EARLY AND LATE STAGE METALS AND SULFIDES IN DIOGENITES. L. C. Sideras, K. J. Domanik, and D. S. Lauretta, Lunar and Planetary Laboratory, University of Arizona, Tucson, AZ 85721-0092.

Introduction: Diogenites are typically highly brecciated orthopyroxenites that contain 84–100 vol.% orthopyroxene [1]. Common accessory minerals include olivine, chromite, Ca-pyroxene, plagioclase, silica, troilite and Fe-Ni metal [2]. Metal and sulfides are minor phases in diogenites with an average abundance of < 1 vol.% and 0–2 vol.% respectively [1,2]. However their presence is important, as they could provide information on T-fO_2-fS_2 conditions and the evolution of the diogenite parent magma during crystallization and/or later metamorphism.

We have examined the occurrence of Fe-Ni metal and sulfides in thin sections of several diogenites including, Johnstown, Manegaon, Roda, Shalka, Bilanga, and Tatahouine using optical microscopy and the electron microprobe. Here, we describe three features of metals and sulfides that are common in most of these diogenites. These are; i) the widespread occurrence of pentlandite associated with copper and copper sulfide minerals, ii) textural evidence that at least some of the metal and sulfide occurring interstitially between, and as inclusions within, orthopyroxene formed from an early immiscible sulfide-oxide liquid, iii) that this sulfide-oxide liquid subsequently fractionated into assemblages containing either Fe-Ni metal, troilite, and chromite or pentlandite, troilite, and copper-bearing sulfide.

Observations: Small amounts of pentlandite [$(FeNi)_9S_8$] occur in Johnstown, Manegaon, Roda, Bilanga, and Tatahouine as 5 to 30 µm patches at the edges of large interstitial troilite grains or in troilite inclusions in orthopyroxene. In all of these except Manegaon, the pentlandite is associated with Cu-bearing sulfide minerals or native copper. In some cases kamacite or tetrataenite is observed nearby but in other occurrences metal is absent.

Fe-rich pentlandite, [average $(Fe_{6.2},Ni_{2.7},Co_{0.1})S_8$] occurs in Johnstown, Manegaon, Roda, Bilanga, and Tatahouine. A second, more Ni-rich pentlandite occurs in Johnstown $(Fe_{4.7},Ni_{4.1},Co_{0.2})S_8$ and Roda $(Fe_{4.6},Ni_{3.3},Co_{1.0})S_8$. The Co-rich nature of the intermediate pentlandite in Roda appears to be consistent with the Co-rich interstitial Fe-Ni metal in this meteorite (15–32 wt% Co) [3].

Cu-bearing sulfides within or adjacent to pentlandite typically appear to have formed by exsolution from the pentlandite (Fig.1). These Cu-rich phases were primarily identified by X-ray mapping and back scattered electron images, and were typically too small to allow good quantitative analyses. However two

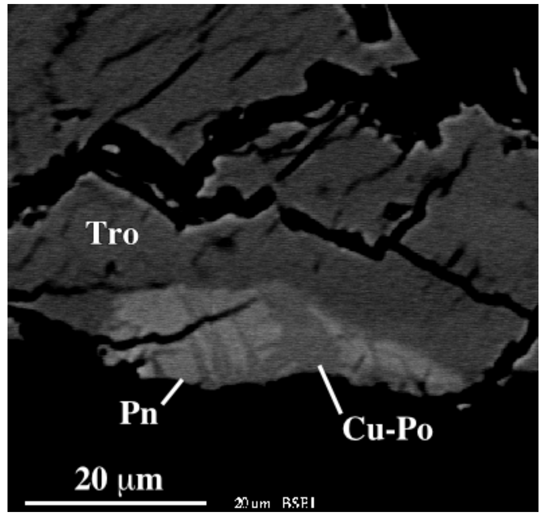

Fig 1: BSE image of pentlandite (Pn) and Cu-pyrrhotite (Cu-Po) in troilite (Tro) in Johnstown.

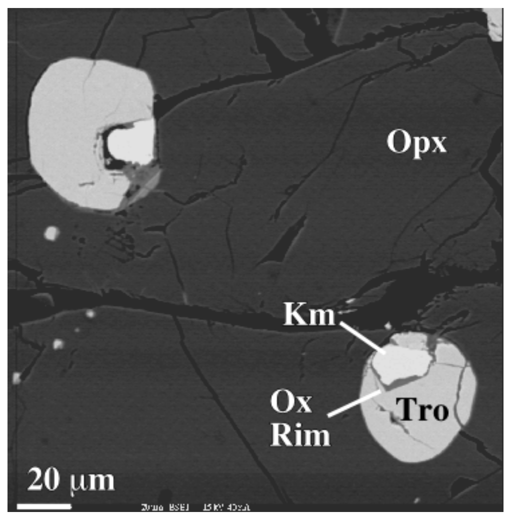

Fig 2: BSE image of zoned Kamacite (Km) – Troilite (Tro) inclusions in orthopyroxene (Opx) in Johnstown.

good analyses of Cu-bearing sulfide occurring with Fe-rich pentlandite in Johnstown suggest that these phases are Cu-bearing pyrrhotite $(Fe_{0.76},Cu_{0.17},Ni_{0.03},\_{0.04})S$. The Ni-rich pentlandite in Roda, contains variable amounts of Cu averaging $Fe_{4.3},Ni_{3.0},Co_{1.0},Cu_{0.7})S_8$. Native copper is associated with Fe-rich pentlandite in Bilanga [4].

