HYDROTHERMAL SYNTHESIS
OF GOLD GRAINS
WITH APPARENT FIVE-FOLD SYMMETRY

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ABSTRACT

Crystals of gold with anomalous symmetry have been synthesized at 300°C, P_{sat} using hydrothermal techniques. Four crystals with diameters of 50 to 60 μm display a pentagonal dipyramidal (decahedral) morphology. More typically, the gold crystals have flattened, pseudohexagonal or elongate, prismatic habits. Some of the latter also appear to possess a five-fold axis of symmetry, and look very similar to gold "fünflings," that have been reported in natural specimens. All of the crystals are gold-rich, with small amounts (< 2 atomic %) of silver and silicon present in solid solution. The unusual morphology is attributed to either noncrystallographic shell packing or multiple twinning. This study is the first to illustrate that gold crystals with external five-fold symmetry can nucleate and grow to sizable dimensions in a hydrothermal environment. The occurrence of multiply-twinned particles of gold and other precious metals may be more widespread in nature then previously recognized.

Keywords: gold, crystallography, hydrothermal, geochemistry, multiply-twinned particles, pentagonal morphology, experimental, ore deposits.

SOMMAIRE

Des cristaux d'or natif possedant une symétrie anormale ont été synthétisés à 300°C, P_{sat} par voie hydrothermale. La dipyramide pentagonale (décaédrique) est la morphologie dominante observée sur quatre cristaux ayant un diamètre de 50 à 60 μm. Typiquement, les cristaux ont un habitus soit applati, pseudo-hexagonal, ou bien prismatique, allongé. Quelques-uns de ces cristaux semblent aussi montrer un axe de symétrie d'ordre 5, et ressemblent aux macles dites "fünflings" que l'on peut observer sur des échantillons naturels d'or natif. Tous les cristaux sont assez purs et contiennent de petites quantités (< 2% atomique) d'argent et de silicium en solution solide. Leur morphologie inhabituelle serait due à soit un empilement non cristallographique de coquilles, soit à un maclage multiple. Cette étude est la première à illustrer le fait que des cristaux d'or qui présentent une symétrie externe quinaire peuvent germiner et croître jusqu'à des dimensions appréciables dans un milieu hydrothermal. Les particules d'or et d'autres métaux précieux sous forme de macles multiples qui miment une symétrie d'ordre 5 pourraient être plus répandues dans la nature qu'on ne le croit.

Mots-clés: or, cristallographie, hydrothermale, géochimie, particules à macles multiples, morphologie pentagonale, experimental, gîtes minéraux.

INTRODUCTION

Pentagonal crystals of gold were observed in nature as early as the turn of the century (Hintze 1904, Goldschmidt 1918). These extremely rare crystals were termed "fünflings" (fivelings), in reference to their unusual habit (Fig. 1), and were explained by a combination of twinning and inhomogeneous growth (Hintze 1904). This phenomenon was essentially ignored until a series of papers documented the propensity of gold, when rapidly evaporated under high vacuum or in an inert gas atmosphere, to nucleate as clusters of atoms with nearly perfect decahedral (*Dh*) or icosahedral (*Ic*) forms (Ino 1966, Schwoebel 1966, Allpress & Sanders 1967, Ino & Ogawa 1967, Kimoto & Nishida 1967, Komoda 1968, Gillet & Gillet 1972, Heinemann *et al.* 1979, Marks & Smith 1981, Duff *et al.* 1987, Mitome *et al.* 1989). Similar particles have been observed for other *fcc* metals (*e.g.*, Ag, Pd, Pt, Ni), as well as Si and Ge (Melmed & Hayward 1959, Gillet 1977, Howie & Marks 1984, Renou & Penisson 1986). The apparent five-fold symmetry of these solids was interpreted to be an artifact of twinning (Ino 1966), hence the term multiply-twinned-particle, or MTP. These solids should not be confused with quasi-crystals (Schechtman *et al.* 1984), the only compounds known to possess exact five-fold symmetry.

