Letters

Discovery of Hg–Cu-bearing metal-sulfide assemblages in a primitive H-3 chondrite: Towards a new insight in early solar system processes

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A B S T R A C T
We report here the discovery of a novel meteoritic paragenesis consisting of sub-micrometric HgS, Cu sulfides, and Hg metal, associated with polycrystalline fine-grained native Cu in opaque mineral aggregates heterogeneously distributed in the matrix of the H-3 Tieschitz unequilibrated ordinary chondrite (UOC).

The systematic association of Hg with Cu in Tieschitz chondrite provides a unique opportunity to place robust constraints on the origin of these assemblages either by condensation and sulfidation in a local nebular reservoir of non-solar composition, followed by gentle and fast accretion, or by sublimation of Hg from the hot interior of the asteroid and recondensation in its cold outer regions. The sulfide phase relations support low temperature conditions (< 300 °C), implying that subsequent to accretion indigenous hydrothermal processing, oxidation/sulfidation, transportation, or shock-induced thermal processing of the assemblage on the parent body earlier proposed are very unlikely and unrealistic. Origin of HgS by sublimation of Hg from the hotter asteroid interior and precipitation as cinnabar in the colder surface regions is discrepant with our findings and can be ruled out because cinnabar occurs only in Tieschitz matrix in alternating rhythmic intergrowth with Cu-sulfide. The sublimation scenario calls for co-evaporation of both the highly volatile Hg as HgS and Hg metal and the moderately volatile Cu both as Cu metal, or their sulfides and deposition as sulfides in alternating episodes. Our findings provide further ample evidence refuting the repeated claim of formation of native copper in chondritic metal by shock-induced impact melting. Cold accretion is the only reasonable possibility to preserve the delicate accretionary intergrowth textures, the polycrystallinity of FeNi-metal, native Cu, Hg-Cu-sulfides and native Hg globules and the high Hg concentration retained in this meteorite. Our findings strongly suggest that Tieschitz resided near the cold surface of the parent asteroid.

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1. Introduction

Mercury (Hg) is the most volatile non-gaseous element. The Hg solar abundance (Lodders, 2003; Lodders et al., 2009) is not precisely known. Its nebular condensation into specific mineral species is still debated because no Hg-bearing minerals have been reported from any meteorite so far. Hg occurs in trace amounts and its distribution in chondrites is inexplicably variable in bulk primitive meteorites. Our present findings are in clear disagreement with Wasson and Kallelmeyn (1988) predictions that Hg should severely be depleted in chondrites because elemental abundances correlate with the condensation temperature. Reed and Jovanovic (1969), and Reed (2000) reported concentrations of bulk Hg in chondritic meteorites and exceptionally high Hg abundances in Tieschitz (7200 ng/g), respectively. Rossman et al. (1980) reported high concentrations of another volatile element, Cd and correlated 116Cd/106Cd isotopic anomalies in Tieschitz, however without localizing the Cd carrier in chondrules and matrix. Rossman et al. (1980) showed that two components may have resulted from heterogeneous mixing of the precursor material or from variable conditions in the nebula. Wombacher et al. (2003) controversially interpreted these results, also without searching for or identifying any Cd-bearing species in any chondrite they investigated. Stepwise heating experiments of chondrites (Jovanovic and Reed, 1980, 1985) and Hg abundance measurements in chondrites (Lauretta et al., 2001) predicted sulfide as host phase for Hg (Palme et al., 1985). Ganapathy and Larimer (1980) also reported unusual volatile-rich fragment in Abee EH chondrite but no Hg-bearing phase was recognized. Computational models predicted that
Hg condenses at very low temperatures (about 160 K) (Larimer, 1967) and it was speculated that Hg is sited as a trace element in troilite (FeS) at 252 K (Lodders, 2003). Recently, Devouard et al. (1998) and Lauretta et al. (1999) claimed that pure HgS is unstable in a vapor of solar composition. Elemental redistribution after condensation onto the surface of the parent body was first proposed by Larimer and Anders (1967). Redistribution of volatile elements in the Tieschitz parent body was proposed by Hutchison et al. (1998) to explain various compositions of chondrule mesostases, and to explore the relationship to its unique matrix. Dreibus and Wänke (1980) and Wombacher et al. (2003) proposed that volatile elements could be transported from the internal and allegedly hotter layers of the meteorite parent body, vaporized into the gas phase and transported within the parent body (Schaeffer and Fegley, 2010).

