Chemistry and thermal history of metal particles in Luna 20 soils

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Abstract—Individual metal particles from Luna 20 thin sections 521, 513 and 514 as well as several small metallic inclusions in silicate particles from Luna 20 thin sections 501 and 502 were examined using optical microscopy and the electron microprobe. All the metallic particles and inclusions analyzed are of meteoritic Co—Ni content as are most of the metallic particles from the Fra Mauro and the Apollo 16 highlands sites. It is proposed that most of the metal at these 3 sites had its origin in the meteoritic projectiles that bombarded and accumulated in the early lunar crust. It is apparent that the metallic particles and some of the metallic inclusions in the Luna 20 soil have been subjected to reheating on the Moon and this process has removed any evidence of the original meteoritic microstructure of the metal.

INTRODUCTION

A small proportion of the minerals found in lunar rocks and soil are metallic. Sources of these metallic phases include the metal in igneous rocks, the metal reduced from Fe-bearing silicate or glass during metamorphism, and the metal phases of meteorites (irons, stones) which have cratered the lunar surface. Because of the relatively simple chemistry and phase equilibrium relationships within the metallic phases, it is often possible to determine unique time-temperature histories for these particles. It is the purpose of this investigation to characterize several Luna 20 metal particles chemically and structurally and to determine their origin (meteoritic vs lunar) and the various effects of shock-reheating events at or near this lunar highlands location.

METHOD

Individual metal particles from polished thin sections (PTS) 521, 513 and 514 as well as several small metallic inclusions in silicate particles from polished thin sections 501 and 502 were examined. These thin sections were prepared by the Smithsonian Astrophysical Observatory for the East Coast Mineralogy and Petrology Consortium. All the particles were chemically analyzed with the electron microprobe. Special attention was given to the compositions at the interfaces between phases (kamacite—phosphide, kamacite—taenite, etc.) since these values probably represent the frozen-in local equilibrium compositions corresponding to the most recent heat treatment of the metal. Estimates of the effective temperatures of final equilibration are made by comparing measured interface compositions with measured or interpolated tie line relationships in the appropriate Fe—Ni (GOLDSTEIN and OGILVIE, 1965) or Fe—Ni—P (DOAN and GOLDSTEIN, 1970) equilibrium diagram. Calculations of reheating times and cooling rates are made with the use of appropriate binary (Fe—Ni) diffusion coefficients for taenite (GOLDSTEIN et al. 1964), and for kamacite (BONG and LAI, 1963) as well as the appropriate ternary (Fe—Ni—P) diffusion coefficients for taenite and kamacite (HEYWARD and GOLDSTEIN, 1972). After microprobe analysis the metal particles were repolished, etched in a 1 per cent nital solution, and examined optically.

RESULTS AND DISCUSSION

The particle sizes, sample numbers, bulk chemical analyses and descriptions of the metallic particles are collected in Tables 1 and 2. The descriptions of the silicate
Table 1. Composition, sizes and descriptions of Luna 20 metal particles

<table>
<thead>
<tr>
<th>PTS number</th>
<th>Composition (wt. %)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 23 in PTS 513</td>
<td>6-0 0.45 0.02 0-02 6-0 0.45 0.02 0-02</td>
<td>Bulk composition and kamacite composition</td>
</tr>
<tr>
<td>No. 13 in PTS 513</td>
<td>10-1 0.72 0-06 0-02 31-0 0.22 0-02 0-02</td>
<td>Kamacite at kamacite/taenite boundary</td>
</tr>
<tr>
<td>No. 28 in PTS 514</td>
<td>8-63 0.46 1.8 3-35 8-63 0.46 1.8 3-35</td>
<td>Bulk composition, remelted metallic particle</td>
</tr>
</tbody>
</table>

Metallic particles

Particle 73 in PTS 521 is an Al-rich alloy fragment containing 1-2 wt.% Mg, 3-3 wt.% Cu, 0-55 wt.% Si, 0-52 wt.% Mn, 0-22 wt.% P, and 0-04 wt.% Zn. It is about 250 μm in its longest dimension, 70 μm in width and its microstructure is shown in Fig. 1. Lunar silicate-glass is attached to several areas of the metal particle. Its chemistry is almost identical to that of the commercial Al alloy 2024. This same alloy is used in the Apollo lunar module in sheet form, 200–500 μm thick, as a heat sink shield to protect the spacecraft from the radiant heat of the engine exhaust (Orrok, 1967). Presumably a similar alloy was used on the Luna 20 vehicle and particle 73 is a fragment which was eroded from the landing vehicle and adhered to some of the lunar soil.

