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Natural and Experimental Clues to Understand the Transport and Deposition of Supergene Gold in Western Australia

INTRODUCTION

Supergene gold deposits are relatively small (<1.5 Mt) and of low grade (1-5 g/t), but provide easy start up options for early cash-flow generation for small mining operations (Butt 1998), and such operations are abundant in Western Australia. One question asked is “can the information provided by studying the supergene Au be used as a vector to primary systems?” Hough *et al.* (2007; 2008) have investigated the morphology and geochemistry of Au to unravel some of the mysteries of nugget and single crystal formation that has indicated a need to look closer at both natural and synthetic Au morphologies and environmental constraints that will assist exploration.

Secondary Au deposition occurs through weathering of a primary hypogene Au deposit, dissolution of the Au from the host quartz or sulfide primary minerals, with the Au being mobilized in solution, transported and then deposited via precipitation at a later stage. Gold is inert

in many weathering conditions, but can mobilize when complexed to stable ligands that are commonly found in soil and groundwater (Gray *et al.* 1992). Thiosulfate, organics and halides are believed to be the main ligands that mobilize Au (Butt 1998). In tropical environments cyanide, hydroxide and ammonia may also be functional ligands (Vlassopoulos & Wood 1990; Howell *et al.* 1993). Bacteria have been shown to influence Au solubility and precipitation (Reith *et al.* 2006; Reith & McPhail 2006). A more detailed understanding of the mechanisms of formation of micro- and indeed nano-particulate Au may lead to a better understanding of supergene Au deposits, distance and conditions of mobilized Au, and in turn develop the capability of using morphology of supergene Au in the near surface environment to target larger hypogene Au systems.

A study of saprock fractures at an abandoned open-pit
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Au deposit was conducted to investigate the morphology of Au in the supergene zone and to search for nanoparticulate components. The pit, south of Southern Cross in Western Australia (Fig. 1), was a small Au deposit where localised

primary mineralisation occurs as small, high grade quartz veins, blanketed by 30 m of weathered cover (Fig. 2).

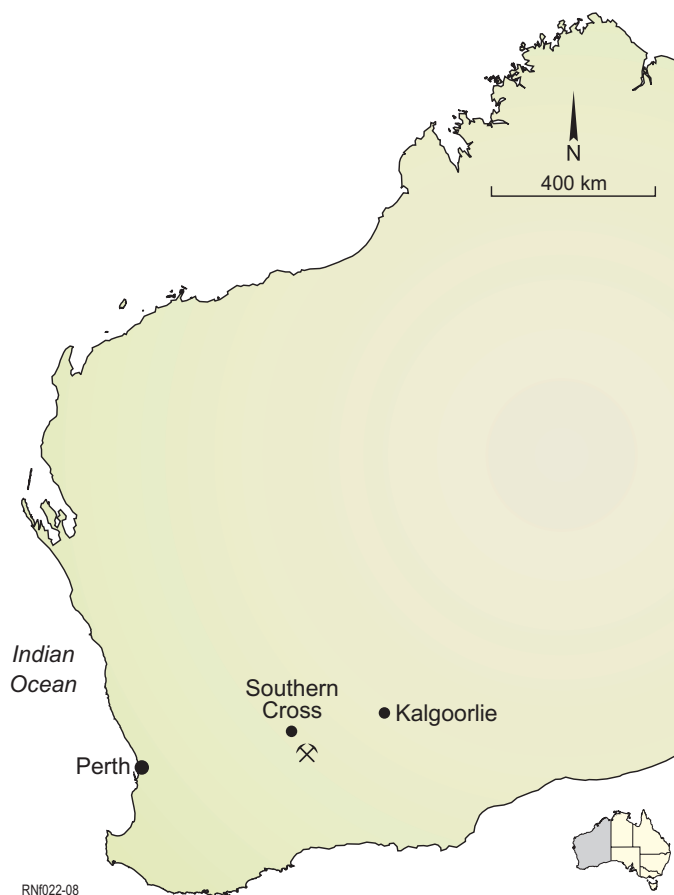


Figure 1. Location of the abandoned open-cut Au pit, approximately 400 km west of Perth, in western Australia.

