MORPHOLOGICAL AND CHEMICAL STUDY OF PLACER GOLD
FROM THE SAN LUIS RANGE, ARGENTINA

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ABSTRACT
The composition of placer gold from the San Luis Range, Argentina, is poorly documented, although these deposits have been known since the 18th century. A detailed study of gold grains collected from different streams in the La Carolina gold district was carried out. We performed 502 analyses on 191 grains. The core composition of the gold grains is heterogeneous, with an average chemical composition of 58 to 74 wt.% Au, 25 to 40% Ag, up to 0.5% Hg, and less than 0.4% Cu. The rim of each grain is generally richer in gold than the core, and the contact between rim and core is very sharp but of irregular shape and complex texture. There are populations with different chemical composition, but the compositional differences among rounded grains and those having a more delicate morphology are not invariably either significant or consistent. All sources are restricted to deposits associated with Tertiary volcanic rocks in the area, and the variable and wide range of fineness points to low-sulfidation epithermal-type deposits as the most likely source. The sharpness of the core–rim contact may result from either electrochemical processes active in the stream or stream sediments, or Au and Ag dissolution processes followed by Au precipitation in surface or near-surface environments. The presence of overgrowths of gold on gold grains suggests that there was secondary precipitation of gold after the host grain was formed. Gold grains do grow in low-temperature geochemical settings, and we believe that their composition becomes more gold-rich as the grains move downstream or are buried in the sediments. Anthropogenic Hg was detected in some of the streams, and even where there are several sources for it, we believe that all of it is coming from the amalgamation processes used by local inhabitants to recover the panned gold.

Keywords: gold grains, gold rims, placer gold deposits, San Luis Range, Argentina.

SOMMAIRE
On connaît mal la composition de l’or dans les placers aurifères de la chaîne de San Luis, en Argentine, quoique ces gisements sont connus depuis le dix-huitième siècle. Nous présentons les résultats d’une étude détaillée de pépites d’or prélevées de divers cours d’eau du district aurifère de La Carolina. Nous avons effectué 502 analyses sur 191 grains. Le coeur des grains est hétérogène, contenant en moyenne entre 58 et 74% Au, 25 et 40% Ag, jusqu’à 0.5% Hg, et moins de 0.4% Cu. La bordure de chaque grain est généralement plus riche en or que le coeur, et le contact entre ce liseré et le coeur est très franc. Les sources de minéralisation sont limitées à des gisements associés au volcanisme tertiaire dans la région, mais la pureté de l’or varie beaucoup, de sorte que des gisements de type épithermal à faible sulfuration semblent rendre compte de la provenance. L’allure abrupte du contact entre le coeur et le liseré pourrait résulter de processus électrochimiques dans le cours d’eau ou dans les sédiments qu’ils

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ont déposés, ou bien d’une dissolution de l’or et de l’argent, suivie de la précipitation de l’or dans un milieu à la surface ou près de la surface. D’après la présence de surcroissances d’or sur des grains d’or, il y aurait eu une précipitation secondaire d’or après la formation du grain principal. Les grains d’or peuvent donc croître dans un milieu géochimique de basse température; nous croyons que la composition devient enrichie en or à mesure que les grains sont transportés dans le cours d’eau ou sont enfouis dans les sédiments. Nous avons décélè des signes de mercure anthropogénique dans certains cours d’eau. Même où il pourrait y avoir plus d’une source du mercure, nous l’attribuons uniquement au processus d’amalgamation utilisé par les habitants locaux intéressés à récupérer l’or exploité à la batée.

(Traduit par la Rédaction)

Mots-clés: grains d’or, liseré d’or, gisements de type placer, chaîne de San Luis, Argentine.

INTRODUCTION

The chemical composition of placer gold from Argentina is poorly documented in the literature. Several studies have been performed on gold grains in the San Luis area (Burmeister 1934, Bassi 1948, Rosello & García 1983, Karlsson & Porta 1991, Guilhou & Cardó 1995, Rosello & Castro 1995, Castro 1999), but none of them have given much information about the composition of the gold grains, which is one of the main objectives of this paper.

