

**FLUID INCLUSION THERMOMETRIC AND STABLE ISOTOPE ( $\delta^{18}\text{O}$ - $\delta\text{D}$ ) EVIDENCE FOR "CRYPTIC BOILING" IN THE PROFITIS ILIAS EPITHERMAL GOLD DEPOSIT, MILOS: A POTENTIAL EXPLORATION TOOL FOR EPITHERMAL GOLD**

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**ABSTRACT**

"Cryptic boiling" has been disclosed throughout the vertical extent of the Profitis Ilias epithermal system (~450 m) by assessing systematic variations in fluid inclusion and stable isotope ( $\delta^{18}\text{O}$ - $\delta\text{D}$ ) data in relation to elevation. Highest gold grades (Au: 2-57.9 g/t) are preferentially concentrated in the upper 200-250 m of the system in a "steam-dominated zone" that is separated from a lower "liquid-dominated zone" (Au < 2 g/t). This distribution of gold may be due to colloidal transport in a boiling epithermal system. The identification of the base of the "steam-dominated zone" using fluid inclusion and stable isotope data may potentially guide exploration drilling to depths with high-grade gold ore in productive epithermal systems.

Key words: fluid inclusions, boiling, isotopes, epithermal gold, exploration

**1. INTRODUCTION**

During the last decade, volcanic-hosted epithermal gold ores have been the focus of intense mineral exploration efforts in Greece (Kilias et al. 2001; Naden et al. 1999; Skarpelis 1999a,b; Skarpelis et al. 1999; Michael et al. 1995; Michael 1993).

Modern exploration strategies rely on conceptual genetic models which explain deposits in terms of causative geological processes. Fluid inclusions (FI) provide one of the best techniques available for defining the physical and chemical environment attending the various geological processes leading to the formation of epithermal gold deposits. In general, the use of fluid inclusions in exploration rely mainly on defining genetic (or empirical) relationships between some inclusion characteristics and mineralisation (see examples in Wilkinson 2001; Roedder and Bodnar 1997). In epithermal precious metal systems, it has been shown that the depth range over which mineralisation occurs corresponds to the range over which co-genetic vapour- and liquid-rich inclusions, defining zones of boiling, are found (e.g. Bodnar et al. 1985).

Fluid inclusion thermometric properties from the Profitis Ilias epithermal Au deposit, Milos island, were found to vary systematically in relation to sample depth and gold grades (Kilias et al. 2001). In this study, the above data are combined with stable isotope ( $\delta\text{D}$ ,  $\delta^{18}\text{O}$ ) analyses of inclusion fluids in an attempt to establish genetic relationships between fluid inclusion characteristics and mineable gold grades with potential use in drilling-target selection of an exploration program for epithermal gold.

**2. THE PROFITIS ILIAS DEPOSIT**

The Profitis Ilias gold deposit, located on the western part of Milos island, approximately 20 km west of the high-enthalpy active geothermal system of central Milos, is the first epithermal gold deposit discovered in the Pliocene-Pleistocene Aegean volcanic arc (Kilias et al. 2001). It is hosted by 3.5-2.5 Ma old silicified and sericitised rhyolitic lapilli-tuffs and ignimbrites, and is closely associated with a horst and graben structure.

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Estimated reserves are 5 million tonnes grading at 4.4 g/t Au and 43 ppm Ag and recently bonanza grades have been discovered in the neighbouring Koumaria and Chondro Vouno (Amethyst) prospects. The deposit consists of a series of interconnected veins and vein sets, which have maximum widths up to 3 m and extend to depths of at least 300 m (relative to the present day surface). The mineralisation occurs in three hypogene stages and one supergene stage. Hypogene mineralisation consists almost entirely of quartz, with minor amounts of adularia, pyrite, galena, chalcopyrite, sphalerite, native gold, electrum and barite.

