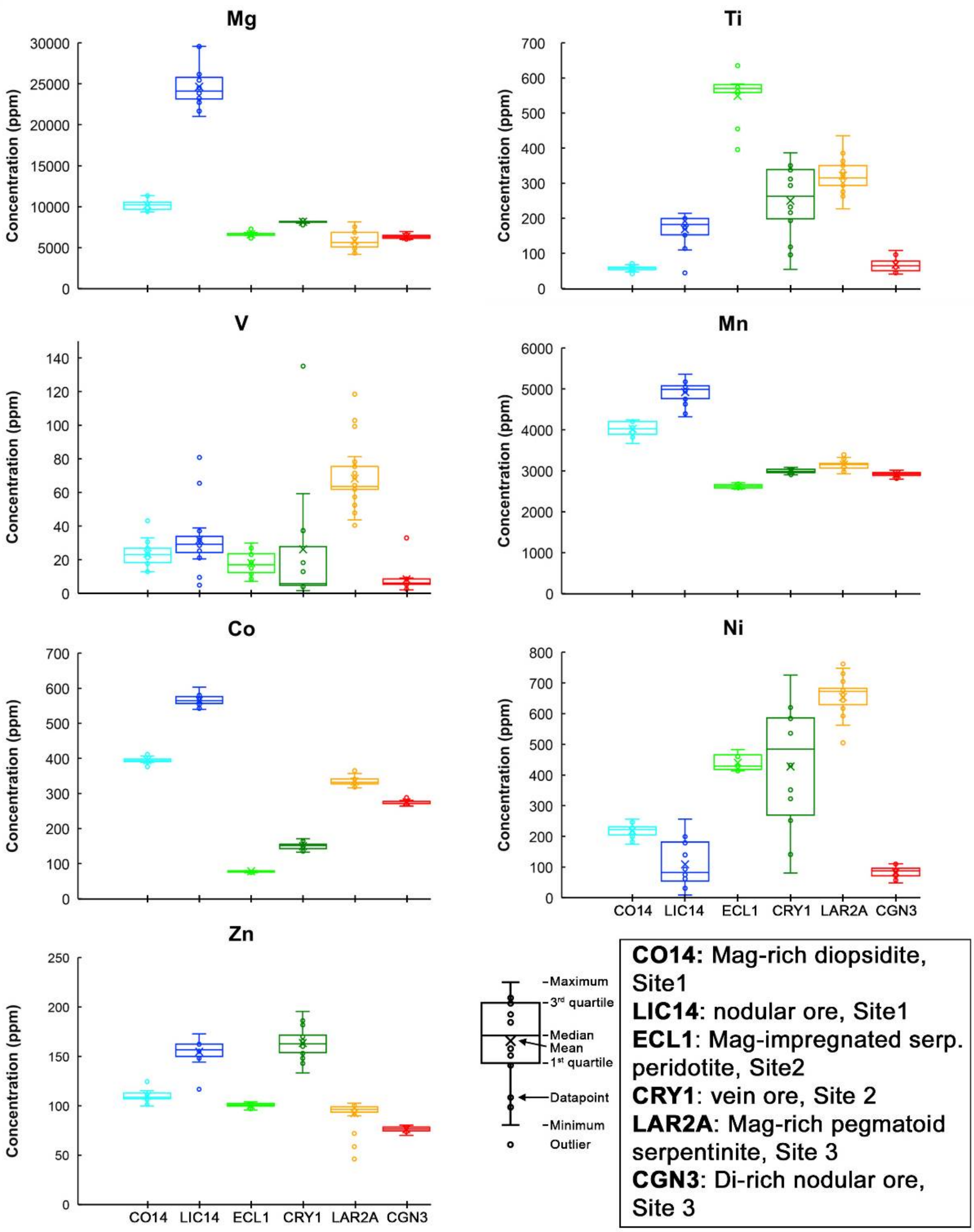


Fig. 8 Box and whiskers plot of magnetite trace element composition. "X" symbol indicates the arithmetic mean.

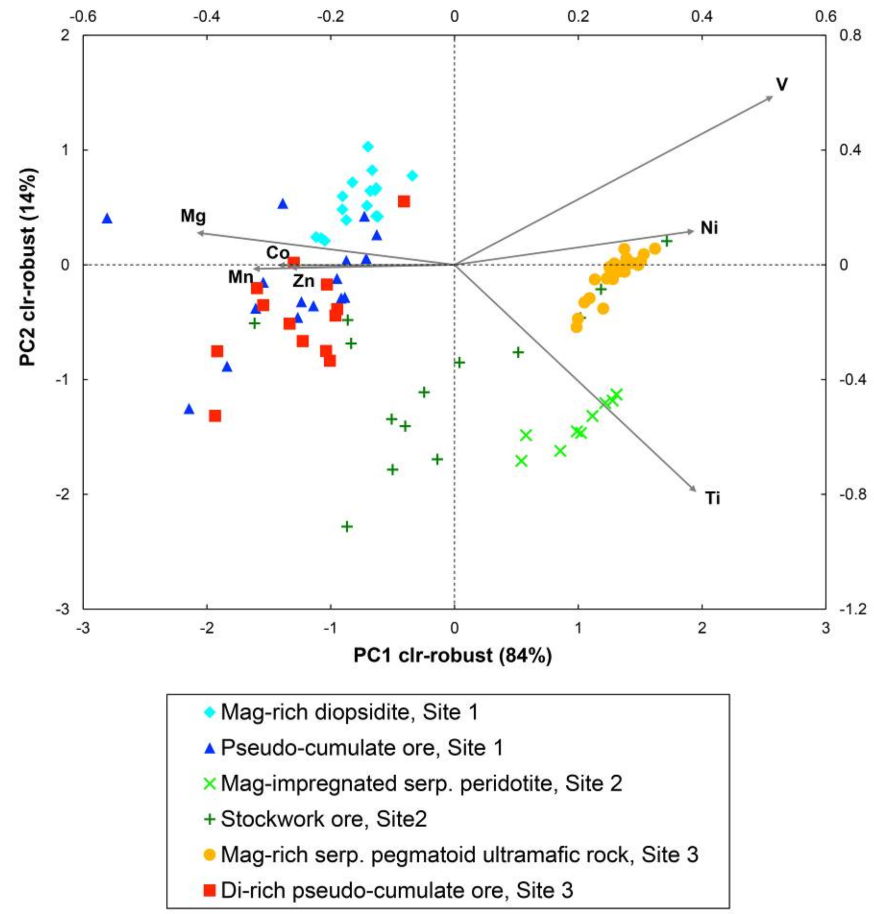


Fig. 9 Robust-PCA of magnetite trace element composition. Coordinates of datapoints (scores) are on left and lower horizontal axes. Coordinates of variables (loadings) are on right and upper horizontal axes.

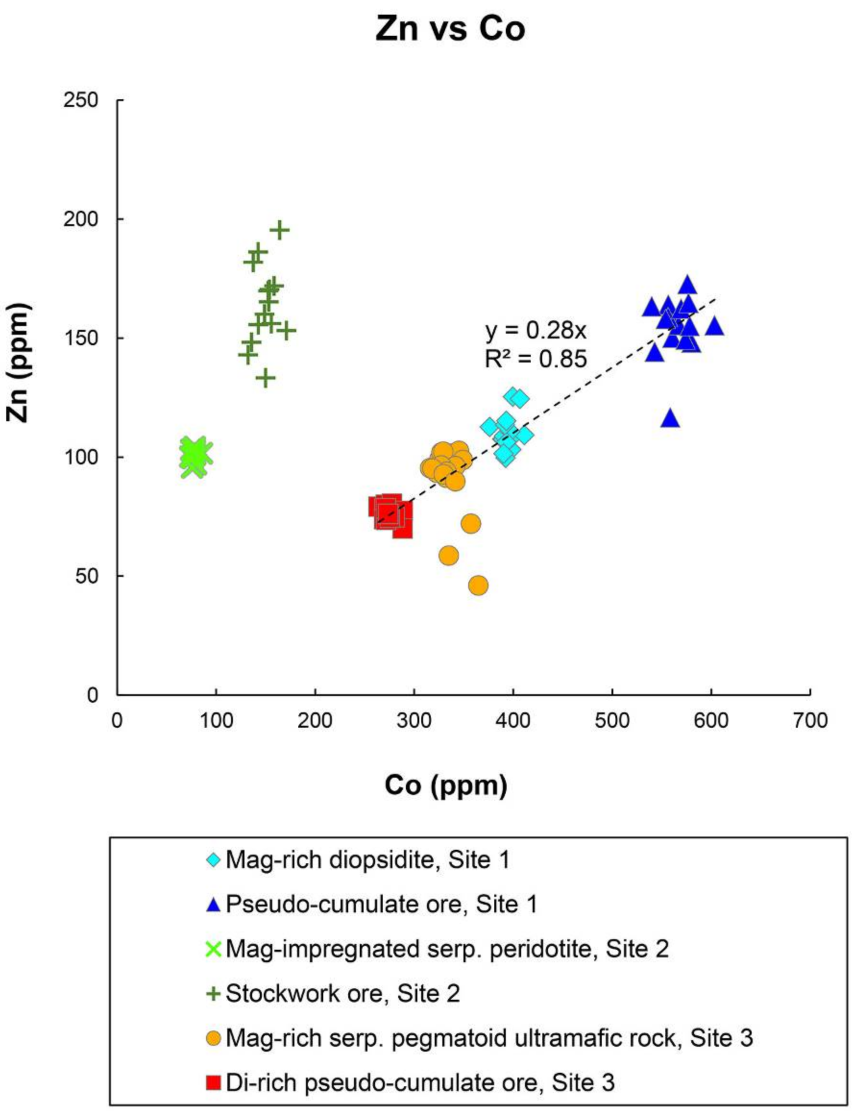


Fig. 10 Co vs. Ni relationships in magnetite. Regression line (dashed) for magnetite-rich samples from Site 1 and 3 shows linear relationship between Co and Ni.