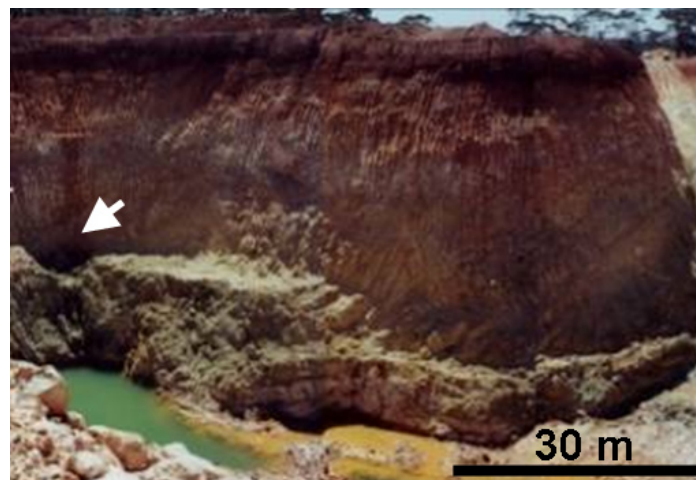


Figure 2. The regolith profile at the abandoned open cut Au pit near Southern Cross. Regolith depth is approximately 30 m, with significant Fe staining of the upper profile. The approximate location of the saprock sample is shown by the white arrow.

Following the field observations, laboratory experiments were conducted to determine if the morphologies of Au observed in nature could be produced synthetically, and as a result indicate potential mechanisms of formation and deposition, as well as to identify key ligands involved in transportation.

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METHODOLOGY

Saprock materials were collected from the open-pit at approximately 30 m depth, above the primary mineralised zone. The fracture surfaces in the quartz blocks from this zone were covered in finely disseminated Au crystals. Selected pieces with this visible Au were then imaged using optical microscopy and Scanning Electron Microscopy (SEM, Philips XL-40) with an Energy Dispersive X-ray Spectrometer (EDS) used to obtain low magnification images using the backscatter electron (BSE) detector and compositional data (EDS), operating at 30 kV. Field Emission Gun Scanning Electron Microscopy (FEGSEM, Zeiss) images were collected at the Centre for Microscopy at the University of Western Australia. A low accelerating voltage of 3kV was used; with 1 kV used for some images to provide true surface images at high magnifications.

Synthetic Au crystals were manufactured in the CSIRO laboratory (Kensington, WA) by evaporation of 500 ppm chloroauric acid at ambient temperature or on a hot plate at approx. 120°C in a fume hood. In some cases additional ligands such as 0.01 M oxalic acid ($C_2H_2O_4 \cdot 2H_2O$) was added to the solution and pH and temperature were adjusted. Characterization of the synthetic Au was conducted in the same manner as with the natural samples.

RESULTS

The use of various microscopy techniques revealed the morphology and chemical composition of the saprock materials. On the surfaces of the fractures, numerous populations of Au crystals were observed with the common euhedral, face centred, cubic, crystal structure. The Au shapes were triangles and hexagons. Other minerals such as halloysite and barite were also detected.

The laboratory work produced Au particles in all experiments. The solutions did not change their absorbance characteristics over time or with the different conditions. Following evaporation, microscopy and EDS analysis showed microparticles and nanoparticles of Au in triangular and hexagonal morphologies. Some variation existed in the number and size of Au particles depending on the treatments of the AuCl solutions.

DISCUSSION

Primary Au typically occurs as a Au-Ag alloy. However, secondary Au is commonly pure, although secondary Au-Ag alloys have also been shown to form in isolated cases (Webster & Mann 1984; Howell *et al.* 1993). Supergene deposits are formed via chemical and mechanical weathering.