### **3. SAMPLING AND ANALYTICAL METHODS**

#### **Sample selection**

Fluid inclusion microthermometry (Kilias et al. 2001) was conducted in 23 samples selected from a total of 130 collected from surface exposures (27) and drill core (100). These cover the vertical extent of the deposit, extending from surface [elevation: 650 m above sea level (m asl)] down to an elevation of 200 m asl. Samples were prepared as free standing, 100-200  $\mu\text{m}$  thick doubly polished wafers. Analyses were carried out using a Linkam TMSG600 heating-freezing stage calibrated with natural carbon-dioxide-bearing fluid inclusions of known composition and commercially available chemical standards. Estimated analytical error is  $\pm 0.2$   $^{\circ}\text{C}$  for low ( $<50$   $^{\circ}\text{C}$ ) and  $\pm 2$   $^{\circ}\text{C}$  for higher ( $>75$   $^{\circ}\text{C}$ ) temperatures. Eleven (11) samples (Table 1) were selected for isotopic analysis based on fluid inclusion microthermometry, elevation and assay data. The first selection criterion was that samples should contain only a single inclusion type with an inclusion population dominated by primary/pseudosecondary inclusions. The second was that the sample suite should cover most of the vertical range of the gold mineralisation.

#### **Bulk volatile analysis of inclusion fluids**

A selected number of samples (9) were prepared and analysed for bulk volatiles ( $\text{H}_2\text{O}$  and  $\text{CO}_2$ ) (Kilias et al. 2001). The main objective of these analyses was to provide estimates of the  $\text{CO}_2$  content of the fluid inclusions which is an important parameter for calculating depth-to-boiling relationships in epithermal systems (Bodnar et al. 1985; Hedenquist and Henley 1985).

#### **$\delta\text{D}$ and $\delta^{18}\text{O}$ analysis of inclusion fluids**

Approximately 10g of quartz from each sample were crushed and sieved to -1000 $\mu\text{m}$  +500 $\mu\text{m}$ . The quartz concentrate was then washed in hot (c. 90  $^{\circ}\text{C}$ ) 6M HCl several times with a final rinse in hot (c. 90  $^{\circ}\text{C}$ ) Milli Q water to remove "soluble" impurities adhering to the surface of the quartz grains (e.g. iron oxides). This was followed by ultrasonic cleaning in cold Milli Q water for 5 minutes, this removed "insoluble" impurities adhering to the quartz grains (e.g. clay minerals). Any impurities left were then removed by careful hand picking under a binocular microscope to give a pure quartz concentrate weighing between 0.5 and 1.0 g. Immediately prior to analysis, the sample was briefly ultrasonically cleaned in dichloromethane to remove any remaining organic contaminants.

The procedure used for determining  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in fluid inclusions is modified from the published methods of Kishima and Sakai (1980), Kazahaya and Matsuo (1984), and Lecuyer and O'Neil (1994). First, between 0.5 and 1g of hand picked quartz grains were degassed at  $\sim 20$   $^{\circ}\text{C}$  overnight under vacuum. The samples were then decrepitated at 600  $^{\circ}\text{C}$  for 30 minutes and the fluid inclusion water collected cryogenically. Water was transferred to a micro-equilibration quartz tube sealed at one end, to which 2 $\text{cm}^3$  of a standard  $\text{CO}_2$  gas was added, and the tube completely sealed. The tube was then weighed and the  $\text{H}_2\text{O}$  and standard  $\text{CO}_2$  gases were left to exchange oxygen isotopes at 25  $^{\circ}\text{C}$  for 7 days. After equilibration samples of  $\text{H}_2\text{O}$  and  $\text{CO}_2$  were separated cryogenically. The water was converted to hydrogen by reduction over hot zinc; ratios were measured on a SIRA 10 mass spectrometer. The  $\text{CO}_2$  was collected and ratios measured on an Optima

mass spectrometer along with a sample of the standard gas used for the equilibration. The  $\delta^{18}\text{O}$  values of the water samples were calculated using the mass balance equation proposed by Kishima and Sakai (1980) and the  $\text{CO}_2\text{-H}_2\text{O}$  fractionation factor at 25 °C determined by O'Neil et al. (1975). The  $\delta^{18}\text{O}$  value of standard  $\text{CO}_2$  used for equilibration was 31.85‰ (SMOW), a value close to that expected for the  $\text{CO}_2$  after equilibration. Since the oxygen isotope ratio of the  $\text{CO}_2$  changes only by a few permil during the equilibration, the precision was not compromised. The weight of fluid inclusion water released from the quartz was calculated from the weights of the collection tubes before and after the  $\text{H}_2\text{O-CO}_2$  collection. The water content of each sample was variable, but in most cases 0.5 to 1 g of quartz yielded between 0.5 and 4 microlitres of water. At each stage in the extraction procedure the line pressure was monitored to check for residual gas. Precision obtained for the laboratory standard water extracted and measured at the same time were 0.1‰ for  $^{18}\text{O}$  and 3‰ for  $\delta\text{D}$  ( $2\sigma$ ) for samples between 1-2 microliter quantities of water. The data are presented as permil deviations from SMOW.