Although it has been proposed that the *Dh* and *Ic* morphologies are the thermodynamically stable forms of gold at very small particle sizes (Howie & Marks 1984, Marks 1984), it has also been assumed that these solids must revert to a more typical *fcc* structure as grain size increases. Most investigators have argued that this transition occurs at particle diameters somewhere in the range 100 to 200 Å. However, gold grains with perfect *Dh* and *Ic* morphology up to 30 µm in diameter were recently synthesized at 40°C in aqueous media (Hernández *et al.* 1991), and Gammons & Williams-Jones (1995) grew similar decahedral crystals of gold up to 60 µm in diameter in a 300°C hydrothermal experiment. These observations prove that five-fold symmetry in gold is not a phenomenon restricted to atomic clusters, but may in fact be assembled in dimensions that are nearly visible to the naked eye.

The purpose of this paper is to record in greater detail the external morphology of the gold crystals synthesized by Gammons & Williams-Jones (1995), and to speculate about their origin. Whereas most of the investigators cited above synthesized their gold particles using methods that have very little in common with geological systems, the studies of Hernández *et al.* (1991) and Gammons & Williams-Jones (1995) indicate that gold fünflings may nucleate and grow from aqueous solutions by a conventional mechanism of precipitation. Therefore, it seems plausible that multiply-twinned particles may play an important role in the growth of gold crystals in natural aqueous environments, a possibility that has previously been overlooked by the geological community.
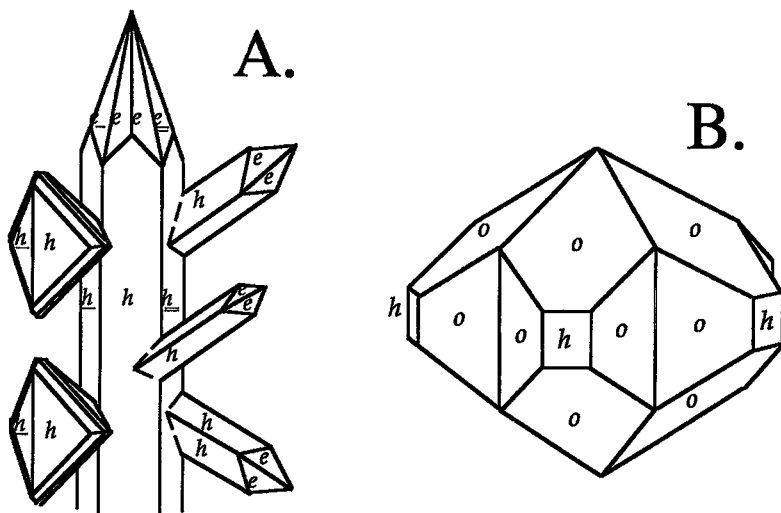

FIG. 1. Line drawings of gold "fünflings", modified after Hintze (1904). No scale was provided in the original reference. The faces labeled *h*, *e* and *o* correspond to the (100), (210), and (111) forms, respectively. The smaller crystals attached to the surface in (a) are unrelated to the twinning. According to Hintze (1904), enlargement of the (100) faces in (b) would lead to a prismatic crystal, as in (a).

METHODS

The discovery of the gold decahedra in this study occurred during the execution of a series of hydrothermal experiments in which the solubilities of gold and silver were measured under conditions of controlled pH and oxidation state. The methodology of this study has been described in detail elsewhere (Gammons & Williams-Jones 1995), and is only briefly summarized here.