The Tieschitz meteorite fell in 1878 in the Czech Republic. It is one of the most primitive unequilibrated ordinary chondrites (UOCs), a conglomerate accreted from various nebular materials that probably formed in different solar environments, including early planetary debris and diverse presolar species (Nittler et al., 1994). This meteorite is chemically unique because of its anomalous Fe-content intermediate between H and L chondrite groups (Sears, 1980; Sears et al., 1980). It also has an unusual textural signature expressed in the presence of what was primarily called black and white matrices on the basis of their individual appearance in transmitted light microscopy (Christophe Michel-Lévy, 1976). This was interpreted to have resulted from leaching of chondrules in order to explain the high porosity of this chondrite (Kurat, 1989). Engler et al. (2003) proposed from the trace element patterns that chondrules in Tieschitz were direct nebular condensates. They suggested that the chondrule formation was followed by metasomatic episodes. In contrast, Hutchison et al. (1998), Alexander et al. (1989) suggested that some elemental redistribution probably took place in some chondrules in which blocky mesostasis are the alteration products similar to the thin white matrix found around them (Christophe Michel-Lévy, 1976).

According to Hutchison et al. (1998) this redistribution could have occurred during accretion.

The cooling rates estimated by Willis and Goldstein (1981) for Tieschitz (2 K/Myr) are twice as fast as those determined by Wood (1967), and are still extremely low, thus contradicting the conclusions drawn by Bevan and Axon (1981). The latter authors interpreted the polycrystalline gamma taenite in Tieschitz matrix, as relic of primary structures formed by rapid cooling non-equilibrium solidification of Fe–Ni–S melts during chondrule formation. Bevan and Axon (1980) introduced controversial interpretation to explain the polycrystallinity of taenite in Tieschitz, the heterogeneous composition of metal grains or misshapen Tieschitz chondrules. They claimed that the grain boundaries could not have been established either by slow sub-solidus cooling of homogeneous gamma taenite or by deformation and annealing, during peak metamorphism in the parent body. In contrast, Scott and Rajan (1981a, 1981b) proposed that metamorphic temperatures were reached during and not after accretion because they did not observe any annealing of small individual metal grains and their coalescence to produce larger grains. This scenario was supported by Hutchison (1996). In short, previous reports published since 1976 on the mineralogy, accretionary, and thermal histories of Tieschitz chondrules and matrix are highly controversial and never reported the presence of any species enriched in volatile (Hg, Cd) or moderately volatile (Cu) elements.

A comparative study of opaque mineral assemblages in UOC that contain native Cu (a moderately volatile element) was initiated and included Tieschitz to clarify the long-debated origin of native Cu in chondritic metal and to constrain the thermal history of these chondrites (Caillet Komorowski et al., 2009). The Tieschitz meteorite is also an unshocked H-3 chondrite. It lacks features characteristic of shocked assemblages e.g. shock-induced high-pressure phases or shock-induced none-venucious melts (Miyahara et al., 2010) but polycrystalline taenite. These features qualify Tieschitz as a perfect research target to address the issue of the origin of native Cu in chondrites.

Rubin (1994) proposed that metallic Cu encountered in association with metallic FeNi and troilite in chondritic meteorites formed by shock melting without outlining any details of his proposed shock-melting mechanism.

We conducted detailed investigations of the metal-sulfide assemblages in chondrules and matrix in Tieschitz also in view of the reported high Cd concentration (Rosman et al., 1980), to determine their individual metal-sulfide inventories and to evaluate their genetic relevance to the formational history of this unique H-3 chondrite. In this article, we report the first finding of the highly volatile metallic mercury, cinnabar (HgS), and Cu-sulfide associated with polycrystalline native Cu in opaque assemblages in the matrix of Tieschitz. We address the mechanisms of formation of this novel paragenesis, which is of prime importance to decipher the record of the solar nebula/parent body processes. We will demonstrate with our novel findings that neither hot accretion nor high temperature metamorphism nor shock on the parent body is compatible with the presence of highly volatile elements in phases such as metallic Hg and other Cu- and Hg-bearing sulfides. We will convincingly show that the high Hg-content in the Tieschitz matrix could not have resulted from sublimation of Hg from the hot interior of the Tieschitz asteroid and re-condensation in the outer colder regions of the asteroid.

2. Experimental methods

We conducted careful field emission secondary electron microscopy FESEM (Zeiss Supra 55VP) observations on several Tieschitz thin and thick sections at an accelerating voltage between 7 and 15 kV without coating the samples with carbon to avoid any contamination and we used low vacuum (25 Pa) and a cooled stage at the SEM to preserve the Hg metal in the samples and to prevent damage of the delicate multi-sulfide intergrowth textures. For the electron microprobe ( Cameca SX100 in Paris) measurements, we used a beam current of 4 nA and an accelerating voltage of 10 kV. Standards used were pure native Cu, FeS, pyrite, Cu-oxide and HgS. We also used a beam current up to 200 nA and an accelerating voltage of 30 kV on a few selected sites for the analyses of minor elements in FeNi metal and FeS troilite.