Two metallic particles were examined in PTS 513. Particle 23 is approximately 370 μm in length and almost completely surrounded by a thin layer of FeS (Fig. 2). Kamacite of 6-0 ± 0.2 wt.% Ni, 0.45 wt.% Co, 0-02 wt.% P, balance Fe is the major metallic phase. A fine ribbon of taenite, approximately 1 to 2 μm in width, was observed in the kamacite phase and the composition of this phase is approximately 18 ± 2 wt.% Ni, 0-28 wt.% Co, 0-02 wt.% P, balance Fe. The Ni compositions of kamacite and taenite indicate an effective temperature of final equilibration at 600°C according to the Fe–Ni equilibrium diagram. The probable history of this particle then includes a final stage in which the kamacite phase is reequilibrated at approximately 600°C where a fine ribbon of isothermal taenite nucleates. A reheating time of approximately several months would be necessary to produce a structure of the size observed.
Fig. 1. Particle 73 in PTS 521—field of view 450 x 350 μm. Etched 1 per cent nital. Al alloy fragment from Luna 20 vehicle. The rounded black areas are bubbles in the epoxy mounting material.

Fig. 2. Particle 23 in PTS 513—field of view 450 x 350 μm. Etched 1 per cent nital. The position of the fine ribbons of taenite in the kamacite matrix is indicated by the arrows.
Fig. 3. Particle 13 in PTS 513—field of view 450 × 350 µm. Etched 1 per cent nital. Complex 3 phase metallic particle. The kamacite along the outside of the particle totally surrounds the taenite–plessite phase field. The taenite at the edge of the plessite is unetched. The phosphide phases are indicated by the arrows and the position of the electron probe scan across a kamacite–taenite interface, Fig. 4, is indicated by the solid line.

Fig. 4. Complex 3 phase metallic particle. The kamacite along the outside of the particle totally surrounds the taenite–plessite phase field. The taenite at the edge of the plessite is unetched. The phosphide phases are indicated by the arrows and the position of the electron probe scan across a kamacite–taenite interface, Fig. 4, is indicated by the solid line.

Fig. 5. Particle 28 in PTS 514—field of view 900 × 700 µm. Etched 1 per cent nital. Oblate shaped remelted metallic particle. The section contains globular metal grains of taenite (light) surrounded by regions of phosphide eutectic (light grey) and troilite (dark grey).

Fig. 6. High magnification view of the phosphide–sulfide rich phases in Particle 28 in PTS 514—field of view 90 × 70 µm. Etched 1 per cent nital. Troilite is dark grey and the eutectic mixture of phosphide and metal is indicated by the open arrow. The elongated phosphide precipitates which appear to have exsolved after solidification are indicated by the solid arrows.
### Table 2. Compositions, sizes, and descriptions of Luna 20 metal inclusions

<table>
<thead>
<tr>
<th>Particle and PTS number</th>
<th>Size of metallic inclusion(s)</th>
<th>Description*</th>
<th>Bulk composition (wt. %)</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>No. 1 in PTS 501</td>
<td>75 × 50 μm</td>
<td>Several interconnected metal particles in a recrystallized and brecciated norite containing ~55% plag., ~41% mafic silicates, ~4% metal and traces of opaques and interstitial glass.</td>
<td>Ni 5.5  Co 0.65  P 0.02  S &lt;0.02  Cr 0.05</td>
<td></td>
</tr>
<tr>
<td>No. 3 in PTS 501</td>
<td>30 × 15 μm</td>
<td>One metallic particle with attached FeS in a recrystallized and brecciated anorthosite containing ~70% plag., ~29% mafic silicates, ~1% metal and traces of opaques.</td>
<td>Ni 5.1  Co 0.65  P &lt;0.02  S &lt;0.02  Cr &lt;0.02</td>
<td></td>
</tr>
<tr>
<td>No. 4 in PTS 501</td>
<td>50 × 25 μm 75 × 8 μm 15 μm dia.</td>
<td>Several metal particles in a probable impact melt. The crystals (pyroxene and plagioclase) look as if they grew from a melt, not upon devitrification from a glass.</td>
<td>Ni 7.8  Co 0.45  P 0.3  S &lt;0.02  Cr &lt;0.02</td>
<td></td>
</tr>
<tr>
<td>No. 7 in PTS 501</td>
<td>70 × 30 μm</td>
<td>One 2-phase (kamacite and taenite) metal particle in a fine-grained, recrystallized area of a relatively coarse-grained, brecciated and slightly recrystallized anorthositic rock.</td>
<td>Ni 7.5  Co 0.5  P &lt;0.02  S &lt;0.02  Cr 0.08</td>
<td>Bulk (estimated) Kamacite (major phase ~80%) Taenite (minor phase ~20%)</td>
</tr>
<tr>
<td>No. 9 in PTS 501</td>
<td>10 μm dia.</td>
<td>One rounded metal particle in a glass-bonded aggregate. It has a few crystals and/or rock fragments included in it.</td>
<td>Ni 5.5  Co 0.2  P 0.35  S 0.4  Cr 0.2</td>
<td></td>
</tr>
<tr>
<td>No. 3 in PTS 502</td>
<td>30 × 20 μm</td>
<td>One metal particle with micro phosphides in a rock close to the border between norite and anorthositic-norite. It has a rather complex history of brecciation and recrystallization.</td>
<td>Ni 4.9  Co 0.5  P 0.15  S &lt;0.02  Cr &lt;0.02</td>
<td>P variable (0.05–0.45) indicating presence of micro phosphides</td>
</tr>
</tbody>
</table>