This two-phase weathering results in Au being mobilized in solution and precipitating as pure secondary Au crystals in other areas. The mobilization of Au is probably in the order of a few metres to a few hundred metres in the Yilgarn Craton (Anand *et al.* 2007; Hough *et al.* 2008). Weathering fractures above primary mineralisation are the ideal place to observe this secondary deposition of Au. Studying the morphologies coupled with laboratory experiments can also provide clues into the natural conditions, mechanisms and associated ligands that are involved in the transport and deposition of Au.

The hypogene quartz veins at the base of the pit contain visible Au with approximately 10% Ag in an Au-Ag alloy. The surrounding groundwater also contains large concentrations of both Au and Ag, 44 and 293 ppt, respectively (Hough *et al.* 2008). A study of saprock fractures above this zone shows significant populations of Au crystals. The Au is pure, and exists as euhedral, isometric crystals. These particles vary in diameter from 300 μm to 0.02 μm (Fig. 3). Initial imaging of these samples did not show

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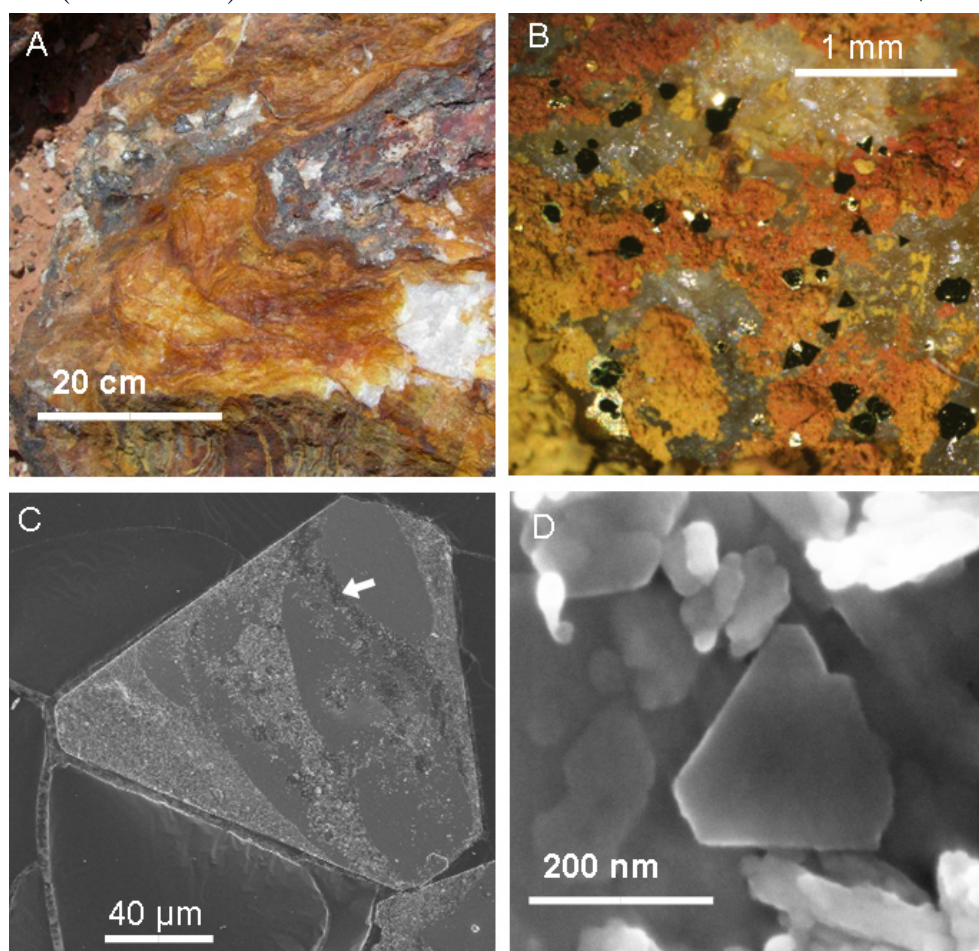


Figure 3. Clockwise from top left, increasing the magnification on the surface of a weathered quartz saprock fracture: A) a larger block of quartz saprock, B) light microscope image of black and shiny Au triangular and hexagonal crystals, C) FEGSEM image of a microparticulate Au crystal, and D) a close up of the darker band shown in C with an arrow, depicting nanoparticulate Au and halloysite.