Our main aim in this research was to study the gold grains collected from various streams and, where possible, in different sections of the same stream, in the La Carolina area, San Luis Province, Argentina. We report on our examination of the morphological developments of the grains, results of our electron-microprobe analyses of different domains of specific grains (border, core, rim and veinlets) for uncontaminated gold grains as well as the ones containing anthropogenic Hg, and an evaluation of the process leading to the formation of the rim, as well as of a possible source-area for the placer gold.

GEOLOGICAL SETTING

The La Carolina district is located in the Departamento Pringles, Provincia de San Luis, Argentina, about 80 km to the north of the capital of the province. The area of the placer deposits forms part of the Pampean Ranges, consisting of a Precambrian–Paleozoic crystalline basement, Tertiary volcanic rocks, Pliocene gravels and Quaternary cover (Bassi 1948, 1990).

Several authors have studied the geology of the crystalline basement, and it is continuously being updated (e.g., Steenken et al. 2002, and references therein). A comprehensive review of the background information, together with a formal description of the geological units, and new geochronological data was made by Sims et al. (1997, 1998). In the present summary, we will follow their general descriptions.

The La Carolina district (Fig. 1) consists of elongate NNE–SSW-faulted blocks of metamorphic rocks belonging to the Pringles metamorphic complex and the San Luis Formation. The Pringles metamorphic complex gives a U–Pb age ca. 480 Ma; it is formed by pelitic and psammitic gneisses and schists, intruded by mafic and ultramafic lenses. The outcrops of the San Luis Formation form two subparallel belts that consist mainly of slates, phyllites, and metaconglomerates intruded by some scarce I-type tonalites and an S-type granite–pegmatite suite with ca. 470 Ma U–Pb ages. The Miocene–Pliocene San Luis volcanic group forms a northwest-trending belt ca. 80 km long, that consists of andesitic to trachyandesitic domes, dikes, sills, lava flows, diatremes and minor pyroclastics rocks. The volcanic suite belongs to a high-K calc-alkaline to shoshonitic suite of arc-related magmas, erupted 700 km inland of the trench in the Pampean ranges, during an episode of flat-slab subduction of the Nazca plate (Kay & Gordillo 1994, Urbina et al. 1997). The epithermal deposits described in this area (Fig. 1) are related with this volcanism (Bassi 1948, 1990, Márquez-Zavalía & Galliski 1994, Rosello & Castro 1995, Urbina et al. 1997), which was followed by sedimentation of the Pliocene gravels and the Quaternary cover that host the placer deposits.

The volcanic effusions delimit the drainage divide, defining catchment basins to the north and south where the placer deposits are situated. Our gold grains come from placer deposits on the southern belt; they are the more important and of higher grade. These placer deposits have been known since pre-Colombian times, and intermittently mined since the last part of the 18th century; they are hosted in the Pliocene gravels and Quaternary cover, overlying the crystalline basement and the volcanic rocks (Rosello & García 1983). Angelelli (1984) gave a mean of 4 g/m³ Au for the richest part of the placer (llampo) and 0.50 g/m³ Au for the barren part, with an irregular distribution. The mass of the gold grains is also irregular; the largest reported mass of gold was 700 g.

MATERIALS AND METHODS

Field site

The gold grains analyzed come from six different areas (Fig. 1): (1) upstream and (2) downstream of Arroyo Cañada Honda (two and five samples were panned in situ, respectively; the two sampling locations were
located 22 km from one another and will be called in this paper 1.CHu and 2.CHd, respectively), (3) upstream and (4) middle stream of Río de La Carpa (two and three samples, respectively, approximately 8 km between the two sampling locations: 3.LCu and 4.LCm, respectively), (5) upstream Río Grande (5.RGu), in the vicinity of the abandoned La Carolina gold mine gallery (five samples), and (6) middle stream of the creek (6.CPm) that runs through Estancia La Primavera, at the foothills of Cerro de Piedra (two samples).

