MINERALOGICAL OBSERVATIONS ON CARBONATE SCALING IN GEOTHERMAL WELLS AT KAWERAU AND BROADLANDS

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ABSTRACT

Variation in the development of prism, scalenohedron and basal pinacoid faces of calcite produces a considerable range in crystal morphology in scale deposits, and platy crystals dominated by the basal pinacoid form are not uncommon. Mechanisms which could produce platy calcite include various combinations of lack of Mg-poisoning, surface charge effects relative to fluid Ca^{++}/HCO_3^-, preferential nucleation of prism rather than basal faces on the pipe wall, or rapid absolute growth rates resulting from high degrees of supersaturation (in turn due to primary fluid composition which may also be consequent upon a pressure decrease or temperature increase and/or high mass flow).

Several wells which have developed scales exhibiting major compositional variations (Mg-calcite, dolomite, talc) occur principally near the margins of the fields and probably result from Mg, Si-enriched groundwater incursions.

INTRODUCTION

Production from more than a dozen wells at Kawerau and Broadlands is hampered to varying degrees by calcite scale depositions within the well casing or liner. Mineralogical study of approximately 70 workover samples has revealed rare variation in crystal structure and major element composition, and common variations in crystal morphology or habit (Table 1). This paper attempts to relate these variations to downhole chemical/physical environments. Unfortunately many scale samples recovered comprise only that material remaining after partial reaming with a drill rig.

All calcite is assumed to have precipitated from the liquid fraction of a two-phase fluid at temperatures of the order of 230-280°C. Basically, flashing leads to loss of CO_2 and increased activity of Ca^{++}, the pH rises and bicarbonate is converted to $CO_3^{=}$ and subsequent supersaturation with respect to calcite leads to its precipitation.

CRYSTAL MORPHOLOGY OF CALCITE SCALE

Mineralogy

Scale fragments recovered after reaming are 1-10 mm thick and consist of aggregates of crystals with individual maximum dimensions of 0.1 - 5 mm. Several growth layers characterise many samples. Crystal morphology varies from prismatic to platy corresponding to the relative development of prism, scalenohedron and basal pinacoid forms.. Combinations of prism and scalenohedron forms predominate at Kawerau but most calcite at Broadlands shows some development of the basal pinacoid and in some cases this form dominates the crystal with length (c-axis): breadth ratios of 0.01. X-ray diffraction patterns of this platy material exhibit anomalously high intensities for the (006) reflection, due to the preferred orientation of platy crystal fragments. If the degree of sample grinding (i.e. grain size) is consistent, the relative intensity of the (006) reflection yields a qualitative estimate of the degree of platiness.

The prismatic forms can be seen under the microscope to develop a dense intergrowth of crystals with the c-axis aligned at a high angle to the pipe wall. Platy crystals grow with their c-axis parallel to the pipe and form a skeletal intergrowth which may contain up to 60% pore space (Fig. 1). In some instances the plates are bent up to 15" up-pipe. Both forms have uniaxial optical signs.

A significant difference exists in the fluid inclusion density of prismatic and platy forms. The latter (BR 19) includes 10-20 vol.% of inclusions compared with a more normal value of 1-2% in the prismatic variety (KA 8). Variable proportions of vapour (30-60%) in the platy variety indicates boiling conditions and precludes temperature determinations.

Representative analyses of prismatic and platy forms are given in Table 2. Platy calcite has a relatively pure composition with decreased Mg, Sr and slightly higher Si relative to prismatic calcite.

Oxygen isotopic compositions are broadly consistent with measured temperatures and reported water compositions, but carbon isotopic compositions apparently differ by 0.8% and 1.7%, from equilibrium fractionation of 13C between CO_2-$CaCO_3$, for prismatic and platy calcite respectively, possibly suggesting a growth rate too rapid for isotopic equilibrium.

Habit	Structure	Composition
prismatic (BR 3, KA 8, 14, 16)	aragonite (BR 6)	dolomite (BR 11, KA 17, 19)
	vaterite (?) (BR 11, KA 17, 19)	**Mg-calcite/talc** **(BR 2)**
platy (BR 2, 7, 8, 11, 19, KA 19, 21)		

Talc is also associated with prismatic calcite in KA 16.
Associated sulphide scales are dominated by pyrrhotite, but include traces of galena, sphalerite, chalcopyrite and covellite.

Table 1. Varieties and principal occurrences of carbonate and associated scale deposits at Kawerau and Broadlands.