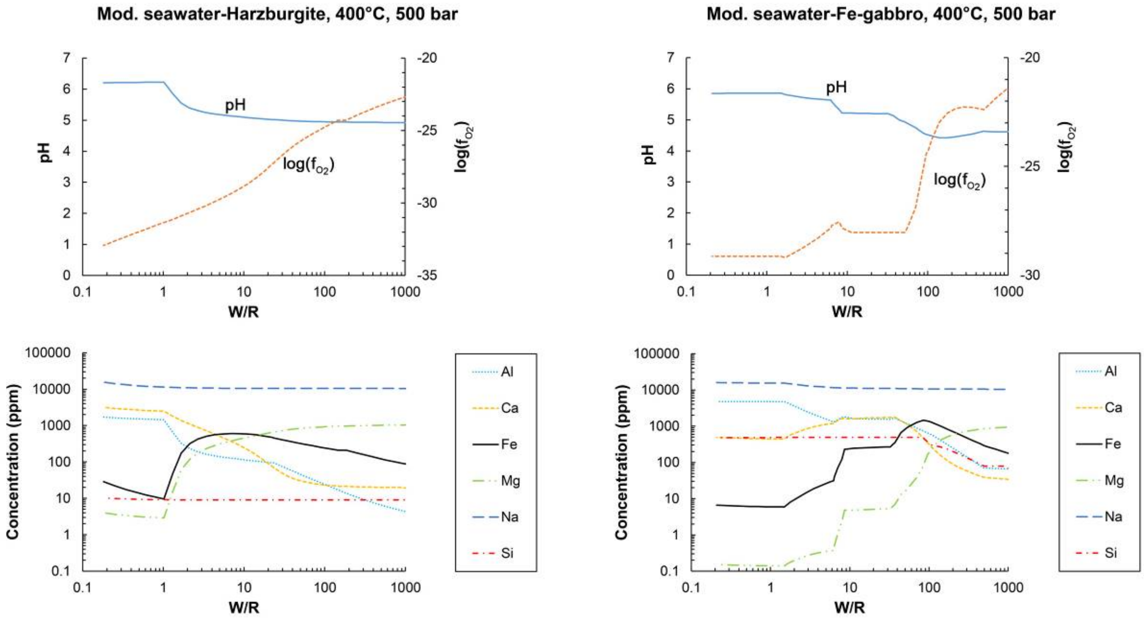
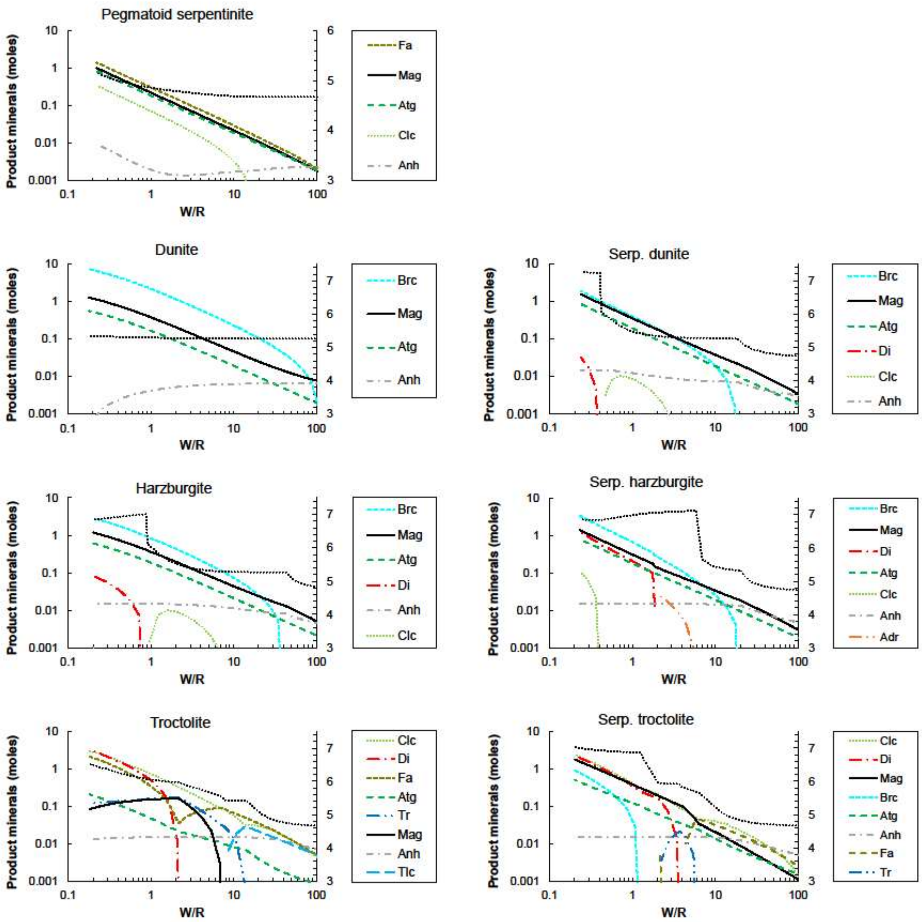


Fig. 11 Variation in pH, fO_2 and element concentrations in fluid equilibrated with harzburgite (a, c) or Fe-gabbro (b, d) at 400°C at various W/R.


Pegmatoid serpentinite
Fa
Mag
Atg
Clc
Anh
Dunite
Brc
Mag
Atg
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Serp. dunite
Brc
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Atg
Di
Clc
Anh
Harzburgite
Brc
Mag
Atg
Di
Anh
Clc
Serp. harzburgite
Brc
Mag
Di
Atg
Clc
Anh
Adr
Troctolite
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Atg
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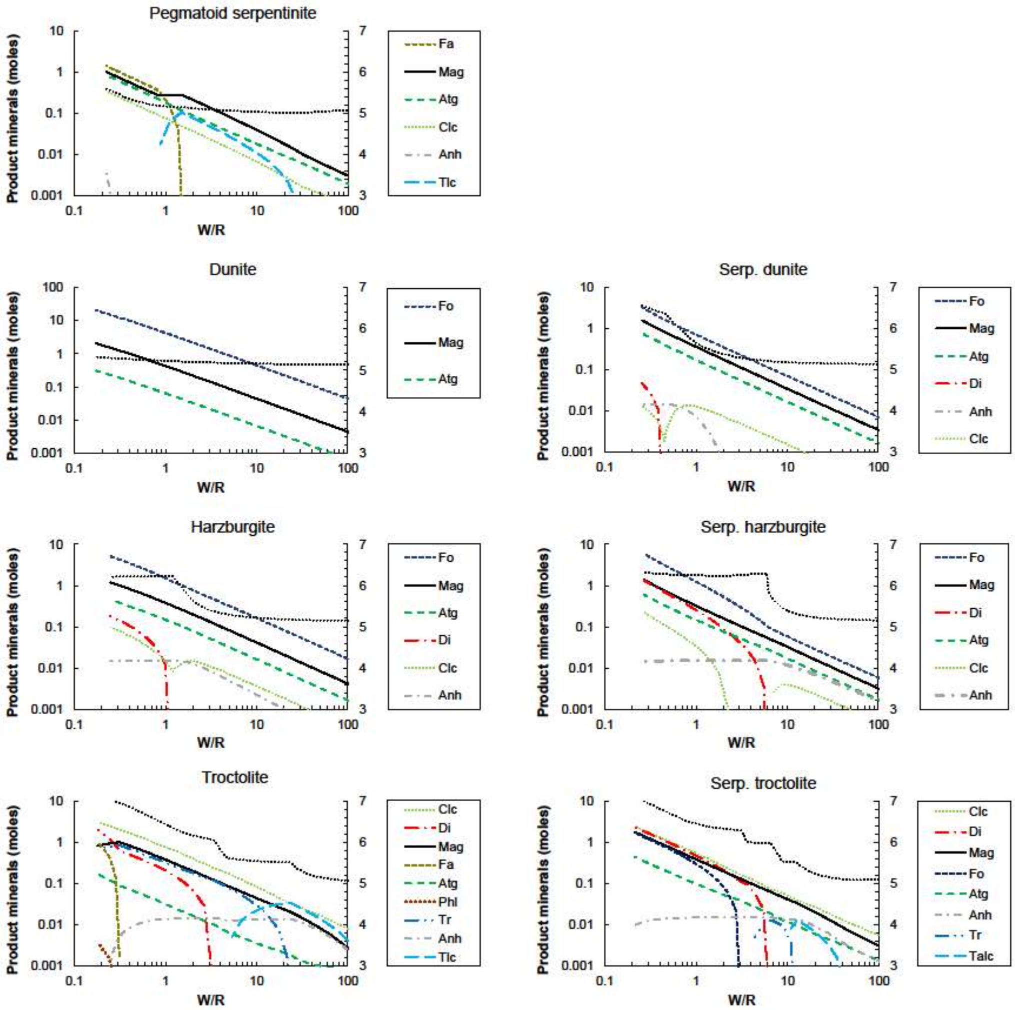
Product minerals (moles)
W/R