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some of the large triangles and hexagons of Au as they are extremely thin (<20 nm; Hough *et al.* 2008). The SEM images produced at the commonly used voltage of 30 kV were seeing “through” these plates as the atomic number contrast was not great enough in the SEM BSE (Fig. 4).

Imaging of the surfaces of the large Au triangles using FEGSEM and secondary electrons revealed banded patterns

that represent the smaller population of Au nanoparticles and halloysite. Hough *et al.* (2008) states that these phases are not coprecipitated (one forming nucleation sites for the other), but they are randomly coexisting in a drying pattern related to differential precipitation during evaporation and particle deposition. The halloysite is supported by a matrix of Au nanoparticles (Fig. 3D), these nanoparticulate Au

crystals may also occur in smaller size fractions (left of centre in Fig 3D). These weathered fractures in the saprock also contain various Fe oxides, clays, sulphates and salts.

The size of these Au populations may be relevant to our understanding of partial extraction results and transport mechanisms. Partial extractions may only dissolve the smaller, nanometre-sized, more labile Au crystals resulting in biased results. Understanding the constraints on Au morphology may reveal more information about the formation of secondary Au deposits and Au fractions in soils, although more work is required. The aim would be to use the chemistry and morphological information of supergene Au to vector in to primary hypogene systems.

Regolith and groundwater chemistry influence the mobility of Au. In the southern areas of Western Australia groundwaters are highly saline, greater than 3x seawater (67,000 mg/L Cl) and acidic (pH down to 3), and soluble Au primarily occurs in solution as the Au-chloride complex (Gray 2001). Evaporation of chloroauric acid (HAuCl₂) was conducted in the laboratory to observe the morphology that can be expected with Cl as the primary ligand and compared to the natural samples (Figs. 3 & 4). Results show the morphology of Au to be similar to those observed in saprolite from the study site (Fig. 5).

Populations of microparticulate and nanoparticulate triangles and hexagons occur on top of Au-

chloride salt crystals as determined by SEM EDS analysis. The triangles and hexagons range in size from 100 μm to 0.060 μm.