**Sampling**

One hundred and ninety one gold grains were selected from a collection of 19 samples, and 502 electron-microprobe analyses were performed. The 19 samples come from six different locations, as explained above, and each of the samples coming from the same sampling site corresponds to pannings done at the very same place but during different field trips. The grains studied were selected using a quarter method, leading to about 10% of the sample recovered. This fraction was examined under the binocular stereo microscope, to check whether it covers all the populations present in the sample. The same was done for the habits; we studied all the grains not selected to see if there was any habit not represented in the quartered sample. In the few cases where that happened, grains were hand-picked and added to the sample to be studied. Multiple grains were mounted in epoxy sections, some with the longer axis horizontal and some vertical, to have a better view of the rim where present. Later, it became clear that there was no difference in the observations performed in horizontally or vertically oriented grains. This mounting process was selected to get all grains exposed; after that, they were cemented in place and then polished in a conventional manner. The Hg-contaminated particles were not removed before the quartering process, so that population would be also included in the samples to be studied.
Analysis of gold grains

Electron-microprobe analyses were performed in wavelength-dispersion mode using a Cameca SX–50 instrument at the Department of Geological Sciences, University of Manitoba, Winnipeg, Canada. We used a beam diameter of 2 μm, an acceleration potential of 20 kV, and a sample current of 20 nA, measured on a Faraday cup, with counting times of 20 seconds for each element. The following standards were used: Au100 (AuMg), Au60Ag40 (AgLa), CuFeS2 (CuKα), HgTe (HgMβ). The lower limits of detection for Cu and Hg are 0.06 and 0.12 wt.% respectively. Data were reduced using the PAP routine of Pouchou & Pichoir (1984, 1985).

The analyses were performed on each of the polished grains; we analyzed both core and rim of each grain. In some grains without rim, or with a discontinuous rim, we found that the margin has a different appearance than the rest of the grain; we have analyzed those areas and called them “borders”.

The analysis of an unusual, cubic mineral phase observed using conventional techniques was performed using a Hitachi S–4500 field-emission gun scanning electron microscope (FEG–SEM) fully equipped with an EDAX™ system. Before energy-dispersion spectroscopy (EDS; EDAX™), the position and “cubic” nature of the grain were confirmed using the back-scatter mode. An area of approximately 100 nm² in the center of the cubic mineral, and a second region located approximately 5 μm into the gold grain from the interface between the cubic mineral and the margin of the gold grain, were analyzed by EDS at an accelerating voltage of 15 kV.

RESULTS: PHYSICAL CHARACTERIZATION OF GOLD GRAINS

The gold grains have different morphologies (Table 1). Many grains from various sampling sites have crystal (or crystal-like) faces, which presumably represent faces on octahedra of gold, or perhaps in some cases, the inherited imprints from former adjacent minerals.

Arroyo Cañada Honda, upstream (1.Chu)

The grains are angular and irregular; a rim is generally absent, but where present, it is thin and discontinuous (Fig. 2b) and only slightly darker than the rest of the grain (Fig. 2c). The presence of “rim”-like enrichments in these grains, which are present along fractures inside the grains, is noteworthy (Figs. 2b, c). Also, some of the grains contain several small (approximately 20 μm) inclusions of galena, quartz, and less abundant, but larger (100 to 500 μm) inclusions of an iron oxyhydroxide. Gold grains of up to 19 g have been recovered from this site (Sr. Lucero 1996, pers. commun.). An unusual crystal (Fig. 2d) recovered during panning, in the foothills of Cerro Tomolasta, and given to the authors by R. Lianza, has 1.5 mm distorted [111] hopper crystal, similar to some crystals found at Mariposa County, California, U.S.A. (Leicht 1982).

Arroyo Cañada Honda, downstream (2.Chd)

The gold grains range from rounded grains (Fig. 3a) to folded leave-like masses (Fig. 3b), flattened grains, to arborescent grains; those arborescent forms are in some cases formed by small crystals “cemented” together