In each experiment, a thin foil of pure gold or Au–Ag alloy (electrum), along with a pressed pellet of AgCl (chlorargyrite), were reacted at 300°C with solutions of varying HCl concentration for a duration of one month. The reactants were contained in sealed silica tubes which, in turn, were placed inside small pressure vessels. Temperature was maintained at $300 \pm 1.0°C$ using a laboratory oven with forced air convection, and pressure was fixed by coexistence of liquid + vapor inside and outside of the tubes. Temperature gradients along the length of each silica tube "autoclave" probably did not exceed 0.1°C at any one time, owing to convection of fluid and steam on both sides of the tube walls. At the end of the experiment, the pressure vessels were inverted and allowed to cool slowly to room temperature. A narrow constriction near one end of the silica tubes prevented the solid reactants from contacting the cool solution during and after the quench. The silica tubes were stored in the dark (to avoid photo-degradation of AgCl), unopened and in their inverted position, for a period of 1 to 2 weeks. During this time, many of the solutions gradually turned yellow, with concomitant precipitation of very fine particles of gold. This phenomenon was interpreted by Gammons & Williams-Jones (1985) as a disproportionation reaction wherein aurous (Au^+) chloride complexes slowly break down upon cooling to a mixture of auric (Au^{3+}) chloride complexes (which are yellow) and metallic gold. The quenched solutions and precipitates were digested and analyzed for ΣAg and ΣAu via atomic absorption spectroscopy (AAS). The solid reactants were recovered, rinsed thoroughly in water, dried, and set aside in the dark prior to analysis via scanning electron microscopy (SEM), electron-dispersion spectrometry (EDS), and wavelength-dispersion spectrometry (WDS), using a JEOL 8900–L electron microprobe.

RESULTS

The results of the solubility experiments were discussed in detail by Gammons & Williams-Jones (1995), who derived equilibrium constants for the dissolution of both gold and silver as chloride complexes ($AuCl_2^-$, $AgCl_2^-$) at 300°C. Because dissolution of the Au–Ag alloys was found to be nonstoichiometric, the composition of the surfaces of

the alloys changed during the experiment, usually becoming more gold-rich. In addition, in some (but not all) experiments, crystals of Au-rich alloy with exquisite morphology nucleated and grew on the surfaces of the AgCl pellets. These are the crystals of interest in this study. Because the solid reactants were separated from the solutions during the quench, these crystals could only have formed during the 300°C experiment.

Although gold crystals were found on the AgCl pellets in several samples, all of the specimens with unusual morphology discussed in this paper grew during a single experiment (#1.4 of Gammons & Williams-Jones 1985). In this run, chlorargyrite and Au–Ag alloy ($X_{Au,initial} = 0.91$) were reacted with a 3.0 m HCl solution for a period of 1 month. The calculated pH, $\log a(Cl^-)$ and $\log f(O_2)$ values at 300°C were 0.14, –0.53, and –26.1, respectively (Gammons & Williams-Jones 1995). For reference, the latter value is approximately 4 log units below the hematite–magnetite boundary. The measured ΣAu and ΣAg solubilities were 610 and 17,100 ppm, respectively. Preferential dissolution of silver from the alloy resulted in a shift to a more Au-rich composition ($X_{Au,final} = 0.98$).

Most of the crystals that nucleated and grew on the surface of the AgCl pellets display a flattened pseudohexagonal or prismatic habit. However, four crystals with decahedral or pseudodecahedral morphology were identified on the surface of the AgCl pellet in experiment #1.4 (Fig. 2). Although the four crystals show a number of differences in detail, all are approximately the same size (50 to 60 µm in diameter). The crystal in Figure 2a has the simplest morphology: a nearly perfect decahedron with sharp, well-defined edges. The form of this crystallite is a pentagonal dipyramid {11.1} with point-group symmetry (by extension of the Hermann–Mauguin international symbols) $10m2$ (Cecil Schneer, pers. comm. 1995). It is identical to the decahedra synthesized at 40°C by Hernández et al. (1991), but is approximately twice as large. The crystal in Figure 2b is a pseudodecahedron in which complicated faceting is displayed around the perimeter of the field of view. Note also the interesting star-shaped indentation at the axis of symmetry, which is in the shape of a regular pentagram. The crystal in Figure 2c is similar to that in Figure 2b, although the indentation is off-center, and the five faces of the decahedron do not meet at a single apex. In addition, a complicated step-like structure is displayed along the five edges that project from the center of the crystal. The crystal in Figure 2d is vaguely similar to the first three grains, but shows considerable deterioration of the decahedron structure at the expense of the more complicated faceting along the perimeter of the crystal.

