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# PETROGENESIS OF MARTIAN SULFIDES IN THE CHASSIGNY METEORITE

JEAN-PIERRE LORAND<sup>1</sup>, SYLVAIN PONT<sup>2</sup>, VINCENT CHEVRIER<sup>3</sup>, AMBRE LUGUET<sup>4</sup>,  
BRIGITTE ZANDA,<sup>2</sup> ROGER HEWINS<sup>2</sup>

*1 Laboratoire de Planétologie et Géodynamique à Nantes, CNRS UMR 6112,  
Université de Nantes, 2 Rue de la Houssinière, BP 92208, 44322 Nantes Cédex 3,  
France. [jean-pierre.lorand@univ-nantes.fr](mailto:jean-pierre.lorand@univ-nantes.fr).*

*2 Institut de Minéralogie, de Physique des Matériaux, et de Cosmochimie (IMPMC) - Sorbonne  
Université- Muséum National d'Histoire Naturelle, UPMC Université Paris 06, UMR CNRS 7590,  
IRD UMR 206, 61 rue Buffon, 75005 Paris, France.*

*3 W.M. Keck Laboratory for Space and Planetary Simulation, Arkansas Center for Space and  
Planetary Science, MUSE 202, University of Arkansas, Fayetteville, AR 72701, USA.*

*4 Rheinische Friedrich-Wilhelms-Universität Bonn, Steinmann Institut für Geologie, Mineralogie  
und Paläontologie, Poppelsdorfer Schloss, 53115 Bonn, Germany.*

Corresponding author: [jean-pierre.lorand@univ-nantes.fr](mailto:jean-pierre.lorand@univ-nantes.fr)

## ABSTRACT

The Chassigny meteorite, a Martian dunite, contains trace amounts (0.005 vol.%) of Fe-Ni sulfides, which were studied from two polished mounts in reflected light microscopy, Scanning Electron Microscope (SEM) and Electron Microprobe (EMP). The sulfide phases are, by decreasing order of abundance, nickeliferous (0-3 wt% Ni) pyrrhotite with an average composition  $M_{0.88\pm 0.01}S$  ( $M = Fe+Ni+Co+Cu+Mn$ ), nickeliferous pyrite (0-2.5 wt% Ni), pentlandite, millerite and unidentified Cu sulfides. Pyrrhotite is enclosed inside silicate melt inclusions in olivine and disseminated as polyhedral or near spherical blebs in intergranular spaces between cumulus and postcumulus silicates and oxides. This sulfide is considered to be a solidification product of magmatic sulfide melt. The pyrrhotite Ni/Fe ratios lie within the range expected for equilibration with the coexisting olivine at igneous temperatures. Pyrite occurs only as intergranular grains, heterogeneously distributed between the different pieces of the Chassigny meteorite. Pyrite is interpreted as a by-product of the low-T (200°C) hydrothermal alteration events on Mars that deposited Ca sulfates + carbonates well after complete cooling. The shock that ejected the meteorite from Mars generated post-shock temperatures high (300°C) enough to anneal and rehomogenize Ni inside pyrrhotite while pyrite blebs were fractured and disrupted into subgrains by shock metamorphism. The negligible amount of intergranular sulfides and the lack of solitary sulfide inclusions in cumulus phases (olivine, chromite) indicate that, like other Martian basalts so far studied for sulfur, the parental melt of Chassigny achieved sulfide-saturation at a late stage of its crystallization history. Once segregated, the pyrrhotite experienced a late-magmatic oxidation event that reequilibrated its metal-to-sulfur ratios.

## INTRODUCTION

Mars is an S-rich planet (King and McLennan 2010 and references therein). Oxidized sulfur is a major component of the Martian regolith (up to 8 wt%  $SO_2$ ; Foley et al. 2003). Martian sulfates originated from magmatic degassing of  $SO_2$  (Tian et al. 2015; Kerber et al. 2015), although

64 a minor contribution from acid weathering of pre-existing Fe sulfides is not unlikely (Dehouck et  
65 al. 2012). Owing to their much higher FeO contents, Martian basalts are able to transfer twice as  
66 much S as dissolved FeS from the mantle to the Martian crust compared to terrestrial basalts (Ding  
67 et al. 2015 and references therein).

68 Mars is the only telluric planet of the solar system that can also be studied from meteorites.  
69 More than a hundred igneous rocks ejected from the Martian crust are now available in our  
70 collections and are referred to as SNC meteorites, in addition to a few meteorites containing pieces  
71 of the lithology of the early Martian crust (McSween and Treiman, 1998; Treiman et al., 2000).  
72 SNC meteorites comprise hypovolcanic porphyritic basalts (Shergottites), clinopyroxene cumulates  
73 (Nakhlites) and dunite cumulates (Chassignites) from extrusive flows (McSween 2001; McSween  
74 and McLennan, 2014 and references therein). Studies of shergottites provided invaluable  
75 information on sulfur and sulfides in the interior of Mars. Accessory pyrrhotite was reported as the  
76 predominant Fe-sulfide, coexisting with pentlandite and chalcopyrite (Lorand et al. 2005;  
77 Gattacceca et al. 2013; Franz et al. 2014; Baumgartner et al. 2017a). It is well known that  
78 pyrrhotite phases are oxygen fugacity sensors because trivalent  $\text{Fe}^{3+}$  can balance the charge  
79 deficiency due to the missing  $\text{Fe}^{2+}$  in the pyrrhotite structure (Pratt et al. 1994; Mycroft et al. 1995;  
80 Mikhlin and Tomashevich 2005; Skinner et al. 2004). The range of metal-to-sulfur atomic ratios  
81 ( $0.99 < \text{M/S} < 0.9$  where M = divalent metals Fe, Ni, Co, Cu, Mn) published for shergottite  
82 pyrrhotites is consistent with the range of  $f\text{O}_2$  conditions inferred for the Martian mantle (FMQ +  
83 0.5 to FMQ-3; Herd et al. 2002; Papike et al. 2009; FMQ = Fayalite-Magnetite-Quartz buffer). Fe-  
84 Ni sulfides also are of prime importance for the budget of highly siderophile elements (Platinum-  
85 group elements-PGEs, Au, Re) of Martian magmas, which behave as strongly chalcophile elements  
86 in metal-free magmatic rocks like SNC meteorites (Baumgartner et al. 2017a).

87 The cumulate nakhlites differ from shergottites by their paucity of Fe-Ni sulfides, which are  
88 mainly composed of strongly metal-deficient pyrrhotite phases ( $\text{M/S} = 0.875 \pm 0.01$ ; Chevrier et al.  
89 2011; see also Day et al. 2006). These pyrrhotite compositions are not in equilibrium with the



redox conditions inferred for the mantle source of parental melts (Chevrier et al., 2011). Moreover, hydrothermal alteration products (e.g., pyrite) have been identified in nakhlites (Bunch and Reid, 1975; Greenwood et al. 2000a). The origin of pyrrhotite non-stoichiometry (magmatic degassing, assimilation of S or post-igneous hydrothermal modification) is still debated (Day et al. 2006; Chevrier et al. 2011; Franz et al. 2014). Chassignites may provide separate constraints because they share many characteristics with nakhlites, including their inferred mode of occurrence as extrusive flow(s) on Mars, their crystallization at ca. 1.3 Ga and their ejection ages at ca. 11 Ma indicating a single ejection event for chassignites and nakhlites (Harvey and McSween 1992; Treiman et al. 2000; Nyquist et al. 2001; McSween 2001). Chassignites consist of only three meteorites, Chassigny (Floran et al. 1978; Johnson et al. 1991), northwest Africa (NWA) 2737, a strongly shocked hot desert find from northwest Africa (Beck et al. 2006) and NWA 8694, a ferroan chassignite recently discovered from northwest Africa (Hewins et al. 2015). However, chassignites remain the least well known of the SNC regarding Fe-Ni sulfides, except the highly shocked sample NWA 2737 that was deeply modified by impact metamorphism (Lorand et al. 2012).

Our paper is focused on the Chassigny meteorite that fell on October 3, 1815 in Haute-Marne, eastern France (Pistollet 1816). It is the oldest fall of a Martian meteorite ever observed on Earth and, as such, the historical starting point of SNC studies. Shock metamorphism effects in this meteorite are much weaker than in NWA 2737 (Langenhorst and Greshake, 1999). Unlike northwest Africa meteorites, it escaped hot desert alteration and the related damage to igneous and hydrothermal sulfide assemblages (Lorand et al 2005; 2015). Chassigny may allow us to address the behavior of Fe-Ni sulfides during cooling and hydrothermal circulation in the cumulate parts of lava flows as well as the timing of S saturation in ferropicritic Martian magmas.

## PETROGRAPHY OF CHASSIGNY

The Chassigny meteorite is a dunitic cumulate composed of cumulus olivine (91.6 vol. %)

116 and chromite (1.4 vol. %), intercumulus pyroxenes (5 vol.%) and feldspar (1.7 vol. %), and  
117 accessory phases (potassium feldspar, apatite, baddeleyite, zirconolite, silica, ilmenite, rutile and Fe  
118 sulfides (Floran et al. 1978; Meyer 2012). The rock microtexture is adcumulate, except where  
119 intercumulus minerals are concentrated (Fig. 1). Olivine is Fe-rich ( $\text{Fo}_{68}$ ). The pyroxenes are Ca-  
120 rich, poikilitic augite ( $\text{Wo}_{33}\text{En}_{49}\text{Fs}_{17}$ ) containing lamellae of exsolved Ca-poor pyroxene  
121 ( $\text{Wo}_3\text{En}_{68}\text{Fs}_{17}$ ) (Johnson *et al.* 1991) and poikilitic pigeonite (Wadhwa and Crozaz 1995).  
122 Interstitial feldspar is Na-rich ( $\text{An}_{32}\text{Ab}_{64}\text{Or}_4$ ). Chassignites are interpreted as cumulates from  
123 ultramafic (ferropicritic) magma(s) emplaced as a komatiitic flow or sill and crystallized at high  
124 oxygen fugacity compared to shergottites ( $\text{FMQ} \pm 1$  log unit vs  $\text{FMQ} + 0.5$  to  $\text{FMQ} - 3$  log unit;  
125 Herd et al. 2002; Papike et al. 2009; Delaney and Dyar 2001; Treiman et al. 2007; McCubbin et al.  
126 2013; Baumgartner et al. 2017b). During cooling and solidification, chromite was likely the first  
127 phase to crystallize because it is found as inclusions in olivine, followed by olivine.

128 Olivine encloses large (up to 350  $\mu\text{m}$  across) spherical to elliptical melt inclusions (Floran  
129 et al. 1978; Varela et al. 2000; McCubbin and Nekvasil 2008; Nekvasil et al. 2007; McCubbin et al.  
130 2013). These melt inclusions are interpreted as entrapment of cogenetic melt during magmatic  
131 growth of olivine (McSween and Treiman 1998). Most of these inclusions are partially crystallized  
132 and contain euhedral minerals interpreted as daughter minerals: low-Ca pyroxene (orthopyroxene)  
133 and high-Ca augitic pyroxene together with Cl-apatite and/or Al-rich chromite, magnetite,  
134 kaersutitic amphibole and Ti-biotite (Johnson et al. 1991; Morikawa et al. 2006; McCubbin et al.  
135 2013). These daughter minerals are embedded in a K-Si-Al-rich alkali feldspar glass (alkali  
136 maskelenyite of McCubbin et al., 2013) showing significant Cl (2500-1500 ppm) and  $\text{H}_2\text{O}$  (0.74  
137 wt%) contents (Boctor et al., 2006; McCubbin and Nekvasil 2008).

138 Secondary minerals of Martian origin (trace amounts of Ca-carbonate, Ca-sulfate and Mg-  
139 carbonate) were identified in some cracks inside Chassigny (Wentworth and Goodings 1994).  
140 Sulfates display non mass-dependent  $\Delta^{33}\text{S}$  isotopic compositions deviating from 0 that support a  
141 pre-terrestrial origin for these minerals (Farquhar et al. 2000; Franz et al. 2014).

## ANALYTICAL METHODS

The samples in this study consisted of two polished mounts of Chassigny ( $\sim 3 \text{ cm}^2$ ), which were provided by the Muséum National d'Histoire Naturelle (MNHN), Paris, France. Sulfides were first characterized with an Olympus BH2 optical microscope operating in reflected light. They were studied in conventional (high-vacuum) mode with a Tescan VEGA II LSU Scanning Electron Microscope (SEM) equipped with a silicon drift (Bruker) Energy Dispersive Spectrometer (EDS) (Muséum National d'Histoire Naturelle-MNHN, Paris, France). Sulfides were localized in the two samples thanks to mosaics composed of stitched BSE maps with a view field of  $905 \mu\text{m}$  each and an overlap of 5% (Fig. 1). These maps allowed sulfide modal abundances to be estimated using their high BSE contrast with non-sulfide minerals (Photoshop<sup>TM</sup> toolbar). The minimum size of sulfide particle that can be resolved this way was around  $10 \mu\text{m}$ . Then, each sulfide detection was checked by optical microscopy and EDS spectra collected during manual scan over the two polished mounts. This procedure helped to take into account the smallest sulfide grains ( $< 5 \times 5 \mu\text{m}$ ) not detected on the BSE maps and avoided overestimation of sulfide abundances from minerals with similar brightness (baddeleyite, ilmenite, chromite).