<table>
<thead>
<tr>
<th>Location</th>
<th>#</th>
<th>Size (mm)</th>
<th>Shape or Habit</th>
<th>Yellow color</th>
<th>Rim</th>
<th>Inclusions</th>
<th>Coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.CHu</td>
<td>24</td>
<td>5 x 3 to 1 x 0.5</td>
<td>Angular, irregular</td>
<td>Pale</td>
<td>Generally absent</td>
<td>Quartz, galena</td>
<td>Common and in large patches</td>
</tr>
<tr>
<td>2.Chd</td>
<td>44</td>
<td>7 x 6 to 2 x 1</td>
<td>Round, arborescent, flat, crystals, leaves, wires</td>
<td>Dark to medium</td>
<td>Discontinuous</td>
<td>Quartz, pyrite</td>
<td>Occasional and thin</td>
</tr>
<tr>
<td>3.LCu</td>
<td>24</td>
<td>3 x 2 to 0.5 x 0.1</td>
<td>Angular, irregular &gt;&gt; arborescent, round</td>
<td>Pale to dark</td>
<td>Generally absent</td>
<td>Quartz &gt;&gt; petzite</td>
<td>Common and in large patches</td>
</tr>
<tr>
<td>4.LCm</td>
<td>18</td>
<td>5 x 3 to 1 x 0.2</td>
<td>Irregular, arborescent &gt;&gt; round, leaves</td>
<td>Pale to dark</td>
<td>Discontinuous</td>
<td>Quartz, pyrite</td>
<td>Omnipresent and thin</td>
</tr>
<tr>
<td>5.RGu</td>
<td>57</td>
<td>1 x 0.5 to 0.1</td>
<td>Irregular (abraded)</td>
<td>Dark</td>
<td>Discontinuous</td>
<td>Quartz</td>
<td>Occasional and thin</td>
</tr>
<tr>
<td>6.CPe</td>
<td>24</td>
<td>2 x 1 to 0.5 x 0.2</td>
<td>Irregular to round &gt;&gt; arborescent</td>
<td>Dark to very dark</td>
<td>Discontinuous</td>
<td>Quartz (rare)</td>
<td>Occasional and thin</td>
</tr>
</tbody>
</table>

Sampling sites 1 to 6 are shown in Figure 1. Symbols: CH: Arroyo Cañada Honda; LC: Río de La Carpa; RG: Río Grande; CP: Creek at foothills, Cerro de Piedra; u: upstream; d: downstream; m: middle stream; #: number of grains studied; Coating: Fe-oxyhydroxide.
Inclusions (approximately 100 for the recovering of gold. A few grains contain small 14.43% at the rim and core, respectively) presumably that possesses a high Hg content (up to 24.87% and cases, the rim has a “brain-like” appearance (Fig. 4b) the pale ones are due to Hg contents in them. In some few grains have both light and dark rims coexisting, and 1 continuous and has a darker color than the core of the grains. In some cases, the core–rim color relation is inverse; a rim is generally absent, but where present, it is discon rounded contours were also observed. In most cases, the rim is generally absent, but where present, it is discontinuous and has a darker color than the core of the grains. In some cases, the core–rim color relation is inverse; a few grains have both light and dark rims coexisting, and the pale ones are due to Hg contents in them. In some cases, the rim has a “brain-like” appearance (Fig. 4b) that possesses a high Hg content (up to 24.87% and 14.43% at the rim and core, respectively) presumably remaining from the amalgamation process used locally for the recovering of gold. A few grains contain small inclusions (approximately 100 μm) of quartz crystals (Fig. 4b) and, in one case, we found a small inclusion (35 × 15 μm) of petzite, Ag₃AuTe₂. Large patches (up to 400 μm) of an iron oxyhydroxide are common within the grains.

**Río de La Carpa, upstream (3.Leu)**

The grains are mostly angular and irregular; some have a well-developed arborescent habit (Fig. 4a), but rounded contours were also observed. In most cases, the rim is generally absent, but where present, it is discontinuous and has a darker color than the core of the grains. In some cases, the core–rim color relation is inverse; a few grains have both light and dark rims coexisting, and the pale ones are due to Hg contents in them. In some cases, the rim has a “brain-like” appearance (Fig. 4b) that possesses a high Hg content (up to 24.87% and 14.43% at the rim and core, respectively) presumably remaining from the amalgamation process used locally for the recovering of gold. A few grains contain small inclusions (approximately 100 μm) of quartz crystals (Fig. 4b) and, in one case, we found a small inclusion (35 × 15 μm) of petzite, Ag₃AuTe₂. Large patches (up to 400 μm) of an iron oxyhydroxide are common within the grains.

**Río de La Carpa, middle stream (4.Lcm)**

The great majority of the grains is irregular, developing an arborescent-like habit (Fig. 5a) and, in some cases, thin leaves (Fig. 5b). Rounded grains are less abundant, but present. The gold grains enclose quartz and pyrite; the grains containing pyrite, almost without exception, have a thin coating of iron oxyhydroxide. Most of the grains have a pale to dark yellow color, commonly with a discontinuous darker rim surrounding them. A few grains possess the brain-like rim, rich in Hg.