Some foils to be studied by transmission electron microscopy (TEM) were carefully cut and extracted from one composite HgS–Hg–Cu–CuS grain by a Focused Ion Beam (FIB) system, JEOL JEM-9320FIB in Sendai, Japan. A gallium ion beam was accelerated to 30 kV during the sputtering of the foils. A dedicated optical microscope with a micromanipulator was employed to recover the targeted cut foils. The extracted TEM foils (120–130 nm in thickness) were adhered on a titanium grid. The targeted cut foils. The extracted TEM foils (120–130 nm in thickness) were adhered on a titanium grid. Details of the FIB procedure are recently described in Miyahara et al. (2008). A JEOL JEM-2010 TEM operating at 200 kV was employed for conventional TEM (CTEM) and selected area electron diffraction (SAED). We also used a scanning TEM (STEM), JEOL JEM-3000F field emission TEM operating at 300 kV equipped with a JEOL energy dispersive X-ray spectroscopy (EDS) detector system. The chemical compositions of individual minerals were obtained by EDS under STEM mode. The compositions were corrected using experimentally determined k-factors (Fe2S (Fei et al., 2000) and covellite) for Fe, Cu and S and a theoretical k-factor for Hg.
Electron backscatter diffraction (EBSD) analyses at a submicrometer scale were performed using the method reported by Ma and Rossman (2009) with an HKL EBSD system on a ZEISS 1550VP SEM, operated at 20 kV and 6 nA in focused beam mode with a 70° titled stage and in a variable pressure mode (25 Pa). EBSD analyses were obtained at California Institute of Technology, USA.

3. Results

3.1. Petrography

We discovered ubiquitous, intimate intergrowth of mercury (Hg) sulfide with Cu sulfide crystals associated with native Cu (Caillet Komorowski et al., 2009). This micrometer-sized mineral assemblage is heterogeneously distributed throughout the matrix of the meteorite. One association was observed in one section while four others were encountered in another one. The assembly typically exhibits a fluffy accretionary texture. Cu- and Hg-sulfides occur mostly as alternating layers of cauliflower-shaped intergrowths objects (Fig. 1a). In this case, we observed delicate rhythmic layering of HgS platelets alternating with Cu-sulfide layers. The two sulfides are also encountered interstitially intergrown within polycrystalline troilite (FeS) (Fig. 1b). Few form cube-shaped grains enclosed in Cu-sulfide (Fig. 1c). They are not found intergrown with silicates but juxtaposed (Fig. 1d) and seldom occur in fractures in pyroxene crystals. An HgS–Cu-sulfide grain was associated with the phosphate merrillite. Another grain was found injected in cracks at the outer margin of a porous silicate opaque-rich chondrule.

We also report the first natural occurrence of native Hg in a meteorite. Nanometer-sized spherules of native Hg were encountered in two distinct associations. The first consists of native Hg globules enclosed in spongy metallic Cu. X-Ray Hg distribution maps reveal that Hg globules and/or nano-grains of HgS are intimately disseminated within polycrystalline and spongy native Cu (Fig. 2a and b). In the second association, tiny, perfectly spherical native Hg is enclosed within cinnabar (HgS) and Cu-sulfides (Fig. 3a–c).

The metallic Hg, Hg- and Cu-sulfides were found in or in close proximity to large opaque assemblages (Fig. 4a) in the fine-grained matrix of Tieschitz. The assemblages are always composed of native Cu grains, together with troilite (FeS), kamacite and taenite exhibiting sharp boundaries with no sulfidation or oxidation products such as magnetite (Fig. 4b).

The native Cu and the FeNi metal are mostly polycrystalline angular mineral aggregates (Fig. 4b). Few exceptions exist: one native Cu area (up to 30 μm in diameter) is encountered in a compact large accretionary layer around a silicate clast (Fig. 5a and b). The second exception is native Cu present in a troilite-metal...
globule within a single porphyritic silicate chondrule fragment (Fig. 6a and b). Metallic Hg nano-globules were neither encountered in this assemblage nor in any chondrule. Metal in these two assemblages is Ni-rich taenite, tetrataenite, and very small Ni-poor kamacite (< 1 wt% Ni) grains only at the contact with native Cu.

Occasionally Cu-sulfide is present without HgS between lobate native Cu and FeS in the matrix (Figs. 7a and b and 8). Both Cu metal and taenite are spongy (Fig. 8). Cu-sulfide was not encountered between native Cu and taenite. No Fe–Cu-bearing sulfides such as bornite, cubanite (CuFe2S3) or chalcopyrite (CuFeS2) were found in any section studied.

Using high contrast BSE–SEM imaging we observed spongy silicates, pores in metals and troilite. The fluffy Cu-sulfide texture underscores the very delicate and fragile nature of the Cu-rich phases that are unstable under high beam current. Standard conditions of analyses were too destructive for these delicate and electron beam unstable assemblages. In a few cases we observed evaporation of metallic mercury beads under focussed electron beam bombardment at the SEM (Fig. 3a–c). The Cu-sulfide was damaged as well. Consequently, we used low vacuum and a cooled stage to prevent further mineral damage.