	Prismatic calcite (1)	Platy calcite (2)	Mg-calcite (3)
CaO	nd	nd	49.40
MgO	0.3	0.06	6.72
MnO	0.3	0.15	0.36
SrO	0.3	0.15	nd
SiO_2	0.06	0.12	0.8
Al_2O_3	0.07	0.07	0.6
Na_2O	0.2	0.2	0.04
BaO	0.005	0.005	nd

Table 2. Compositions of calcite scalings from Broadlands and Kawerau. Samples: (1) KA 16, workover of 8 5/8 casing of 6/79, NZGS colln. P42302; (2) BR 19 6 5/8 liner 9/80, P42602; (3) BR 2, 6 5/8 liner 5/71, P39702. 1 and 2 by emission spectrography, 3 by electron microprobe.

Occurrence

Most calcite is deposited within 100-300 m above the major feed zones where water entering the well begins to boil, and in general the platy variety is restricted to the upper part of this deposition zone. Platy calcite is more common at Broadlands than at Kawerau, consistent with a number of possible causes outlined below.

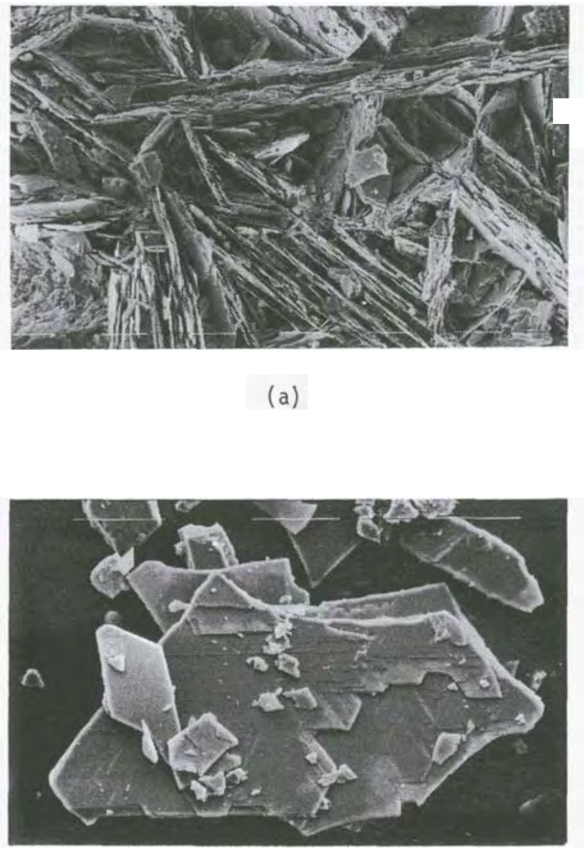
Platy calcite is a relatively uncommon form in nature, where needles (inverted from aragonite) crystallise from sea water and equant rhombs form from fresh water.

Mechanisms which may affect calcite morphology

Possible controls on differential growth rates of calcite crystal faces in the geothermal environment are outlined below:

1. Skeletal crystallisation resulting from a rapid absolute growth rate. SEM images suggest abundant growth defects are present (probably also indicated by the high volume of fluid inclusions), a characteristic of rapid growth. However, calculated on the basis of time between workovers and taking into account the pore space of platy calcite scales there appears to be little difference in the mass precipitation rate of the two forms, although these estimates are poorly constrained and rates may not be constant with time. In BR 19 a possible correlation of growth zones with observed changes in WHP (J.A. Southon, pers. comm.) allows a rate of $\sim$ 0.1 mm/day to be calculated. Rapid growth would result from high degrees of supersaturation, but not so high such that the nucleation rate dominated and a very fine grained precipitate resulted. Growth rates at least as high as those suggested at Broadlands and Kawerau produced aragonite and non platy calcite at Kizildere (James 1977) indicating that rapid growth is not sufficient to produce this form in the absence of a suitable chemical environment. The degree of supersaturation could be increased in a number of ways in the geothermal well environments over and above field differences in the degree of supersaturation of the primary fluid (higher supersaturation with respect to calcite at Broadlands relative to Kawerau is indicated by higher CO_2, greater salt concentrations and higher pH):

(a) Pressure decrease - platy calcite develops upwell of prismatic calcite where flashing is more advanced. It can also be correlated with orifice effects at 6 5/8" - 8 5/8" pipe diameter changes, and in-pipe from slots where a pressure gradient exists between reservoir and pipe and where turbulence produces local flashing zones. In one



(a)

(b)

Fig. 1. SEM micrographs of platy calcite. Scale bars are 100 µm.
a) Face-on picture of scale comprising porous intergrowth of calcite plates, c-axis parallel to page.
b) Platy calcite crystal, c-axis normal to page. Note that all these rhombohedral cleavages can be seen.

well (BR 19) the relative thickness and degree of platiness of two growth zones appear to correlate with two sharp drops in WHP immediately prior to a workover in August 1980, and the correlation may extend to two other wells which record drops in WHP.