The crystals in Figures 3a and 3b, which also nucleated on the AgCl pellet in experiment #1.4, have forms that are more typical: an elongate prism
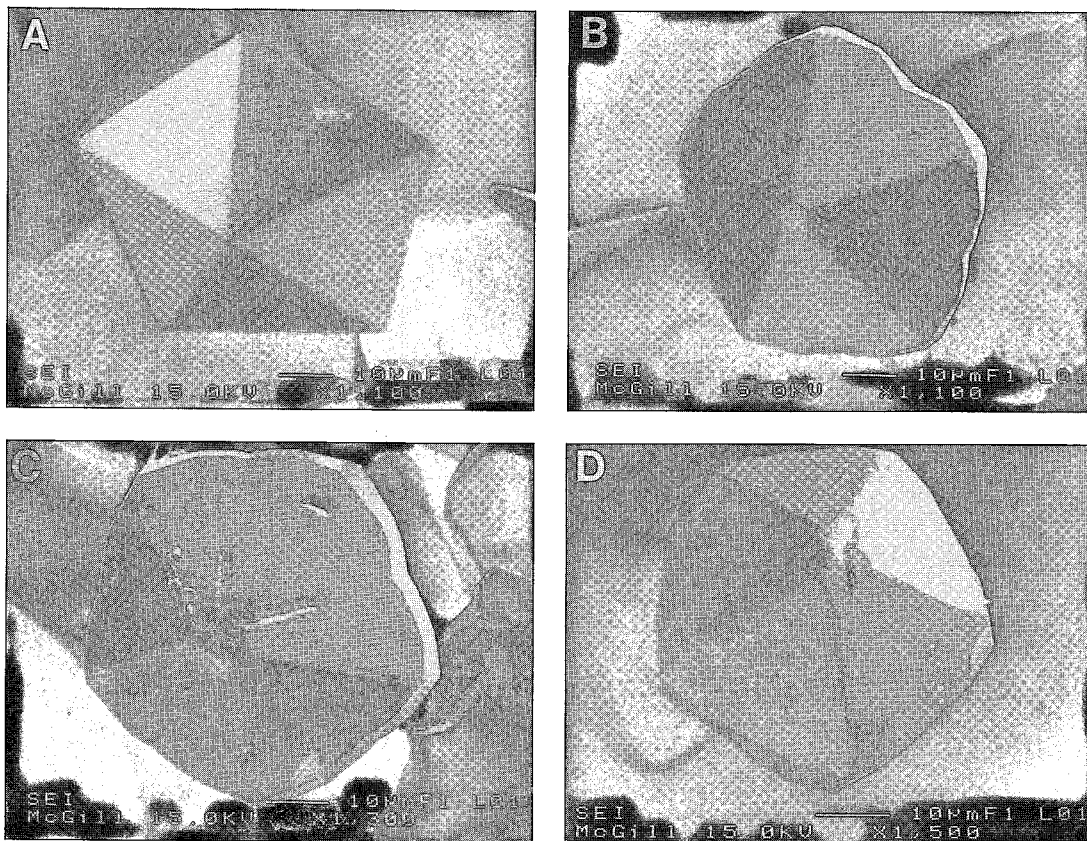
Fig. 2. Scanning electron microscopy (SEM) images of pentagonal gold crystals formed during the 300°C hydrothermal experiment. The substrate is AgCl. The four decahedra in (a) to (d) formed at 300°C, and have been arranged in a sequence considered to reflect the decay of the decahedral shell at the expense of more complex crystal faceting around the perimeter of each grain. This change in texture may be due to hydrothermal annealing during the 30-day experiment.

(Fig. 3a), and a flattened, hexagonal plate (Fig. 3b). Although only three faces are visible in the grain of Figure 3a, this crystal may also be a fünfling, very similar to the specimen observed by Hintze (1904) and shown in the drawing (Fig. 1a). The synthetic crystal contains two small twins projecting from its lower end, which bear a certain resemblance to the crystals attached to the surface of the gold crystal drawn by Hintze. More importantly, the angles and overall shape of the two fünflings, as they appear in their respective two-dimensional illustrations, are nearly identical.