The Hg–Cu constituents of the assemblages (20–50 nm) are finer-grained than silicate dark matrix in Tieschitz reported by Töpel-Schadt and Müller (1985). The small grain-size hindered us...
Fig. 4. BSE images showing (a) a large opaque assemblage in Tieschitz matrix and (b) part of it taken at 7 keV exhibiting a fine-grained polycrystalline aggregate of nanometric Cu particles and taenite crystallites.

Fig. 5. BSE images depicting (a) large native Cu area in an opaque rim around silicate clast. (b) Enlargement of (a) displaying the contact of native Cu juxtaposed to taenite with Ni-poor kamacite in between them.

Fig. 6. BSE images displaying (a) an opaque-rich silicate clast with porphyritic olivines enclosing an opaque globule containing native Cu associated with FeS, kamacite and taenite. (b) Enlargement of the opaque globule. Native Cu and FeS show idiomorphic shapes.

Fig. 7. (a) BSE image of a FeS-rich opaque assemblage showing Ni-rich metal coexisting with native Cu. (b) The enlargement shows that native Cu exhibit a scalloped border. It is surrounded by Cu-sulfide that was partially removed and/or transformed, at the contact with FeS.
in most cases from conducting any further quantitative investigation of chemical compositions of the individual sulfides with conventional micro-analytical wavelength dispersive techniques. The gray brightness of HgS (associated together with Cu-sulfide) as observed in reflected light at the optical microscope may feign the presence of metacinnabar, the high temperature polymorph of HgS.

Finally, we did not encounter metal–troilite eutectic textures that would indicate fusion, or shock melt veins or dense minerals that could indicate a dynamic high-pressure event. Nor do FeS grains show finely spaced twin lamellae/(10–21) or recrystallization.

We observed for the first time a phyllosilicate in the matrix of Tieschitz, but it was never encountered in association with Hg or Cu minerals. The exact nature of the phyllosilicate could not be determined in this study to set an upper temperature limits for its formation.

3.2. TEM and EBSD investigations

EBSD study confirmed HgS has the cinnabar structure (Fig. 9a), and the structure of FeS as troilite, the structure of kamacite and taenite as well. It showed that native Cu crystals in the opaque assemblages enclose nm-sized inclusions of olivine (Fo50) and/or CaPO₄ (possibly apatite). All the Cu-sulfide areas contain traces of HgS. Many cinnabar grains are poikilitically enclosed in Cu-sulfide. We could confirm by EBSD the crystal structure of native Cu in the matrix and in the porphyritic clast as well that revealed an Fm3m structure (Fig. 9b). However, the fine-grained nature of the polycrystalline native Cu angular crystal aggregate did not allow us to obtain meaningful EBSD patterns. The Cu-sulfide showed low quality EBSD patterns, likely due to small crystal sizes and surface layer deformation induced during sample preparation. The EBSD patterns of cinnabar are poor as well because it is beam-sensitive and its surface layers might be disturbed during polishing.

Cu-sulfide grains intergrown with Hg components were studied by a FIB–TEM technique (Fig. 3c). The SAED patterns and chemical compositions obtained by STEM–EDS indicate in this case that the Cu-sulfide is indeed CuS (covellite). The covellite includes many HgS grains with a dimension of < ~50 nm thus indicating their growth in free space around HgS. The HgS grains are confirmed to be cinnabar, based on their SAED patterns (Fig. 10a–d). We could not measure the individual compositions of covellite and cinnabar grains even by STEM–EDS, due to the intimate intergrowth of nm-sized cinnabar grains with covellite, thus leading to mixed analyses (Table 1). Many voids with a dimension of < ~100 nm are also present in the covellite grains. It is likely that the voids were originally filled with native

![Fig. 8. BSE image taken in another opaque assemblage showing identical occurrence to that in Fig. 7b. Cu-sulfide is only present between native Cu and FeS. Notice the numerous pores and inclusions present in the metals and FeS.](image)

![Fig. 9. (a) Electron back-scattered diffraction (EBSD) pattern of a cauliflower-shape cinnabar in Fig. 1a. The pattern is perfectly indexed with the cinnabar structure. (b) EBSD of native copper in Fig. 2a indexed with a Cu Fm3m structure. EDS shows a composition of Cu₉₅,Fex₄₋₄, The given Fe-content of 4.4% is probably an artifact resulting from secondary fluorescence of the Fe Kα X-rays by the emitted Cu-Kα line.](image)
Hg globules. Native Cu crystallites occur around the covellite grains.