**Río Grande, upstream (5.Rgu)**

The old La Carolina (Fig. 1) gold mine (gallery mouth) is in the vicinity, upstream from the sampling site. Most of the grains are abraded and irregular, their color in most cases is dark yellow, or pale yellow where Hg-contaminated. In either case, the rim is discontinuous and invariably darker than the core. We note the unusual presence of small (up to 4 μm), cubic [100] crystals (Figs. 6a, b), composed of gold (Figs. 5c, d). In some of the grains, the rim has the “brain-like” appearance as described above (Fig. 4b).
grains having more delicate morphologies (for simplification, we describe the latter as arborescent in general). The core compositions of the gold grains in samples 4.LCm range between 67 and 77 wt.% for the arborescent varieties, and between 73 and 76 wt.% for the populations of rounded grains.

In most of the cases, the rim is richer in gold than the core, but a few grains have an Au-depleted rim. The latter case is especially common, but not limited, to the presence of mercury contamination. Anthropogenic mercury, a remnant from the amalgamation process used in the area, seems to be restricted to samples from Río de La Carpa and Río Grande. Where Hg is present, it is localized primarily along the rim of the gold grains, although two analyses from the core revealed 1.6 and 14.4 wt.% Hg. Where the mercury contamination reaches values higher than 14%, it corresponds to a pale yellow, “brain-like”, spongy crown. When the content in Hg is lower than 14%, it only affects the color (the higher the Hg content, the lighter the yellow color), but not the texture of the rim.

One of the gold grains from the 5.RGu sampling site, possessing unusual cubic-section crystals occurring along the margin of the gold grain (Fig. 6a) was examined using back-scattered FEGSEM images (Fig. 6b); these reveal a porous, submicrometric sponge-like structure composed of gold (Fig. 6c), in contrast to the border within the gold grain, which is composed of gold and silver (Fig. 6d).

Fig. 2. Typical versus unusual features. SEM back-scattered electron images of gold grains. Scale bar: 100 μm. (a) From sample site 6.Cpm, grains showing unusual internal zonation: dark area with lower content of gold (65% Au) than the brighter, outer area (75% Au). (b) Sample site from 1.CHu, possessing the typical, discontinuous rim around the border and internal “rims” along fractures. (c) A reflected-light micrograph (site 2.CHd) of a gold grain containing a common discontinuous rim along the border and fractures. (d) From site 1.CHu, an unusual flattened and distorted hopper crystal of gold.
FIG. 3. Typical morphologies of gold grains recovered from the sampling site 2.CHd; scale bar: 300 μm. (a) Rounded gold grain. (b) Folded leaf of gold, giving the appearance of a rounded gold grain. (c) Slightly rounded arborescent masses of branching distorted octahedra of gold. (d) Leaf of gold with overgrowth of small flattened, distorted octahedra of gold. (e) Wire gold. (f) Gold crystal.
**DISCUSSION**

The sources of placer gold

For several reasons, we suspect that there are multiple sources for the detrital gold encountered in the La Carolina area. Most important is the coexistence at the same sampling site of rounded grains and others that have a more delicate habit (Fig. 2). The delicate nature of the arborescent grains and the ease with which they are deformed in the placer environment suggest that they may come from a source closer than either the rounded grains or the associated folded leaves. Supporting this interpretation is the coexistence of families of grains with different core compositions at the same sampling site, which also suggests multiple sources of the gold.
grains (Knight et al. 1999b). There is also a tendency toward enrichment of the minimum fineness of the core (Table 2) from the three sampling sites to the west (3.LCu, 4.LCm and 6.CPm) compared with placer gold sampled eastward (1.CHu, 2.CHd and 5.RGu).

The average Au content of the core, 58–74 wt.%, indicates that the source(s) that supplied the material had gold of a low fineness. The variable and broad range of fineness of the gold grains found in the area is typical of low-sulfidation epithermal-type deposits (Morrison et al. 1991). This suggestion agrees with the composition of gold particles described from a primary gold-bearing deposit in the area, La Estancia at (Fig. 1), a low-sulfidation epithermal-type deposit characterized by coexistence of Au–Ag alloy and gold; the former predominates and has an average fineness of 670 (Márquez-Zavalía & Galliski 1994).