Major element compositions of sulfides were first determined with the SEM-EDS at the MNHN using 15 keV accelerating voltage with a PhiRoZ EDS standardless procedure and a working distance of 15.4 mm corresponding to the geometrical configuration of the chamber of the Tescan VEGA II LSU SEM for semi quantitative analyses. Each grain texture was carefully studied in BSE mode at high magnification to avoid analytical contribution of silicate microinclusions or alteration products. The spatial resolution of the SEM (a few hundred nanometers) allowed tiny contaminants to be resolved and discrete sulfide inclusions inside olivine-hosted melt inclusions to be analyzed semi quantitatively. Contaminants, however small, were monitored by analyzing silica and phosphorus which are major elements in the minerals

usually surrounding sulfides. Only the analyses giving undetectable amount of Si and P (<0.1 wt%) were considered to be reliable. Moreover, the accuracy and precision of SEM analyzes were checked by replicate analyses of a terrestrial troilite (Del Norte County; California) previously analyzed with both EMP and SEM (Table 1).

Ninety percent of the sulfides analyzed with EDS were reanalyzed with EMP using wavelength dispersive spectrometer (WDS; Table 2 and supplementary data). The analyses were done with the Camparis (Centre d'analyse microsonde de Paris) SX 100 and SXFive Cameca electron microprobes, at 15 KeV accelerating voltage, a beam diameter of 2–3  $\mu\text{m}$  and a 20 nA as beam current sample. Elemental concentrations were determined using the following standards: natural pyrite for S and Fe, sphalerite for Zn and pure metals for Fe, Ni, Co, Cu, As. Silica and oxygen were added to the analytical routine to check any possible contribution of the sulfide analyses by surrounding silicates. Hematite ( $\text{Fe}_2\text{O}_3$ ) and wollastonite ( $\text{CaSiO}_3$ ) were used as external calibration standard for these two elements. The accuracy of EMP analyses was checked by repeated analysis of the Del Norte County natural troilite. This external standard was analyzed every 10–15 analyses to evaluate potential variation on metal-to-sulfur ratios (M/S). Comparisons with the published electron microprobe analyses of this troilite indicate that the accuracy and precision of the EMP determination of the pyrrhotite (M/S) ratio is currently better than  $\pm 1\%$  (Lorand et al. 2012; Chevrier et al. 2011; Gatacceca et al. 2013; Table 1).

Olivine in our pieces of Chassigny was analyzed by WDS on the Camparis Cameca SXFive electron microprobe at the Université Paris VI, using 15 keV and 10 nA, a beam diameter of 2–3  $\mu\text{m}$  and natural (wollastonite, rutile, albite, forsterite, rhodonite, K feldspar, hematite) and synthetic minerals ( $\text{Mn}_2\text{O}_3$ ,  $\text{Cr}_2\text{O}_3$ , NiO) as standards (Table 3 and supplementary data). Count times were 10 s/peak, 10 s/backgrounds. Detection limits were 0.05 wt% for major elements. The mean composition of olivine is shown in Table 3.

## RESULTS

### Sulfide mineralogy

Five sulfide phases were identified in our polished mounts of Chassigny. These are by decreasing order of abundance: pyrrhotite, pyrite, pentlandite, Cu-sulfides and millerite. Sulfides occur as both enclosed and intergranular sulfides.

### **Enclosed sulfides**

The sulfides do not occur as solitary sulfide blebs in cumulus minerals (olivine and chromite). Enclosed sulfides occur exclusively inside melt inclusions in olivine (Fig. 2a). Olivine-hosted enclosed sulfides are a pyrrhotite phase of very small size (1 x 1 to 5 x 3  $\mu\text{m}$ ). Pyrrhotite may occur as prismatic crystals with hexagonal cross sections that may occasionally be ragged on one face (Fig. 2a). The pyrrhotite is commonly associated with chromite, apatite, orthopyroxene, clinopyroxene and kaersutite, which represent crystallization products from the melt fraction trapped inside the melt inclusions (McCubbin and Nekvasil 2008). The sulfide grain usually occurs close to the inner walls of the cavity; it may also be occasionally located within polycrystalline aggregates of pyroxenes, chromite and apatite.

### **Intergranular sulfides**

Intergranular sulfides range in size from less than 100  $\mu\text{m}^2$  to 600  $\mu\text{m}^2$  for the largest ones (30  $\mu\text{m}$  x 20  $\mu\text{m}$ )(Fig. 3). Their surface area represents less than 0.005 vol. % of the total surface investigated in this study. Intergranular sulfides are randomly scattered throughout our two polished mounts of Chassigny (Fig. 1). They fill space at boundaries between olivine grains as well as triple junctions between olivine and pyroxenes, or olivine and chromite. Some intergranular sulfides are partly embedded inside intergranular feldsparic melt pockets (Fig. 2b). The shape of intergranular sulfides depends on their location in the meteorite. Sulfide grains embedded in feldsparic melt pockets may preserve rounded morphologies (Fig. 2c). Intergranular sulfide may show straight contacts against olivine crystals (Fig. 2d). Those grains located at triple junctions between cumulus minerals (olivine, chromite) or intercumulus pyroxenes are ellipsoidal to polyhedral bodies with convex-inward grain boundaries and low dihedral angles (Fig. 2e).

Intergranular sulfides consist of either predominant pyrrhotite or pyrite. Pyrrhotite exhibits

a strong optical anisotropy in reflected light while the pyrite is isotropic, enabling easy distinction with marcasite. Pyrrhotite and pyrite are randomly distributed throughout the two polished mounts investigated. Pyrrhotite is predominant in one polished mount while pyrite is for the second one. Pyrrhotite and pyrite have been found to coexist in a handful of single grains. In that case, a pyrite rim is observed around the pyrrhotite and the interface between the two phases is corrugated.

Pyrrhotite grains are either optically homogeneous or cut by contorted fracture planes (Fig. 2c-e). However, pyrrhotite is slightly fractured compared with major silicates, chromite, and pyrite (see below). Pentlandite was identified with its optical properties in reflected light (Fig. 2d) and EDS spectra in five pyrrhotite blebs over the several tens studied in detail with the SEM. In those grains pentlandite is concentrated as tiny discrete bodies toward the margins of their host pyrrhotite (granule exsolution, Fig. 2d,e). Copper was detected in two EDS spectra of pyrrhotite/pentlandite and pyrite suggesting that Cu-sulfides too small to be accurately identified may also be present in Chassigny intergranular sulfides. One pyrite bleb encloses a Ni-rich sulfide (millerite-NiS) which was identified with the SEM (Table 2).

Euhedral pyrite crystals have not been observed. Intergranular pyrite grains show the same size and morphologies as pyrrhotite grains: rounded to ellipsoidal bodies or polyhedral grains with low dihedral angles when forming triple junctions with surrounding olivine (Fig. 2f-h). On average, pyrite appears to be more fractured compared to pyrrhotite. Fracture networks are evenly distributed, ranging from a few parallel cracks to regularly spaced cell-like systems; in most extreme cases, pyrite crystals were fragmented into particles of less than 1-2 micrometres across (Fig. 2f-h). Fracture planes are generally confined to the pyrite alone (i.e., they do not cut across surrounding silicates). Pyrite shows incipient alteration by Fe-oxyhydroxides that selectively replace pyrite along its fracture planes (Fig. 2h).

## PHASE CHEMISTRY

Only a few olivine-hosted pyrrhotite microinclusions were large enough for EMP analysis.

246 Their metal-to-sulfur atomic ratio ranges from 0.86 to 0.90 (Fig. 4; Table 2). These compositions  
247 correspond to hexagonal ((Fe,Ni)<sub>9</sub>S<sub>10</sub>) and monoclinic ((Fe,Ni)<sub>7</sub>S<sub>8</sub>) crystal structures in the low-  
248 temperature phase diagram of natural pyrrhotites (Kissin and Scott, 1982). Nickel concentrations  
249 vary between 1.3 and 2.8 wt% (Fig. 5).

250 Intergranular pyrrhotite exhibits very similar compositions to those of enclosed pyrrhotite  
251 (Fig. 4). EDS and WDS analyses provided reproducible results, as long as the grains analyzed were  
252 more than 10 µm across and devoid of any pentlandite exsolutions (Table 2 and Table S1). The  
253 M/S of intergranular pyrrhotites spread over a restricted range (0.87 - 0.92), with an average  
254 centered on  $0.88 \pm 0.01$  (one standard deviation). The lowest ratio corresponds to intergranular  
255 pyrrhotite showing incipient crystallization of pyrite. The highest ratios (>0.9) were found in the  
256 pyrrhotite grains showing pentlandite micro-exsolution (e.g., Po1a16; Table 2) and/or Cu-rich areas  
257 (e.g., Po7c10; Table 2). These metal-rich pyrrhotite compositions were probably contaminated by  
258 pentlandite exsolutions. Nickel concentrations range between 1 and 3 wt% Ni, irrespective of the  
259 M/S ratios and the occurrence of pentlandite (Fig. 5). The highest Ni contents (>2 wt%) were found  
260 in interstitial pyrrhotite grains located between cumulus olivine crystals. Cobalt contents are below  
261 limits of detection (<0.2 wt%) as are Cr contents except in the vicinity of chromite. Pyrrhotite is  
262 also poor in oxygen (< 1 wt%; Fig. 6).

263 The few EDS analyses of pentlandite correspond to Fe-rich compositions (Table 2), as  
264 expected for this sulfide when it is associated with pyrrhotite (Misra and Fleet, 1973).

265 Pyrite is slightly metal enriched compared to stoichiometric FeS<sub>2</sub> (Fe/S atomic ratio = 0.50-  
266 0.54; Fig. 6). EDS and EMP analyses show heterogeneous distribution of Ni, without any well-  
267 defined Ni-rich spots as reported in NWA 7533 euhedral pyrite grains (Lorand et al. 2015). On  
268 average, pyrite is depleted in Ni compared to pyrrhotite (<0.1-1 wt%; Fig. 5). Its Co content is  
269 below limits of detection for most analyses (Table 2). Among other minor and trace elements,  
270 pyrite contains copper (up to 0.23 wt%) and some oxygen. High oxygen contents (3.4 wt%)  
271 correlate with high M/S ratios thus indicating decreasing S content at increasing oxygen content

(Fig. 6).

## DISCUSSION

The sulfide phases documented here were previously reported by Floran et al. (1978) and Greenwood et al (2000b). The olivine-hosted sulfides and intergranular sulfides define two sulfide assemblages I) pyrrhotite ( $\pm$  pentlandite  $\pm$  Cu sulfides), II) pyrite ( $\pm$  millerite  $\pm$  Cu-sulfides). Assemblage I is typical of SNC igneous meteorites either as intergranular assemblages (Lorand et al. 2005; Chevrier et al. 2011; Franz et al. 2014) or as olivine-hosted sulfides reported in Iherzolitic and picritic (olivine-rich) shergottites (Gattaccecca et al. 2013; Baumgartner et al. 2017a). The igneous origin of assemblage I in the Chassigny meteorite is supported by its occurrence in olivine-hosted melt inclusions and the shape of intergranular pyrrhotite grains ranging from nearly spherical droplets to polyhedral grains with concave-inward margins. By its compositions and its shape, assemblage I can be interpreted as a solidification product of magmatic sulfide melts (e.g. Naldrett et al. 1967; Craig and Kullerud 1969; Raghavan 2004; Naldrett 2005 and references therein). By contrast, pyrite is a post-igneous replacement product of the original magmatic sulfide assemblage on Mars because it occurs only as an intergranular, heterogeneously distributed mineral in the intercumulus spaces, while showing similar crystalline shape as pyrrhotite. Before further discussion of their origin, it is necessary to assess the effect of shock metamorphism and post-shock alteration that affected both sulfide assemblages.