3.3. Chemical compositions

Representative electron microprobe analyses (EMPA) of opaque minerals are presented in Table 2. Troilite is stoichiometric and it does not have any measurable traces of Hg but it contains some nanometer-sized Cu-rich domains (Fig. 2a). The Hg content of metal is below detection limit.

In two cases, SEM–EDS analyses and EMPA conducted on the assemblages revealed that this particular kamacite is exceptionally poor in Ni, less than 1 wt%, both in assemblages juxtaposed in between a large elongated native Cu grain and taenite in the opaque rim (Fig. 5) around a silicate assemblage (Table 3) or in the olivine porphyritic clast (Fig. 6). The Ni-poor kamacite is similar to that reported by El Goresy et al., but in comparison without any Co.

4. Discussion

The discovery of native Hg opens the interesting possibility that – in contrast to the CAIs that have registered the conditions prevailed during high temperature condensation of minerals – some nanometer-sized matrix minerals have registered low temperature conditions. It is thus important to investigate the extent to which the occurrence of native Hg and Cu could unfold the mechanism of their direct condensation from the solar gas.

The discovery of HgS–CuS (and/or Cu2S) and specifically metallic Hg in intimate and systematic coexistence with native Cu leads to several significant implications.

4.1. Origin of metallic copper in Tieschitz and other chondrites

First, the polycrystallinity of opaque phases and especially of native Cu that occasionally encloses metallic Hg nano-globules provides conclusive evidence that settles the long debate on the origin of native Cu and clearly refutes the claim that native Cu might have formed by shock melting of FeNi metal (Rubin, 1994). We demonstrate that its occurrence and texture cannot be related to dynamic events. Rubin (1994) claimed a positive correlation between the intensity of shock and the abundance of native Cu in chondritic FeNi metal by merely counting the number of native Cu grains inside chondritic FeNi metal grains without presenting any reliable evidence for shock-induced melting of FeNi. However, we never encounter metal–troilite eutectic textures evidencing fusion, nor do we observe shock melt veins or minerals indicating high-pressure phase transformations, as are found in other shocked L6 meteorites (Chen et al., 1996). Furthermore, there are no shock-induced finely spaced twin lamellae/(10–21) or re-crystallization in FeS grains, that would evidence shock-induced deformation twinning and re-crystallization at high post-shock temperatures.
It has also been statistically demonstrated that metallic Cu is more abundant in H than in L or LL chondrites, regardless of the shock stage of the meteorite (Ramdohr, 1963, 1973; Caillet Komorowski, 1973). The lack of sublimation of Hg globules (boiling point: 357°C) or decomposition of HgS (<273°C after accretion) constitutes further unambiguous evidence against the claimed shock-induced origin of native Cu.

Our findings also cast considerable doubt on the TL sensitivity results namely the metamorphic grades reported for Tieschitz by Sears (1980) thought to be similar to the highly shocked meteorites Farmington or Barratta. Metamorphic grade estimates by Quirico et al. (2003) are also clearly discrepant with our findings. Even if the organic matter they measured in Tieschitz could have possibly been not correctly sampled because of the presence of two distinct types of matrices in Tieschitz (Christophe Michel-Lévy, 1976). It has been demonstrated that some meteorites contain higher Hg bulk concentrations than others regardless of the claimed metamorphic grades (Jovanovic and Reed, 1985; Luck et al., 2003). In addition, the reported concentrations of Hg do not seem to correlate either with their class or with the estimated parent body alteration grade.

Furthermore Tieschitz matrix is porous (Ashworth, 1981) and lacks evidence of compaction. Sulfide minerals, metals and olivine are also porous in some chondrules but we do not see petrographic evidence of leaching or metasomatism as reported by Kurat (1969). The porosity observed in metals and sulfides, associated with native Cu suggests the former existence of inclusions such as Hg-spherules in pores in metals and sulfides. The metastable nature of Cu- and Hg-sulfides may have contributed to the degree of porosity of the meteorite matrix as well.

Formation of native Cu in the large rim around the clast (Fig. 5) or in the chondrule rim (Fig. 6) but barren of any Hg mineral in its interior must have taken place through another process. In these two special cases, the Ni-poor kamacite associated with native Cu probably emerged from a breakdown process of a parental Fe-, Cu, bearing, Ni-poor but Co-free sulfide that is similar to the reaction described by El Goresy (2006). In contrast, native Cu and kamacite in the matrix could not have exsolved from the taenite because they exist as polycrystalline aggregate of micron-sized to sub-micron angular grains. Therefore, the two kinds of chemical compositions of kamacite (different Ni-concentrations) strongly suggest that native Cu in the Tieschitz meteorite had at least two different modes of formation: direct condensation as metal and for some exceptions through a breakdown process of a Cu-rich sulfide. This is strongly suggestive of different nebular sources for matrix and chondrules in Tieschitz.