(b) An upward temperature increase in wells with inversions, as relatively cool waters rise into hotter feed zones, will increase calcite supersaturation in accord with its retrograde solubility.

(c) Mass output. High output wells have been recognised as being the most problematical regarding calcite scaling and it is further noted here that the platy variety is largely restricted to the higher of these high mass output wells.

2. Selective inhibition of growth normal to the c-axis. Two mechanisms have been proposed by sedimentary petrologists. Folk (1974) suggested that incorporation of Mg ions would distort the lattice and inhibit sideways growth in waters with high Mg/Ca ratios. Lahann (1977) suggested that different surface charges on different crystal faces would lead to preferential growth in the c-axis direction depending on the Ca^{++}/HCO_3^- ratio of the fluid. There is a good correlation of the degree of platiness of scale calcite with the former, but not the latter, of these ratios. Thus Mg/Ca for wells developing platy calcite averages 0.04 compared to 0.17 for wells with prismatic calcite and ∿ 3 for sea water. This correlation is supported by the low Mg compositions of platy calcite discussed above

3. Preferential nucleation of basal or prism faces on pipe wall. Once nucleated a crystal would grow normal to the wall. Different surface charge characteristics of crystal faces may respond to variations in the well wall environment, or the restriction to high output wells might suggest mechanical inhibition of crystals which are aligned with their $Ca^{++}/CO_3^=$ sheet structures parallel to the mass flow direction (i.e. crystals with c-axes parallel to wall are preferred).

MAJOR COMPOSITIONAL VARIATIONS

Mg-calcite. Scale from a 1971 workover of BR 2 consists of calcite containing an average of 14.7 mol.% $MgCO_3$ (Table 2). Microprobe analyses and backscattered electron images show Mg/Ca distribution to be heterogeneous, which together with the presence of associated talc suggests an origin by replacement of dolomite. Low Mg in well fluid analyses suggests the scale developed in response to a unique event in which steam heated Mg, Si-rich groundwater entered the well, consistent with suggestions (R.W. Henley, pers. comm.) for such an incursion at the base of the casing.

Dolomite. In three wells (BR 11, KA 17, 19) minor (∿ 5%) dolomite occurs with calcite and possible vaterite. This assemblage is repeated in two consecutive workovers. The calcite is platy, possibly because all available Mg was partitioned into the dolomite. The well fluids are slightly enriched in Mg and are situated near the field margins.

Talc. In addition to the occurrence in BR 2, talc also occurs as a thin (0.5 mm) pale brown layer between two layers of prismatic calcite in KA 16 (also located near the margin of the Kawerau field).

VARIATION IN CRYSTAL STRUCTURE

One and possibly two metastable polymorphs of calcite occur at Kawerau and Broadlands. Aragonite has been described by Browne (1973) from BR 6. Recent experimental work (Katz, 1973) suggests that calcite could not have precipitated from fluids of BR 6 (Mg/Ca) composition, regardless of precipitation rate.

Vaterite (?) is a possible constituent of scales which contain dolomite. It is a metastable pseudohexagonal form of $CaCO_3$ and its occurrence in boiler scale has previously been attributed to low Mg, Sr water compositions.

ASSOCIATED SULPHIDE SCALES

Thin (generally < 1 mm) black sulphide scales are dominantly pyrrhotite, but traces of galena, sphalerite, chalcopyrite and covellite have been noted. An antipathetic relationship with calcite can be observed in some wells, with sulphide scales increasing up well, as calcite decreases, presumably due to their opposite solubilities with respect to temperature. The thin regular sulphide layers are considered to have deposited when the wells were shut in and the temperature declined in the upper parts of the holes. Although some pyrrhotite can be regarded as in situ corrosion it is not uncommon for such scale to be separated from the casing by a layer of calcite.

CONCLUSIONS

A platy form of calcite, generally uncommon in nature, is strongly developed some geothermal wells due to combinations of various contributing factors, of which the root cause is probably a lack of Mg-inhibition of growth normal to the c-axis. Rapid growth from waters highly supersaturated with respect to calcite aided such growth, but cannot develop this morphology if the fluid chemistry is not broadly appropriate. For the same mass of calcite precipitated the platy form will clog a well approximately twice as fast as the prismatic form. Some control over its formation (addition of trace Mg?) may thus be useful in some cases.

Minor development of Mg-phases (dolomite, Mg-calcite, talc) occurs principally near field margins due to incursions of steam-heated groundwater.

The mineralogical stratigraphy of scale deposits has considerable potential to record (chronological and depth) variations in fluid compositions etc.

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