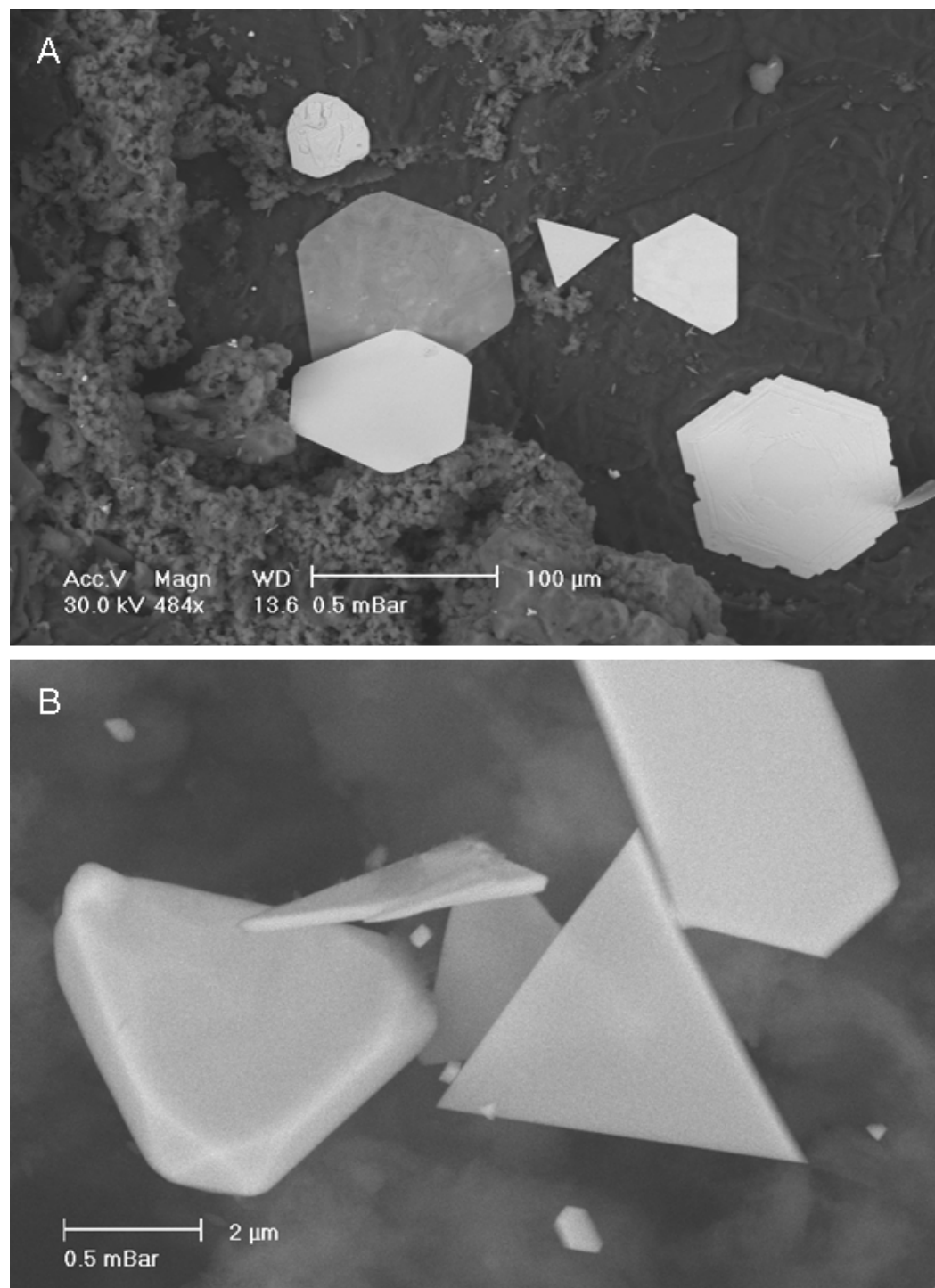


Figure 4. Naturally occurring hexagons and triangles of Au in the saprock fractures. Some of these plates are very thin and are partially transparent, showing the underlying Fe oxides and silicates (A), whereas others are growing into cubic pyramidal forms (B).

