



# **HYDROTHERMAL ALTERATION MINERALOGY IN GEOTHERMAL FIELDS WITH CASE EXAMPLES FROM OLKARIA DOMES GEOTHERMAL FIELD, KENYA**

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## **ABSTRACT**

In geothermal environments, primary minerals usually tend to alter to secondary (hydrothermal alteration) minerals that are either stable or at least metastable in these environments. The formation of these hydrothermal alteration minerals is usually dependent on the temperature, permeability, pressure, fluid composition, initial composition of the rock and the duration of the hydrothermal activity. These factors are largely independent, but the effects of one or more of the factors can exert a dominant influence in the location and extent of hydrothermal alteration. Case study examples have been derived from studies done on the three exploration wells at Olkaria Domes geothermal field where appraisal drilling is currently underway. The main hydrothermal minerals in the geothermal field are albite, amphibole (actinolite), biotite, calcite, chlorite, chalcedony, epidote, fluorite, garnet, illite, K-feldspar (adularia), mordenite, secondary Fe-Ti oxides, sulfides (pyrite), titanite (sphene) and quartz. In addition, minor amounts of wairakite and prehnite are present. The occurrences and distribution of these hydrothermal minerals indicate that the minerals in all the wells show prograde variation patterns. The correlation of between the formation, interpreted hydrothermal alteration and fluid inclusion temperatures indicate that there have been temporal changes in the Olkaria Domes systems with part of the field indicating cooling whereas other parts indicate heating.

## **1. INTRODUCTION**

### **1.1 Definitions and Terminology**

#### **1.1.1 Minerals**

A mineral is defined as an element or a chemical compound that is normally crystalline and has formed as a result of geologic processes. Although any of the hundreds of minerals can group together to form a rock, only six are very common. These common minerals are referred to as the “rock forming minerals” and include quartz, feldspars, micas, amphiboles, pyroxenes and olivine. Others include ferromagnesian minerals, oxides, sulfides, carbonates and native elements.

### 1.1.2 Rock

By definition, a rock is a solid mass or compound consisting of at least two minerals (although there are some exceptions when a rock may consist entirely of one mineral). The minerals comprising the rock can be identified using common field-testing methods for individual minerals, particularly where the texture is sufficiently coarse-grained enough to distinguish the individual minerals with the naked eye or a hand lens. Where the grain sizes of the minerals comprising the rock are too fine-grained to recognize discrete minerals, petrographic methods can be used for reliable identification in many cases.

Petrographic methods involve the use of a microscope to examine the optical properties of discrete minerals magnified through the microscope lens. Properties include the behaviour of refracted, reflected and transmitted light either through a thin slice of the rock (called a thin section), or of a sample plug (for reflected light). The light source is adjusted to provide light, which polarized in one or two directions. Different minerals have characteristic optical properties, which can be used with tables of optical mineral properties to identify the mineral.

## 2. HYDROTHERMAL ALTERATION MINERALOGY

### 2.1 What is hydrothermal alteration?

Rock alteration simply means changing the mineralogy of the rock. The primary minerals are replaced by the secondary minerals because there has been a change in the prevailing conditions subjected to the rock. These changes could be changes in temperature, pressure, or chemical conditions or any combination of these. Hydrothermal alteration is a change in the mineralogy as a result of interaction of the rock with hot water fluids, called “hydrothermal fluids”. The fluids carry metals in solution, either from a nearby igneous source, or from leaching out of some nearby rocks.

Hydrothermal fluids cause hydrothermal alteration of rocks by passing hot water fluids through the rocks and changing their composition by adding or removing or redistributing components. Temperatures can range from weakly elevated to boiling. Fluid composition is extremely variable. They may contain various types of gases, salts (briny fluids), water, and metals. The metals are carried as different complexes, thought to involve mainly sulphur and chlorine.

### 2.2 Sources of hydrothermal fluids

There are three main possible sources of hydrothermal fluids, though it could be a combination of any or all the three:

- I. Near surface groundwater (called “meteoric” water) is the main source of hydrothermal fluids. Evidence from some ore deposits suggests meteoric waters may mix with juvenile or metamorphic waters during late stages of mineralization.
- II. Another source can be the magmatic rocks themselves, which exsolve water (called “juvenile” water) during the final stages of cooling.
- III. In metamorphic terranes a potential source of the fluids is dehydration reactions, which take place during the metamorphic event. With increasing temperature of metamorphism, early, low temperature, hydrous minerals recrystallize into new, higher temperature, anhydrous minerals. The excess water circulates through the surrounding rocks and may scavenge and transport metals to sites where they can be precipitated as ore minerals.

Hydrothermal fluids in plutonic settings are thought to circulate along a large-scale convective path. It would be analogous to a pot of boiling water: hottest water rises fastest directly above the heat source,

and at the surface changes flow direction to horizontal, and finally downwards along the sides of the pot. In a similar manner, hydrothermal fluids circulate upward and outward from an igneous intrusion at depth. Porous and permeable host rocks (those containing lots of interconnected pore spaces) allow this to happen more readily, for example, in coarse-grained sandstone. Some types of rocks, like shale or slate, are extremely impermeable. A layer of shale can cause damming or ponding of the hydrothermal fluids, which can lead to a concentration of mineralization behind the impermeable barrier. Fluid migration can be also facilitated by the presence of lots of thin layers.

Hydrothermal fluids also circulate along fractures and faults. A formation, which has a well-developed fracture system, may serve as an excellent host rock. Veins form where the fluids flow through larger, open space fractures and precipitate mineralization along the walls of the fracture, eventually filling it completely. Fault zones are excellent places for fluids to circulate and precipitate mineralization. Faulting may develop breccia and gouge, which is often a good candidate for replacement style mineralization. The form of mineralization and alteration associated with faults is highly variable, and may include massive to fine-grained, networks of veinlets, and occasionally vuggy textures in some breccias.