### **Shock effect and terrestrial alteration.**

Both pyrrhotite and pyrite are fractured, especially the pyrite. Fracture affects all minerals in the Chassigny meteorite, silicates, phosphates, oxides and sulfides. Olivine-hosted melt inclusions are surrounded by radial fracture planes which may reach intergranular pores of the rock. These fracture networks are usually ascribed to the shock event that launched the meteorite into space, ca 11 Myr ago (Langenhorst and Greysake 1999, Malavergne et al. 2002; Meyer 2012

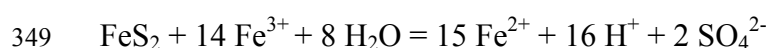


298 and references therein). However, pyrite displays a much higher density of fracture, resulting  
299 locally in finely granulated pyrite blebs (Fig. 2h). Pyrite behaves as an extremely brittle mineral  
300 resulting in cataclastic deformation during deformation and metamorphism (McClay and Ellis  
301 1983). One may note that at temperatures up to 400°C and confining pressures up to 1000 MPa,  
302 pyrite strain rates range from  $10^{-4}$  to  $10^{-7}$  sec<sup>-1</sup> (McClay and Ellis 1983 and ref. therein). Generally,  
303 the brittle deformation results in randomly fractured fragments (cataclastic texture), as documented  
304 in Chassigny pyrite (Fig. 2g,h). Pyrrhotite behaves more plastically and recrystallizes easily (Cox  
305 1987). Langenhorst and Greshake (1999) studied in detail the shock metamorphism features of the  
306 Chassigny meteorite by optical and transmission electron microscopy (TEM). These authors  
307 documented i)-the activation of numerous planar fractures and dislocations in olivines coexisting  
308 with discontinuous fractures, strong mosaicism and clino-/orthoenstatite inversion, ii)-fracturing,  
309 reduced birefringence (conversion to diaplectic glass (maskelynite), and planar deformation  
310 features in the plagioclase. Taken altogether, these shock features indicate a shock pressure of  
311 about 35 Gpa with a post-shock temperature of about 300°C (Malavergne et al. 2002) without the  
312 impact melting found in other Martian meteorites. The post shock temperature of 300°C proposed  
313 for Chassigny was too low to remelt pyrite which is a stable phase below 743°C under P-T  
314 conditions of planetary surfaces (Toulmin and Barton, 1964). However it was high enough to  
315 anneal and rehomogenize any pentlandite exsolution inside the pyrrhotite: at this temperature, the  
316 Chassigny pyrrhotite compositions plot in the single-phase domain corresponding to monosulfide  
317 solid solution (Mss), the high-temperature precursor of pyrrhotite and pentlandite in the Fe-Ni-S  
318 ternary diagram of Fig. 7. It may be deduced from Fig. 7 that the few pentlandite blebs observed in  
319 Chassigny pyrrhotite exsolved during post-shock cooling by heterogeneous nucleation (Etschman  
320 et al. 2004).

321 The persistence of pyrite and metal-deficient pyrrhotite in the Chassigny meteorite is  
322 consistent with a much lower post-shock temperature and weaker shock effect compared to NWA  
323 2737. Bogard and Garrison (2008) suggested that NWA 2737 experienced a post-shock

324 temperature to 300–500 C, perhaps 800 C. i.e. closer to the upper thermal stability of pyrite.  
 325 Indeed, Lorand et al. (2012) reported for this meteorite, minute amounts (0.01 vol.%) of a pyrite-  
 326 free, metal-saturated Fe-Ni sulfide assemblage consisting of a Ni-poor troilite (FeS, sometimes Cr-  
 327 bearing) coexisting with micrometer-sized native Ni-Fe alloys, in addition to a few Os-Ir alloys.  
 328 Lorand et al. (2012) proposed that the high shock pressure (55 Gpa) coupled with strong heating  
 329 triggered sulfur degassing that reduced pyrite and metal-deficient pyrrhotite into FeS and native  
 330 metal alloys. This shock-induced S loss is supported by the highly resorbed and denticulated shape  
 331 of sulfide blebs and their spongy textures (Lorand et al., 2012). An FeS phase was reported to  
 332 occur locally in the Chassigny meteorite by Floran et al. (1978). Chevrier et al. (2011) interpreted  
 333 this phase as an analytical artifact in the EMP analyses of pyrrhotite. However, as shown by the  
 334 sulfide assemblage of NWA 2737, it may have been produced by local S loss during shock  
 335 metamorphism. Gattaceca et al. (2013) reported similar evolution of pyrrhotite compositions  
 336 toward FeS in the highly shocked olivine-phyric shergottite Tissint. If present, this stoichiometric  
 337 FeS phase is likely a very minor phase in the Chassigny meteorite. We did not identify it in our two  
 338 polished mounts (Fig. 4). Franz et al. (2014) did not detect the Acid Volatile Sulfides (AVS)  
 339 fraction that would correspond to this FeS phase in their chemical extraction of sulfur from  
 340 Chassigny.

341 Pyrite has been oxidized after crystallization as shown by its elevated (though variable)  
 342 oxygen contents detected by EMP analyses and local replacement by Fe oxyhydroxides. The latter  
 343 alteration of pyrite by Fe oxyhydroxides is a typical feature of weathering that releases S as soluble  
 344 sulfate while leaving insoluble trivalent Fe as Fe oxyhydroxides (Wattmuff 1974; Thornber 1975;  
 345 Lorand et al. 2005; Zurfluh et al. 2013; Hayes et al. 2014). In humid and aerated conditions, pyrite  
 346 can be oxidized by oxygen or trivalent Fe following the reactions below (Jerz and Rimstidt 2004;  
 347 Liu et al. 2009; Huminicky et al. 2009) :



350 This alteration event is likely a terrestrial feature because Fe oxyhydroxides were observed to occur  
351 only within the finely granulated pyrite blebs showing cataclastic microtextures (Fig. 2h).  
352 However, the Chassigny meteorite is an observed fall and not a hot desert find: its pieces were  
353 collected immediately after their arrival on the Earth surface (Pistollet, 1816), which certainly  
354 prevented them from extensive weathering by atmospheric agents (Meyer, 2012). However,  
355 oxidation may have occurred during the curation of the meteorite for the last 200 years in the  
356 MNHN collection. It is well known from museum curators and mining operation that pyrite can  
357 alter over days or months if kept in a humid and oxygenated environment (Huminicky et al. 2009).  
358 There is independent evidence of terrestrial contamination and/or alteration involving water, sulfur  
359 and sulfides in the Chassigny meteorite. Wentworth and Gooding (1994) reported traces of  
360 massive, fine-grained Ca-sulphate in some vugs in Chassigny's fusion crust which could indicate  
361 either terrestrial contamination or post-fall leaching of hygroscopic, pre-terrestrial salts from the  
362 interior. Terrestrial hydrogen exchange was documented by Leshin et al. (1996) via D/H ratios.  
363 Brandon et al. (2000) documented disturbance in the bulk-rock  $^{187}\text{Re}/^{188}\text{Os}$  ratio of Chassigny  
364 possibly due to late terrestrial remobilization of Re liberated from altered pyrite.

365 The sensitivity of Chassigny pyrite to oxidation can be ascribed to the extensive fracturing  
366 that generated highly granulated domains inside pyrite grains. In impact regolith breccia NWA  
367 7533, terrestrial weathering was guided by shock-induced microfracturing of pyrite (Lorand et al.  
368 2015). The size of the pyrite grains plays a key part in the oxidation process which destroys  
369 museum samples of pyrite and marcasite (Rimstidt and Vaughan 2003). It is well known that  
370 milling and grain size reduction increases the rate and susceptibility of Fe-bearing phases to  
371 oxidation processes (Williamson and Rimstidt 1994; Pratt et al. 1994; Nesbitt et al. 1998; Thomas  
372 et al. 1998, 2001). Conchoidal fractures that produce surface sites of reduced coordination with  
373 dangling bonds are more reactive compared to normal crystallographic surfaces sites (Chandra and  
374 Gerson 2011; Todd et al. 2003). Compared with pyrite, Chassigny pyrrhotite shows almost  
375 unaltered, oxygen-poor compositions which are at odds with theoretical expectations. Pyrrhotite is

376 expected to be far more reactive to oxidation than pyrite (Janzen et al. 2000; Mikhlin and  
377 Tomashevich 2005). The weathering of pyrrhotite under the influence of atmospheric oxygen  
378 proceeds approximately 20–100 times faster than that of pyrite (Belzile et al. 2004). This faster  
379 oxidation rate is usually ascribed to the lower crystal symmetry of pyrrhotite that results from the  
380 vacancy of Fe atoms in the crystal structure (Janzen et al. 2000, Harries et al. 2013). Concerning  
381 Chassigny pyrrhotite, its very low degree of alteration could be due to extensive recrystallization  
382 at 300°C during the shock metamorphism event that probably healed fracture planes, thus reducing  
383 preferential pathways for oxidation.

384

#### 385 **Martian hydrothermal alteration and the origin of pyrite.**

386 By its location in interstitial pores, pyrite clearly postdates solidification of the cumulate  
387 phases of the Chassigny meteorite. Crystallization of pyrite at the igneous stage is very unlikely as  
388 it is not stable above 743°C (Toulmin and Barton 1964). Moreover, its precipitation at this  
389 temperature would require unrealistically high sulfur fugacity (close to the domain of liquid native  
390 S) compared with that indicated by pyrrhotite composition (Fig. 8). Both lines of evidence make  
391 pyrite a subsolidus phase. Pyrite can exsolve from pyrrhotite by cooling but exsolution should  
392 produce Py inside Po, as wormlike textures (e.g., Lorand and Alard 2011) or discrete granules as  
393 usually observed in magmatic sulfide assemblages (Craig and Vokes 1993; Hall 1986; Hollwell et  
394 al. 2017 and references therein). Precursor high-temperature monosulfide solid solution (Mss) can  
395 produce only 30% pyrite by weight this way (Naldrett et al. 1967). Assuming that pyrite exsolved  
396 from metal-deficient pyrrhotite with a general composition of  $M_{0.88}S$ , the exsolution process should  
397 have followed path B in Fig. 8 on cooling; hence the pyrrhotite should display increasing metal-to-  
398 sulfur ratio down to 0.92 at  $T < 200^\circ\text{C}$ , significantly off the compositional range measured for the  
399 Chassigny meteorite (Fig. 4). If exsolved from the pyrrhotite, then pyrite should be homogeneously  
400 distributed within our two polished mounts of Chassigny, and observed both as inclusions and  
401 intergranular sulfides.

402 The shape of pyrite grains that display the same morphologies as coexisting igneous  
403 pyrrhotite grains argues instead for local replacement of the pyrrhotite by pyrite. The same  
404 replacement reaction was postulated for pyrite from other Martian meteorites (e.g. ALH 84001;  
405 Shearer et al. 1996; the nahklites Nakhla, Governador Valadares and Lafayette; Bunch and Reid  
406 1975; Greenwood et al. 2000a; Franz et al. 2014). In the  $\log fS_2$ -T diagram of Fig 8, single-phase  
407 pyrite grains observed in Chassigny reflect local excursion of the fugacity of sulfur within the  
408  $\log fS_2$ -T area of pyrite stability, i.e. well above the FMQ-Po reference curve taken as a marker of  
409 redox conditions for Chassigny. This cooling path may track input of external S raising the  
410 apparent fugacity of sulfur (Hall 1986). There is published evidence for post-igneous external input  
411 of S in the Chassigny meteorite. Wentworth and Gooding (1994) reported discontinuous veins of  
412 Ca-sulphate (gypsum ( $CaSO_4 \cdot 2H_2O$ ) or bassanite ( $CaSO_4 \cdot \frac{1}{2}H_2O$ )), Ca-carbonate, and Mg-  
413 carbonate along fractures in primary igneous minerals. These sulfate and carbonate salts also  
414 contain traces of Cl and P, which supports their precipitation from short-lived, cold, saline, aqueous  
415 solutions well after the igneous crystallization of the Chassigny cumulate (Bridges et al., 2001).  
416 Sulfur isotopic compositions measured on the Chassigny meteorite add further constraints on the  
417 origin of pyrite. Greenwood et al (2000b) provided seven *in-situ* ion microprobe analyses of this  
418 sulfide; all show negative Canyon Diablo Troilite (CDT)-normalized  $\delta^{34}S$  ( $-4.6\text{‰} < \delta^{34}S < -1.5\text{‰}$ ),  
419 off the baselines for mantle-derived Martian sulfur ( $\delta^{34}S = 0$ ) as defined from shergottite meteorites  
420 (Franz et al. 2014). Greenwood et al (2000b) inferred low-temperature (200°C) exchange of  
421 volatile components (S, C, H) between olivine cumulate flows and regolith by hydrothermal fluids.  
422 Likewise, Franz et al. (2014) documented mass-independent fractionation (MIF) in Chassigny Ca  
423 sulphates ( $\Delta^{33}S = 0.0336 \pm 0.008 \text{‰}$ ) which also indicates recycling of surface sulfur.

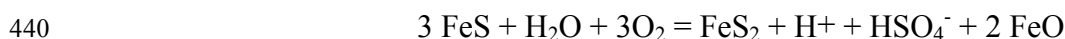
424 Chassigny pyrite may have formed from direct sulfurization of preexisting igneous  
425 pyrrhotite by S-bearing hydrothermal fluids because the latter imparted their S isotopic  
426 composition to the pyrite, different from that of initial igneous sulfides. Different pathways can be  
427 assumed for this transformation, depending on the initial assemblage of the igneous sulfide and

chemical exchanges between sulfides and hydrothermal fluid. For example, the NiS-rich mineral identified as millerite with the SEM in one pyrite grain could derive from a pyrrhotite-pentlandite precursor, if this reaction also operated with Fe loss to the fluid (Fig. 9). Pyrite and millerite are stable together below 230°C (Craig 1973; Misra and Fleet 1973), in agreement with the temperature range inferred for hydrothermal contamination of the Chassigny meteorite (Greenwood et al., 2000b). A volume loss of several tens percent of original sulfides is expected for this reaction (e.g. Holwell et al. 2017, and ref. therein) but hard to quantify as the Chassigny sulfides experienced shock effects that heavily fractured the pyrite and modified its porosity.