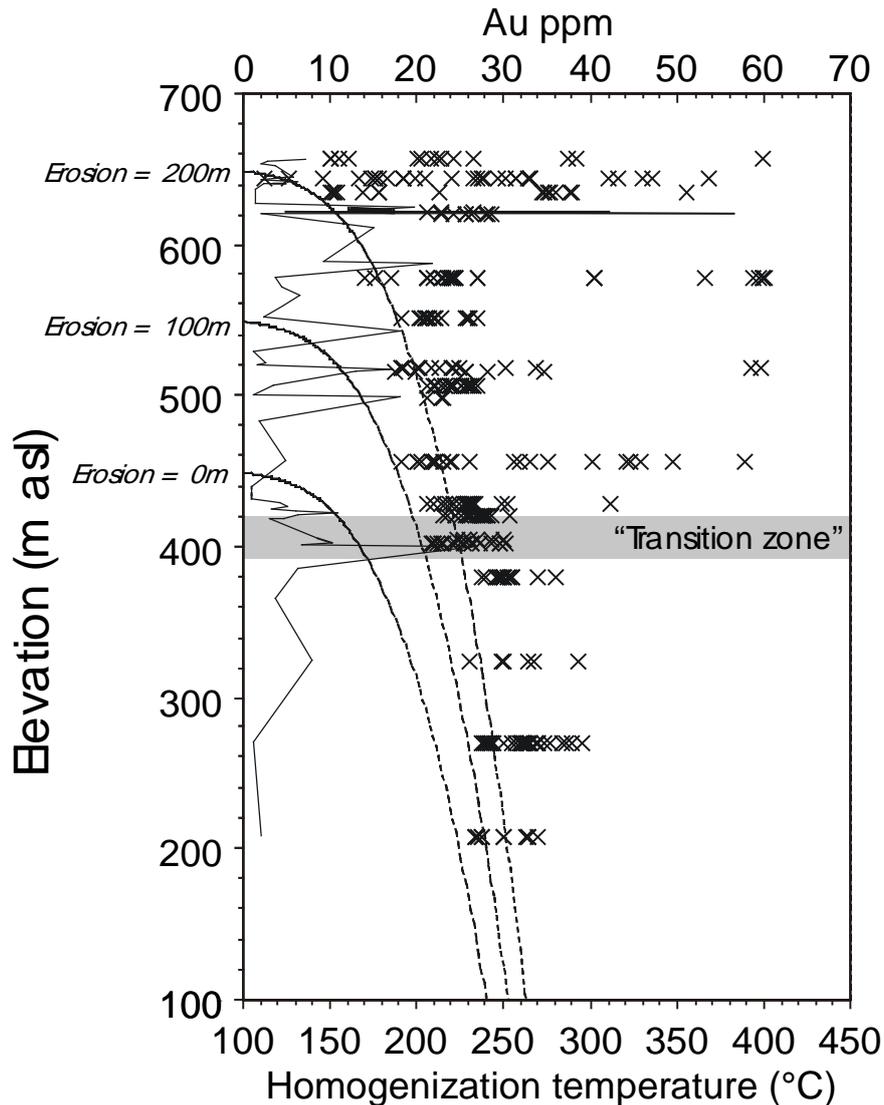
#### 4. FLUID INCLUSION MICROTHERMOMETRIC DATA--"CRYPTIC BOILING"

Most fluid inclusions (>95 % by number) that are intimately associated with gold grains contain only two phases at room temperature: an aqueous solution and a vapour bubble occupying 10-30 % of the inclusion volume. Vapour-rich two-phase aqueous inclusions occur rarely. Microthermometric data show the hydrothermal system that formed the PI deposit boiled (Kiliass et al. 2001). Boiling, and fluid heterogeneous trapping, were disclosed by assessing salinity versus homogenisation temperature trends discriminated by sample elevation, and homogenisation temperature--sample elevation relationships (Fig. 1,2), rather than routinely used petrographic evidence of co-genetic liquid- and vapour-rich fluid inclusions with respective overlapping bubble point and dew point homogenisation temperatures. Consequently, the new term "cryptic boiling" was introduced in order to describe boiling in hydrothermal fluids that is only seen by examining the relationship between depth (elevation) and fluid inclusion microthermometric data.

