TOWARDS A UNIFIED THEORY ON CALCITE FORMATION IN BOILING GEOTHERMAL SYSTEMS

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SUMMARY: The formation of hydrothermal calcite relates to the movement of carbon dioxide in a geothermal system as governed by boiling, dilution and condensation. Replacement calcite forms in rock-dominated environments where sub-boiling liquids contain relatively high concentrations of dissolved carbon dioxide, while platy calcite forms in fluid-dominated environments where rising two-phase fluids exsolve carbon dioxide through boiling. The distribution of these two occurrences reflects the distribution of boiling conditions within a phase of steady hydrothermal activity. In the ideal situation, platy calcite forms along the inner margin of the two-phase zone, having the shape of an inverted cone, whereas replacement calcite mostly forms in the surrounding one-phase liquid-only zone. The sparse occurrence of calcite at ≤800 m depth in the central upflow of the Ohaaki sector at Broadlands-Ohaaki is compatible with this model and appears related to the exsolution of dissolved carbon dioxide through boiling'deeper in the system.

1.0 INTRODUCTION

Hydrothermal calcite commonly forms in active geothermal systems, with its formation controlled by *f* CO_2, pH, temperature and aqueous calcium ion activity (e.g. Fournier, 1985); however, for most geothermal systems *f* CO_2 appears to be the limiting factor (e.g. Browne and Ellis, 1970; Giggenbach, 1981, 1984, 1988). Since many hydrothermal fluids are close to calcite saturation, indicating that calcite plays a major role as a mineral-gas buffer, the presence or absence of calcite in a hydrothermal mineral assemblage directly reflects the concentration of aqueous carbon dioxide of the coexisting fluid (Ellis, 1969, 1970; Ellis and Mahon, 1977; Arnórsson, 1978; Giggenbach, 1981, 1988). Since boiling and fluid mixing are the main hydrologic processes that affect the concentration of aqueous carbon dioxide in the upper one to two kilometers of a geothermal system, calcite formation in this environment should be sensitive to the flow of carbon dioxide. Here, we present an interpretive framework for calcite formation in a boiling geothermal system based on research at Broadlands-Ohaaki, the details of which are published elsewhere (Simmons and Christenson, 1993).

2.0 CALCITE OCCURRENCE AT BROADLANDS-OHAAKI

Calcite and siderite are the two main hydrothermal carbonates at Broadlands-Ohaaki, and their distribution is shown in cross-sections (Fig. 1). Two different styles of carbonate occurrence have been distinguished (Browne and Ellis, 1970), referred to here as replacement and platy calcite. The adjective replacement refers to hydrothermal carbonate surrounded by rock-forming minerals and volcanic glass; relict igneous textures and metastable phases suggest that hydrothermal fluids reacted with a precursor solid phase to produce carbonate. Platy calcite, by contrast, describes the distinct habit of calcite that precipitates in open spaces, infilling natural vugs and fractures or forming pipe scale in geothermal wells. The adjective platy denotes the crystal shape dominated by the basal pinacoid form. Other crystal habits of carbonate infilling open space also exist, but these are less common (Browne and Ellis, 1970; Tulloch, 1982).

Replacement calcite occurs with a diversity of other alteration minerals over a temperature range from <125° to >290° C; its total abundance rarely exceeds 5 % by volume of the rock (Browne and Ellis, 1970; Browne, 1973). Below about 170" C, calcite replacement is confined to pumice clasts and glass shards and is associated with clays, smectite, interlayered illite/smectite, kaolinite), mordenite, cristobalite and quartz, with the intensity of alteration being low. Siderite is also common and appears to be a key indicator mineral of this cooler assemblage, but it rarely constitutes more than 1% of the total rock volume. Figure 1 shows that siderite is widespread in the shallow and marginal parts of the system (Browne and Ellis, 1970). Above about 170" C, calcite replaces primary plagioclase (andesine) phenocrysts, in addition to volcanic glass, and is associated with quartz, illite, adularia, chlorite and pyrite of low to moderate, or locally, high intensity alteration. This hotter replacement calcite, while being widespread, mostly occurs at sub-boiling temperatures (Fig. 1). Minor coexisting epidote occurs where temperatures exceed 250° C (Fig. 1), and siderite is uncommon, being noted in only a few isolated occurrences (Wood, 1983).