Pegmatoid serpentinite
Dunite
Serp. dunite
Harzburgite
Serp. harzburgite
Troctolite
Serp. troctolite
Product minerals (moles)
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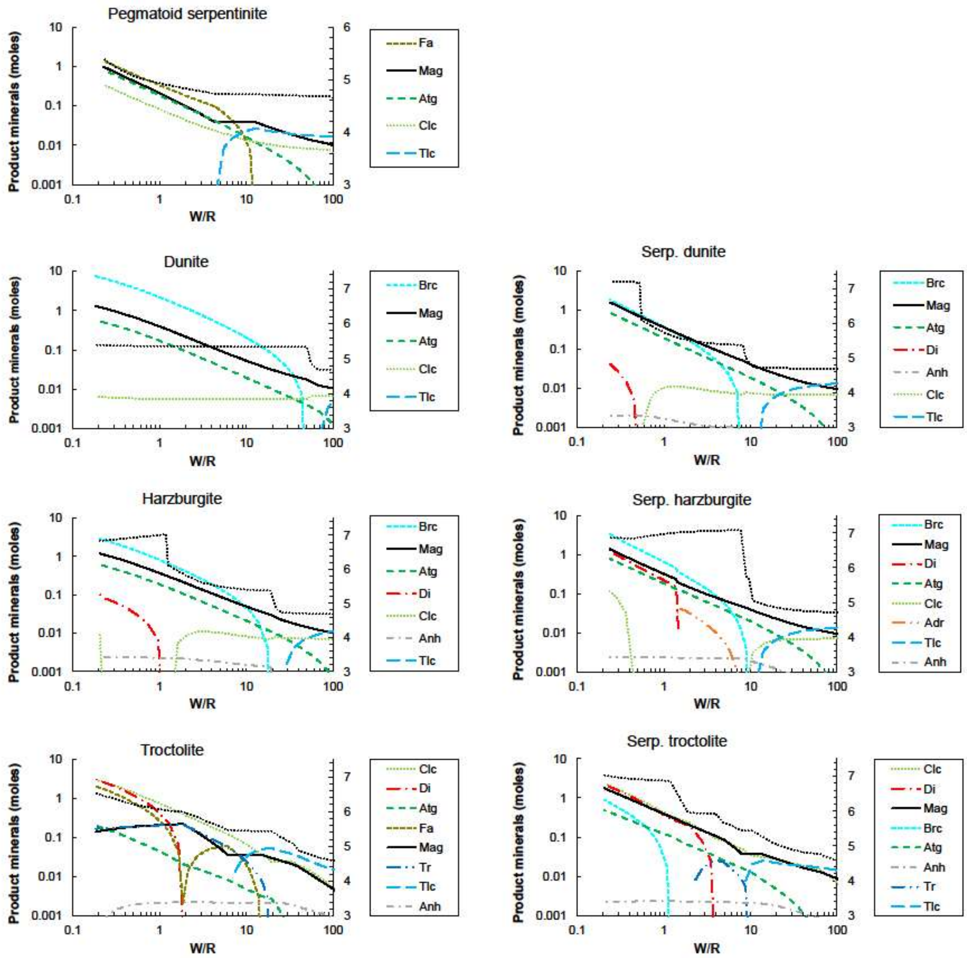
Talc

1457


Pegmatoid serpentinite
Dunite
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Harzburgite
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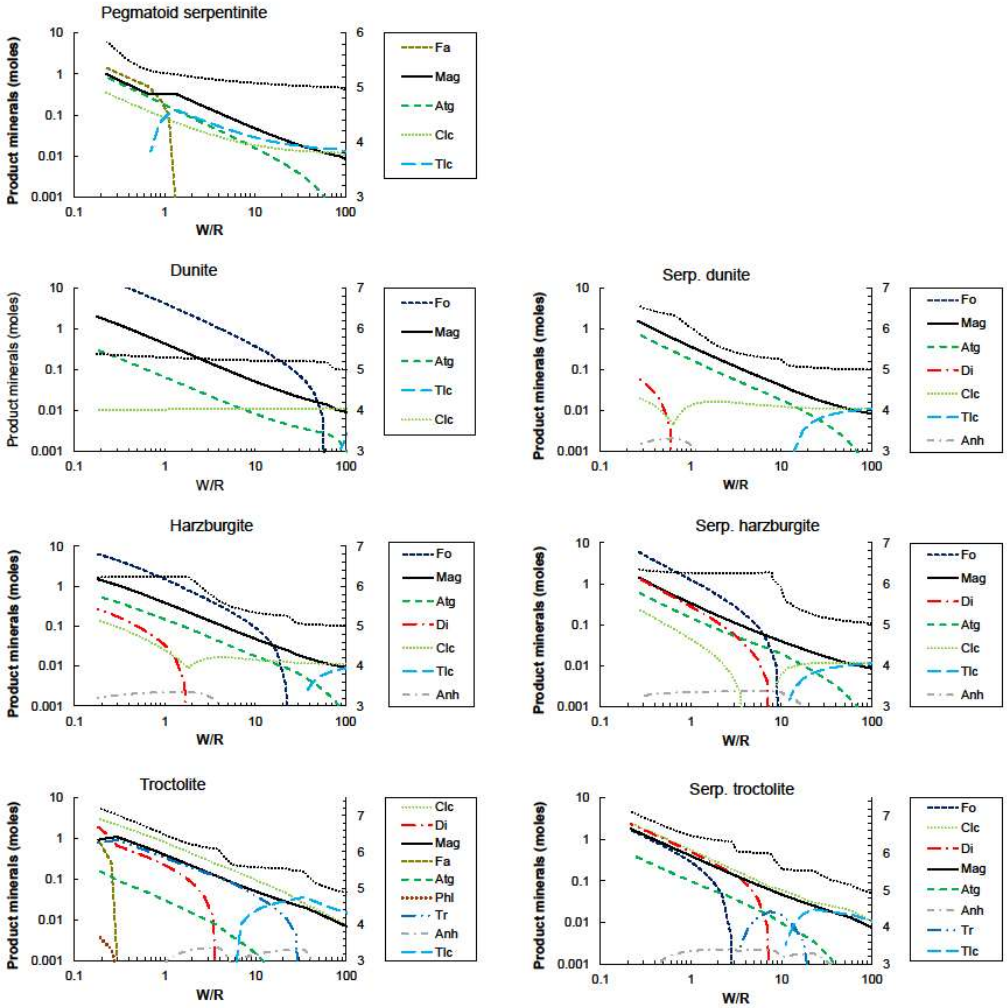

1460

1461 **Fig. 12** Mineral assemblages produced by reaction of model hydrothermal fluids with selected rock
1462 types. Harzburgite-reacted fluid reacting with rocks at a) 300°C and 500 bar c) 400°C and 500 bar.
1463 Fe-gabbro-reacted fluid reacting with rocks at b) 300°C and 500 bar d) 400°C and 500 bar.
1464