There are other possible pathways for pyrite formation in the Chassigny meteorite. Pyrrhotite can be oxidized into pyrite via reactions such as:



or



in humid and aerated conditions (Watmuff 1974; Pratt et al. 1994; Harries et al. 2013; Kanipayacharoen and Boudreau 2013). However, such reactions are considered to be much less likely because the Chassigny cumulate flow was exposed to subsurface conditions of dry Amazonian Mars (Nyquist et al., 2001), a period of little water and dissolved oxygen available for oxidative dissolution of pyrrhotite.

Our study, coupled with literature data, reveal strong heterogeneity in the distribution of pyrite both within and between each piece of the same meteorite. The pyrite/pyrrhotite modal ratio is estimated to vary from ca 1 to 2 between our two polished mounts. Greenwood et al (2000b) identified only pyrite in a sulfide-poor chip of Chassigny. This heterogeneity is an expected outcome of the numerous parameters that drive pyrite-producing reactions. For instance, pyrrhotite armored inside olivine-hosted sulfide inclusions escaped to alteration while unarmored portions within intercumulus material have been heterogeneously replaced. One may also argue that pyrite did not systematically nucleate because its formation is very sluggish below 200° C (Craig, 1973;

454 Rickard and Luther 2007 and references therein). Additional evidence of internal heterogeneity is  
455 the heterogeneous distribution of marcasite. Floran et al. (1978) identified this sulfide, based only  
456 on its optical properties, while we did not find it in our polished mounts of Chassigny. Marcasite  
457 was reported to form at  $T < 150^{\circ}\text{C}$  and  $\text{pH} < 4$  by Fleet (1978) and Craig and Vokes (1993 and  
458 references therein). One may argue that the post-shock annealing event at  $300^{\circ}\text{C}$  converted  
459 marcasite to pyrite. On Earth, for example, marcasite in sulfide ore deposits is converted to pyrite  
460 by natural annealing at relatively low ( $< 200^{\circ}\text{C}$ ) temperatures (Fleet 1978; Hall 1986; Murowchick,  
461 1992). The heterogeneous distribution of marcasite may thus fingerprint some heterogeneities in  
462 the Chassigny meteorite related to shock metamorphism, as do the occasional occurrences of FeS  
463 (troilite).

464

## 465 **Petrogenesis of the igneous sulfide assemblage I.**

### 466 **Sulfur ultradepletion in Chassigny indicates sulfur-undersaturated parental melt.**

467 The lack of single-phase pyrrhotite inclusions indicates that the parental melt for the  
468 Chassigny meteorite presumably did not segregate immiscible sulfide liquids over the interval of  
469 olivine and chromite crystallization. Sulfur dissolves in reduced Martian basalts as  $\text{FeO} + 1/2\text{S}_2 =$   
470  $\text{FeS} + 1/2\text{O}_2$  (Ding et al., 2015 and references therein). The S content necessary to saturate the  
471 hypothetical parental melt of Chassigny is available from experiments relevant to Martian lavas  
472 (Ding et al. 2015), coupled with the FeOT content (19.95 - 20.33 wt%; Johnson et al. 1991;  
473 Filiberto 2008; He et al. 2013). Giesting et al. (2015) estimated that partial melting started at  $P > 2$   
474 Gpa (170 km) so this putative melt was able to dissolve at best  $4000 \pm 1000$  ppm S (Ding et al.  
475 2015). Its actual S content can be estimated around 3600 ppm by coupling the most conservative  
476 estimate of the S content of the Martian mantle ( $360 \pm 120$  ppm S; Wang and Becker 2017) with  
477 the degree of partial melting estimated for Chassignites (10%; Wadhwa and Crozaz 1995). Of  
478 course, melting degrees in excess of 10% would have decreased the S content of the melt  
479 proportionally, thus making it S-undersaturated once leaving its mantle source. Our conclusion is

480 supported by platinum-group element (PGEs) analyses. Baumgartner et al (2017b) reported  
481 detectable concentrations of Ru (up to ~160 ppb Ru) in chromite of Chassigny and NWA 2737.  
482 This element (and other PGEs as well) should have been preferentially incorporated into sulfide  
483 melts if any sulfide had been present during chromite precipitation (Brenan et al., 2016 and  
484 references therein). Baumgartner et al (2017b) concluded that the parental melt of Chassigny  
485 started crystallizing chromite under sulfide-undersaturated conditions, as documented for other  
486 Martian magmas sampled by shergottites (e.g. Brandon et al. 2012; Baumgartner et al. 2017a).

487         The late-magmatic achievement of S saturation is also consistent with the very low amount  
488 of Fe-Ni sulfides in the Chassigny meteorite. Previous studies reported bulk-rock S contents of  
489 similar order of magnitude in Chassigny (mean  $260 \pm 130$  ppm S; McSween, 2014) and nakhlites,  
490 corresponding to ca.,  $0.06 \pm 0.03$  wt% Fe-Ni sulfides composed of 50% pyrite and 50% pyrrhotite.  
491 By contrast, our two polished mounts are depleted in Fe-Ni sulfides by a factor 10 (Table 4). The  
492 same depletion was also reported by Franz et al. (2014) who concluded that over 99% of the sulfur  
493 recovered by their chemical extraction from Chassigny ( $65 \pm 1$  ppm) correspond to Ca-sulphates,  
494 while a negligible fraction ( $< 3$  ppm) correspond to sulfides (pyrite and metal-deficient pyrrhotite,  
495 i.e. Chrome Reduced Sulfide, CRS). The bulk-rock Ni budget also reflects the negligible volume of  
496 Fe-Ni sulfides in Chassigny. Olivine alone is able to balance the bulk rock Ni contents ( $500 \pm 70$   
497 ppm; Papike et al. 2009) if we combine our analyses of olivine in Table 3 ( $530 \pm 30$  ppm Ni) with  
498 the olivine modal proportions reported in the literature (91%; Meyer, 2012). By contrast, the  
499 contribution of Fe-Ni sulfides is at best 1-2 ppm (within the analytical error of the bulk-rock Ni  
500 content) for the maximum Ni concentration of 3 wt% in the sulfides and a modal volume of 0.005  
501 % (Fig. 7).

502         The amount of sulfide precipitated in Chassigny is negligible compared to the expected  
503 huge amount of S the parental melt was able to dissolve. Because Fe-Ni sulfides preferentially  
504 segregated in the intercumulus pores of the meteorite, their amount primarily reflects the low  
505 amount of trapped intercumulus silicate melt. Other parameters may also have contributed in



506 producing negligible amount of sulfides, i-an unrealistically high degree of partial melting  
507 compared to the accepted values, ii-second stage melting of a S-depleted, LREE-depleted olivine-  
508 augite mantle source, iii-late-stage migration/removal of intergranular sulfides by percolating  
509 fluid(s), iv- S outgassing or sulfide resorption driven by late-stage melt decompression that was  
510 coeval with the extrusion of the Chassignite cumulate pile to near-surface conditions. Any further  
511 discussion of these parameters will require detailed in-situ geochemical studies of trace metals in  
512 Fe-Ni sulfides, which were hitherto made impossible by the very small size of these sulfides  
513 (Baumgartner et al., 2017a,b).

#### 514 **In-situ nucleation of Ni-pyrrhotite**

516 Models based on previously published S contents of Chassigny ( $260 \pm 130$  ppm S)  
517 suggested that Chassigny Fe-Ni sulfides originated from mixing between cumulates from S-  
518 undersaturated melts with S-saturated melts or externally derived evolved melt (see Ding et al.  
519 2015, Baumgartner et al 2017b). The new bulk-rock S estimates (Franz et al. 2014) and our own  
520 observations make such interpretations disputable. In-situ nucleation of sulfides from the trapped  
521 intercumulus melt is more likely, especially by considering sulfides from olivine-hosted melt  
522 inclusions. Such enclosed sulfides resemble early solid micro - precipitate growth in a fluid  
523 medium. One may surmise that sulfides appeared very early in these inclusions because the trapped  
524 silicate melt fractions were strongly FeO-depleted after massive precipitation of olivine; olivine  
525 melt inclusions started crystallizing at high pressure, under conditions of lowered S saturation  
526 according to experiments on terrestrial (e.g. Mavrogenes and O'Neill, 1999) and martian basalts  
527 (Ding et al., 2015). Pressure above 0.4 GPa to as high as 2 GPa were suggested by Nekvasil et al.  
528 (2007, 2009), Filiberto (2008) and Giesting (2015). McCubbin et al. (2008) estimated  $P = 0.9$  GPa  
529 from the crystallization path of Chassigny melt inclusions that contain 0.48–0.67 wt% H<sub>2</sub>O (He et  
530 al. 2013). These high water contents, coupled with high alkali contents, delayed full solidification  
531 of olivine-hosted melt inclusions down to  $T = 700^{\circ}\text{C}$  (McCubbin et al. 2013). Enclosed pyrrhotites  
532 in theory have a solidification temperature of ca.  $1200^{\circ}\text{C}$  at 1 bar (Craig and Kullerud, 1969 and

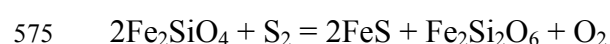
references therein) that accounts for their segregation as euhedral solid crystals along with apatite and low-Ca pyroxene.

The shape of intergranular assemblages, i.e. ovoid grains or triangular-shaped grains showing convex-inward margins and low dihedral angles with matrix silicates are characteristic of immiscible sulfide blebs forming isolated pockets in cumulate rocks (Naldrett 2005 and references therein). Textural reequilibration that typically affects sulfides in cumulate igneous rocks is recognized through straight triple junctions with olivine and chromite meeting at  $120^\circ$  indicating surface energy minimization between solids. According to Giesting et al (2015), after accumulation of olivine at  $T = 1230^\circ\text{C}$  and 0.9-1.7 Gpa, the putative lava flow was decompressed from 1 to 0.02 Gpa and cooled rapidly from a point where temperatures were 800–850  $^\circ\text{C}$  at a depth of no more than  $\sim 200$  m (Treiman et al. 2007; McCubbin et al. 2013). The interstitial magma that cooled to form the mesostasis of olivine cumulates experienced retrograde boiling and degassing of volatiles, especially  $\text{H}_2\text{O}$  (McCubbin and Nekvasil 2008; McCubbin et al. 2013; Giesting et al., 2015). This degassing also triggered complete solidification of the mesostasis at higher  $T$  ( $>900^\circ\text{C}$ ) compared to melt inclusions in olivine, thus preventing sulfide melts from migrating through the cumulate pile. Chemical equilibrium between sulfides and olivine can be tested with the partitioning behavior of Ni. Despite between-grain variations of Ni/Fe on a localized scale, the mean partition coefficient  $K_d$  ( $\text{Ni/Fe}_{\text{sulfides}}/\text{Ni/Fe}_{\text{olivine}}$ ) calculated from our olivine and pyrrhotite compositions (Fo 68, 0.06 wt% NiO for olivine, Table 3 and supplementary data;  $2 \pm 0.5$  wt% Ni for pyrrhotite) is in good agreement with the experimental values determined at magmatic temperatures ( $19 \pm 5$  vs. 13 to 15; Brenan, 2003). Thus, an overall state of equilibrium seems to have existed between intergranular (and enclosed) Chassigny pyrrhotite and coexisting olivine as regard the Ni-Fe partitioning. This is expected where sulfides segregated in-situ.

### **Pyrrhotite compositions track late-magmatic oxidation-crustal contamination**

Our data show that a metal-deficient pyrrhotite composition of general formula  $\text{M}_{0.88}\text{S}$  (M

559 = Fe + Ni + Co + Cu + Mn) is the main igneous sulfide in the Chassigny meteorite. It has long been  
 560 suggested that disseminated sulfides in volumetrically dominant silicate rocks reequilibrate through  
 561 redox equilibrium involving coexisting silicate assemblages (Barton 1970). The Chassigny  
 562 pyrrhotite compositions cluster within a narrow  $\log f_{S_2}$ -T domain of Fig. 8, well above the  
 563 reference buffer curve Fayalite-Magnetite-Quartz-Pyrrhotite (FMQ-Po) at solidus temperature. The  
 564 accepted magmatic  $f_{O_2}$  conditions for Chassigny are slightly below FMQ (FMQ-1.25 log units;  
 565 McCubbin et al 2013), whether calculated with the equilibrium olivine + low-Ca pyroxene + Cr-  
 566 spinel (Treiman et al. 2007) or from V valence-state oxybarometer (Baumgartner et al. 2017b; see  
 567 also Beck et al. 2006). For such  $f_{O_2}$  conditions, the igneous pyrrhotite compositions should be  
 568 more metal-rich ( $M_{0.96}S$ ) at magmatic temperatures compared to the measured composition (Fig.8).  
 569 Of course, the latter may not be representative of the high temperature pyrrhotite composition  
 570 because of subsolidus reequilibration. A cooling path following the FMQ-Po reference buffer curve  
 571 can lower pyrrhotite M/S ratios down to at best 0.91 before pyrite starts exsolving at ca 250°C  
 572 (path A; Fig. 8). Nevertheless, the latter value still excludes almost all the measured pyrrhotite  
 573 compositions. The fugacity of oxygen necessary to reproduce the composition of the Chassigny  
 574 pyrrhotite can be estimated from the sulfidation reaction of olivine



576 Eggler and Lorand (1993) calibrated this equilibrium as a barometer for oxygen and sulfur  
 577 fugacity. The fugacity of S is deduced from the FeS isopleths in Fig. 8. Using the compositions of  
 578 olivine and low-Ca opx in Chassigny (Fa<sub>32</sub> and En<sub>70</sub>; Meyer, 2012 and Table 3), the sulfidation  
 579 reaction of olivine indicates an  $f_{O_2}$  value close to FMQ + 2 log units at 800-900°C (equation 46 in  
 580 Eggler and Lorand 1993). Such conditions are significantly more oxidizing compared to the  $f_{O_2}$   
 581 range deduced from Cr spinel compositions (McCubbin et al., 2013; Baumgartner et al. 2017b).