"Cryptic boiling" is characterised by the following systematic variations in microthermometric data:

- a) A high-salinity trend, where moderate-temperature (300 to 250 °C) moderate-salinity brines (c. 3 wt % NaCl equiv.) trend to high-salinity (up to 15 wt % NaCl equiv.) fluids with lower (c. 25 to 50 °C) homogenisation temperatures. This is seen mainly below 430-450 m asl;
- b) A high- $T_h$  trend where moderate-salinity and moderate-temperature brines (200 to 250 °C; 3 wt % NaCl equiv.) develop into low-salinity (<1 wt % NaCl equiv.) high-temperature (>350 °C) fluids, which is found either alone, or combined with the high-salinity trend, exclusively above the 430-450 m asl level;
- c) Tightly clustered homogenisation temperatures occur below 430 m asl (variation: 30-50°C);
- d) Extremely variable homogenisation temperatures occur above 430-450 m asl (locally > 150 °C).

Based on these relationships the 430-450 m asl level divides the Profitis Ilias hydrothermal system into a lower liquid-dominated segment and an upper vapour-dominated segment (Kiliass et al. 2001). Note that below 400 m asl only three assays (among a few tens of assays) above 2 ppm have been recorded, whereas above 400 m asl the number of gold assays greater than 2 ppm increases and locally gold grades reach 57.9 ppm (Fig. 2). The low gold grades correlate with the lower liquid-dominated segment and the narrow range in  $T_h$ , whereas Au grades >2 ppm correlate very well with the wide range in homogenisation temperatures and the upper vapour-dominated segment of the system. Elevation data and Au grades were provided by Midas S.A., Milos.

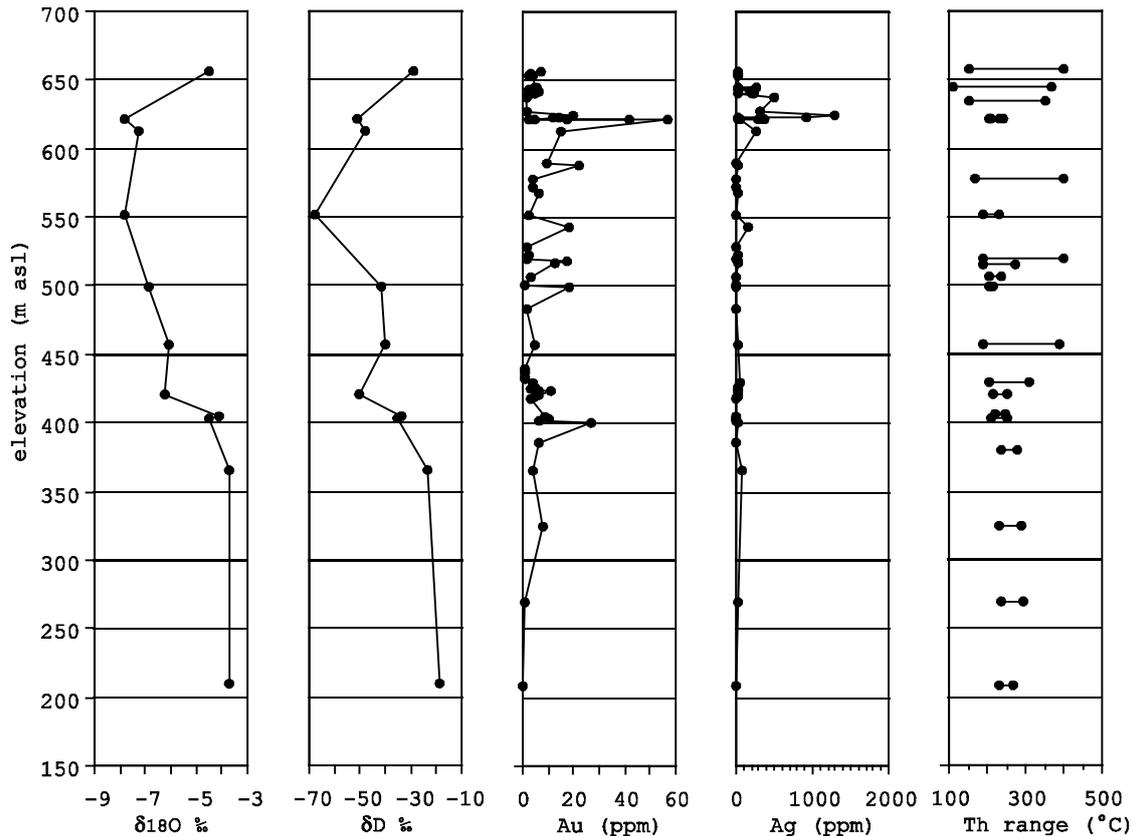


**Figure 1:** Relationships of fluid inclusion  $T_h$  versus elevation and Au assay for the Profitis Ilias deposit. Superimposed on the diagram are three depth-to-boiling curves calculated assuming net erosion of 0 m, 100 m and 200 m, since the mineralisation formation (see text for discussion).