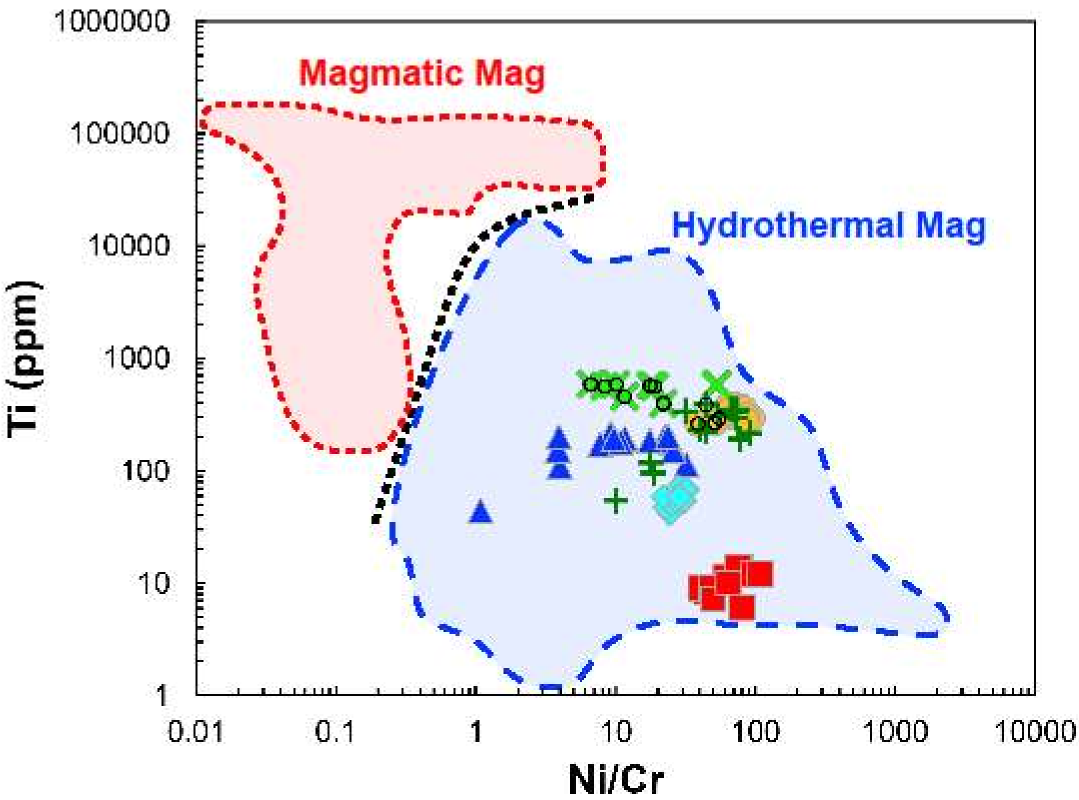

Fig. 13. Compositions of Cogne magnetites plotted in the discrimination diagram by Dare et al. (2014). Magnetites with Cr contents above detection limit are circled. The other data points are plotted assuming a Cr value equal to the detection limit of 8 ppm. Although this may have unduly shifted the points to lower Ni/Cr ratios, the strong hydrothermal character of the Cogne magnetites remains evident.

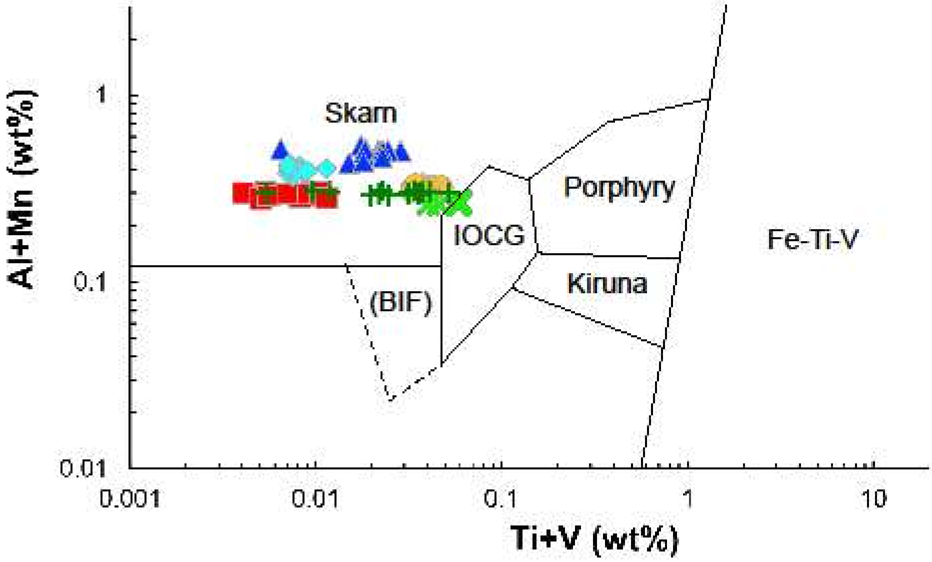

Fig. 14. Compositions of Cogne magnetites in the discrimination diagram of Dupuis and Beaudoin, 2011. LA-ICP-MS data are not available for Al (generally <<0.1 wt% based on EPMA data), therefore the plotted (Mn + Al) contents should be considered as minimum values.

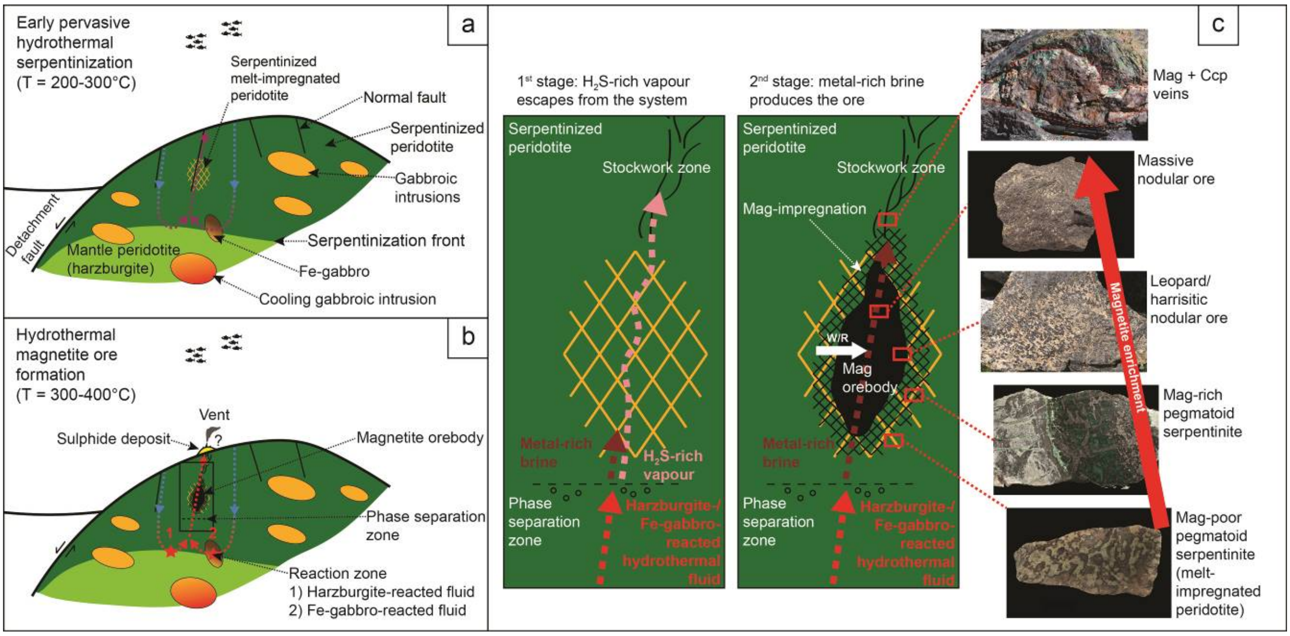

Fig. 15. Interpreted schematic evolution of the Cogne deposit. a) Formation of an oceanic core complex made up of mantle peridotites intruded by gabbros and Fe-gabbros, and locally impregnated by melts. Early circulation of hydrothermal fluids produces extensive serpentinization at relatively low-T (lizardite stability field). High water/rock ratios are possibly attained thanks to fluid focussing along fractures and faults. b) Convective circulation of seawater produces high-T hydrothermal fluids that leach metals from harzburgites and Fe-gabbros. These fluids undergo phase separation and produce a magnetite-rich body at depth and a sulphide mound on the seafloor. A magnetite-sulphide stockwork zone marks the transition between the magnetite orebody and the sulphide mound. c) Close-up of the framed region in b). Phase separation produces an H2S-rich vapour that quickly escapes from the system and a dense metal-rich brine. Then, the upwelling brine reacts with the serpentinites at various fluid/rock ratios and precipitates magnetite, producing fine-grained disseminated, nodular and replacive massive ores. Further upwelling of the magnetite-saturated fluids along fractures produces magnetite + chalcopyrite veins (stockwork zone) and fine-grained disseminations in shallower serpentinites.