A few samples of gold crystals that precipitated from the quenched solutions after cooling to room temperature were examined by SEM–EDS to compare with the crystals that formed at high temperature. Figures 3c and 3d show some of the more common morphologies encountered: flat, pseudohexagonal or trigonal plates (Fig. 3c), slender, acicular to rod-shaped prisms (Figs. 3c, d), and small, equidimensional twins with cubic habit (Fig. 3d). Although some of these grains have dimensions comparable to those that formed at high temperature, no examples with five-fold symmetry were found.

Semiquantitative EDS analysis of the decahedra confirmed that they are gold, with minor amounts of silver and silicon present in solid solution. Owing to the irregular topography of the decahedra, a quantitative analysis was not possible. However, WDS analyses of neighboring grains with a flattened pseudohexagonal habit, as well as the reacted surface of the electrum foil, yielded concentrations of silver in the range 0.1 to 2 mol % Ag. Thus, it is probable that the decahedra also contain up to 2 mol % Ag. In contrast, the gold crystals that formed at 25°C *via* the disproportionation reaction contain no detectable impurities.
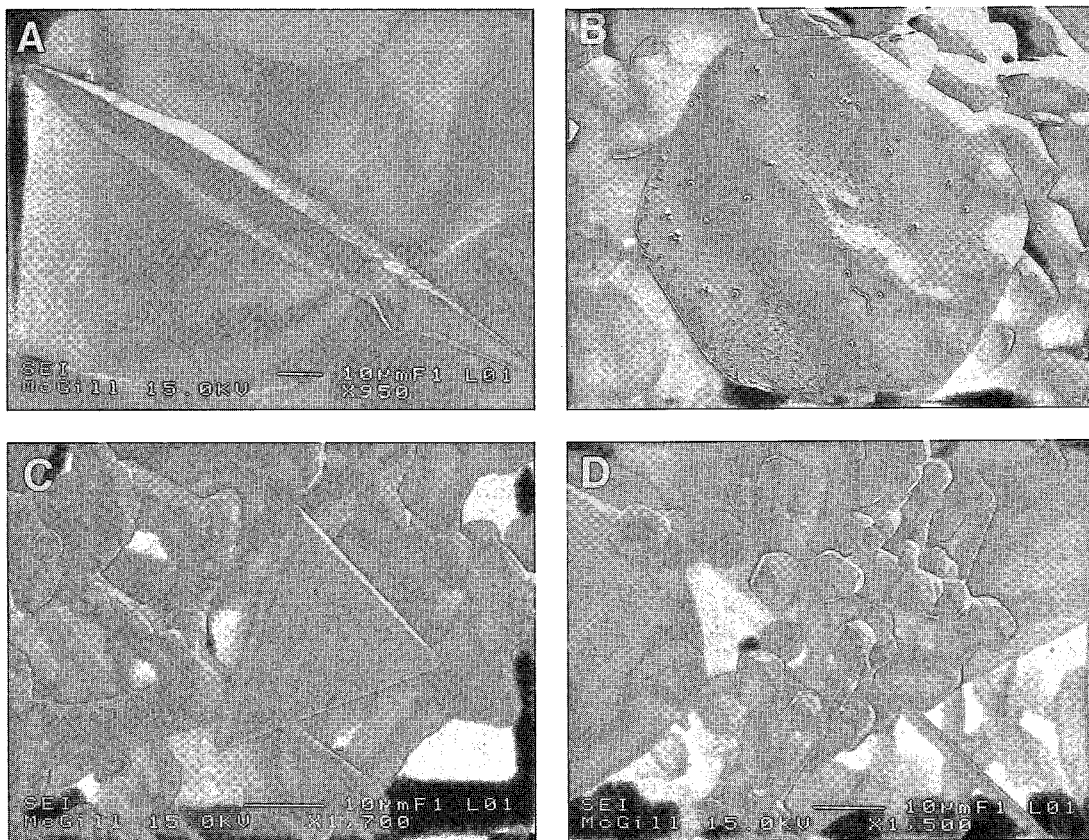
Fig. 3. Additional SEM images. The grains in photos (a) and (b) grew in the same 300°C experiment as the decahedra in Figure 2. Although only three faces are visible for the prismatic grain in (a), this crystal may also be a "fünfling" (cf. Fig. 1a). The hexagonal crystal in (b) is unusually large (500 μm diameter), and is also exceptionally thin, and was deformed during handling. The surface coating is secondary AgCl deposited during the quench, and the botryoidal substrate is the AgCl pellet. A number of smaller crystals of gold also are visible in (b). The gold crystals in (c) and (d) formed at room temperature by the slow disproportionation of aurous chloride complexes to auric complexes + metallic gold. Although a wide variety of morphologies is evident, no examples with obvious five-fold symmetry were found.