In addition, depth-to-boiling curves were calculated according to the methodology of Hedenquist and Henley (1985) with conversion of pressure to depth assuming a hydrostatic gradient. The concentration of  $\text{CO}_2$  was estimated from gas analysis (Kiliyas et al. 2001) and 5 wt% NaCl corresponds reasonably closely to the Median salinity of the Profitis Ilias fluids. Depth-to-boiling curves were plotted against elevation- $T_h$  data, taking into consideration three scenarios regarding the relative position of the paleo-surface to present day elevations. The three scenarios assume that net uplift and erosion have resulted in the present day surface being at the same elevation (+0m curve, Fig. 1), or, 100 m (+100 m curve, Fig. 1) or 200 m (+200 m curve, Fig. 1) below the paleo-surface, respectively. The position of the +200 m depth-to-boiling closely follows the lowest homogenisation temperatures and suggests that approximately 200 m of the deposit has been eroded since the Late Pliocene.

##### 5. STABLE ISOTOPES ( $\delta\text{D}, \delta^{18}\text{O}$ ) IN INCLUSION FLUIDS

Stable isotope ( $\delta\text{D}, \delta^{18}\text{O}$ ) data for extracted inclusion fluids (FI water) along with a summary of fluid inclusion microthermometry and Au assay-elevation data



**Figure 2.** Relationships between isotopic ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) composition of hydrothermal fluids, Au and Ag assay, and fluid inclusion homogenisation temperature distribution, in relation to the studied vertical extent of the Profitis Ilias boiling hydrothermal system (See text for discussion).

are presented in Table 1. The inclusion-fluid data are consistent with boiling and heterogeneous trapping, which agrees with the microthermometry data (Naden et al. 1999).  $\delta\text{D}_{\text{FIwater}}$  values when plotted against  $\delta^{18}\text{O}_{\text{FIwater}}$  show sub-linear fractionation trends consistent with single-stage steam separation; the trends parallel the Mediterranean Meteoric Water Line, and are broadly comparable to the currently active Milos geothermal system (Naden et al. 1999).

$\delta^{18}\text{O}_{\text{FIwater}}$  and  $\delta\text{D}_{\text{FIwater}}$  data shows a systematic antipathetic correlation with sample-elevation and gold assay (Fig. 2).  $\delta^{18}\text{O}_{\text{FIwater}}$  and  $\delta\text{D}_{\text{FIwater}}$  values generally increase with depth (Fig. 2), from -3.7 ‰ at 210 m asl to -7.3 ‰ at 613 m asl. An exception is the sample from the highest elevation (657 m, sample G2185), which has a  $\delta^{18}\text{O}_{\text{water}}$  of -4.5 ‰. As with the oxygen data,  $\delta\text{D}_{\text{FIwater}}$  vary from the lightest values (-47.8 ‰) at high elevations (613 m asl) to the heaviest values (-19 ‰) at the lowest elevation (210 m asl). In addition, highest gold grades (> 2ppm) are preferentially concentrated in the upper levels of the system (>400 m asl), and this "gold grade enrichment" correlates very well with the observed "depletions" in  $\delta^{18}\text{O}_{\text{FIwater}}$  and  $\delta\text{D}_{\text{FIwater}}$ . Furthermore, the observed dramatic shift of the isotopic data to more negative values >400 m asl (Fig. 2) is consistent with trapping "steam". This adds additional evidence to support a "steam-dominated zone" above 430 m asl. Also, the increase in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  in the uppermost elevations (> 630 m asl) (Fig. 2) is consistent with condensation and mixing with groundwater, thus defining the steam-heated zone in the system.

