
Excesses of $^{107}$Ag ($^{107}$Ag*) exist in iron meteorites of different classes (IVA, B, IIIAB, anomalous). This $^{107}$Ag* is correlated with Pd and is inferred to be the daughter of extinct $^{107}$Pd ($T=9.4\times10^{6}$y) (1). Intensive efforts have been made to establish internal isochrons on iron meteorites using coexisting phases. While a general correlation has been found, there are discrepancies in some cases (Santa Clara and Gibeon). The study of $^{107}$Pd-$^{107}$Ag systematics involves not just the isotopic chemistry but also the cooling history and later stage events. Gibeon is a meteorite that has undergone shock melting and later heating and forging. The evolution and modification of the phases are thus critical to understanding the silver isotopic evolution. For this reason we have undertaken a petrographic study of the sulfide inclusions and the metal host in the specific samples that have been used for isotopic analyses.

Special attention was given to the relationships between the metal phase and the sulfide nodules at the metal-sulfide interface. Three samples from Gibeon (ASU Lion River, USNM #3187, USNM #679) and one from Santa Clara (ASU #1060.2.5.1) were investigated. Two important diagnostic features can be used to recognize heating effects by humans from heating induced by an impact event: 1) Thermal treatment of an iron meteorite after terrestrial weathering will modify the textures of sulfides, metals and iron oxides resulting in an intimate intergrowth of magnetite + troilite and metal + magnetite. 2) Heating effects induced by an impact event will usually be confined to the troilite-metal interface resulting from partial melting and eutectic intergrowth of FeS and FeNi. These latter textures do not involve magnetite. An important question is to ascertain how each of these heating events would influence the chemistry of Pd and Ag and whether they would result in a late stage separation of these elements between the sulfide and the metal phase.

Results: The Lion River sample consists of troilite and minor pentlandite in a texture of polygonal equant grains of 10μm. The sample closest to the metal, magnetite was found in intimate intergrowth with troilite and pentlandite. Spherical cavities of ~1 μm are commonly found in the troilite throughout the inclusion that appear to be the walls of bubbles. The above texture appears to be novel. Textural relationships in troilite nodules in Gibeon USNM #3187 and USNM #679 are distinctive from the observed features in Lion River. The inclusions are contained in a metal phase with a well developed Widmannstätten pattern. The texture of the sulfides consists of a fine-grained intergrowth of troilite with common daubreelite in the interior. The boundaries of the inclusions with metal are comprised of patches of troilite + daubreelite + kamacite + taenite. The proportions of metal and FeS vary widely to the metal-rich area occurring in globular patches. In these regions daubreellite may occur as rounded blebs surrounded by troilite-free kamacite rims. Large exsolution lamellae of daubreellite were found to show different degrees of breakdown to form a Cr-bearing metal phase. This follows the idealized reaction: FeCr$_2$S$_4$ + FeCr$_2$ + 2S$_2$ (gas) [1]. The newly formed Cr-bearing alloy can be recognized from kamacite and taenite through its faint greenish tinge. EMP analyses of the new alloy associated with the breakdown reaction show 0.10-2.28%Cr, 2.13-3.81%Ni, 95.4-98.1%Fe, and 0.35-1.70%Co. This is the first report of such a reaction in meteorites. Some taenite grains adjacent to the breakdown assemblage also contain considerable Cr (0.53-1.31%). Santa Clara #1060.2.5.1 consists of an elongated and offset troilite nodule embedded in the FeNi metal ground mass. The core of the
sulfide inclusion contains a fine-grained intergrowth of polygonal grains of troilite + magnetite + metal. At the sulfide-metal groundmass interface patches of a eutectic intergrowth of metal + troilite + magnetite were encountered. The Widmannstätten pattern of the metal groundmass is destroyed and instead a fine-grained texture of wormy intergrowth of kamacite + taenite + schreibersite was found.

Thus it appears that both of the Gibeon samples analyzed for Pd and Ag (1) underwent later heating episodes. The Lion River sample was heated to below the Fe-FeS eutectic possibly to below the breakdown temperature of pentlandite - 610°C (2). The presence of magnetite and the bubbles indicates that some heating took place after oxidation. This last event is presumably post impact oxidation weathering and is most reasonably associated with human treatment. The bubbles may plausibly be associated with the formation of SO₂ gas as a result of heating the sulfides in an oxidizing atmosphere (air). It is also possible that troilite recrystallization is a result of a shock deformation followed by heating. The breakdown reactions and the eutectic features in the other Gibeon samples (USNM #3187 and USNM #679) appear to be a result of heating to above the FeS-FeNi eutectic and is attributed to shock melting upon impact. The absence of magnetite in the eutectic intergrowth would indicate that this mass of Gibeon was not heated after oxidation weathering. In addition studies of Santa Clara (#1060:2.5:1) show textures that indicate severe thermal treatment after weathering as evidenced from the magnetite-FeS-metal intergrowth in the troilite nodule, the magnetite-FeS-metal eutectic at the nodule rim, and the destruction of Widmannstätten pattern in the metal ground mass. These observations are in agreement with reports by V. Buchwald (3).

Discussion: As a result of the heating events indicated above, fractionation of Pd and Ag could have taken place. If the temperature is high enough (at the troilite-metal interface), Ag vapors could migrate from the metal and react with FeS and deposit on the sulfide according to 2Ag+FeS → Ag₂S+Fe [2]. On the other hand S₂ vapors released from the breakdown of daubreelite will definitely scavenge for Ag from the surrounding metal and deposit it along with FeS on the surface of troilite. Accordingly, in a late heating event (extraterrestrial or terrestrial) sulfide nodules are perfect sinks for mobile Ag in the metal phase. Since evidence for severe heating and melting and for sulfur release was presented, some of the 1⁰⁷Ag* in the sulfide nodules could be explained as a result of reactions 1 and 2 due to migration of Ag from the metal phase to the troilite nodules. This would separate 1⁰⁷Ag* correlated with Pd in the metal phase and provide very radiogenic Ag to the sulfide. The proportions of material involved are ~1:1 by volume (1). This could in principle generate multiple sites in the troilite nodules with distinctive Pd-Ag characteristics and possibly different chemical behavior. A consequence of this model is that regions of FeNi metal poor in 1⁰⁷Ag* should be found near sulfide nodules.

We cannot provide a detailed explanation which could account for the relatively large volume of metal (~2cc) required to provide the 1⁰⁷Ag*. Nevertheless, it is certain that late metamorphism by shock heating and human intervention may play a significant role in disturbing the Pd-Ag system in these meteorites.