* Description of PTS provided by G. J. Taylor, Smithsonian Astrophysical Observatory.
Particle 13 in PTS 513 contains 10.1 wt.% Ni, 0.72 wt.% Co, 0.06 wt.% P, <0.02 wt.% S, balance Fe and is approximately 350 μm in length and 160 μm in width. The particle contains 3 phases, kamacite, taenite, and phosphide, and its microstructure is shown in Fig. 3. The kamacite outlines the particle and surrounds the taenite–plessite phase field while phosphide is located in isolated areas along the outside of the particle. The metallographic structure is different from that of a chondritic metal particle since in the chondritic particle taenite usually abuts on silicate and is not observed to be surrounded by swathing kamacite (Wood, 1967).

Figure 4 shows a Ni profile taken across a kamacite–taenite interface. The γ-taenite is zoned and a small dip in the Ni concentration in α-kamacite from 7.5 to 7.0 wt.% Ni near the α/γ boundary is observed. The Ni contents, 7.0 wt.% in kamacite and 31 wt.% in taenite at the kamacite/taenite interface, indicates an effective temperature of final equilibration of 400°C and 500°C, respectively, according to the Fe–Ni binary diagram. Considering the difficulty of obtaining the maximum Ni content of the taenite due to the severe chemical gradient and the finite 1 μm resolution of the electron probe, the 400°C equilibration temperature obtained from the kamacite measurement is more correct. The P contents, 0.08 wt.% in kamacite and 0.02 wt.% in taenite at the two phase interface also indicate equilibration between 450 and 400°C according to an extrapolation of the Fe–Ni–P diagram. Also measurements of the Ni and P compositions at phosphide–kamacite interfaces (44 wt.% Ni, 15.5 wt.% P in the phosphide and 7.0 wt.% Ni, 0.04 wt. P in the kamacite) suggest a final equilibration temperature of around 400°C.

The shape of the Ni gradient across the kamacite–taenite interface in this particle (Fig. 4) is qualitatively similar to that obtained at 2-phase interfaces in stony or iron meteorites. However 2-phase kamacite–taenite interfaces in meteorites usually
have lower Ni contents in kamacite and higher Ni contents in taenite (Wood, 1967; Short and Goldstein, 1967), indicating final equilibration temperatures below 400°C.

Detailed calculations of kamacite growth during the cooling of chondrites and iron meteorites (Wood, 1967; Goldstein and Short, 1967) have been made. These computer simulations are based on the assumption that growth is controlled by Fe–Ni diffusion in taenite and that equilibrium at the kamacite–taenite interface is given by the Fe–Ni phase diagram. The results of these calculations give the expected Ni concentration gradients in kamacite and taenite for various cooling rates. Agreement between measured and calculated Ni gradients in the metallic phases of chondrites and iron meteorites generally occur at cooling rates between 1° and 10°C per million years. Final equilibration temperatures of about 350°C according to the Fe–Ni phase diagram are usually found for these meteorites. The computer growth calculations also show that as the cooling rate for meteoritic metal increases the final equilibration temperatures of kamacite and taenite as indicated by the Ni content at the kamacite–taenite interface increases. This effect occurs because the time available for Ni diffusion and for equilibration at the lower temperatures decreases as cooling rate increases. The effective temperature of final equilibration (460–400°C) for particle 13 therefore indicates a faster cooling rate for the particle than for meteorites in general. We estimate cooling rates for particle 13 of approximately 1°C per thousand years.