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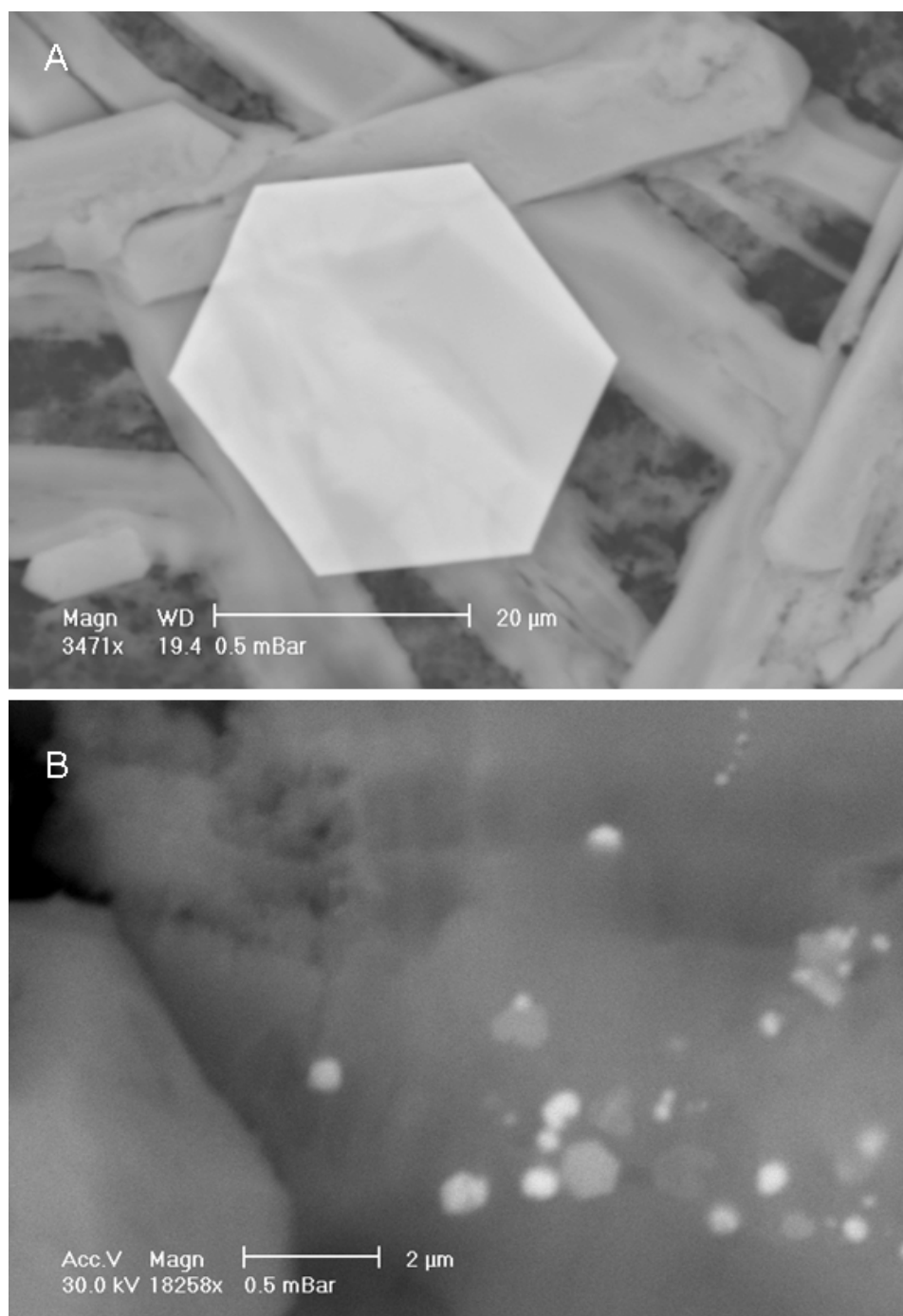


Figure 5. A) Gold formed from the evaporation of Au-chloride. The common hexagonal pure Au crystal is sitting on top of Au-chloride crystals. B) An additional nanometre sized population of Au hexagons is also present.

The Au-chloride solution was not evaporated immediately, and the visible light absorption was measured over time. Previous work in the area of materials science and nanoparticles has shown those Au colloids forming in solution change the solution colour as the reaction progresses, with colour controlled by the size of the colloidal Au. Using evaporation as the mechanism of formation, the absorption did not change during the experiments, indicating the Au is not colloidal during this time and formed after the solution was placed on the slide as a result of evaporation.

Other organic ligands may also be important for

particulate Au formation; combining Au-chloride with oxalic acid produced numerous forms of Au (Fig. 6). Not only were the common hexagons and triangles observed, but also larger 3D pyramids and wires of Au. The reduction of the Au-chloride by the oxalic acid rapidly precipitates Au crystals in minutes compared with the hours of formation via evaporation. In natural conditions, a Au-chloride bearing solution would form supergene Au quickly, particularly in the presence of oxalic acid (or other strong reductants). Organic compounds are usually used in the nanotechnology manufacturing as capping agents to control size and shape of Au (Bi *et al.* 2008; Tan *et al.* 2003). The common supergene environment (especially in this study region) does not contain a large concentration of organic ligands, and in turn these compounds are unlikely to act as controlling variables, hence the bulk of formation is likely driven by slightly slower, inorganic evaporation.