582 The same discrepancy between expected and measured pyrrhotite compositions was  
 583 documented for nakhlites (Chevrier et al. 2011). Indeed, in addition to their occurrence as extrusive

584 flows, nakhlites and chassignites share many features as regards their sulfide assemblages, i.e.  
 585 metal-deficient pyrrhotite predominating over pentlandite and Cu-sulfides. Our pyrrhotite  
 586 compositions overlap the pyrrhotite compositions so far published for nakhlites (Table 4). Chevrier  
 587 et al. (2011) suggested that nakhlite pyrrhotites experienced deuteric oxidation resulting from water  
 588 dissociation and devolatilization of intercumulus melts. Deuteric oxidation results from  
 589 accumulation of  $\text{Fe}^{3+}$ -rich minerals raising oxygen fugacity in the latest magmatic differentiates  
 590 after massive precipitation of  $\text{Fe}^{2+}$ -rich minerals such as olivine (e.g. Czamanske and Wones 1973).  
 591 McCubbin and Nekvasil (2008), McCubbin et al. (2013) and Giesting et al. (2015) suggested that  
 592 degassing changed significantly the  $\text{H}_2\text{O}$  content of the interstitial magma in the Chassigny  
 593 cumulate during uplift and eruption or near-surface emplacement. According to these authors,  
 594 retrograde boiling and degassing may increase oxygen fugacity through the loss of hydrogen while  
 595  $\text{H}_2\text{O}$  losses may account for the lack of biotite and amphibole in the intergranular mesostasis of the  
 596 Chassigny meteorite. McCubbin and Nekvasil (2008) and McCubbin et al. (2013) interpreted the  
 597 Cl-enrichment of intercumulus apatites (compared to the olivine-hosted F-rich apatite  
 598 compositions) as resulting from addition of an exogenous Cl-rich fluid to the intercumulus regions  
 599 of the Chassigny meteorite above 700 °C. This late-percolating fluid may also have disturbed  
 600 pyrrhotite compositions if it was introduced into the cumulate horizon sampled by Chassigny  
 601 immediately after formation and accumulation of the cumulus olivine.

602 Another potential source of alteration of igneous pyrrhotite composition is assimilation of  
 603 crustal sulfur coeval driven by magmatic crystallization (Assimilation-Fractional Crystallization  
 604 process), as suggested by Franz et al (2014) for nakhlites. These authors found Mass Independent  
 605 Fractionation (MIF) in the S isotopic composition of sulfides chemically extracted from Nakhla  
 606 ( $\Delta^{33}\text{S} = -0.08 \text{ ‰}$ ), and Miller Range (MIL) 03346 ( $\Delta^{33}\text{S} = 0.434 \pm 0.008 \text{ ‰}$  to  $-0.5386 \pm 0.008$   
 607  $\text{‰}$ ). SIMS in-situ analyses confirmed these bulk-rock analyses of MIF, within the error of the  
 608 chemical extraction analysis for Nakhla, and more variable values for individual pyrrhotite of MIL  
 609 03346 ( $-0.306 \pm 0.13 \text{ ‰} < \Delta^{33}\text{S} < -1.116 \pm 0.13 \text{ ‰}$ ). Franz et al (2014) concluded that sulphur salts

610 (Ca sulfates) or sulphur-bearing fluids were assimilated by parental melts at the time the nakhlite  
611 flows were extruded. If valid for nakhlites, this model of exogenous sulfur assimilation at the  
612 magmatic stage is plausible for Chassigny that was part of a subaerial flow erupted on the S-rich  
613 Martian surface. However, the very small size of igneous pyrrhotite grains made in-situ SIMS  
614 analyses of S isotope compositions impossible (J. Farquhar, personal communication to J.-P.  
615 Lorand). Only a bulk analysis of the Chrome Reducible Sulfide fraction is available ( $\Delta^{33}\text{S} = 0.004$   
616  $\pm 0.008$  ‰; Frantz et al, 2014), which, however is a mixture of both igneous metal-deficient  
617 pyrrhotite and hydrothermal pyrite. Fig. 10 clearly shows that the assemblage Ca sulfates + a  
618 metal-deficient pyrrhotite ( $\text{Fe}_{0.88}\text{S}$ ) produce the same oxidizing conditions (FMQ + 1.5 log unit) as  
619 those defined by the sulfidation reaction of olivine. One may speculate that, because of its  
620 exceedingly low modal volume, Chassigny pyrrhotite reequilibrated under the redox conditions  
621 imposed by assimilation of sulfates, without reequilibrating for S isotopic compositions. Of course,  
622 such a reequilibration is assumed to have started before isolation of olivine-hosted melt inclusions  
623 inside olivine.

624

## 625 CONCLUSION

626

627 Like other Martian basalts so far studied for sulfur and strongly chalcophile elements (i.e.  
628 PGEs), the parental melt of the Chassigny dunitic cumulate achieved sulfide-saturation at a late  
629 stage of its crystallization, after olivine and chromite precipitation. Igneous sulfides precipitated in-  
630 situ as magmatic sulfide melt of low-Ni pyrrhotite bulk composition, either inside porphyritic  
631 silicate melt inclusions in olivine or as polyhedral or near-spherical blebs in intergranular spaces  
632 between cumulus olivine. The igneous pyrrhotite displays Ni/Fe ratios within the range expected  
633 for equilibration with the coexisting olivine at igneous temperatures.

634 Chassigny sulfides bear imprints of each petrogenetic process experienced by the Chassigny  
635 meteorite. Once segregated, the pyrrhotite experienced a late-magmatic reequilibration of its metal-

to-sulfur ratios toward a general formula  $M_{0.88\pm0.01}S$  ( $M = Fe+Ni+Co+Cu+Mn$ ). This reequilibration may result from retrograde boiling, volatile loss, or contamination by crustal sulfates, perhaps driven by post-cumulus circulation of late-magmatic differentiated melts.

Hydrothermal fluids operated pervasively over different temperatures well after complete cooling of the Chassigny dunite. Magmatic pyrrhotite was converted to pyrite along with other accessory sulfides (e.g. millerite), in line with low-temperature precipitation of Ca sulfate + Ca carbonate deposition. The shock that ejected the Chassigny meteorite from Mars generated post-shock temperatures high enough (300°C) to anneal and rehomogenize Ni inside pyrrhotite while pyrite blebs were fractured and disrupted into subgrains by shock metamorphism. Owing to its high density of fractures, pyrite was preferentially oxidized on Earth compared to pyrrhotite.

Hydrothermal alteration and shock metamorphism generated strong heterogeneity inside the Chassigny meteorite. This is demonstrated by the distribution of pyrite, marcasite, and an FeS phase (troilite) between each piece of the meteorite investigated so far for Fe-Ni sulfides.

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## Figure captions

FIGURE 1: Low-magnification backscattered electron (BSE) image of the Chassigny meteorite showing the distribution of Fe-Ni sulfides (white star) in one of the two polished mounts

1030 investigated in this study.

1031

1032 FIGURE 2: Microphotographs of Chassigny sulfides. 2a: pyrrhotite included in an olivine-hosted  
1033 melt inclusion (reflected light optical microscope). 2b: intergranular pyrrhotite hosted in a feldspar  
1034 pocket enclosing euhedral chromite (reflected light optical microscope); 2c: detail of Fig. 2b  
1035 showing a two-phase (pyrrhotite + pentlandite) ellipsoidal magmatic sulfide grain associated with  
1036 a euhedral apatite inclusion inside the feldspar glass (BSE image). 2d: intergranular pyrrhotite (+  
1037 pentlandite) at triple junction of olivine crystals (reflected light optical microscope). 2e:  
1038 polyhedral intergranular pyrrhotite (+ pentlandite) showing convex-inward grain boundaries (BSE  
1039 image). 2f: highly fractured, rounded pyrite grain showing incipient replacement by an NiS phase  
1040 (BSE image). 2g: intergranular pyrite showing formation of subgrains (BSE image). 2h: rounded  
1041 and highly granulated pyrite (white) showing incipient alteration in Fe oxyhydroxides (reflected  
1042 light optical microscope; oil immersion objective). Ol: olivine; Opx: orthopyroxene; Chr:  
1043 chromite; Ap: apatite; Amph: amphibole; Fs: feldspar; Po: pyrrhotite; Py: pyrite; Pn: pentlandite;  
1044 Fe oxhyd: Fe oxyhydroxide.

1045

1046 FIGURE 3: Distribution of sulfide grain sizes in the Chassigny meteorite.

1047

1048 FIGURE 4: Metal-to-sulfur atomic ratios (M/S;  $M = \text{Fe} + \text{Ni} + \text{Co} + \text{Cu} + \text{Mn}$ ) of Chassigny  
1049 pyrrhotite (WDS analyses only).  $\text{Fe}_7\text{S}_8$  : monoclinic pyrrhotite;  $\text{Fe}_9\text{S}_{10}$  : hexagonal pyrrhotite  
1050 (Kissin and Scott, 1982)

1051

1052 FIGURE 5: Ni concentrations (wt%) in pyrrhotite and pyrite (WDS analyses only). N = number of  
1053 analyses.

1054

1055 FIGURE 6: Metal-to-sulfur atomic ratio vs. oxygen contents for pyrrhotite and pyrite (WDS

1056 analyses only).

1057

1058 FIGURE 7: Plot of Chassigny pyrrhotite compositions (squares) in the Fe-Ni-S system at 300°C.  
1059 Compositional range and phase relationships of Mss (monosulfide solid solution) from Naldrett et  
1060 al (1967), Craig (1973) and Rhagavan, (2004). Fe<sub>7</sub>S<sub>8</sub>: monoclinic pyrrhotite; Fe<sub>9</sub>S<sub>10</sub>: hexagonal  
1061 pyrrhotite; FeS: troilite (Kissin and Scott, 1982).

1062

1063 FIGURE 8: Plot of the mean composition of Chassigny pyrrhotite (M<sub>0.88</sub>S; white star) in the log  
1064 fS<sub>2</sub>-T diagram for the Fe-S-O system (after Lorand et al., 2005 and Chevrier et al., 2011).  
1065 Pyrrhotite isopleths of metal-to-sulfur atomic ratios, pyrrhotite iron (Fe-Po) and sulfur vapor-sulfur  
1066 liquid (Svap-Sliq) reaction curves from Toulmin and Barton (1964). The curves labeled with  
1067 oxygen fugacity are for the reaction: 3FeS + 2O<sub>2</sub> = Fe<sub>3</sub>O<sub>4</sub> + S<sub>2</sub> (pyrrhotite-magnetite equilibrium);  
1068 FMQ-Po buffer from Eggler and Lorand (1993). We present two possible subsolidus evolutions for  
1069 the Chassigny igneous pyrrhotite. Path A assumes subsolidus re-equilibration controlled by the  
1070 FMQ-Po buffer curve (see text for description of the buffer). Note that path A precludes pyrrhotite  
1071 M/S ratios < 0.91. Path B assumes cooling of the Chassigny pyrrhotite at constant M/S ratio. Path  
1072 A should trigger pyrite exsolution at high temperature, and then increasing M/S ratios in the co-  
1073 existing pyrrhotite down to 0.91.

1074

1075 FIGURE 9: Low-temperature (135°C) phase relationships in the Fe-Ni-S system (wt %) after Craig  
1076 (1973) and Rhagavan (2004)(wt%). This diagram illustrates a putative reaction path (arrow) at  
1077 decreasing Fe/Ni ratio producing pyrite + NiS from the igneous sulfide assemblage of Chassigny  
1078 (pyrrhotite + pentlandite). Mss1 and Mss 2: compositional field of monosulfide solid solutions 1  
1079 and 2 from Craig (1973). Py: pyrite; Mpo: monoclinic pyrrhotite (Fe<sub>7</sub>S<sub>8</sub>); Hpo: hexagonal  
1080 pyrrhotite (Fe<sub>9</sub>S<sub>10</sub>); Tr: troilite (FeS); Pn: pentlandite, Mi: millerite; Vs: vaesite; Vi: violarite; Gd:  
1081 godlevskite; Hz: heazlewoodite.