In the study area, there are several small epithermal deposits, such as La Carolina, La Estancia and La Rica mines, and possibly La Juana and La Carpa mines (Fig. 1, Table 6). The La Carolina mine is located near sampling site 5.RGu, La Estancia and La Rica mines are nearer sampling site 1.CHu, whereas the other two mines, La Juana and La Carpa, are located between sampling sites 3.LCu and 4.LCm. In the area, there are also several linear zones of alteration, where the disseminated mineralization consists of gold and silver associated mainly with pyrite; one sample of pyritic schist gave 1 g Au/t, 2 g Ag/t and traces of As (Bassi 1990).

We are not aware of any other epithermal-type deposit in this area; using the Klondike placers as an analogy (see Knight et al. 1999b), however, we concede that some occurrences may be either unexposed at present or have been erosionally stripped. Unfortunately, there are no values of fineness of gold available from any of the mines except La Estancia.

Even if grain morphology is generally a less reliable indicator of provenance than fineness (Grant et al. 1991), or at least not a sufficient argument for determining the existence of multiple sources, we know of the existence of several gold deposits in the area (Fig. 1, Table 6) and at least some must have supplied the gold, if not all of them. In the La Estancia epithermal-type deposit (Fig. 1), fine-grained (1–10 μm), pure gold and the more abundant and coarser (10–100 μm) irregular grains of Au–Ag alloy coexist. Besides, an interpretation of multiple sources may indicate as well, according to Giusti & Smith (1984), that either the gold is derived from different areas, or that gold of different compositions was derived from a single deposit with gold derived from more than one stage of emplacement. Suffice it to say, all the sources are restricted to the deposits from Tertiary igneous rocks in the area (see also Bassi 1948, Rosello & Castro 1995).

Finally, in one sample (6.CPm), we found rounded grains of gold together with one crystal of petzite with some of its crystal faces still perfectly preserved. This fact also suggests multiple sources for the material, because petzite is both soft (hardness 2.5–3) and brittle, so that any significant transportation would obliterate its crystal faces.

### Formation of the rim

The Au and Ag values of the core and rim of grains collected in the two streams with upstream and downstream depositional affinities (Arroyo Cañada Honda: 1.CHu and 2.CHd, and Río de La Carpa: 3.LCu and 4.LCm; Fig. 1, Table 4) suggest that the Au-rich compositions in the rim possibly reflect a combination of distance and duration of transport (Fig. 7). Evidence for progressive growth of the gold grains with transportation is indicated by the fact that those grains collected upstream generally lack a rim, whereas grains sampled further downstream generally have a rim, even if it is discontinuous (Table 1). Together with observations of grain-growth in placer gold in New Zealand (Craw & Youngson 1993, Youngson & Craw 1993, 1995), this would suggest that the gold grains collected at the downstream site have grown larger and more homogeneous than those collected at the upstream site.
phenomenon may reflect the overall process: the further the gold grain is transported downstream, the more enriched the rim becomes, the greater the proportion of the grains that possess a rim, and the thicker the rim becomes.

Gold grains recovered from the downstream sites Arroyo Cañada Honda (2.CHd) and Río de La Carpa (4.LCm) are generally depleted in silver in their core and rim. We attribute this to enrichment of gold in the rim during rim accretion and possibly to selective leaching of Ag either during transport or even after deposition.

In some cases, we observed thin “veins” that locally penetrate and dissect some of the grains along fractures or cracks; these veins have compositions different from the core, and generally they are also distinct from rim compositions. These veins, also described by Robinson et al. (1999), may result from precipitation of gold in open fissures in gold grains, either during transportation or after deposition in the placer, unless they represent a region where two or more smaller grains of gold were “glued” together. Hence, the mechanism that produces a rim (Craig & Callahan 1989) and the one forming these veins may have similarities.

The contact between core and rim is invariably very sharp, and may result from electrochemical processes active either in the stream or in the stream sediments (Mann 1984, Groen et al. 1990, Krupp & Weiser 1992, Knight et al. 1999a), or from processes of dissolution of gold and silver followed by gold precipitation in sur-
face and near-surface environments (Wilson 1984, Groen et al. 1990, Southam 1998). We consider the latter model more likely because electrochemical leaching of Ag would most likely produce a regular rim rather than the discontinuous rim observed (Figs. 2b, c). The presence of a discontinuous rim is also considered to occur in active abrasive sediments (Knight et al. 1999a). The rim may also exhibit an irregular shape and a complex texture, which might be a result of solid-state reactions rather than deposition from solution, with the reaction front moving inward, at different rates in different directions and locations (Robinson et al. 1999).