Additional evaporite minerals are also evident in the study area and indicate that the evaporation mechanism of Au deposition is plausible. Gold microparticles are clearly visible in barite crystals (Fig. 7). Once bound in the barite, this Au is much less easily mobilized, which again indicates the importance of understanding the morphology as well as the host minerals of secondary Au in the near surface and deeper environments. This understanding may have significant implications for i) the formation and deposition of supergene Au, ii) secondary mineral fractions removed from soils in partial extractions with relation to Au, and iii) the ability to develop methods of using partial extractions and secondary mineral fractions to vector to mineralisation.

CONCLUSIONS

Studying the natural Au crystal morphologies, coupled with laboratory experiments has provided insight into the environmental conditions, mechanisms and associated ligands that may be involved in the transport and deposition of supergene gold in Western Australia. In the southern Yilgarn Craton supergene gold deposits are most likely formed through the evaporation of AuCl complexes in a relatively short time. Whether the use of the secondary Au crystal characteristics and associated minerals can be linked

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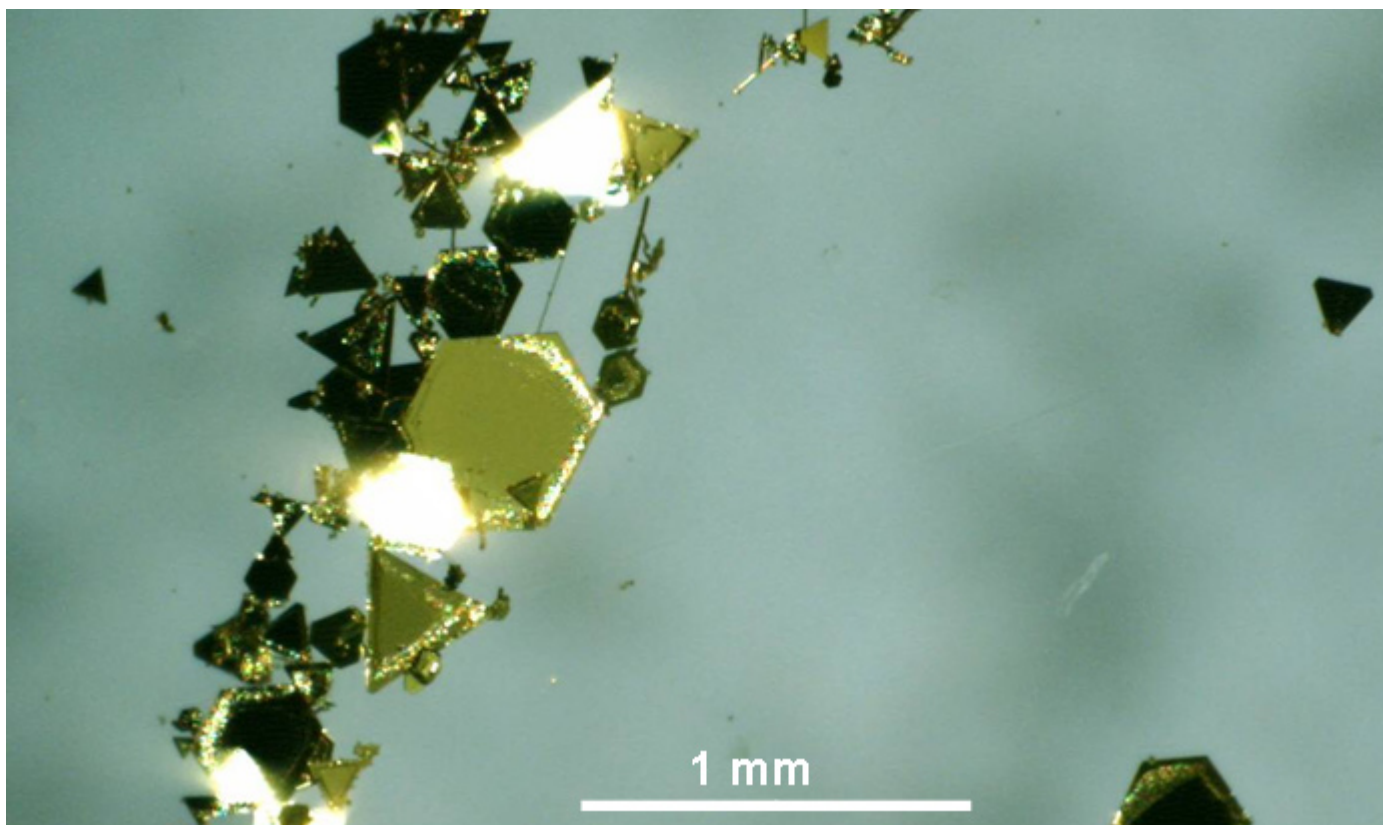
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Figure 6. Particulate Au triangles and hexagons formed from the reduction reaction with oxalic acid.