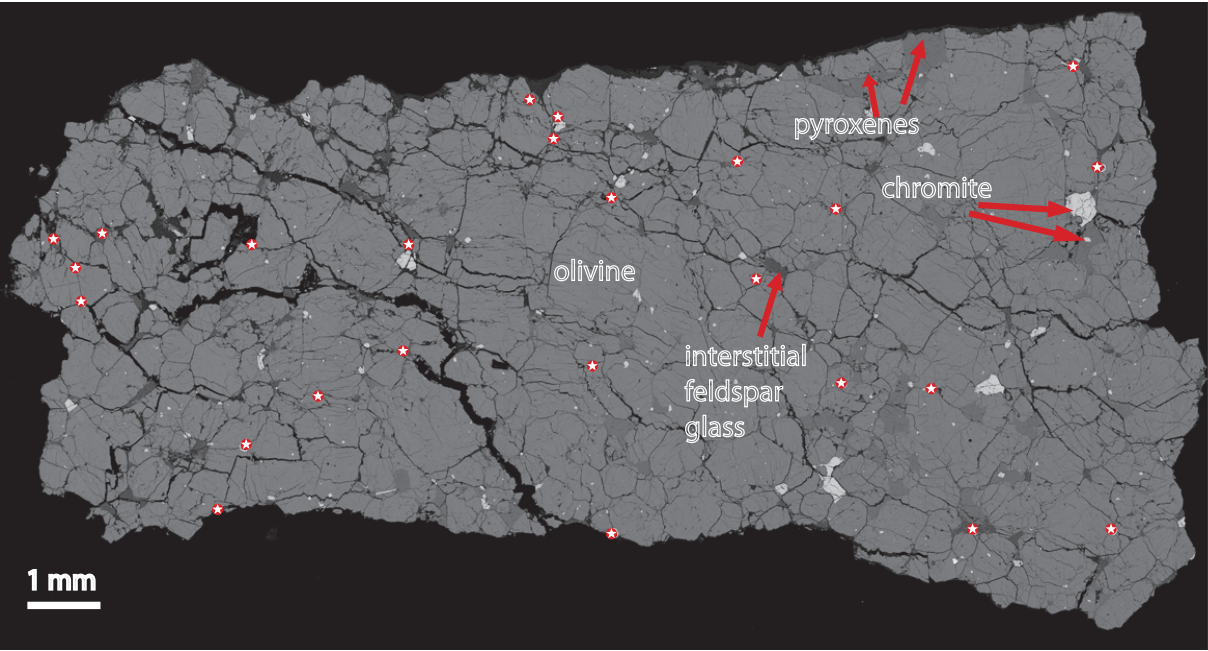
1082

1083 FIGURE 10: Log  $fS_2$  vs. log  $fO_2$  diagram for the Fe-S-O system at 800°C (after Parat et al., 2011).

1084 The compositional range of Chassigny pyrrhotite can coexist with anhydrite if the oxygen fugacity

1085 is above that defined by the synthetic assemblage FMQ (Fayalite-Magnetite-Quartz);  $Fe_7S_8$ :

1086 monoclinic pyrrhotite;  $Fe_9S_{10}$ : hexagonal pyrrhotite (Kissin and Scott, 1982).