DISCUSSION

Although it is difficult to prove how the decahedral crystals of gold formed in this study, a number of hypotheses merit further discussion. First, a mechanism must be proposed to explain why gold dissolved from the Au–Ag alloy and then reprecipitated on the AgCl substrate during the 300°C experiment. In this respect, it is probable that considerable strain was induced into the Au–Ag alloy starting material during the fabrication of the thin foils. Dissolution of gold (and silver) would have been enhanced at highly strained sites on the surface of these foils (e.g., see Fig. 3c of Gammons & Williams-Jones 1995). It is likely that dissolution of gold was especially vigorous at the early stages of the experiment (first several days), owing to the presence of residual $O_2(g)$ in the HCl solutions and also in the vapor space of the tubes.

To maintain equilibrium, gold subsequently reprecipitated at favorable loci elsewhere in the capsule. Apparently, the botryoidal surface of the AgCl pellet was a more effective substrate for nucleation of new crystals of gold than the surface of the strained foils.

If the above model is correct, the gold decahedra would have formed early, and then persisted more or less intact throughout the 30-day duration of the experiment. The differences in morphology of the crystals may reflect the slow transformation from a simple (but unstable) decahedral structure (Fig. 2a), to a more complex (but stable) arrangement depicted by the intricate faceting around the perimeter of many of the grains (Figs. 2b, c, d). The obvious question is then raised: if the decahedral form is unstable, why did the gold atoms arrange themselves in a five-fold manner to begin with? Two possible explanations have been advanced, and are referred to here as the "decahedral

shell packing" (DSP) and "multiply-twinned particle" (MTP) models. They are described separately below, although the author recognizes that the two models are not necessarily mutually exclusive.

Prior to the discovery of pentagonal clusters of gold in the mid-1960s, Mackay (1962) demonstrated that a dense, noncrystallographic arrangement having the outward morphology of an icosahedron can be formed by packing spheres (*i.e.*, individual, uncharged atoms) about a nucleus consisting of 13 closest packed units. Addition of successive layers or shells produces progressively larger icosahedra that obey the geometric relationship:

$$I_n = \tfrac{1}{3}(10n^3 + 15n^2 + 11n + 3) \qquad (1)$$

where n is the number of shells, and I_n is the total number of atoms contained in an icosahedron with n shells. Thus, the first five "Mackay icosahedra" contain 13, 55, 147, 309, and 561 atoms, respectively. Mackay (1962) pointed out that the bulk density of a particle formed by icosahedral shell packing (ISP) will decrease as each successive shell is added, eventually reaching the limit $\rho_{isp} = 0.92937 \cdot \rho_{fcc}$. Some examples of solids that seem to follow this ISP model were recently discussed by Schneer (1988).