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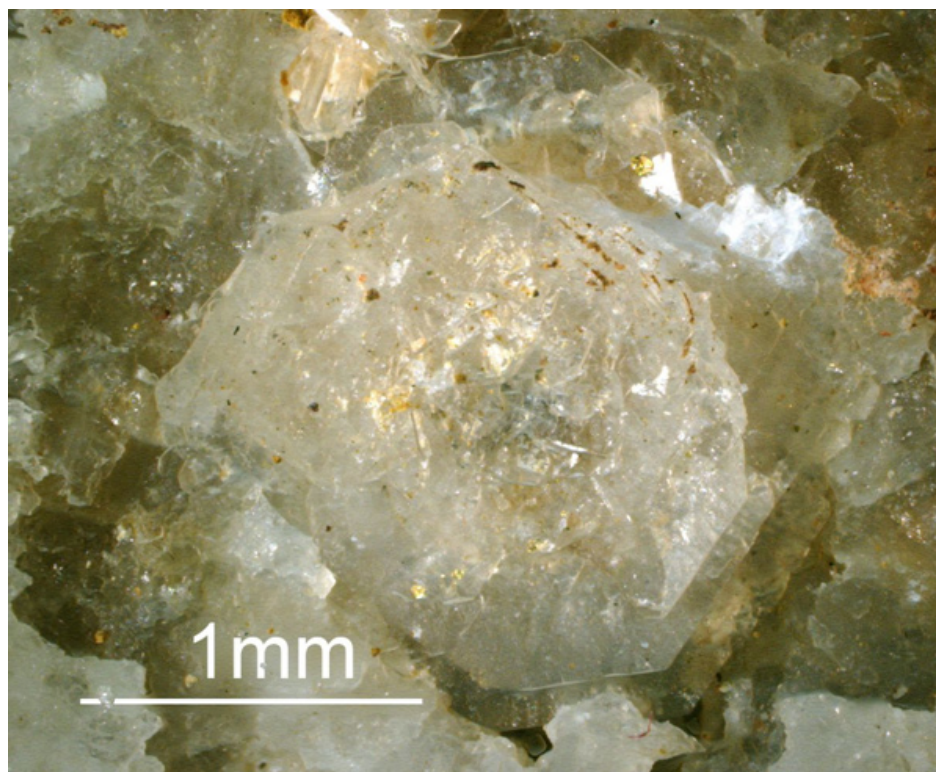


Figure 7. Visible Au formed within barite.

to primary hypogene systems is unclear, but it provides an ultimate goal and direction for future research.

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