Fe-Ni metal in these diogenites often occurs in a distinctive textural relationship with troilite and chromite. In these assemblages the metal is partially included in troilite (sometimes separated by an oxide layer) with chromite generally occurring at the outer edges of the troilite. These assemblages occur as large inclusions in orthopyroxene in Johnstown, Manegaon, and possibly Roda; and interstitially between orthopyroxene in Johnstown and Bilanga. The only diogenite in which this texture was not observed was Tatahouine, where the metal and troilite in inclusions are complexly intergrown.

In the inclusions, metal usually occurs at one edge with troilite making up the remainder (Fig. 2). The metal, (or the outline of the metal after formation of an oxide rim), is often euhedral-subhedral. Chromite occurs in the troilite, and sometimes forms euhedral-subhedral crystals. Diopside constitutes 0-50 vol.% of these inclusions. Ca-phosphate and/or silica also occur in some inclusions. The association of metal with troilite in these inclusions is common, inclusions containing only metal are very rare and inclusions containing metal and chromite without troilite were not observed. Interstitial metal occurring with chromite is always associated with troilite. Metal occurring by itself is more common in this setting.

Previously research has shown that the composition of metal in diogenites is variable both within and between samples [3,5]. Our observations confirm this variability, although, in some cases, patterns in diogenite metal composition can be discerned. In Johnstown, a few inclusions exhibit metal compositions ranging up to 7 wt%, Ni and 1.6 wt% Co, while most of the metal occurring intersitially and in inclusions has a composition of 96.5 wt% Fe, 3 wt% Ni, 0.5 wt% Co. Although rare, a significant compositional variation can also be observed in Johnstown among metal inclusions within single orthopyroxene crystals. In Manegaon, the compositions of interstitial metal, (average 2.3wt% Ni), appears to be systematically lower in Ni from the metal occurring in inclusions, (average 3.9 wt% Ni). The Co contents are roughly the same between the two types of occurrences.

Conclusions: In the Fe-Ni-S system pentlandite has a maximum thermal stability of 610 ^{o}C [6]. The stability of pentlandite in the Fe-Ni-Co-S system has been studied by [7] and we rely on these studies to interpret the history of these assemblages. Pentlandite has a limited range of Fe/Ni ratios that are highly temperature dependent. The majority of diogenite pentlandite is Fe-rich. This composition is stable over a very narrow temperature range of 400 to 550 ^{o}C. The Co-rich pentlandite in Roda is stable from 300 to 550 ^{o}C, while the Ni-rich pentlandite in Johnstown is in equilibrium with endmember troilite at 550 ^{o}C. The Fe/Ni ratio in pentlandite is sensitive to sulfur fugacity (fS_2) [7]. The Fe-rich pentlandite is consistent with formation at fS_2 of 10^{-13} bars. In contrast the Ni-rich pentlandite equilibrated under a much higher fS_2 ($\sim 10^{-10}$ bars). We conclude that the pentlandite and troilite formed by exsolution from monosulfide solid solution (mss) either late in the crystallization of the magma or during subsequent metamorphism. The difference in Fe content of the pentlandite is likely the result of variable fS_2 within each immiscible droplet.

Previous workers [3,8] suggest that inclusions of metal and troilite in diogenite orthopyroxenes formed by exsolution of metal followed by sulfurization of metal to troilite. However, our observations suggest that the larger metal inclusions in orthopyroxene represent trapped immiscible sulfide melt.

The euhedral to subhedral metal, which occurs at one end of the inclusions with troilite in the center, is not what would be expected if exsolution/sulfurization had produced these inclusions. If this were the process, we would expect to see that the orthopyroxene surrounding the inclusions reflect the initial shape of the metal, with later sulfurization producing a, circular rim of troilite on the outer edge of the metal grain. Instead the texture observed suggests that metal crystallized first, leaving a residual sulfur-rich melt.

The presence of Ca-phosphate in these inclusions is particularly difficult to explain by exsolution. We suggest rather that these inclusions represent immiscible sulfide liquid along with varying amounts of silicate melt that were trapped during orthopyrene crystal growth. Metal, troilite, and possibly chromite may have formed by fractional crystallization of the sulfide oxide liquid during cooling. Diopside and Ca-phosphate, appear to have formed from the trapped silicate liquid after the orthopyroxene component of the melt had crystallized out and plated the walls of the inclusion. That we see a similar texture of metal and troilite occurring interstitially between orthpyrexene crystals suggests that these may also have formed from an immiscible liquid.

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