Rock Type	Fe-gabbro[1]	Dunite[1]	Serp. Dunite[2]	Harzburgite[1]	Serp. Harzburgite[2]	Cumulate Harzburgite[3]	Serp. Cumulate Harzburgite[3]	Troctolite[1]	Serp. Troctolite[4]
Ox. wt%									
SiO_2	47.94	40.87	39.24	44.31	39.38	47.09	38.98	42.90	37.95
Al_2O_3	12.19	0.00	0.19	0.42	0.59	1.30	0.71	9.58	6.12
FeO	18.87	9.77	7.57	8.97	6.61	6.74	6.24	9.06	8.44
MgO	4.85	49.35	38.79	45.81	38.37	44.20	40.31	32.39	34.73
CaO	13.17	0.00	0.08	0.48	1.69	0.68	0.21	5.39	2.87
Na_2O	2.99	0.00	0.13	0.00	0.05	0.00	0.00	0.67	0.41
H_2O	0.00	0.00	13.99	0.00	13.30	0.00	13.55	0.00	9.47
Tot.	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

[1] "Artificial" rock

[2] Andreani et al. (2014)

[3] Paulick et al. (2006)

[4] Sanfilippo et al. (2014)

Location	Site 1					Site 1																			
Sample	LIC12					LIC14, LIC15																			
Rock type	Serpentinized peridotite					Pseudo-cumulate ore																			
Mineral	Antigorite		Spinel			Magnetite		Antigorite				Lizardite				Olivine		Brucite				Clinochlore		Ti-chondrodite	
Additional information			core Mg-Al-chromite	middle Ferrian chromite	rim Magnetite					Included in Mag				Included in Mag						Included in Mag		Included in Mag			
Ox. wt%	Mean (6)	s				Mean (9)	s	Mean (22)	s	Mean (5)	s	Mean (9)	s	Mean (4)	s	Mean (6)	s	Mean (5)	s	Mean (10)	s	Mean (19)	s	Mean (2)	s
SiO_2	42.80	2.03	0.00	0.34	0.01	0.13	0.20	44.69	0.58	44.55	0.53	37.99	2.063	38.84	0.88	41.55	1.645	3.62	2.14	0.46	1.29	33.97	1.27	34.81	0.11
TiO_2	0.01	0.02	0.03	0.14	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.02	0.03	0.02	0.00	0.09	0.13	0.00	0.00	0.01	0.01	0.01	0.01	5.33	0.13
Al_2O_3	1.00	0.51	25.73	0.62	0.00	0.04	0.04	0.57	0.26	0.79	0.41	4.65	0.246	5.16	0.91	0.00	0.00	0.30	0.24	0.01	0.02	14.70	3.02	0.05	0.07
Cr_2O_3	0.44	0.16	43.72	38.69	3.51	0.01	0.01	0.01	0.01	0.02	0.03	0.00	0.008	0.02	0.02	0.01	0.014	0.01	0.01	0.01	0.02	0.02	0.02	0.01	0.01
FeO	1.87	0.44	17.89	46.45	87.50	88.15	1.37	1.30	0.45	1.75	0.43	4.61	0.836	4.64	0.45	1.12	0.08	0.65	0.11	1.94	1.08	3.59	0.75	2.64	0.09
MnO	0.09	0.01	0.29	4.73	0.57	0.60	0.07	0.04	0.03	0.05	0.02	0.02	0.021	0.03	0.02	0.36	0.053	0.08	0.02	0.11	0.04	0.06	0.04	0.81	0.00
MgO	41.09	1.12	12.80	3.94	1.45	4.52	1.01	41.44	0.50	40.72	0.22	39.06	0.309	38.42	0.42	56.99	1.175	68.98	1.28	72.96	3.03	35.40	1.04	52.37	0.37
CaO	0.02	0.02	0.00	0.02	0.01	0.01	0.01	0.02	0.02	0.02	0.02	0.02	0.016	0.04	0.04	0.00	0.004	0.02	0.02	0.01	0.01	0.02	0.02	0.00	0.01
K_2O	0.00	0.01	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.008	0.01	0.01	0.00	0.007	0.00	0.01	0.00	0.01	0.01	0.01	0.00	0.00
Na_2O	0.00	0.01	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.002	0.01	0.01	0.00	0.006	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.00
Total	87.32		100.46	95.00	93.06	93.48		88.09		87.92		86.38		87.19		100.12		73.67		75.51		87.79		96.02	
Mg#	97.5	0.6	58.1	25.5	8.4			98.2	0.7	98.1	0.5	97.0	0.8	95.0	1.0	98.9	0.1					96.0	0.5		

Location	Site 2												Site 3							Site 3	
Sample	ECL1												LAR4A							LAR2C	
Rock type	Mag-impregnated serpentinized peridotite												Serpentinized peridotite							Mag-rich diopsidite	
Mineral	Magnetite	Antigorite					Diopside	Lizardite		Spinel			Magnetite		Antigorite		Lizardite	Clinochlore		Magnetite	
Additional information				Bastite core	rim	Vein		Vein		core Mg-Al-chromite	middle Ferrian chromite	rim Magnetite									
Ox. wt%		Mean (3)	s					Mean (2)	s				Mean (4)	s	Mean (6)	s		Mean (5)	s	Mean (8)	s
SiO_2	0.07	44.72	0.30	45.56	43.70	44.59	55.98	41.45	0.33	0.03	2.42	0.12	0.03	0.02	43.78	0.32	39.38	35.63	0.47	0.16	0.21
TiO_2	0.08	0.01	0.01	0.01	0.02	0.05	0.00	0.04	0.01	0.10	0.43	0.09	0.06	0.01	0.01	0.01	0.03	0.02	0.01	0.06	0.03
Al_2O_3	0.02	0.94	0.32	3.89	1.79	1.35	0.00	4.73	0.48	23.76	2.11	0.04	0.00	0.00	1.42	0.23	6.64	11.67	1.18	0.00	0.01
Cr_2O_3	0.60	0.07	0.06	0.90	0.90	0.07	0.07	0.06	0.01	45.20	39.04	0.47	1.90	1.43	0.39	0.09	0.14	0.96	0.73	0.00	0.01
FeO	90.53	2.27	0.90	1.91	2.03	1.98	0.82	3.54	0.22	18.00	40.94	90.38	89.59	1.72	2.28	0.05	4.06	3.22	0.50	90.93	0.25
MnO	0.38	0.08	0.00	0.06	0.05	0.05	0.06	0.05	0.01	0.48	4.34	0.34	0.41	0.20	0.14	0.01	0.10	0.09	0.02	0.40	0.05
MgO	1.05	40.09	0.68	35.43	38.89	39.77	18.33	37.05	0.29	12.52	6.13	1.13	0.54	0.07	40.09	0.32	37.80	36.24	0.29	1.17	0.20
CaO	0.07	0.02	0.01	0.02	0.05	0.02	26.01	0.03	0.01	0.00	0.01	0.00	0.05	0.06	0.00	0.00	0.05	0.02	0.01	0.10	0.06
K_2O	0.02	0.01	0.02	0.00	0.00	0.00	0.00	0.06	0.00	0.00	0.01	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Na_2O	0.02	0.01	0.01	0.01	0.00	0.03	0.00	0.04	0.02	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.02	0.03
Total	92.84	88.22		87.79	87.43	87.91	101.27	87.05		100.09	95.43	92.57	92.58		88.11		88.20	87.85		92.84	
Mg#		96.9	1.2	97.1	97.2	97.3	97.6	94.9	0.3	57.7	34.2	6.5			96.9	0.1	94.3	95.6	0.2		

Location	Site 3								Site 3													
Sample	LAR2C								LAR2B													
Rock type	Mag-rich diopsidite								Mag-rich serpentinized pegmatoid ultramafic rock													
Mineral	Diopside				Antigorite		Lizardite		Magnetite		Antigorite						Lizardite		Clinochlore			
Additional information	Fine-grained		Di + Lz vein				Di + Lz vein				Atg-only "pseudomorphs"		Corona between the pseudomorphs		Lz + Clc + Mag "pseudomorphs"		Lz + Clc + Mag + Atg "pseudomorphs"		Lz + Clc + Mag "pseudomorphs"		Included in Mag	
Ox. wt%	Mean (5)	s	Mean (2)	s	Mean (6)	s	Mean (2)	s	Mean (25)	s	Mean (4)	s	Mean (4)	s	Mean (9)	s	Mean (13)	s	Mean (4)	s	Mean (4)	s
SiO_2	55.42	0.36	55.37	0.03	44.11	0.69	40.69	0.11	0.14	0.26	44.17	0.26	43.77	0.62	44.08	0.36	38.17	1.16	35.38	1.28	34.18	0.97
TiO_2	0.01	0.01	0.01	0.02	0.01	0.01	0.02	0.01	0.04	0.02	0.00	0.01	0.00	0.00	0.00	0.01	0.04	0.01	0.01	0.02	0.02	0.00
Al_2O_3	0.05	0.05	0.12	0.07	1.26	0.65	5.65	0.03	0.01	0.02	1.24	0.44	1.01	0.19	1.20	0.20	6.93	0.49	13.45	2.44	15.21	2.22
Cr_2O_3	0.00	0.00	0.00	0.00	0.01	0.02	0.00	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01	0.01	0.01	0.02	0.02	0.01	0.01
FeO	0.98	0.22	1.24	0.34	2.49	0.52	3.57	0.14	91.91	1.48	2.21	0.17	2.21	0.19	2.53	0.34	4.02	0.22	3.25	0.37	4.01	1.31
MnO	0.13	0.03	0.08	0.04	0.12	0.02	0.07	0.03	0.38	0.04	0.10	0.02	0.11	0.02	0.10	0.04	0.05	0.02	0.07	0.03	0.09	0.01
MgO	18.26	0.23	18.23	0.25	40.14	0.42	37.70	0.11	0.85	0.26	40.41	0.14	40.41	0.14	40.16	0.54	37.65	0.37	35.42	0.75	35.52	0.79
CaO	25.73	0.32	25.97	0.05	0.03	0.02	0.07	0.02	0.03	0.08	0.00	0.01	0.00	0.01	0.01	0.01	0.03	0.01	0.01	0.02	0.02	0.01
K_2O	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01
Na_2O	0.01	0.00	0.01	0.02	0.00	0.00	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.00	0.00
Total	100.59		101.03		88.17		87.78		93.39		88.14				88.12		86.92		87.61		89.07	
Mg#	96.9	0.7	96.3	1.0	96.6	0.7	95.0	0.2			97.0	0.3	97.0	0.2	96.6	0.4	94.5	0.4	95.1	0.5	95.5	0.5