Platy calcite occurs at depths ranging from 100 to >1000 m, and it forms pipe scale in wells where ascending fluids are two phase (steam and liquid). Some of these occurrences at Broadlands-Ohaaki and Kawerau were described by Tulloch (1982). He noted three relevant features: 1) calcite formation is restricted to within 300 m above the zone where fluids in the well begin to boil; 2) platy crystals grow outward from the wall of the pipe in a direction perpendicular to the c-axis;

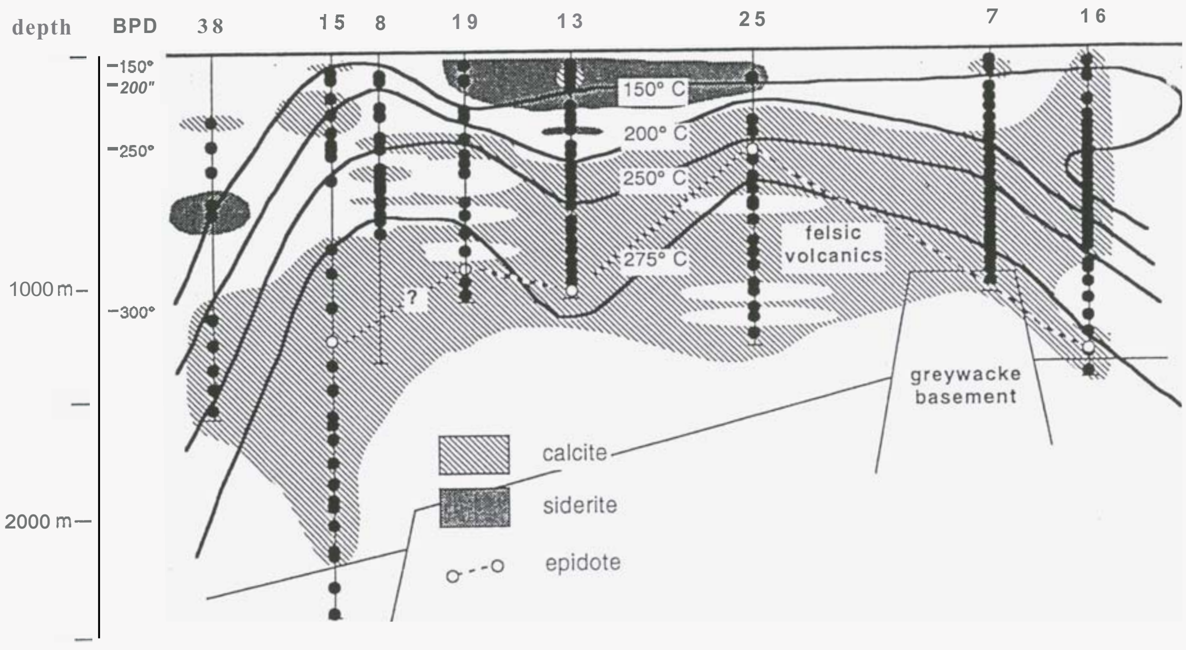

Figure 1. **A** NW-SE cross section showing the distribution of calcite and siderite within the Broadlands-Ohaaki geothermal system based on petrographic descriptions of cores **and** cuttings (Browne, 1971; Wood, 1983; Simmons and Christenson, 1993). No distinction is made between calcite occurrence (i.e. replacement or platy), but note that most are replacement occurrences (P. R. L. Browne, personal communication, 1991). Filled circles represent sample locations. In some samples calcite and siderite coexist, however where both occur siderite is shown Although rare at Broadlands-Oh&, the first downhole occurrence of epidote is also indicated. Isotherms are from Hedenquist (1990); boiling point for depth (BPD) temperatures are provided for comparison.