4.2. Origin of Hg- and Cu-sulfides in Tieschitz

Second, a further important implication of our discovery regards the co-genetic relationship between Cu and Hg through their systematic coexistence as native metals and sulfides, and their presence as intimate and delicate sulfide intergrowths which provides evidence for the simultaneous nucleation and growth of Cu-sulfide and HgS.

<table>
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<tr>
<th>Table 2</th>
<th>Representative electron microprobe analyses (in wt%) of Cu- and Hg-sulfides, native Cu and taenite.</th>
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<td>42</td>
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bd: below detection (10,000 ppm for Hg, Cu and Ni, 6000 ppm for Fe and 1900 ppm for S) Average detection is high at 10 kV and 4 nA. The minerals are beam sensitive. The metastable nature of Cu- and Hg-sulfides may have contributed to the degree of porosity of the meteorite matrix as well.

Much more importantly, native Cu, troilite and FeNi grains in Tieschitz are polycrystalline aggregates of individual angular grains, a texture that would have been replaced by individual large and massive metal or troilite grains if annealing had taken place (e.g. Scott and Rajan, 1981a, 1981b).

This indicates cold accretion and probably only low-temperature little thermal annealing. Fast cooling of metal would never have produced multigrain assemblage of angular grains. Therefore, Cu could not have formed by diffusion from the FeNi-metal. The native Hg found in Cu assemblages would never have survived a shock event involving high temperatures during the dynamic event or at high post-shock temperatures. In addition, the tiny perfect spheres of native Hg in metals and sulfides in Cu assemblages and the Cu–Hg-sulfide association in Tieschitz demonstrate that accretion occurred at very low temperatures and suggest that native Hg was sequestered in the spongy and polycrystalline native Cu grains before accretion hence in a closed system that pre-existed in the meteorite matrix that accreted in Tieschitz near the surface of the parent body. Native Cu could be one of the host phases for the volatile chalcophile element Hg (together with HgS). It is well known that Hg does not alloy with Fe, Ni, or Co, but it does alloy with Cu (Hansen, 1958) and chemisorbs onto Fe metal surfaces (Jones and Perry, 1981).
Whereas Hg has the lowest condensation temperature of metals fully condensed in Cl-chondrites, Cu condenses at fairly higher temperatures and the Cu-content is thought to be constant in various types of chondritic meteorites (Keyes et al., 1971) indicating that Cu and Cu-sulfides should normally occur at much higher temperatures than formation of Hg and Hgs in a solar environment. Investigation of the S vapor pressure curves for Cu metal/Cu$_2$S and liquid Hg/HgS according to Barton and Skinner (1967) shows that both sulfides could not co-exist at any temperatures in a vapor of solar composition.

The scenario of condensation of sublimated Hg and Cu vapors from the hot interior of the asteroid would inevitably call for sequential raise and drop of temperatures in the asteroid interior in order to account for repeated volatilization of Hg, Cu and their sulfides followed by their condensation in the cold regions of the asteroid. These requirements are discrepant with the findings. A possible explanation for the occurrence of both sulfides association in Tieschitz would imply that Cu$_2$S formed first at high temperature and lower partial S pressure and that HgS formed at lower temperature and higher partial S pressure and that both formed rapidly before all the Cu metal was consumed to form sulfides. However this explanation is not valid because the preservation of delicate associations of sulfides with metals requires an intimate crystallization process and suggests simultaneous formation of sulfides from the vapor phase.

The coexistence of cinnabar and Cu-sulfide in such alternating and rhythmic layers cast considerable doubt on the proposed enrichment in HgS and Hg by condensation of Hg as HgS and/or metallic Hg possibly sublimated from the hotter H-3 asteroid interior and re-condensation in the colder outer regions. This scenario is discrepant with the encountered metal-sulfide textures and assemblages. Furthermore, nanometer-sized inclusions of HgS grains in Cu-sulfide is an evidence against evaporation of Hg from the asteroid interior because it would require that Cu-sulfide also formed by sublimation from the asteroid interior and condensed in the cold region explicitly using HgS as nucleation sites similar to that reported by El Goresy et al. in comparison without any Co. Nanometer-sized inclusions of olivine (Fo$_{50}$) and phosphates inside cinnabar in Tieschitz matrix are incompatible with the evaporation–condensation scenario because such scenario would also imply a common source from the asteroid interior and formational mechanism by evaporation and condensation of volatile sulfides, and the more refractory olivine and phosphates inside cinnabar.