A similar model of decahedral shell packing (DSP) may be used to explain the origin of gold particles with pentagonal dipyramid (*Dh*) morphology. The first and second decahedra formed in this way are illustrated in Figure 4. Each new layer adds

$$1 + \sum_{x=1}^{n} 5 \cdot x \qquad (2)$$

atoms to the pre-existing structure, where n is the shell number. The total number of atoms for a *Dh* particle consisting of n shells is given by:

$$I_n = \sum_{x=0}^{n} [1 + \sum_{y=1}^{x} 5 \cdot y] \qquad (3)$$

Thus, the nucleus ($n = 1$) consists of 7 closest packed gold atoms, and the next four decahedra contain 23, 54, 105, and 181 atoms, respectively. It is important to note that both the DSP and ISP models produce solids that have perfect 5-fold external symmetry, but an aperiodic translation structure (Schneer 1988, pers. comm. 1995).

Based on a consideration of surface and volume energetics, Fukano & Wayman (1969) concluded that *Ic* and *Dh* particles of gold formed by shell packing could be stable at very small particle sizes (<200 atoms), but that octahedral (*fcc*) symmetry is favored by increase in grain size. A shell packing model was also adopted by Gillet & Gillet (1972), on

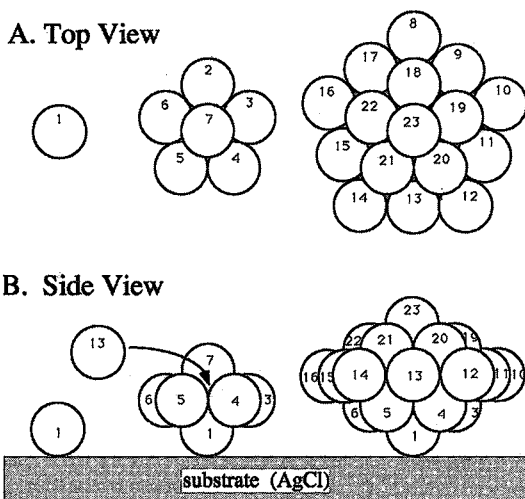## A. Top View

B. Side View

Fig. 4. Sketches summarizing the "decahedral shell packing" model for a *Dh* gold grain. Each sphere represents an individual gold atom, and has been assigned a number from 1 to 23. From left to right, the sketches show the assembly of the first ($n = 7$) and second ($n = 23$) decahedral shells from an aerial perspective (top) and a side view (bottom). In this model, crystal growth occurs by adsorption of a single gold atom onto the substrate, followed by addition of successive layers of pentagonally arranged gold atoms along vectors that propogate away from the substrate.

the basis of high-resolution electron microscopy of *Dh* and *Ic* gold particles that failed to show any crystal defects, as would be expected assuming the MTP model (see below). In contrast, Komoda (1968) proposed that gold particles with *Dh* and *Ic* morphology initially form by a shell packing process, but quickly arrange themselves into multiple twins from a very early stage in the deposition and growth process (*e.g.*, particle diameters <20 Å).

The MTP model of Ino (1966) attempts to explain the unusual morphology of *Dh* and *Ic* gold particles by crystal twinning. Following Ino (1966), a single *Dh* gold particle is comprised of five separate tetrahedra arranged in such a way that each shares two of its four (111) faces, thereby producing an overall decahedral shape (Fig. 5a). However, the fit is not perfect: assuming that each tetrahedron has the normal *fcc* structure of gold, a "gap" of approximately 7° must be made up by strain (Fig. 5a). Numerous diffraction studies have failed to find any evidence for such a misfit (Ino 1966, Allpress & Sanders 1967, Ino & Ogawa 1967, Kimoto & Nishida 1967, Komoda 1968, Gillet & Gillet 1972, Yang 1979, Renou & Penisson 1986), indicating that the strain must be delocalized along twin planes (*i.e.*, edges), or homogeneously distributed throughout the entire crystal (Marks &
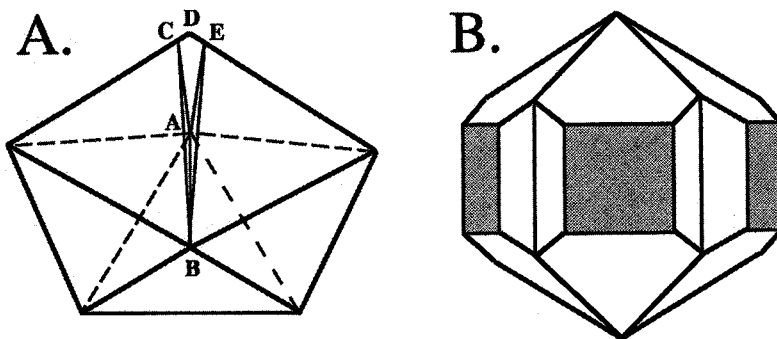
Fig. 5. Sketches summarizing the "multiply-twinned particle" model for a *Dh* gold grain. The simple decahedron in (a) is formed by five adjoining *fcc* tetrahedra twinned about edge A–B. A solid angle misfit of 7° is produced along E–B–C, which must be made up by strain in the crystal structure (from Fig. 9a of Ino 1966). This strain could be partly alleviated by crystal faceting, as in (b), which is taken from Figure 10b of Marks (1984). Note the similarity between this theoretical particle and the natural specimen shown in Figure 1b.