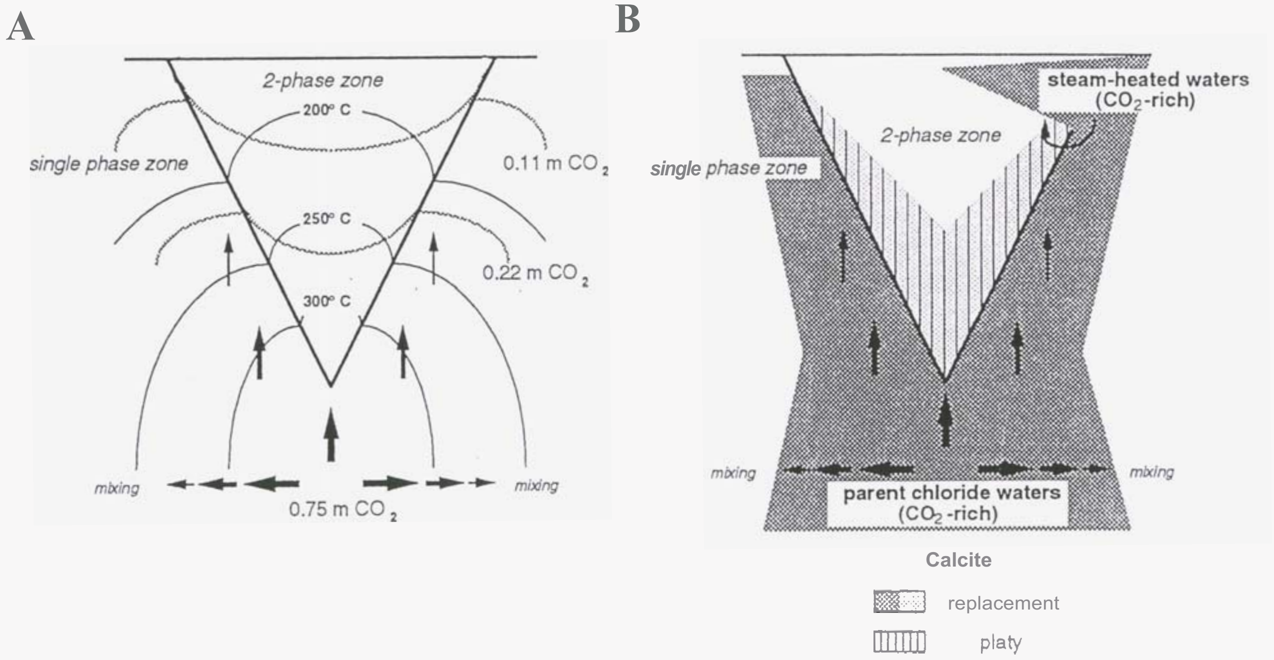

Figure 2. Schematic diagrams showing the relationship between variation in aqueous carbon dioxide concentration and the distribution of calcite in a boiling geothermal system. **A)** The cone of boiling model (Christenson, 1987). B) Distribution of replacement and platy calcite based on hypothetical cone of boiling model. The contrast between dense **and** light stipple for replacement calcite represents relative abundance of more and less, respectively.

and **3)** the estimated rate of calcite growth is about 0.1 mm/day.

3.0 MECHANSISMS FOR CALCITE PRECIPITATION

The formation of hydrothermal calcite is governed by the aqueous parameters that include $f\,CO_2$, pH, temperature and calcium ion activity. Other than the initial input of carbon dioxide into the deep hydrothermal system, these parameters are dictated by fluid-mineral equilibria, permeability (water-rock ratios), boiling and fluid mixing.

Hydrolysis-Calcite replacement forms via hydrolysis reactions involving calcium alumino-silicates indicated by the common association of clays with calcite. Representative reactions are given by Giggenbach (1984), involving plagioclase (anorthite), clinozoisite or wairalcite at >200° C, and laumontite at <200° C:

$$\text{anorthite} + \text{K-feldspar} + CO_2 + H_2O = \text{calcite} + \text{K-mica} + 2\ SiO_2$$

$$0.5\ \text{clinozoisite} + 0.75\ \text{K-feldspar} + CO_2 + 0.5\ H_2O = \text{calcite} + 0.75\ \text{K-mica} + 1.5\ SiO_2$$

$$\text{wairakite} + \text{K-feldspar} + CO_2 = \text{calcite} + \text{K-mica} + 4\ SiO_2 + H_2O$$

$$\text{laumontite} + \text{K-feldspar} + CO_2 = \text{calcite} + \text{K-mica} + 4\ SiO_2 + 3\ H_2O$$

Volcanic glass is also susceptible to calcite replacement by hydrolysis, and this non-stoichiometric reaction occurs over the full temperature range.

In the above reactions the presence of carbon dioxide plays the dual role of 1) making the fluid reactive by supplying hydrogen ions (H_2CO_3 being the dominant aqueous carbon species), which promotes hydrolysis (Giggenbach, 1981; 1984; 1988) and releases calcium into solution, and 2) supplying the dissolved carbonate necessary for calcite formation. As shown by Ellis (1969) and Browne and Ellis (1970), it is the relatively high carbon dioxide concentration of the solution in the presence of a mineral pH buffer that causes calcite to form in place of other calcium alumino-silicates. Calcite replacement by hydrolysis is thus favored in a "rock dominated" environment where a slow-moving fluid has the opportunity to react with the rocks under sub-boiling conditions.

Boiling-In a "fluid dominated" environment (i.e. in the absence of the mineral pH buffer), increasing dissolved carbon dioxide concentration (up to about 1 m) has the effect of increasing (rather than decreasing) calcite solubility, with aqueous carbonate species mostly controling pH (e.g. Ellis, 1959, 1963; Ellis and Golding, 1963). Therefore in a boiling environment calcite precipitates in open spaces upon loss of carbon dioxide. Platy calcite formed in this way can be described by the reaction:

$$2HCO_3^- + Ca^{++} = \text{calcite} + H_2O + CO_2$$

Platy calcite is thus likely to deposit in vertical channels where rising, carbon dioxide-bearing fluids decrease pressure **and** boil.