However, the textural relationship showing some Cu-sulfides without HgS between lobate native Cu and FeS leads us to the conclusion that the Cu-sulfides were formed during a nebular condensation and less likely sulfidation event after formation of the assemblages but not in the parent body, because sulfidation would also have created troilite rims around FeNi-metal. Finally, we note that the stoichiometry of troilite with FeS activity of 1 should not allow troilite to take more that 0.2 wt% Cu, Ni or Co in solid solution (Kullerud, 1967). There is no possibility that either Cu$_2$S or CuS could have exsolved from troilite because no solid solution exists between FeS and Cu$_2$S and/or CuS (Craig, 1982). Therefore the nanometer-sized Cu-rich areas in troilite suggest that nanometer-sized Cu-sulfides were enclosed as primordial inclusions in the troilite grains.

Phase relations of sulfide systems (Sack and Ebel, 2006; Fleet, 2006) show that the assemblage chalcocite, cinnabar and metallic Hg is a stable phase association below 300 °C. We also found no Fe-bearing Cu-sulfide that should co-exist with FeNi-metal, Cu metal and troilite at low temperature (Cabri, 1973; Craig, 1982). In fact, the textural relationships together with experimentally determined phase relations in the systems Hg-S, Cu-Hg-S and Cu-Fe-Hg-S (Kullerud, 1965; Potter and Barnes, 1978; Doctor and McCallister, 1978; Ollitrault-Fichet et al., 1984) show that chalcocite and cinnabar could coexist as stable phases below 300 °C. Hg metal and HgS are a stable assemblage below 345 °C (Potter and Barnes, 1978).

4.3. Possible mechanisms for enrichment of Tieschitz matrix in Hg minerals

Two contrasting scenarios were alternatively proposed to explain the relatively high abundance of Hg minerals in the Tieschitz matrix: (1) the Tieschitz matrix condensed and accreted at low temperatures incorporating high portion of the volatile Hg, or (2) high abundance of Hg is due to evaporation of volatile elements from the hot interior of the Tieschitz asteroid and its recondensation in the outer colder regions of the asteroid. The first scenario calls for different degrees of Hg incorporation in chondrules and matrix. Although both scenarios require enrichment in other volatile elements like Cd as well, the second scenario calls for homogeneous distribution of Hg (and Cd) among chondrules and matrix.

There are several lines of evidence that are not compatible with the second scenario proposed by Wombacher et al. (2003): (1) such a scenario would also require that Hg allegedly evaporated from the hot asteroid interior should equally re-condense proportional to the chondrule/matrix ratio both in Tieschitz matrix and in chondrules. However, Hg-bearing assemblages are confined to the matrix alone and they are heterogeneous distributed throughout the meteorite matrix demonstrating that Hg was not mobilized prior to accretion, (2) we did not encounter any independent Cd sulfide in chondrules or matrix of Tieschitz: the hexagonal-structured greenockite, or hawleyite, the sphalerite-structured polymorphs. Hence, we anticipate that volatile Cd, by analogy to the also volatile Hg, is incorporated in cinnabar or Hg metal preferentially in the Tieschitz matrix. (3) Much more importantly, the rhythmic alternating mineral layers of HgS and Cu-sulfide demonstrate that they formed during genetically and timely related events. The assemblage accreted as such in the fluffy matrix of Tieschitz. This intergrowth which according to the parent body scenario (Wombacher et al., 2003) would have emerged from the interior of the hot asteroid would require simultaneous mobilization, cogeneric sublimation of the Hg, Cd, and Cu sulfides from the parent body interior followed by their simultaneous re-condensation in the outer cold regions and only in the Tieschitz matrix. This is unlikely due to the stark differences in the Hg and Cu volatilities and the lack of reasoning why Hg and HgS should only condense in the Tieschitz matrix and not in chondrules or their fragments; (4) occurrence of sponge metallic Cu with Hg metal globules in their pores. There is no plausible explanation for formation of sponge metallic Cu during a re-condensation process of Cd and Hg preferentially in a polycrystalline metallic Cu in the parent body. (5) Occurrences of micrometer-sized inclusions of Fo50 olivine and a phosphate inside native Cu would also not have originated with the same scenario by sublimation from the hot asteroid interior. It rather demonstrates that Tieschitz contains heterogeneous accretionary assemblages. (6) Lack of Cd isotopic fractionation in Allende and Murchison chondrules in comparison to the presence of isotopically fractionated Cd in Tieschitz shows that the degree of Cd isotopic fractionation is different in C-chondrites from Tieschitz. Allende and Murchison are highly oxidized C-chondrites in comparison to the reduced H-3 Tieschitz. Zn is expected to be in solid solution in olivine in C-chondrites. The carrier phases of Cd in chondrules and matrices in C-chondrites are unknown. (7) In addition, the absence of FeS and iron oxides such as magnetite and/or FeOOH polymorphs around FeNi-metal does not support such a parent body remobilisation. The hypothesized formation of Hg–Cu-bearing assemblages from secondary aqueous alteration processes on their parent bodies (Lauretta et al., 1999) requires the occurrence
of pre-existing minerals (such as HgS dissociating to Hg+S) and unknown enrichment mechanisms for both Hg and Cu in only a few chondrites. In addition, native Cu is not observed in a corroded state. Cuprite, the first product of oxidative corrosion of native Cu on Earth (McNeil and Little, 1992), was not found. Phyllosilicate has no chemical or genetic relationship to the Hg-Cu assemblage and could have formed in the nebula (Ciesla et al., 2003). (8) Furthermore, the occurrence of metallic Cu, kamacite, and taenite in Tieschitz matrix as aggregates of angular grains clearly advocates for their origin of cold accretion thus negating any thermal or dynamic event. (9) Should not meteorites with high petrologic grades (allegedly from a more internal part of perhaps the same UOC parent body) also be enriched in Hg? Furthermore, this scenario would inevitably lead to the formation of chalcopyrite (CuFeS2) which would have formed below 557 °C in the presence of Fe and which is not observed.