Particle 28 in PTS 514 (Fig. 5) is a remelted metallic globule, 300 x 400 μm in size, similar to those found at the various Apollo sites (Mason et al., 1970, Wänke et al., 1970 and Goldstein and Yakowitz, 1971). The bulk analysis of 8.63 wt. % Ni, 0.46 wt. % Co, 3.35 wt. % S, 1.8 wt. % P, balance Fe is approximately the same as the average composition of a large number of remelted metal particles from the various Apollo soil samples. As shown in Fig. 5, the microstructure of this oblate shaped particle is indicative of rapid solidification of a molten alloy. The section contains globular metal grains of taenite surrounded by regions of metal–phosphide eutectic and troilite. The metal grains probably are primary crystals of nickel–iron which solidified before the rest of the phosphide–sulfide rich liquid. The structure of the primary metal crystals is different from that found in metal globules collected from the plains surrounding the Canyon Diablo Crater in Arizona, USA. In Canyon Diablo, the metal forms in a dendritic, tree-like intergrowth (Blau et al., 1973) while in Particle 28 the metal is globular in shape and the metal areas are isolated from each other.

Flemings, Barone and Brody (1967) have proposed a method by which the rates at which alloy castings cooled through the solidification range may be estimated from measurements of the primary metal crystals in the final cast structure. They observed a straight line log–log relationship for Fe–Ni alloys between the cooling rate and the primary crystal size. Blau et al. (1973) have used this relationship to estimate cooling rates, during solidification, of Canyon Diablo spherules. The average crystal spacing of Particle 28 is 25 μm and indicates a cooling rate of approximately 45°C per second over the freezing range.

A high magnification view of the phosphide–sulfide rich phases is shown in Fig. 6. The region shown by the open arrow is a eutectic containing phosphide and metal. Microprobe measurements show approximately 13 wt.% Ni and 11.9 wt.% P in the
eutectic which is just equivalent to the composition of the liquid in equilibrium with \( \alpha, \gamma \) and phosphide at 1000°C in the Fe–Ni–P diagram. Particular attention should be paid to the elongated phosphide precipitates \( \sim 1 \mu m \) in width depicted by the solid arrows. Phosphides of this type are not found in most lunar globules or in experimental alloys cooled directly from the melt (Goldstein et al., 1970). These elongated phosphides appear to have exsolved from the metal below the solidification temperature (<1000°C) when the cooling rate of the metallic globule was greatly decreased. A similar type of phosphide exsolution was described by Goldstein et al. (1970) for a metallic particle in Apollo 11 breccia rock 10046-18A. The taenite composition at the taenite phosphide interface is 9.2 wt. % Ni and 1.02 wt. % P and corresponds to an effective final equilibration temperature of about 950°C. Based on ternary diffusion data we have estimated that this exsolution occurred in about 10 to 10^4 sec, much more slowly than the time available during the solidification process.

In light of the preceding discussion, particle 28 was likely to have formed in the same way as most of the molten metallic globules found on the Moon, that is by a meteorite impact in which metallic metal/troilite/phosphide interfaces in the meteoritic metal are shock melted to form a S and P rich liquid (Blau et al., 1973). Once formed, the ejected liquid breaks up into droplets of varying sizes. Particle 28 in particular solidified rapidly (~45°C/sec), losing its heat by radiation and then landed on the lunar surface in a mass of hot ejecta where the cooling rate was greatly slowed. This final step allowed sufficient time (~ hours) for the phosphides to precipitate from the phosphorus-supersaturated nickel–iron matrix.

The thickness of the blanket of hot ejecta in which particle 28 was incorporated can be estimated using the method of Taylor and Heymann (1971). The temperature–time profile for the center of a silicate ‘slab’ of thickness \( h \), originally at a uniform temperature \( T_0 \) is calculated. A temperature \( T_0 \) of 1200°C, a thermal diffusivity of 0.01 cm^2/sec, and a cooling period of 10^4 seconds during the temperature interval (1000–900°C) in which the phosphides exsolved was assumed for the calculation. A hot ejecta blanket about 1 meter in thickness is sufficient to allow the necessary cooling period. The proposed model also provides for the fact that particle 28 is oblate in cross-section since the solidifying globule may still have been partially molten and/or plastic enough to deform into its present shape when it landed. The ‘Minimoon’ from Apollo 11 is another such oblate metallic particle (Mason et al., 1970; Goldstein et al., 1970).