Location	Site 3												Site 3											
Sample	CGN8												CGN3											
Rock type	Pseudo-cumulate ore												Di-rich pseudo-cumulate ore											
Mineral	Magnetite		Antigorite				Clinochlore		Lizardite		Andradite		Magnetite		Diopside		Clinochlore						Antigorite	Andradite
Additional information					Included in Mag		Included in Mag		Included in Mag		Included in Mag						Fine-grained, interstitial		Large, tabular crystals		Included in Mag			Included in Mag
Ox. wt%	Mean (6)	s	Mean (5)	s	Mean (7)	s	Mean (10)	s	Mean (2)	s	Mean (3)	s	Mean (7)	s	Mean (10)	s	Mean (2)	s	Mean (7)	s	Mean (6)	s		
SiO_2	0.22	0.20	43.94	1.08	44.12	0.49	34.29	1.07	39.59	0.33	35.21	0.31	0.07	0.06	55.47	0.20	35.66	0.03	32.07	1.32	33.60	1.32	42.45	34.77
TiO_2	0.00	0.00	0.01	0.01	0.00	0.01	0.01	0.01	0.02	0.03	0.14	0.13	0.03	0.02	0.00	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.26
Al_2O_3	0.10	0.05	1.57	0.88	0.99	0.35	13.42	2.26	6.40	0.10	0.28	0.17	0.02	0.04	0.03	0.04	11.73	0.26	18.06	1.92	14.92	2.80	3.35	0.34
Cr_2O_3	0.01	0.02	0.01	0.02	0.01	0.01	0.02	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.00	0.01	0.00	0.00
FeO	93.53	0.47	2.83	0.46	2.88	0.46	4.22	0.45	4.77	0.20	29.31	0.44	91.06	0.34	0.86	0.25	3.67	0.03	4.02	0.61	3.78	0.76	4.09	27.26
MnO	0.46	0.05	0.12	0.02	0.14	0.03	0.09	0.03	0.10	0.03	0.17	0.11	0.39	0.06	0.13	0.08	0.06	0.02	0.09	0.03	0.07	0.02	0.06	0.27
MgO	1.15	0.29	39.47	0.62	39.51	0.42	34.96	0.86	37.14	0.02	0.20	0.02	1.10	0.05	18.46	0.16	36.38	0.21	33.08	1.07	35.57	1.00	38.61	0.29
CaO	0.02	0.04	0.01	0.01	0.01	0.01	0.04	0.03	0.10	0.02	33.57	0.31	0.01	0.01	25.97	0.19	0.03	0.02	0.03	0.02	0.04	0.04	0.03	33.39
K_2O	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.03	0.04	0.01	0.01	0.01	0.01	0.01	0.00
Na_2O	0.01	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.00	0.03	0.02	0.00	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.00	0.01	0.02	0.00
Total	95.51		87.98		87.66		87.06		88.13		98.92		92.69		100.94		87.57		87.38		88.00		88.62	96.58
Mg#							94.2	0.5	93.3	0.3					97.5	0.7	95.2	0.7	93.6	1.0	95.7	0.4		

s: sample standard deviation

Mineral abbreviations: Mag, magnetite; Atg, antigorite; Lz, lizardite; Clc, clinochlore; Di, diopside

Location	Site 1	Site 1	Site 1	Site 1	Site 2	Site 2	Site 3	Site 3	Site 3	Site 3	Site 3
Sample	LIC1B	LIC12*	LIC14*	LIC15	ECL1*	CRY1	LAR4	LAR2-1*	LAR2-2*	CGN3*	CGN8*
Rock type	Serpentinite	Serpentinite (harzburgite)	Pseudo-cumulate ore	Pseudo-cumulate ore	Mag-impregnated serp. peridotite	Stockwork ore	Serpentinite	Mag-rich serp. pegmatoid ultramafic rock	Mag-rich diopsidite	Di-rich pseudo-cumulate ore	Pseudo-cumulate ore
Ox. wt%											
SiO_2	41.91	39.49	22.38	20.51	32.20	24.60	39.06	33.14	42.40	6.52	10.06
TiO_2	0.02	0.02	0.06	0.02	0.04	0.04	0.10	0.03	0.02	0.02	0.02
Al_2O_3	1.04	1.01	0.62	1.08	0.92	0.43	2.67	2.31	0.27	0.86	0.31
Fe_2O_3	5.46	8.31	41.04	47.34	31.09	43.44	4.94	28.03	21.44	85.73	78.70
MgO	38.28	37.57	28.22	21.07	25.72	22.35	33.39	30.69	16.01	3.90	9.17
MnO	0.11	0.10	0.31	0.31	0.17	0.20	0.16	0.17	0.17	0.35	0.40
CaO	0.26	0.02	0.11	2.21	2.63	0.04	5.84	0.14	18.19	1.50	0.03
Na_2O	0.04	0.03	0.02	0.02	0.03	0.02	0.03	0.04	0.02	0.02	0.01
K_2O	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.01	0.01	0.01	0.01
P_2O_5	0.01	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01
LOI	12.19	12.57	6.88	7.09	7.09	6.75	13.21	5.18	98.54	0.21	0.32
Total	99.32	99.14	99.66	99.66	99.90	97.87	99.42	99.76	0.72	99.13	99.04
ppm											
Be	-	<1	<1	-	1.00	-	-	<1	<1	<1	<1
S	53	1194	245	193	948	3290	946	124	104	14	6
Sc	BDL	6	<1	BDL	6	BDL	BDL	2	1	<1	<1
V	31	26	<8	BDL	31	55	47	20	12	<8	<8
Cr	2391	2395	<14	BDL	2196	78	2132	<14	<14	21	<14
Co	87.0	117.4	236.8	345.0	97.8	133.0	111.0	105.8	72.3	260.9	295.2
Ni	1596	2403	93	12	1005	511	1542	275	97	110	42
Cu	22	20	36	29	209	14659	23	70	77	45	38
Zn	47	54	82	111	129	140	44	66	38	83	84
Ga	BDL	0.8	1.3	BDL	<0.5	BDL	BDL	8.3	2.0	3.5	0.8
Rb	BDL	<0.1	<0.1	BDL	<0.1	BDL	BDL	0.1	<0.1	<0.1	<0.1
Sr	BDL	<0.5	1.3	87.0	1.0	BDL	115.0	<0.5	12.4	1.8	0.6
Y	BDL	0.5	0.5	BDL	0.2	BDL	BDL	1.0	3.4	0.5	0.4
Zr	BDL	3.4	5.8	BDL	0.7	BDL	BDL	1.9	2.8	1.0	0.8
Nb	BDL	<0.1	0.6	BDL	<0.1	BDL	BDL	<0.1	0.9	0.4	<0.1
Sn	-	<1	<1	-	<1	-	-	<1	<1	<1	<1
Cs	-	<0.1	<0.1	-	<0.1	-	-	<0.1	<0.1	<0.1	<0.1
Ba	BDL	1.0	<1	BDL	<1	BDL	17.0	1.0	3.0	<1	<1
Hf	-	<0.1	0.2	-	<0.1	-	-	<0.1	0.1	<0.1	<0.1
Ta	-	<0.1	<0.1	-	<0.1	-	-	<0.1	<0.1	<0.1	<0.1
W	-	1.1	4.0	-	<0.5	-	-	<0.5	<0.5	<0.5	<0.5
Pb	9.0	38.0	16.0	10.0	10.0	20.0	16.0	29.0	22.0	10.0	BDL
Th	BDL	<0.2	0.9	BDL	<0.2	BDL	BDL	0.3	0.5	<0.2	<0.2
U	BDL	<0.1	2.9	BDL	<0.1	BDL	BDL	1.3	2.0	0.8	2.4
La	BDL	0.9	0.4	BDL	0.2	BDL	BDL	0.8	3.3	0.9	0.3
Ce	BDL	0.7	0.6	BDL	0.1	BDL	BDL	0.9	5.8	1.1	0.7
Nd	BDL	0.4	0.7	BDL	<0.3	BDL	BDL	0.3	3.8	0.7	0.4