1087

Fig. 1

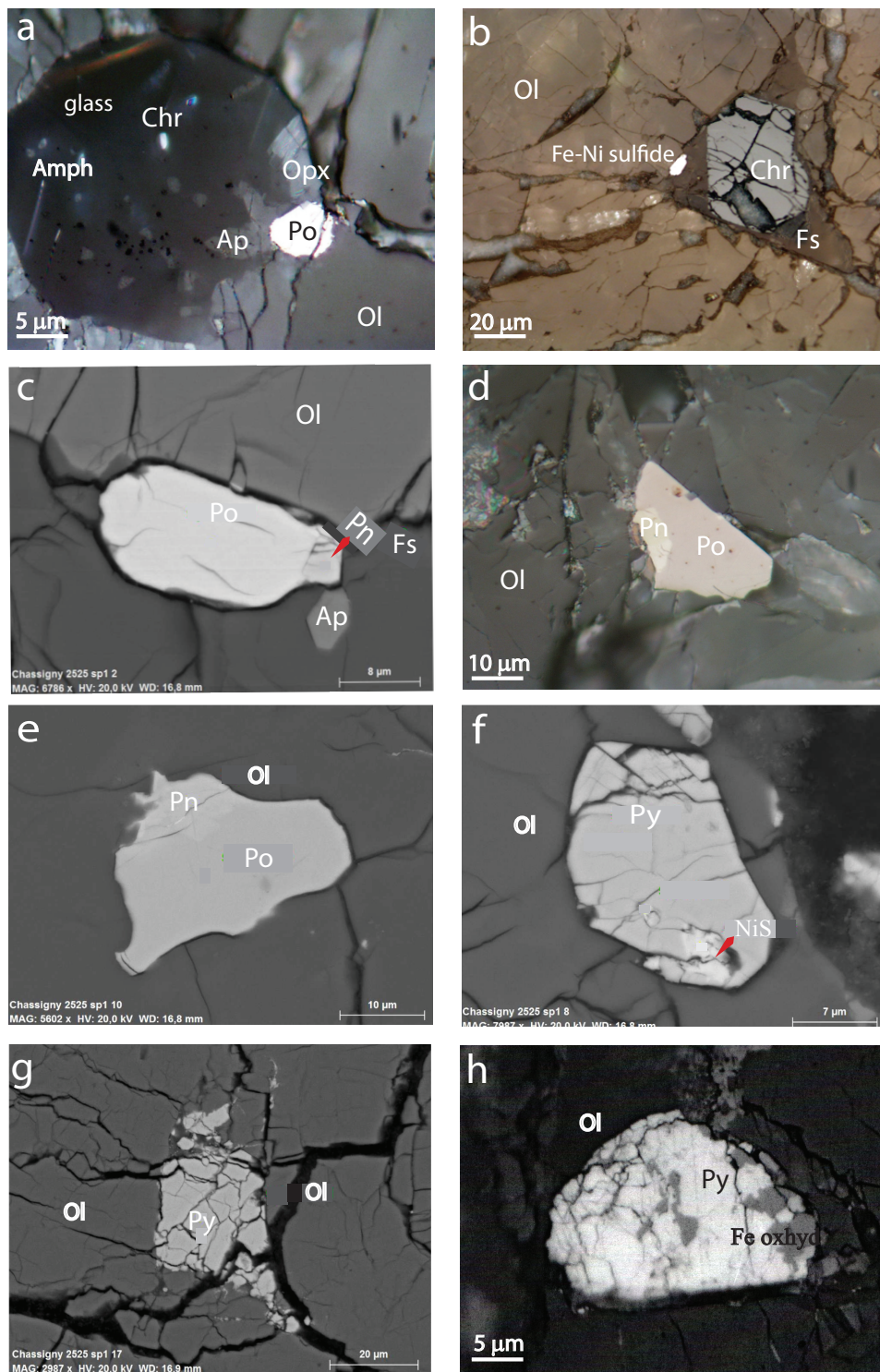


Fig. 2



Number of sulfide grains

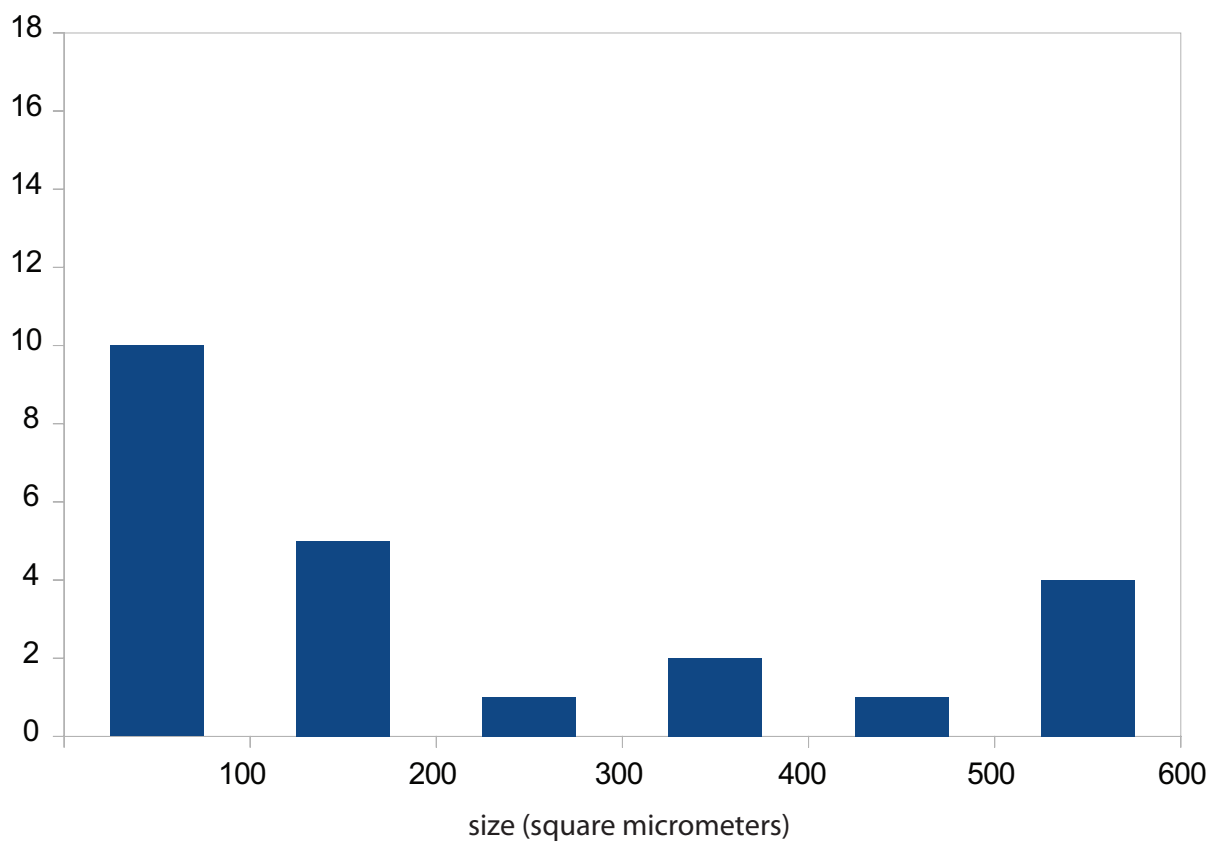


Fig. 3

number of  
analyses

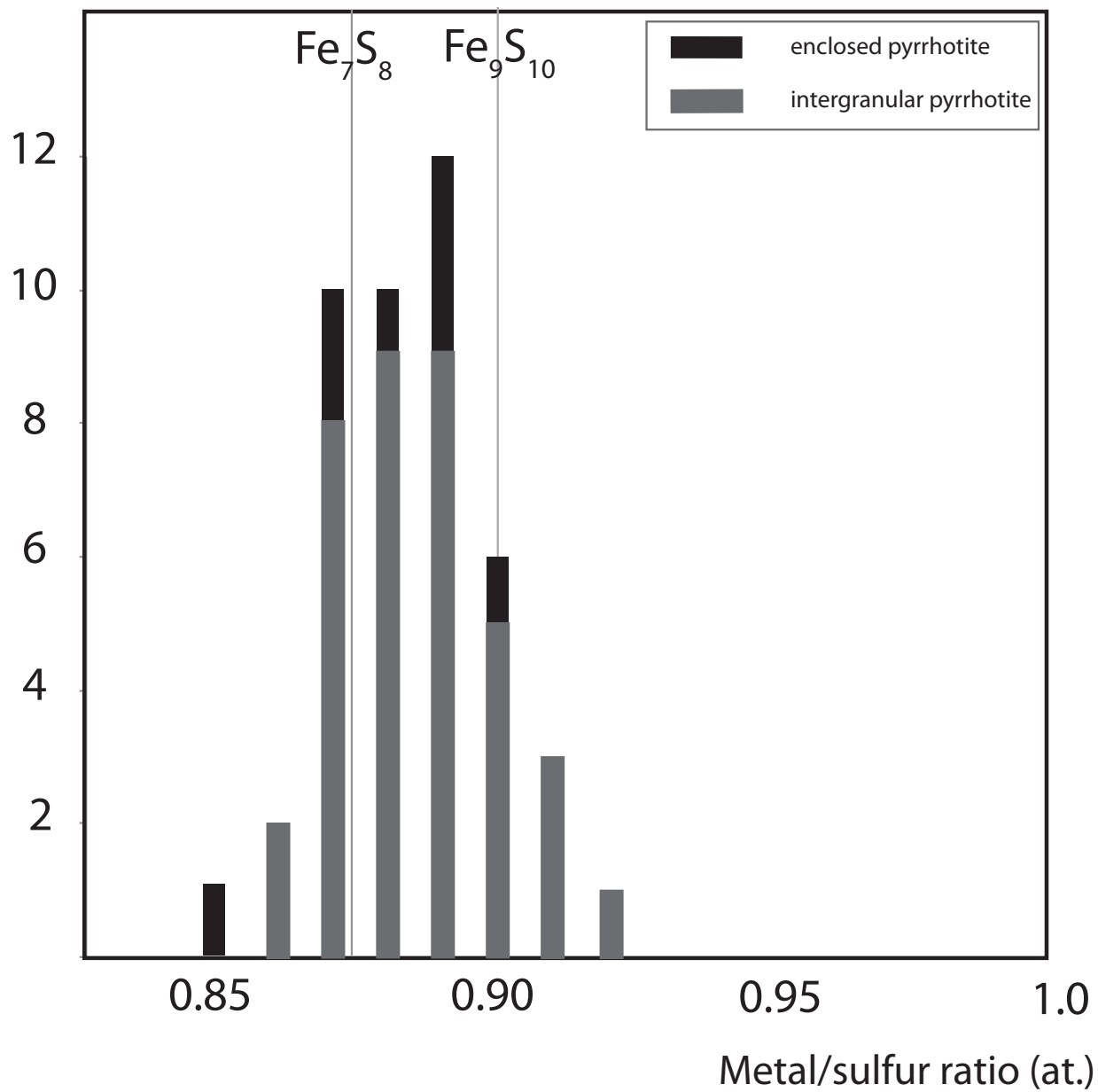


Fig. 4

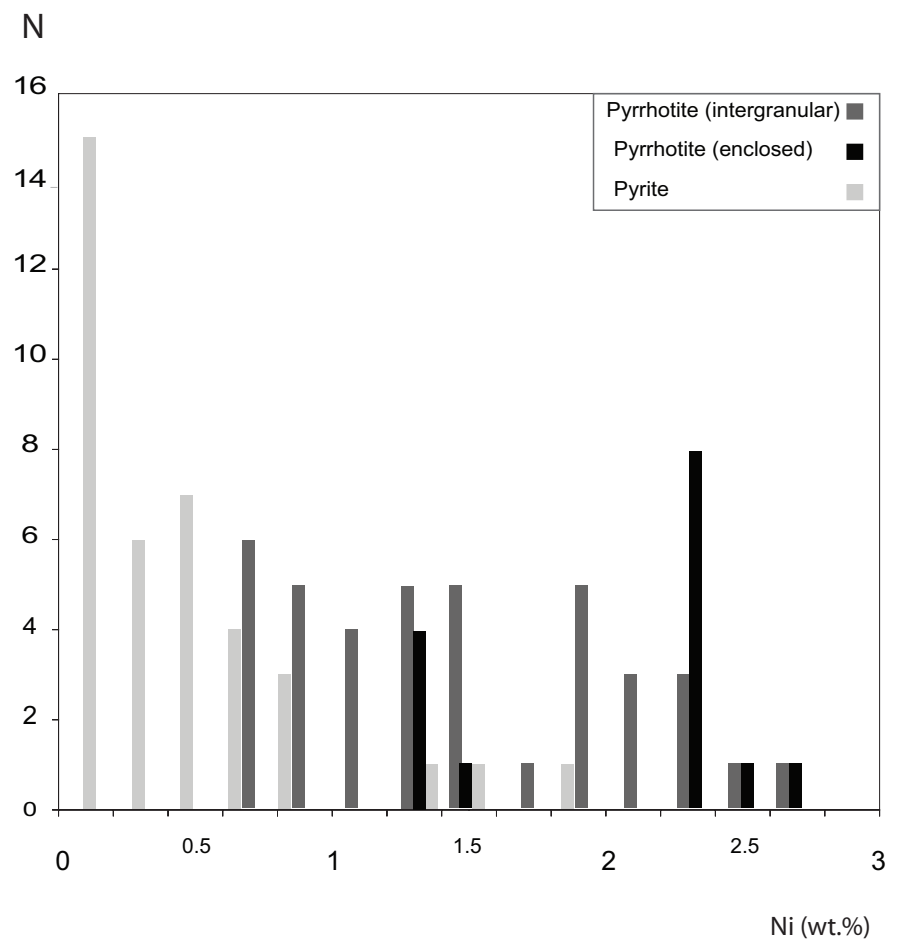


Fig. 5

metal/sulfur(at.)