## 6. DISCUSSION

"Imaginative application of conceptual models of ore genesis is of paramount importance to the contemporary exploration geologist" is a statement (Bodnar et al. 1985) that can hardly be overemphasised. Based on genetic models that have

been developed for epithermal gold deposits, it has been suggested that highest gold grades often occur at and above the "boiling horizon", whereas deeper portions of the epithermal system are barren or contain only base metals (Roedder and Bodnar 1997). Boiling causes gold deposition through either destabilisation of gold-bisulphide complexes (sulphur loss to the vapour phase) or the destabilisation of gold-chloride complexes (rapidly changing pH conditions) (e.g. Drummond and Ohmoto 1985). In this context, fluid inclusion data (usually thermometric only) indicative of boiling has been suggested as a practical guide to that part (depth) of the epithermal system where mineralisation is most likely to have occurred.

**Table 1:** Stable isotope data for Profitis Ilias inclusion fluids. Also shown are gold assays for each sample.

Sample no.	Elevation (m asl)	Sample wt. (g)	FI water weight (mg)	$\delta^{18}\text{O}\%$ FI water	$\delta\text{D}\%$ FI water	Au (ppm)
G2185	657	1.4	0.5	-4.5	-28.7	7.18
G1746	621	0.5	2.5	-7.8	-51.0	56.50
G1810	613	0.5	0.3	-7.3	-47.8	n.d.
G2374	551	1.5	1.2	-7.8	-68.0	4.22
G2245	499	0.5	3.7	-6.9	-41.5	18.00
G2255	457	0.5	1.6	-6.1	-39.8	4.84
G2424	421	0.7	1.2	-6.2	-50.5	6.32
G2267	405	1.4	3.7	-4.1	-33.3	8.51
G2268	403	1.2	2.5	-4.5	-34.9	10.20
G2283	365	1.2	0.3	-3.7	-23.8	10.20
PD9380	210	0.5	1.2	-3.7	-19.0	2.00

The presented systematic variation of fluid inclusion thermometric and stable isotope data with sample elevation, provide undisputed evidence that boiling is an integral part of the genetic model of the Profitis Ilias epithermal gold deposit. The novelty of our results lies in the recognition of "cryptic boiling" (see definition above) and the preservation of a "boiling signature" in fluid inclusion stable isotope compositions. Furthermore, as emphasised earlier, there is a close spatial association between samples that exhibit heterogeneous fluid trapping and the distribution of the highest gold grades (Fig. 1,2). This indicates that fluid inclusion data, stable isotope composition and gold are genetically related. However, at Profitis Ilias, the hydrothermal fluids boiled throughout the studied depth intervals and gold is preferentially concentrated in the vapour-dominated part of the system (upper levels). Thus, the distribution of gold cannot be explained by boiling alone. Saunders and Schoenly (1995) show that boiling induces rapid gold precipitation, which leads to the formation of gold colloids. The colloids are then transported by high velocity (vapour-rich fluids) where they grow as they move up the fracture system. Ultimately, they reach a critical size and aggregate at higher levels in the system and precipitate, possibly due to partitioning of gold colloids into the continuously diminishing liquid phase and accompanying increasing gold concentration. Thus, colloidal transport of gold offers and explanation as to why the highest gold grades at Profitis Ilias are correlated with the zone where the inclusions exhibit heterogeneous trapping (vapour-dominated segment of the system), rather than uniformly distributed throughout the deposit. Also, recent drilling by RoyalGold Inc. at nearby prospects (East Amethyst and Amethyst Ridge) records high-grade gold (30 to 178 g/t) in the upper 50 metres of drilling, while at deeper levels (100 to 150 m) gold grades are much lower (mainly below 5 g/t) (RoyalGold news release -- [www.royalgold.com/news/990105.htm](http://www.royalgold.com/news/990105.htm)).

## 7. CONCLUSIONS

From an exploration point of view, our results from Profitis Ilias suggest that:

1. Boiling, as a guide to the location of gold mineralisation, is seen by examining the relationship between depth, fluid inclusion and stable isotope data ("cryptic boiling"). This is important as direct evidence from fluid inclusion petrography (coexisting and co-genetic liquid- and vapour-rich inclusions), microthermometric data (overlapping dew- and bubble-point homogenisation temperatures) and mineralogy (i.e. adularia) may not be present. This is obtained by examining one drill-core from within the epithermal system.
2. It is the identification of the depth of the "transition zone" between "liquid-dominated" and the "vapour-dominated" parts of a boiling hydrothermal system that is important. Because it defines the volume of rock that has good potential for high-grade gold. For example a "transition zone" close to the surface will have a low potential while a deep one, as at Profitis Ilias will be much higher.

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