* integrated with data from ICP-MS

Location		Site 1			Site 1			Site 2			Site 2			Site 3			Site 3		
Sample		CO14			LIC14			ECL1			CRY1			LAR2A			CGN3		
Rock Type		Mag-rich diopsidite			Pseudo-cumulate ore			Mag-impregnated serpentinized peridotite			Stockwork ore			Mag-rich serp. pegmatoid ultramafic rock			Di-rich pseudo-cumulate ore		
Element (ppm)	DL (ppm)	n = 16			n = 16			n = 10			n = 14			n = 25			n = 13		
		min	Max	Median	min	Max	Median	min	Max	Median	min	Max	Median	min	Max	Median	min	Max	Median
^{25}Mg	11	9357	11350	10216	21021	29568	24112	6149	7259	6696	7773	8481	8146	4173	8150	5629	5992	6945	6311
^{29}Si	1020	BDL			BDL			BDL			BDL			BDL			BDL		
^{43}Ca	325	BDL			BDL			BDL			BDL			BDL			BDL		
^{47}Ti	6	42	75	59	44	214	182	396	635	570	54	387	263	227	435	315	41	108	70
^{51}V	0.3	12.9	43.1	23.0	4.9	80.8	29.1	7.1	29.9	17.0	<0.3	135.1	5.0	40.4	118.4	63.6	BDL	33.0	6.2
^{53}Cr	8	BDL			BDL			<8	154	32	BDL			BDL			BDL		
^{55}Mn	4	3669	4246	4025	4318	5360	4991	2558	2706	2620	2903	3086	2984	2927	3394	3154	2797	3016	2940
^{59}Co	0.8	376.2	411.2	393.2	539.9	603.3	564.7	74.0	85.7	78.1	132.4	171.2	151.2	316.0	364.8	332.4	264.1	288.5	272.9
^{60}Ni	8	175	257	223	9	256	82	413	482	429	80	726	484	505	762	672	49	111	89
^{66}Zn	2	100	125	109	117	173	157	96	104	101	133	195	163	46	103	96	70	80	77
^{98}Mo	0.5	BDL			BDL			BDL			BDL			BDL			BDL		
^{90}Zr	0.1	BDL			BDL			BDL			BDL			BDL			BDL		