**Metallic inclusions in silicate**

Metal inclusions in 5 silicate particles from PTS 501 and 1 silicate particle from PTS 502 were examined. The compositional data and descriptions of the metal and the surrounding silicate are collected in Table 2. Most of the inclusions were one-phase and chemically homogeneous. The metal in particle 7 in PTS 501 however was 2-phase, with a matrix of kamacite and a 2–5 \( \mu m \) wide region of high-Ni taenite on two sides. The kamacite contained 6.8 wt. % Ni but near the kamacite–taenite border decreased to 6.1 wt. % Ni. The formation of the high-Ni (25 wt. %) taenite and the Ni gradient in kamacite indicate a reheating of the metal phase to approximately 550°C. A reheating time of approximately several years at 550°C is necessary to produce a structure of the observed size. The metal in particle 3 in PTS 502 was
also two-phase, with evidence of micro-phosphides precipitated in a matrix of kamacite. The P content of the metal is 0.15 wt.% P and the temperature of phosphide precipitation was estimated, according to the solubility limits of P in kamacite from the ternary diagram, to be below 500°C. If cooling through this temperature region is rapid, faster than a month, the phosphide particles will grow only to submicron size.

**Composition and origin of the metal particles**

The bulk Co and Ni contents for metallic particles 23 and 13 in PTS 513 and for the metallic globule 28 in PTS 514 are plotted as open circles and as a cross, respectively, on the Co–Ni diagram, in Fig. 7. Three Co–Ni ranges are also indicated on Fig. 7: (1) the Co–Ni range for meteoritic metal as given by GOLDSTEIN and YAKOWITZ (1971), (2) the high Fe range with low Ni (<1 wt.%) and low Co (<0.5 wt.%) characteristic of metal in Apollo 11 lunar basalts, and (3) the high Co range which encompasses the Co–Ni contents of metal from Apollo 12 and 15 lunar basalts. All three of these particles apparently are of meteoritic composition and origin. VINOGRADOV (1972) also reports that the anorthositic regolith contains fragments of meteoritic alloys. It is important to note that all of the metallic particles we have studied have been reheated in the lunar environment and that their original meteoritic microstructure has been completely lost.

The bulk Co and Ni contents of the metallic inclusions are also plotted on the Co–Ni diagram, Fig. 7 as solid squares. All of the metal inclusions are apparently of meteoritic composition and origin. VINOGRADOV (1972) has also reported that metal in the crystalline rocks contains Ni. The surrounding silicate in 4 of the particles analyzed is recrystallized (reheated) and brecciated and the other 2 particles were remelted (Table 1). None of the particles seem to be metal inclusions from igneous rocks. It is probable that the meteoritic metal was incorporated in the rocks during the brecciation and recrystallization event(s).
Although the number of Luna 20 metallic particles we have analyzed is small, their Co–Ni contents are meteoritic and this result is quite similar to the results obtained for metallic particles at the Apollo 14 site (Wlotzka et al., 1972; Goldstein et al., 1972) and to our observations on the Apollo 16 highlands site. Most of the metal found in the soil and in the reprocessed rock fragments had its origin in the meteoritic projectiles that bombarded and accumulated in and on the early lunar crust (Goldstein et al., 1972).

**Conclusions**

1. The metallic particles and some of the metallic inclusions in the Luna 20 soil have been subjected to reheating processes on the Moon extending from 500 to >700°C and for periods of time from several seconds to several years. One metallic particle was formed from the explosively melted portion of a meteoritic projectile and was relatively slowly cooled on the lunar surface after solidification.

2. The metallic particles and inclusions all have meteoritic Ni–Co contents. Most of the metal had its origin in the meteoritic projectiles that bombarded and accumulated in and on the early lunar crust. The Ni–Co contents of the metal at the Luna 20 site is quite similar to that found for the Apollo 14 and the other highlands site, Apollo 16.

3. The structure of the silicate surrounding the metallic inclusions is compatible with the incorporation of meteoritic metal into the rocks at some stage. The metamorphic processes to which the metal was subjected while incorporated in the fragmental lunar rocks and during later events have removed any initial meteoritic microstructure of the metal.

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**References**