Formation of secondary gold

Several samples from Cañada Honda (2.CHd) possess overgrown gold crystals over gold grains (e.g., Fig. 3d), suggesting that secondary precipitation of gold had occurred only after the host grain was formed. In a Brazilian placer system, secondary crystals of gold were recovered by gravity separation several years after placer mining had recovered rounded grains, indicating that the new secondary gold had formed either in situ after mining or had been transported into this system from a nearby source (Freise 1931).

The cubic habit of gold shown in Figure 6a and 6b represents an unusual development of secondary gold that presumably resulted as a Au–Hg amalgam (Desborough & Foord 1992) from the Hg present in this system, followed by removal of Hg, which was not detected by EDS analysis (Fig. 6c). The submicrometric structure of this porous, spongy gold is finer than that typically associated with the reaction of Hg with surfaces of grain grains which produce a “brain-like” ap-
pearance (Fig. 4b; Knight 1993), but it is consistent with the ≤5 μm monoclinic, pseudo-orthorhombic Au–Hg mineral described by Desborough & Foord (1992).

The presence of metal sulfides within some of the grains and local iron oxyhydroxide coating suggests a primarily oxidizing environment of weathering. The transformation of metal sulfides to iron oxyhydroxides is an indication that chemical and bio-oxidation of metal sulfides has either occurred or is still occurring in this placer system (Nordstrom & Southam 1997). Furthermore, the formation of sulfoxyanions through either abiotic or biotic mechanisms (Schippers et al. 1999) could have contributed thiosulfate as an effective gold-complexing agent to promote weathering and dissolution (Vlassopoulos & Wood 1990), leading to formation of secondary gold. This weathering environment was undoubtedly aided by plant (Baker 1978, Bowell et al. 1993) and even bacterially derived organic phases (Korobushkina et al., 1974, 1976, Vlassopoulos et al. 1990, Southam & Beveridge 1994, 1996) that would also have facilitated formation of secondary gold.

**Anthropogenic Hg**

Where present, Hg is encountered mostly in the rims of the grains. However, two analyses performed in the core area gave high Hg values (1.6 and 14.4 wt.% Hg). The composition of those grains, from sampling sites 5.RGu and 3.LCu, respectively (Au, Ag, Cu, Hg) is: 93.76, 5.59, 0.00, 1.64 and 78.76, 4.82, 0.03, 14.43. For these compositions, we strongly believe that the rim was thick enough to still be covering the grain after the grinding and polishing process, and that they have the appearance of rimless grains.

We interpret all the Hg in the grains as being anthropogenic. Weishanite, (Au,Ag)1.2Hg0.8, the only IMA-approved mineral containing Au and Hg, was not recognized in the samples. Even though there are numerous sources for anthropogenic mercury, such as fertilizers, medical compounds (antiseptics and diuretics), and some now-prohibited agricultural fungicides and herbicides (Meisser & Brugger 2000), we believe that all the Hg identified here is from the amalgamation processes used to recover the gold.

The placer gold from the San Luis Range of Argentina is a good example of a natural environment that possesses a limited anthropogenic impact. In this environment, gold grains possessing a core of Au–Ag alloy have become enriched in higher-fineness gold as a surface coating. The gold grains are also “glued” together to form larger grains (aggregates). Gold grains do grow in low-temperature geochemical settings but, more importantly, they become gold-enriched either by loss of silver or by loss of silver followed by reprecipitation of gold. The net effect, recognized long ago and confirmed here, is that the overall composition becomes more gold-

![Fig. 7. Histograms of core (plain gray pattern) and rim (dotted gray pattern) compositions of gold grains collected from the six sampling sites: Arroyo Cañada Honda upstream (1.CHu) and downstream (2.CHd), Río de La Carpa upstream (3.LCu) and middle stream (4.LCm), Río Grande upstream (5.RGu) and Creek at the foothills of Cerro de Piedra, middle stream (6.Cpm).](image-url)
rich as the grains move downstream or sit in the sedimentary environment.

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