Rare delicate HgS–Cu-sulfide layered associations located in one pyroxene and at the border of a porous chondrule might indicate that these silicates formed close to the opaque assemblages in the nebula before being accreted into the Tieschitz parent body. Nevertheless, our results show that particles previously condensed as fine-grained dust, i.e. primordial material, such as the submicrometer-sized assemblages of juxtaposed Hg, HgS, Cu-sulfides associated with polycrystalline aggregate of angular native Cu were the last phases to accrete at very low temperatures onto a parent body. The unexpected preservation of these low T mineral assemblages attest that there were no post-accretionary events, either by high temperature metamorphism or by impact on the parent asteroid, that could have induced mineralogical changes and high-pressure phase transitions. This implies that water ice was absent on Tieschitz since we find no evidence for aqueous alteration, and that accretion was fast, to prevent the Hg from being totally sulfidized.

Tieschitz differs from other chondrites with respect to its chemistry, mineralogy, and not only because of a late post accretion history. Moreover, Tieschitz formed in a region that sampled a large range of low temperature primary condensates from different reservoirs providing us with valuable information about cooling of the local dense solar nebula, gentle accretion until very low temperatures (Hezel and Palme, 2010), and also the preservation of fine-grained dust that was not dissipated in the nebula prior to fast accretion. It would be worthwhile to study other primitive carbonaceous chondrite that have a high Hg-bulk content and search for the Hg-bearing assemblages similar to those encountered in this study.

5. Conclusions

We discovered a unique occurrence of metallic Hg, cinnabar (HgS) and Cu-sulfide in fine-grained polycrystalline native Cu-bearing assemblages in the Tieschitz unequilibrated H3 ordinary chondrite.

We discussed two alternative possibilities for the formation of these assemblages: the first scenario implies condensation of opaque assemblages (FeNi-metal–FeS-native Cu) followed by sulfidation in a reservoir of strictly non-solar composition in the nebula to explain the Hg–Cu-sulfide association. Condensation would be followed by gentle and fast accretion at low temperatures. The second scenario, proposed by Wombacher et al. (2003) and others, involves parent body processes including impact shock, metamorphism evaporation of volatile elements (Hg, Cd) from the asteroid interior and their re-condensation in the outer colder regions of the parent body. Our detailed evidence refutes processing of the assemblage after accretion in the parent body. We unambiguously demonstrate that the native Cu could not have been produced by shock melting of metallic FeNi. Shock effects would have homogenized the metal and destroyed the delicate intergrowths, rather than exsolved traces of Cu from the FeNi metal melt. In addition the Hg-bearing minerals could not have survived at high temperatures near the surface of a parent body. Neither heating events nor hot accretion can satisfactorily explain our findings. We maintain that cold accretion is the only viable hypothesis to preserve the fluffy fine-grained mineral assemblages and their delicate textures, the polycrystallinity of FeNi-metal, angular aggregates of native Cu and sulfides and the high Hg concentration in this meteorite. Furthermore, we have no evidence of hydrothermal processing, kamacite oxidation and sulfidation and native Cu corrosion and no association of phyllosilicates. The sulfide phase relations indicate low temperature conditions (< 300 °C). Our observations provided a unique opportunity to place robust constraints on the origin by fast accretion at low temperature of the Hg–Cu-minerals on Tieschitz.

Finally, the presence of these aggregates together with the high bulk content of Hg suggests its residence in a closed system near the surface of the parent body of Tieschitz. The discovery of new low temperature metal-sulfide assemblages in the matrix of the Tieschitz chondrite calls for reinvestigations of elemental abundances in UOC and the meticulous search for the carriers of volatile elements like Cd, Hg and Zn, in chondrules and matrices separately, which expectedly occur as individual sulfides; new studies of their solid-solutions prior to any isotopic investigations of these elements in bulk meteorites; and further understanding of the origin and formation of the matrices on the chondrite parent bodies.

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