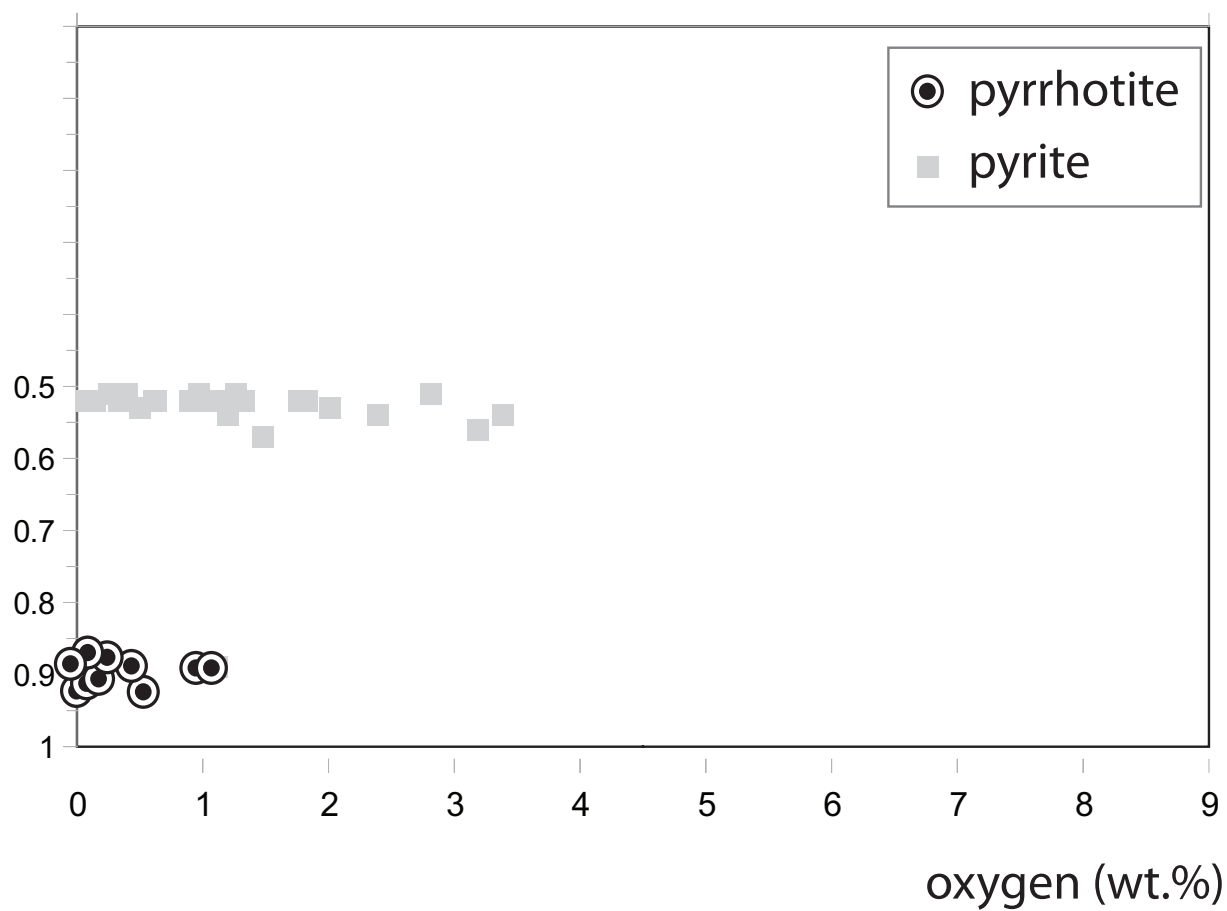


Fig. 6

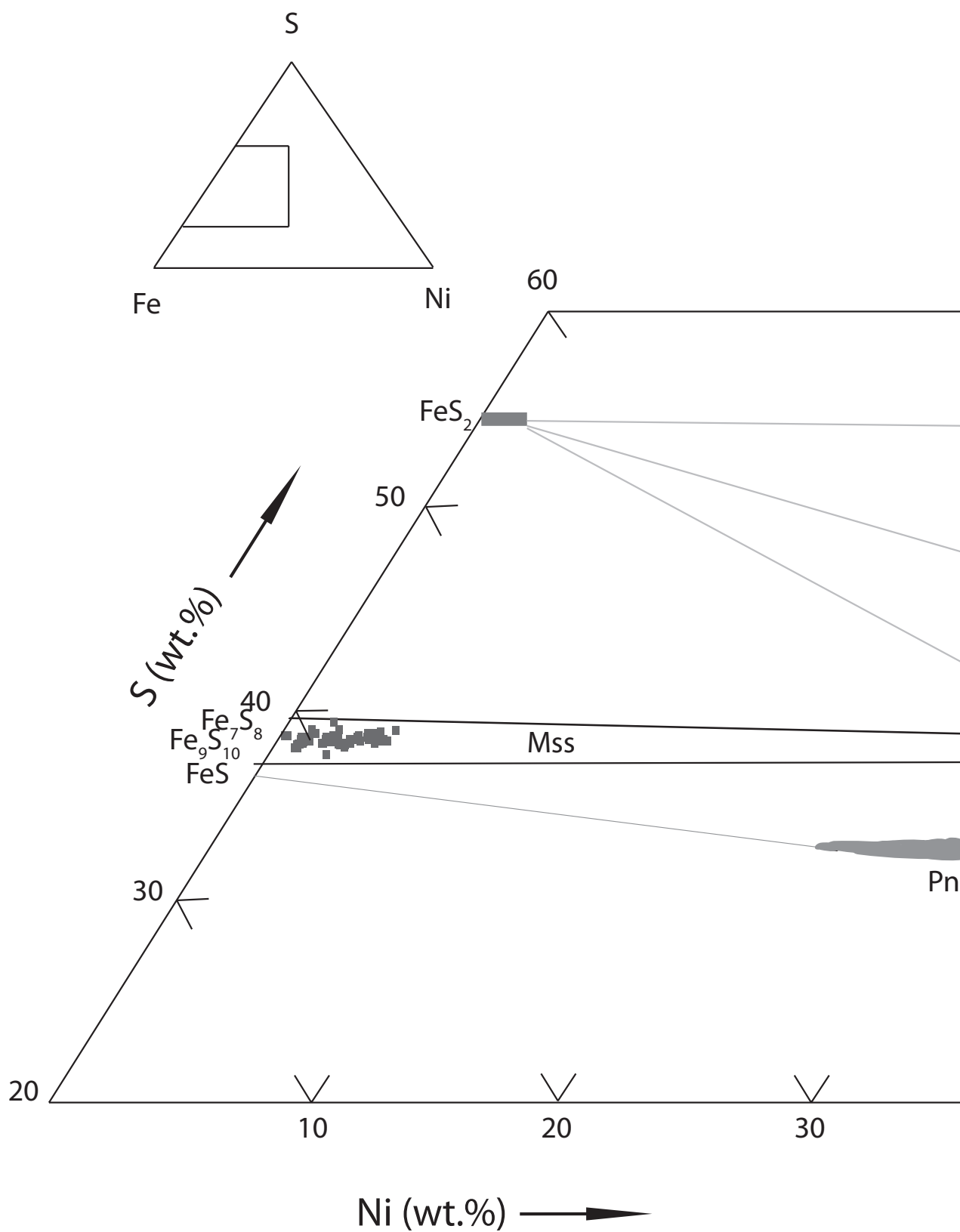


Fig. 7

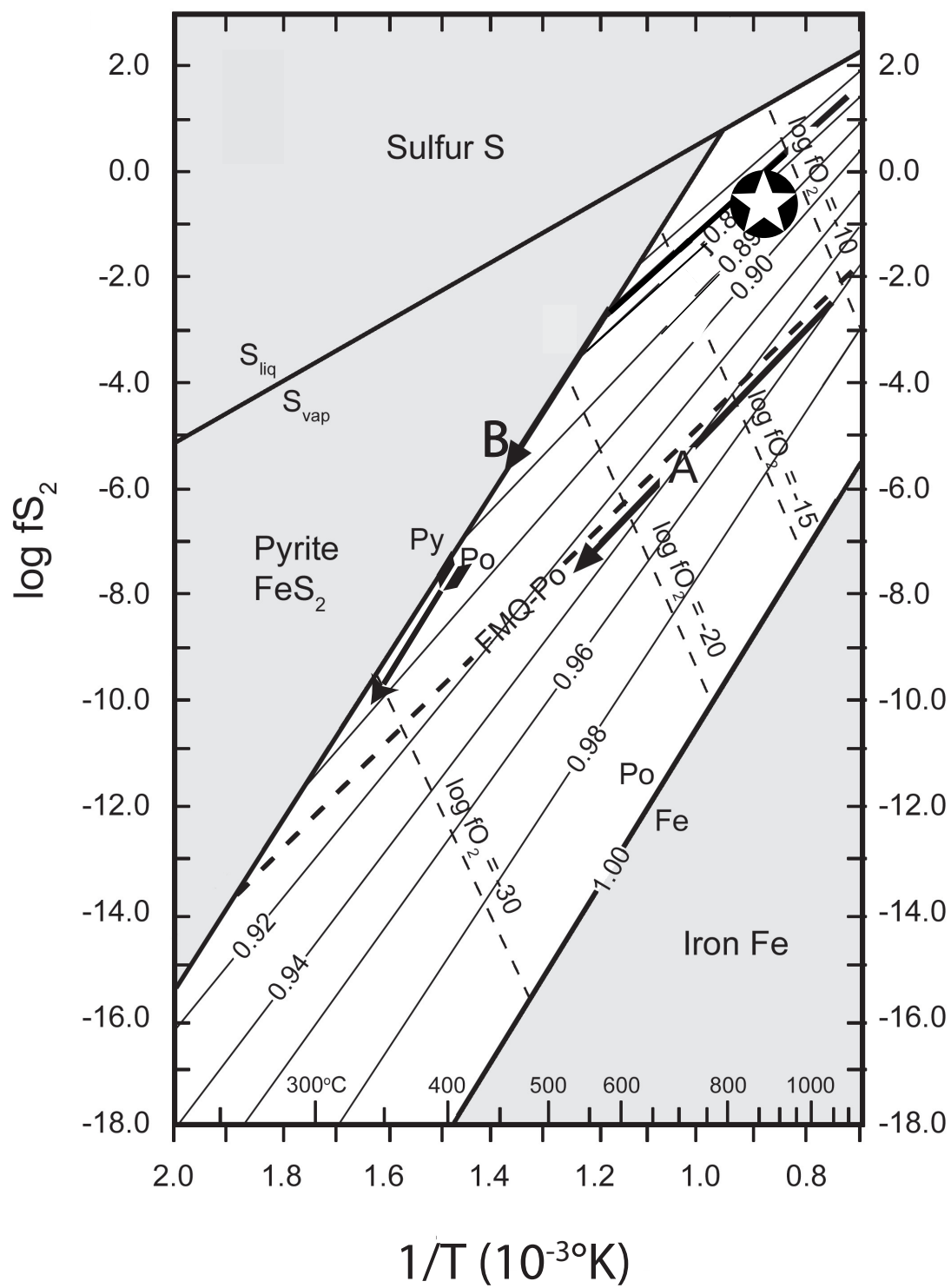


Fig. 8

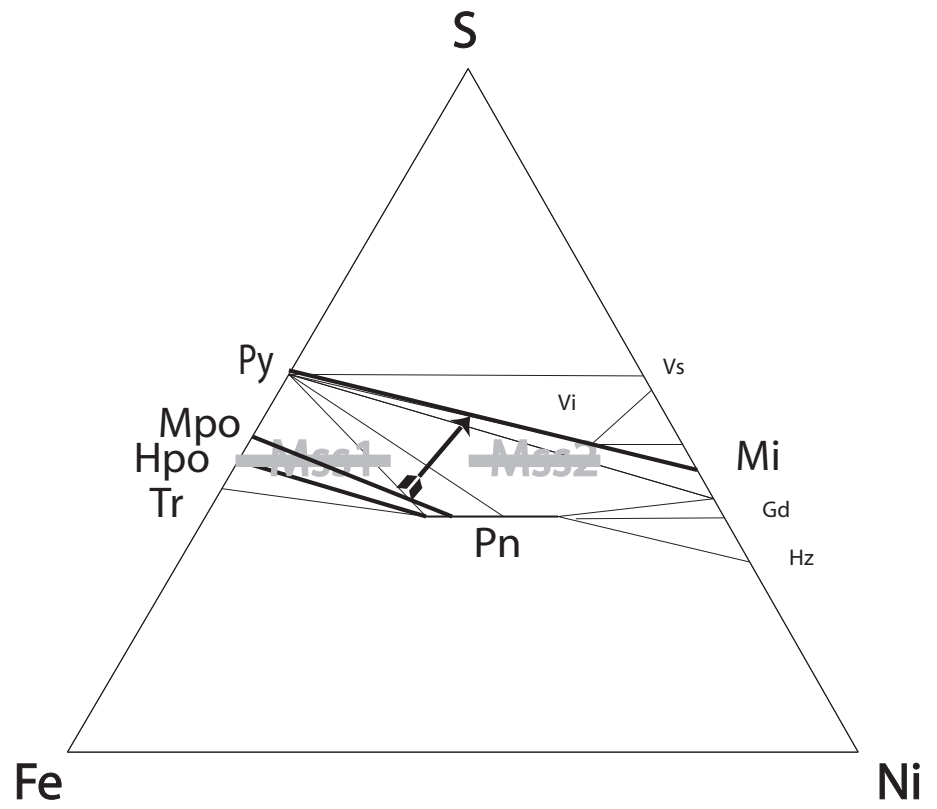


Fig. 9

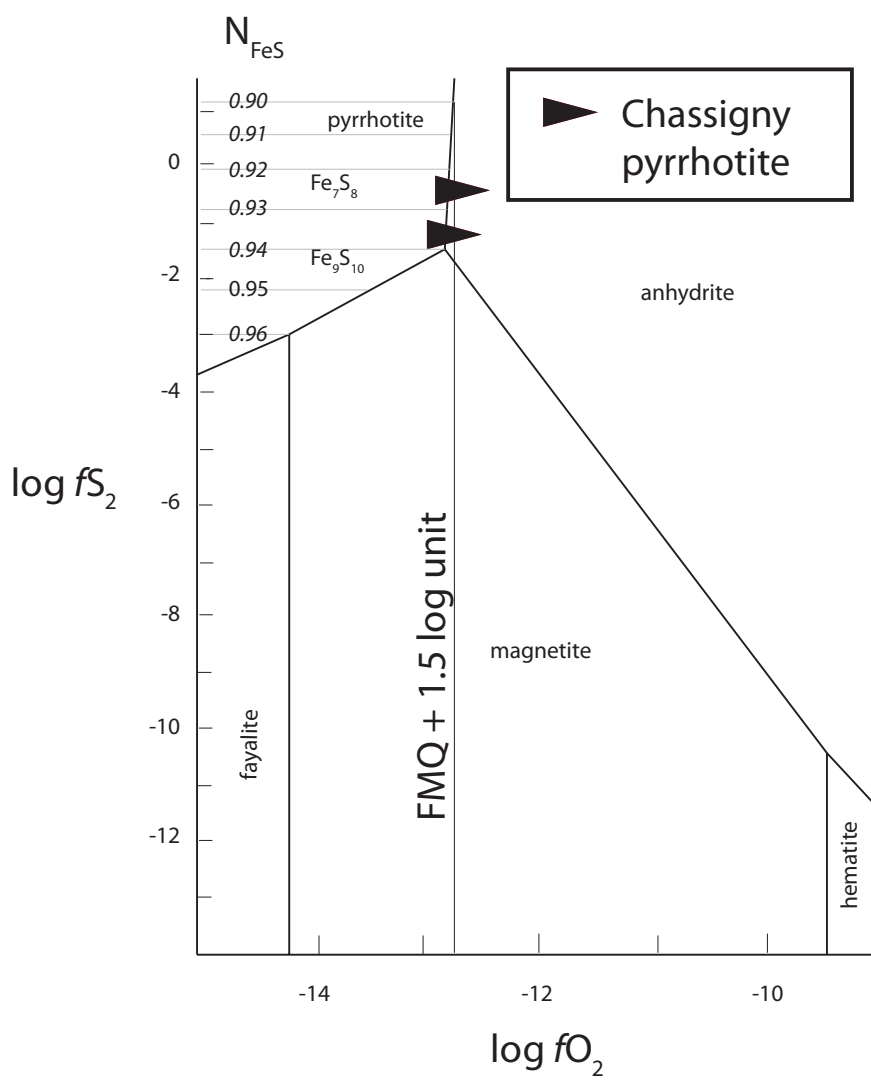


Fig.10



1099 **Table 1: Replicate analyses of Del Norte County troilite (Oregon, USA).**

1100

1101

1102

	(A) n = 5	(B) n = 36	(C) n = 10
wt%			
Fe	63.45 ± 0.05	63.43 ± 0.23	63.30 ± 0.30
Ni	-	-	-
Co	-	-	-
S	36.53 ± 0.03	36.56 ± 0.20	36.31 ± 0.20
total	99.98	99.99	99.61
M/S	0.999	0.998	1.000
	SEM	EMP	EMP

1114

1115 A : Gattaceca et al. (2013), B : Chevrier et al. (2011), C : Lorand et al. (2012). = : number of analyses. M/S :  
1116 metal/sulfur atomic ratio (M = Fe+Ni+Co). - : below detection limit (<0.05 wt%). SEM : scanning electron microscope  
1117 standardless procedure (Muséum National d'Histoire Naturelle, Paris); EMP : electron microprobe analysis  
1118 (Camparis).  
1119  
1120

**Table 2: Representative analyses of Fe-Ni sulfides from the Chassigny meteorite**

mineral	E Po	E Po	E Po	I Po	I Po	I Po	I Po
sulfide grain	Po5l13	Pod10	Pod10	Pod11	Pod11	Pod11	Po3h2
wt%							
Fe	59.08	56.15	58.0	57.73	57.27	58.24	58.51
Ni	1.5	2.77	2.54	2.52	2.62	2.50	2.37
Co	-	0.09	-	-	-	-	0.26
Cu	-	-	0.15	-	-	0.17	-
Mn	-	0.1	-	-	-	0.05	-
Zn	-	-	-	0.08	-	-	-
S	38.8	39.78	39.1	39.57	39.67	39.17	39.60
O	-	-	-	na	na	0.20	0.18
Total	99.38	98.89	97.79	99.90	99.56	100.34	100.92
M/S	0.89	0.87	0.88	0.88	0.88	0.89	0.88
mineral	I Po	I Po	I Po	I Po	I Po	I Po	*I Pn
sulfide grain	Po3h2	Po3h2	Pol1a16	Pol1a16	Pol1a16	Po7C10	Pol1a16
wt%							
Fe	58.02	58.14	58.8	60.45	59.57	60.65	32.88
Ni	2.35	2.14	1.75	1.4	2.0	1.03	32.94
Co	0.05	0.17	0.2	-	-	-	-
Cu	-	-	-	-	0.15	-	-
Mn	-	-	-	-	-	-	-
Zn	-	0.08	-	-	-	-	-
S	39.62	39.22	38.6	39.36	39.16	38.80	34.18
O	0.08	na	na	0.05	0.07	0.07	na
Total	100.12	99.75	99.41	101.26	100.95	100.55	100.0
M/S	0.88	0.875	0.90	0.88	0.89	0.91	1.08
mineral	I Py	I Py	I Py	I Py	I Py	I Py	*I Mi
sulfide grain	Pyb7	Py6e17					
wt%							

Fe	46.57	45.54	47.28	46.23	45.35	44.24	3.89
Ni	0.1	0.94	0.46	0.46	1.49	0.53	61.89
Co	-	-	-	-	-	0.11	-
Cu	0.05			-	0.06	0.05	-
Mn	-	-	-	-	-	-	-
Zn	-	-	-	0.18	0.49	0.90	-
S	53.23	53.91	52.37	51.7	48.65	48.07	34.5
O	na	na	0.63	1.19	3.19	4.26	na
Total	99.94	100.39	100.74	99.66	99.13	98.16	99.28
M/S	0.5	0.51	0.54	0.52	0.56	0.53	1.04

E Po : enclosed pyrrhotite ; I Po : intergranular pyrrhotite ; I Pn : intergranular pentlandite  
I Py : intergranular pyrite ; I Mi ; intergranular millerite ; EMP analyses except \*  
(EDS analyses) ; na : not analysed ; - : below detection limits (<0.05 wt%).

**Table 3: Electron microprobe analyses of Chassigny olivine**

	Mean (27 analyses)	Standard deviation
Wt%		
SiO <sub>2</sub>	37.40	0.26
TiO <sub>2</sub>	-	-
Al <sub>2</sub> O <sub>3</sub>	-	-
Cr <sub>2</sub> O <sub>3</sub>	-	-
FeO	28.1	0.26
MgO	34.13	0.38
MnO	0.50	0.15
NiO	0.06	0.03
CaO	0.13	0.03
Total	100.32	
Mg/Mg+Fe <sup>2+</sup> (at.)	0.68	

- : below detection limit (<0.05 wt %)

1134 **Table 4: Sulfide modal abundances and pyrrhotite compositions in Nakhrites and Chassignites.**

1135			
1136		sulfide modal content (vol.%)	pyrrhotite metal-to-sulfur
1137			ratio
1138			
1139	<b>Nakhrites</b>		
1140	NWA 817	0.02 ± 0.01 <sup>1</sup>	0.874 ± 0.01 <sup>1</sup>
1141	MIL nakhrites	0.042 <sup>2</sup>	0.89 <sup>2</sup> -0.90 <sup>3</sup>
1142	Yamato nakhrites		0.86-0.88 <sup>4</sup>
1143	Nakhla	0.04 ± 0.013 <sup>1</sup>	0.88 ± 0.02 <sup>1</sup>
1144			0.88 <sup>5</sup>
1145	Governador Valadares		0.87 <sup>5</sup>
1146		0.037 ± 0.012 <sup>1</sup>	0.88 ± 0.016 <sup>1</sup>
1147	Lafayette		0.87 <sup>5</sup>
1148	NWA 998	0.08 ± 0.03 <sup>1</sup>	0.881 <sup>1</sup>
1149		0.04 <sup>6</sup>	
1150	<b>Chassignites</b>		
1151	Chassigny	0.005 <sup>7</sup>	0.88 ± 0.01 <sup>7</sup>
1152	NWA 2737	0.01 ± 0.005 <sup>8</sup>	1.05 <sup>8</sup>
1153			

1154 1 : Chevrier et al (2011); 2 : Day et al. (2006), 3 : Frantz et al., (2014); 4 : Imae and Ikeda (2007); 5 : Greenwood et al.  
1155 (2000a); 6 : Irving and Treiman (2008); 7 : This study; 8 : Lorand et al. (2012).