Location	Sample		Ox. wt%[1]								ppm			U/Th	Age (Ma)	Error[2] ± (Ma)
			UO_2	ThO_2	PbO	MgO	SiO_2	FeO	CaO	Total	U	Th	Pb			
Site 1	LIC16	S5-1	86.81	7.06	1.99	0.04	0.40	1.92	0.06	98.28	765231	62044	18474	12	166	8
		S5-2	86.79	6.84	1.93	0.04	0.20	1.72	0.15	97.67	765054	60111	17917	13	161	8
Site 1	LICONI	S7-1	91.68	4.34	1.98	0.04	0.34	2.36	0.11	100.84	808160	38140	18381	21	158	8
		S7-2	87.14	7.92	1.95	0.02	0.34	2.50	0.05	99.92	768140	69602	18102	11	162	8
		S4[3]	88.37	7.01	1.98	0.03	0.32	2.13	0.09	99.92	778982	61570	18344	13	162	8
Site 1	CDP7	S1-2	74.22	13.00	1.57	0.01	0.27	1.08	1.07	91.21	654250	114246	14575	6	149	7
		T1-1	71.24	16.43	1.44	0.05	0.65	3.24	0.77	93.83	627981	144389	13368	4	140	7
		T1-2	70.91	16.68	1.51	0.03	0.66	3.14	0.83	93.76	625072	146586	14018	4	148	7
		T1-3	68.18	17.13	1.57	0.03	0.47	2.52	0.53	90.43	601007	150540	14575	4	159	8
		T1-4	72.72	14.15	1.57	0.01	0.28	2.22	0.54	91.49	641027	124352	14575	5	151	8
		T1-5	74.19	12.28	1.71	0.02	0.34	2.00	1.16	91.70	653985	107918	15874	6	163	8
		T1-6	74.97	12.34	1.60	0.03	0.46	1.91	1.20	92.51	660861	108445	14853	6	151	8
		T1-7	73.58	11.84	1.52	0.06	0.32	1.65	1.00	89.98	648608	104051	14110	6	146	7
		T1-8	71.99	13.94	1.61	0.03	0.30	1.49	0.91	90.27	634592	122506	14946	5	157	8
		T1-9	69.77	15.37	1.52	0.03	0.38	1.36	0.67	89.10	615023	135073	14110	5	152	8
		T1-10	71.17	15.32	1.55	0.02	0.40	1.24	0.58	90.28	627364	134634	14389	5	152	8
		T1-11[4]	*84.63*	*5.84*	*0.68*	*0.03*	*0.27*	*1.10*	*1.31*	*93.87*						
		T1-12	*88.19*	*5.00*	*0.59*	*0.04*	*0.37*	*1.06*	*1.11*	*96.36*						
		T1-13	*80.50*	*9.34*	*1.09*	*0.03*	*0.25*	*0.99*	*0.99*	*93.19*						
		T1-14	76.19	12.33	1.57	0.03	0.28	0.88	0.94	92.23	671615	108358	14575	6	146	7
		T1-15	*69.01*	*18.10*	*1.31*	*0.05*	*0.27*	*0.83*	*0.69*	*90.27*						
		T1-16	*79.82*	*8.04*	*0.72*	*0.26*	*0.25*	*0.78*	*0.98*	*90.85*						
		T1-17	*82.57*	*6.53*	*0.68*	*1.49*	*0.28*	*0.83*	*1.20*	*93.58*						
		T1-18	*70.16*	*15.44*	*1.41*	*0.02*	*0.30*	*0.69*	*0.78*	*88.80*						
		T1-19	*72.26*	*13.55*	*1.41*	*0.04*	*0.43*	*0.68*	*0.69*	*89.06*						
		T1-20	*77.04*	*10.07*	*1.11*	*0.04*	*0.30*	*0.70*	*0.96*	*90.23*						
		T1-21	*83.87*	*5.76*	*0.69*	*0.04*	*0.30*	*0.69*	*1.11*	*92.45*						
		T1-22	*74.85*	*13.37*	*1.08*	*0.02*	*0.32*	*0.70*	*0.59*	*90.92*						
		T1-23	75.35	12.05	1.60	0.01	0.28	0.74	0.44	90.47	664211	105897	14853	6	150	8
		T1-24	72.12	14.77	1.59	0.01	0.52	0.80	1.18	90.99	635738	129801	14760	5	154	8
		T1-25	65.48	19.20	1.42	0.02	0.28	0.98	0.68	88.07	577207	168732	13182	3	148	7
		T1-26	65.97	17.38	1.48	0.03	0.58	0.99	0.75	87.18	581526	152737	13739	4	154	8
		T1-27	*76.54*	*9.75*	*0.92*	*0.52*	*0.37*	*1.30*	*0.69*	*90.08*						
		T1-28	*70.36*	*17.59*	*1.07*	*0.09*	*0.50*	*1.44*	*0.54*	*91.59*						
		T1-29	*68.29*	*17.48*	*1.11*	*0.02*	*0.26*	*2.25*	*0.71*	*90.11*						
		T1-30	*83.32*	*5.04*	*0.54*	*0.13*	*0.28*	*4.53*	*0.99*	*94.84*						
Site3	CGN3	S1-2	84.95	9.61	1.84	0.03	0.26	1.41	0.14	98.24	748835	84454	17081	9	156	8
		S1-3	84.91	8.92	1.84	0.02	0.23	1.71	0.60	98.24	748482	78390	17081	10	156	8
		S1-4	85.75	8.28	1.82	0.03	0.27	1.25	0.65	98.05	755887	72766	16895	10	153	8
		S1-5	83.56	10.35	1.86	0.02	0.22	1.22	0.31	97.55	736582	90957	17267	8	159	8
		T1-1	85.17	8.37	1.79	0.03	0.29	0.86	0.81	97.31	750774	73557	16617	10	152	8
		T1-2	84.53	8.61	1.75	0.01	0.27	0.92	0.81	96.90	745133	75666	16246	10	149	7
		T1-3	83.51	9.46	1.73	0.01	0.35	0.87	0.77	96.70	736141	83136	16060	9	149	7
		T1-4	84.90	8.68	1.84	0.02	0.26	0.91	0.73	97.34	748394	76281	17081	10	156	8
		T1-5	85.45	8.57	1.83	0.02	0.26	1.06	0.76	97.94	753242	75314	16988	10	154	8
		T1-6	83.44	9.60	1.71	0.02	0.23	0.95	0.66	96.61	735524	84366	15874	9	147	7
		T1-7	*81.99*	*10.85*	*1.28*	*0.03*	*0.37*	*1.07*	*0.55*	*96.14*						
		T1-8	*80.25*	*12.60*	*0.99*	*0.03*	*0.23*	*1.05*	*0.29*	*95.44*						
		T1-9	*82.19*	*11.57*	*1.04*	*0.01*	*0.24*	*1.11*	*0.38*	*96.54*						
		T1-10	*81.58*	*11.11*	*1.40*	*0.04*	*0.29*	*1.20*	*0.49*	*96.11*						
		T1-11	82.11	11.08	1.63	0.04	0.26	1.12	0.38	96.62	723800	97372	15132	7	142	7
		T1-12	81.94	10.71	1.71	0.13	0.48	1.21	0.17	96.35	722302	94121	15874	8	149	7
		T1-13	82.81	10.44	1.76	0.07	0.39	1.32	0.13	96.91	729971	91748	16338	8	152	8
		T1-14	83.48	10.49	1.82	0.03	0.29	1.33	0.10	97.53	735877	92187	16895	8	156	8
		T1-15	*82.37*	*10.84*	*1.54*	*0.03*	*0.28*	*1.45*	*0.27*	*96.78*						
Site3	CGN3	*T1-16*	*82.18*	*11.36*	*1.29*	*0.03*	*0.27*	*1.58*	*0.38*	*97.09*						
		T1-17	*82.82*	*11.07*	*1.26*	*0.02*	*0.38*	*1.61*	*0.38*	*97.54*						
		T1-18	*86.21*	*8.31*	*1.60*	*0.02*	*0.37*	*1.75*	*0.50*	*98.76*						
		T1-19	86.98	6.88	1.75	0.04	0.38	2.08	0.65	98.76	766729	60462	16246	13	146	7
		T1-20	85.81	8.27	1.80	0.04	0.34	1.97	0.36	98.58	756416	72678	16710	10	151	8
		T1-21	86.35	8.19	1.82	0.04	0.33	2.31	0.25	99.28	761176	71975	16895	11	152	8
		T1-22	84.73	9.10	1.83	0.02	0.30	2.17	0.42	98.56	746896	79972	16988	9	155	8
		T1-23	86.42	8.31	1.83	0.00	0.29	2.53	0.22	99.60	761793	73029	16988	10	153	8
		T1-24	*71.05*	*7.37*	*1.48*	*0.05*	*0.62*	*9.28*	*0.52*	*90.37*						
		T1-25	79.68	8.45	1.70	0.05	0.99	4.91	0.53	96.31	702380	74260	15781	9	154	8
		T1-26	*68.06*	*6.29*	*1.08*	*0.11*	*1.71*	*6.43*	*0.65*	*84.34*						
		T1-27	*70.34*	*6.67*	*1.40*	*0.20*	*0.55*	*13.20*	*0.54*	*92.90*						
		T1-28	*77.26*	*7.21*	*1.50*	*0.13*	*0.46*	*7.12*	*0.59*	*94.27*						
		T1-29	*29.24*	*3.76*	*0.69*	*0.81*	*0.27*	*66.02*	*0.24*	*101.02*						
		T1-30	*4.54*	*0.65*	*0.10*	*0.98*	*0.25*	*87.94*	*0.04*	*94.50*						
		T1-31	*10.58*	*1.41*	*0.25*	*0.97*	*0.22*	*83.28*	*0.10*	*96.81*						
		T1-32	*0.47*	*0.04*	*0.01*	*1.06*	*0.29*	*90.47*	*0.01*	*92.36*						
		T1-33	*0.18*	*0.00*	*0.00*	*1.08*	*0.30*	*90.93*	*0.01*	*92.49*						
		T1-34	*0.23*	*0.01*	*0.02*	*1.10*	*0.26*	*91.09*	*0.02*	*92.73*						
		T1-35	*0.15*	*0.00*	*0.05*	*1.07*	*0.29*	*91.43*	*0.01*	*93.00*						
		T1-36	*0.14*	*0.00*	*0.01*	*1.06*	*0.28*	*91.25*	*0.01*	*92.75*						
		T1-37	*0.14*	*0.04*	*0.07*	*1.11*	*0.33*	*90.99*	*0.01*	*92.68*						
		T1-38	*0.11*	*0.00*	*0.03*	*1.19*	*0.34*	*91.11*	*0.01*	*92.78*						
		T1-39	*0.14*	*0.00*	*0.01*	*1.07*	*0.28*	*91.49*	*0.00*	*93.00*						
		T1-40	*0.11*	*0.00*	*0.04*	*1.10*	*0.28*	*91.56*	*0.01*	*93.10*						
		T2-1	83.84	9.41	1.78	0.02	1.05	0.82	0.53	97.45	739050	82696	16524	9	153	8
		T2-2	83.66	10.01	1.79	0.06	0.89	0.83	0.44	97.68	737463	87969	16617	8	153	8
		T2-3	83.57	10.31	1.77	0.05	0.54	0.87	0.40	97.51	736670	90606	16431	8	152	8
		T2-4	82.66	10.59	1.75	0.15	0.57	0.90	0.35	96.97	728648	93066	16246	8	151	8
		T2-5	81.14	10.56	1.71	0.13	1.32	0.90	0.36	96.12	715250	92803	15874	8	151	8
		T2-6	80.17	10.56	1.70	0.29	1.68	0.94	0.36	95.69	706699	92803	15781	8	152	8
		T2-7	*81.04*	*11.83*	*1.35*	*0.04*	*0.29*	*1.07*	*0.44*	*96.07*						
		T2-8	81.46	11.34	1.79	0.08	0.27	1.10	0.37	96.41	718070	99657	16617	7	157	8
		T2-9	83.04	10.10	1.77	0.03	0.28	1.19	0.25	96.65	731998	88760	16431	8	153	8
		T2-10	84.43	8.72	1.77	0.04	0.27	1.23	0.27	96.74	744251	76632	16431	10	151	8
		T2-11	*80.24*	*8.46*	*1.52*	*1.56*	*1.55*	*1.54*	*0.38*	*95.25*						
		T2-12	*77.39*	*7.90*	*1.47*	*3.01*	*2.88*	*1.71*	*0.34*	*94.70*						
		T2-13	*15.58*	*1.81*	*0.44*	*22.15*	*25.96*	*3.93*	*0.12*	*69.99*						
		T2-14	*6.79*	*0.66*	*0.24*	*24.85*	*30.41*	*4.32*	*0.08*	*67.35*						
		T2-15	*1.77*	*0.19*	*2.01*	*30.08*	*30.31*	*4.07*	*0.05*	*68.47*						
		T2-16	*1.23*	*0.12*	*3.19*	*29.35*	*32.56*	*4.19*	*0.06*	*70.69*						
		T2-17	*0.78*	*0.08*	*1.14*	*32.48*	*29.60*	*4.09*	*0.04*	*68.21*						
		T2-18	*0.49*	*0.03*	*0.08*	*31.29*	*33.54*	*4.27*	*0.03*	*69.74*						
		T2-19	*0.45*	*0.06*	*0.06*	*31.76*	*29.96*	*4.01*	*0.05*	*66.35*						
		T2-20	*0.45*	*0.06*	*0.02*	*28.89*	*31.78*	*4.38*	*0.03*	*65.62*						
		T2-21	*0.67*	*0.09*	*0.02*	*30.20*	*29.41*	*4.18*	*0.04*	*64.61*						
		T2-22	*0.71*	*0.09*	*0.00*	*26.53*	*28.45*	*5.08*	*0.04*	*60.90*						
		T2-23	*1.94*	*0.23*	*0.02*	*28.73*	*24.13*	*4.84*	*0.05*	*59.94*						
		T2-24	*2.64*	*0.44*	*0.01*	*24.24*	*21.32*	*9.06*	*0.07*	*57.78*						
		T2-25	*8.42*	*1.24*	*0.07*	*17.84*	*11.61*	*30.10*	*0.13*	*69.41*						
		T2-26	*10.07*	*1.47*	*0.09*	*15.36*	*9.57*	*38.33*	*0.15*	*75.03*						
		T2-27	*34.76*	*5.62*	*0.29*	*1.96*	*0.99*	*46.75*	*0.27*	*90.63*						
		T2-28	*34.48*	*5.12*	*0.26*	*0.76*	*0.41*	*47.89*	*0.22*	*89.15*						
		T2-29	*73.21*	*10.51*	*0.69*	*0.16*	*0.60*	*7.42*	*0.40*	*93.00*						
		T2-30	*80.12*	*10.55*	*1.10*	*0.04*	*0.63*	*3.21*	*0.56*	*96.22*						

[1] Ti and Cr are systematically below the detection limit, therefore they are not reported

[2] 5% relative error (equivalent to the accuracy on Pb analysis; Bowles 1990)

[3] Average of 5 repetitions on the same point

[4] Rejected analyses (out of plateau or mixed) are in italics

	Hydrothermal fluids		
	Harzburgite-reacted	Fe-gabbro-reacted	Rainbow
Na	459.0	456.4	570.0
Ca	19.3	5.4	67.7
Mg	12.4	14.4	1.7
Si	0.3	18.4	7.3
Fe	2.0	10.4	22.2
Al	0.0019	0.0023	0.0029
Cl^-	535.3	523.9	757.0