Heating-Heating also affects calcite (and siderite) precipitation due to its inverse solubility (Ellis, 1959). Most fluids at Broadlands-Ohaaki are close to calcite saturation at in situ conditions (e.g. Hedenquist, 1990), therefore any slight fluid heating will precipitate calcite. Fluid heating can occur where cooler marginal fluids come into contact with hotter rocks. For a geothermal system undisturbed by drilling, this process is likely to be restricted to the margins and shallow parts of a system, where temperature gradients are sharp. Alternatively, formation of shallow calcite scales in production wells may result from heating of descending steam-heated bicarbonate waters if a means if fluid access exists; e.g. shallow casing corrosion. During the late-stage collapse of the convection when marginal waters invade the pre-existing zone of upflow, calcite deposition through heating is also possible, and this may explain the common occurrence of barren late stage calcite in epithermal deposits.

4.0 CALCITE DISTRIBUTION, CARBON DIOXIDE MOVEMENT AND HYDROLOGY

Calcite deposits in both rock and fluid dominated environments of a boiling hydrothermal system. In the rock dominated environment it forms as a replacement phase in the presence of a fluid containing relatively high dissolved concentrations of carbon dioxide, whereas in the fluid-dominated environment calcite precipitates in response to carbon dioxide loss **due** to boiling, or fluid heating. The distribution of calcite thus reflects the movement of carbon dioxide through the system (Fig. 2).

Figure 2a schematically shows how decrease in the concentration of dissolved CO_2 due to dilution shallows the depth of first boiling for a rising column of fluid in a matrix of isotropic permeablility (Christenson, 1987). The parent fluid (initial concentration of $0.75m\ CO_2$) rises, cooling conductively until it intersects the boiling curve at about 2000 m and 320" C for hydrodynamic flow. This undiluted parent fluid initiates boiling at the deepest level forming the vertex of the cone. Outward from the center of the rising fluid column aqueous carbon dioxide concentration is gradually diluted, which decreases the fluid pressure and shallows the depth of first boiling. For this ideal situation, the two phase region is outlined by the shape of an inverted cone with concave CO_2 isopleths and convex isotherms.

This model is extended in Figure 2b to show the hypothetical distribution of calcite with respect to the two-phase region in an active geothermal system. **A** modification in the upper right corner is made to portray the influence of CO_2-rich steam-heated waters on calcite formed at shallow depths; in this case, two-phase conditions are suppressed by incursion of steam-heated waters. The relatively high concentration of dissolved carbon dioxide in the sub-boiling fluid promotes the formation of replacement calcite through hydrolysis in the single phase zone surrounding the inverted cone. In contrast, platy calcite is restricted to a narrow vertical interval (e.g. ≤300 m) along the inner margin of cone controlled by exsolution of dissolved carbon dioxide. **As** carbon dioxide is lost in the two-phase zone, the effect of hydrolysis also diminishes and hence, although overlap between the domains of platy and replacement calcite exist, replacement calcite decreases in abundance towards the interior of the cone.

The result is a V-shaped pattern of platy calcite distribution, with a gap in the distribution of calcite at shallow to intermediate depths in the central upflow zone. The calcite-depositing capacity of fluids at these depths is exhausted due to boiling. Isotopic evidence from Broadlands-Ohaaki and Waiotapu indicates that platy calcite can precipitate from either a deep chloride water or a shallow steam-heated water (Hedenquist and Browne, 1989; Simmons and Christenson, 1993). Thus under certain hydrologic conditions steam-heated waters boil. A possible fluid path for this is schematically portrayed by the arrow in upper right side of Figure 2b where a packet of fluid on the margin is cycled into the two-phase cone.

The models in Figure 2 are hypothetical and are based on the assumption of isotropic permeability and constant gas composition of the unboiled parent fluid during steady-state upflow. In a real hydrothermal system, however, the distribution and persistence of two-phase conditions, and therefore also the distribution of calcite, are likely to be far more complex as a consequence of anisotropic permeability and changes over time.

At Broadlands-Ohaaki, sub-boiling temperatures prevail in the upflow zone of the Broadlands sector (Fig. 1), and this is possibly due to permeability being influenced more by horizontal aquifers rather than vertical fractures. Consequently, calcite is widespread in the subsurface region here. Calcite occurrences within the Ohaaki sector, however, diminish at depths shallower than 800 m. The reduction and local absence of calcite here overlaps with zone of boiling upflow (and fracture dominated permeablity) and resembles the hypothetical distribution of calcite in Figure 2b. The calcite distribution in a real system is highly variable over short distances (<100 m) as influenced by the distribution of boiling and sub-boiling conditions.

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