Smith 1981). Theoretical studies (Marks 1984) suggest that some of the internal strain could be alleviated by crystal faceting or re-entrants, leading to more complex geometries, as in Figure 5b. This phenomenon could explain the complex faceting observed around the perimeter of the synthetic crystals in Figure 2. The striking similarity between Figure 5b (drafted according to theory) and Figure 1b (a natural mineral specimen) should also be noted.

Regardless of whether one favors the DSP or MTP models, the photographs in Figure 2 leave little doubt that growth of gold grains with *Dh* morphology is possible to micrometric dimensions. The unusual size of the gold decahedra in the present study and that of Hernández *et al.* (1981) suggests that growth rates are much faster in aqueous media as opposed to the vacuum or inert gas atmospheres employed in previous crystal-growth studies. Once formed, conversion of a decahedral crystal 60 µm in diameter to a more stable structure must involve considerable atomic reorganization, and would therefore be kinetically inhibited (Howie & Marks 1984). The survival of the near-perfect decahedron in Figure 2a proves that this is the case, even in a 300°C hydrothermal solution. However, with time, the decahedra must reorder their internal and external structure to a lower energy state. Changes in external morphology would most likely take place *via* a dissolution – reprecipitation mechanism (Ostwald ripening) along zones of high strain, and would result in a gradual rounding of the overall decahedron shell at the expense of new equilibrium crystal faces or re-entrants (Marks & Howie 1979, Marks 1984). The sequence of photographs in Figures 2a–d indicates that disintegration of the decahedra does indeed appear to take place preferentially at grain edges and corners (Figs. 2b, c and d), concomitant with rounding and an

increase in surface roughness (Fig. 2d).

CONCLUDING REMARKS

This study documents the synthesis of large (up to 60 µm) crystals of gold with anomalous five-fold symmetry, and is the first to show that pentagonal crystals of gold can grow under hydrothermal conditions (300°C, P_{sat}). The crystals in question are nearly visible to the naked eye, but in detail exhibit varying degrees of annealing, presumably to more stable atomic configurations. Because the physicochemical conditions of the experiment are similar to those of ore-forming environments (with the notable exception of pH), it is tempting to consider that gold crystals in nature may, in some cases, grow *via* a similar process. In fact, it is conceivable that growth of gold crystals from supersaturated solutions may *routinely* take place *via* a pentagonal precursor (*e.g.*, by either a shell packing or MTP model). This could have important ramifications for studies of gold adsorption and precipitation from low-temperature solutions (*e.g.*, in weathering or supergene environments), as well as higher-temperature ore fluids. To the author's knowledge, no geochemical or mineralogical study to date has specifically addressed this possibility, although the drawings of Hintze (1904) prove that gold "fünflings" do indeed occur in nature.

It should be emphasized that, out of several dozen solubility experiments, only four decahedral grains have thus far been identified, all of which formed in the same experiment. Other than the presence of the decahedra, there was nothing unusual about this particular experiment. More work clearly is needed to better understand the mechanisms by which gold decahedra are formed and, subsequently, are destroyed.

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