### **3. SAMPLING**

#### **3.1 Rig site during drilling of geothermal wells**

Cuttings from geothermal wells are normally sampled after every 2 m interval, but in cases where the sample was too little and unrepresentative, up to 4 m depth interval is sampled. Preliminary analysis of the cuttings and cores are normally done at the rig site by use of a binocular microscope and specimen samples which are representative of all the rock units penetrated are selected for detailed laboratory analysis of hydrothermal alteration minerals and fluid inclusion studies. For exploration drilling a few cores can be cut, but for appraisal and production drilling, cores are rarely cut because the stratigraphy and the formations are well understood and also the fact that it costs more to cut a core.

The problem with cuttings generally, is that the rock chippings in some of the samples are fine, usually smaller than the crystals hence bringing about difficulty in identifying some lithologic units conclusively. Also when the soft parts of the hydrothermally altered rock are ground during drilling, only the harder components reach the surface, hence less representative of the rock unit penetrated. Another problem is when cutting chips derived from a specific depth may have fallen from a shallow level due to cave-ins resulting to mixing of cuttings. Geosweeps are, however, carried out where mixing of cuttings is suspected. Time delays in sample cuttings to reach the ground result in depth difference between the true and the indicated depth and are usually greater for deeper samples. This anomaly is however corrected by reconciling the depths with the drill logs and calculating for the error.

#### **3.2 Field sampling during geological surface exploration**

In the field, hydrothermally altered samples are found where there are active or extinct hydrothermal activities. Hydrothermal minerals such as quartz, sulphur, zeolites, silica and clays are deposited at the vents where hydrothermal fluids leak on the surface. The sample here is scooped, and detailed descriptions are made including the sampling location. The sample is then stored in the sample bags for further laboratory analyses.

## **4. ANALYTICAL METHODS**

### **4.1 Stereo microscope analysis**

Binocular analysis of the cuttings, cores or field samples are done using the binocular microscope. A sample is scooped from the sample bag into a petri dish and washed with clean water to remove impurities and dust. Wetting the cuttings is necessary to enhance visibility of samples and obscure features such as finely disseminated sulphides e.g. pyrite. The sample is then placed on a mounting stage of the binocular microscope and among the essential features noted are the colour(s) of the cuttings, rock type(s), grain size, rock fabrics, original mineralogy, alteration mineralogy and intensity.

### **4.2 Petrographic microscope analysis**

Representative samples from all the lithologic units encountered in the well/field are selected and thin sections are prepared for petrographic studies. The thin sections are analyzed using the petrographic microscope. The petrographic microscope is used to confirm the rock type(s) and the alteration minerals, additional alteration minerals not observed by the binocular microscope, and to study the mineralogical evolution of the alteration minerals.

### **4.3 X-ray Diffractometer analysis**

The X-ray Diffractometer is used to qualitatively or quantitatively identify individual minerals e.g. clays and zeolites. Samples are selected from all the lithologic units and analysed for clays. The <4 microns fractions are prepared for x-ray diffraction by use of a mechanical shaker to separate the phyllosilicates from the rock matrix. Count data were collected from 2°-14° at intervals of 0.02°, 2θ for a time of 1 second. Crystals of the mineral to be identified e.g. zeolites, carbonate, clays and sulphides are picked from the rock samples and ground by using an automatic milling machine. Count data were collected from 4°-56° at intervals of 0.04°, 2θ for a time of 1 second. The procedure of preparing clay and zeolite samples for XRD analysis is shown in Appendices I and 2.

### **4.4 Fluid Inclusion analysis**

Double-polished thick sections (approximately 70 microns) of cuttings, which contain abundant quartz and calcite in veins, are used to prepare samples for fluid inclusion analysis. Fluid inclusions are small portions of fluid, which are trapped in a solid crystal as it grew or recrystallized. The fluids are thus samples of the original brine from which the crystal grew or a later fluid which bathed the crystal during crystallization. Primary fluid inclusions are concentrated along the first-order growth discontinuities or occur as isolated inclusions distributed within the crystals. Secondary fluid inclusions are trapped along healed cracks. If the crystal cools, the liquid will contract at a faster rate than the solid and a vapor bubble will form. At ambient temperatures, all types of inclusions contain a liquid aqueous solution and a gas bubble. This bubble forming process could be reversed to determine the temperature of mineral formation or temperature of homogenization (Th). The inclusion is heated until the fluid homogenizes in a single phase (i.e. bubble disappears) and the Th is measured.

### **4.5 Electron Microprobe analysis**

Electron microprobes permit the non-destructive, major and trace element analysis of small areas (~4 µm diameter) of solid materials in situ. Thin sections, which contain the minerals that are required for to be analysed in abundance e.g. epidote, are prepared for analysis. The analysis of minerals is carried

out using Scanning Electron Microprobe Quantometer (SEM-Q). The analysis is normally done at 15 kV with sample current of 15 nA and a beam diameter of 2-3 micrometers.

## 5. APPLICATION OF HYDROTHERMAL ALTERATION IN GEOTHERMAL SYSTEMS

### 5.1 Geothermometers

Hydrothermal minerals commonly used as geothermometers based on studies carried out in the Olkaria field are shown in Figure 1. First appearance of well-crystallized epidote indicates temperature of over 240°C in Olkaria field. Presence of chlorite and epidote indicate temperatures of 220-340°C and appearance of actinolite-tremolite occurs at 280-350°C. Presence of garnet normally indicates temperatures of over 300°C. Smectite is an indicator of temperatures of less than 220°C.

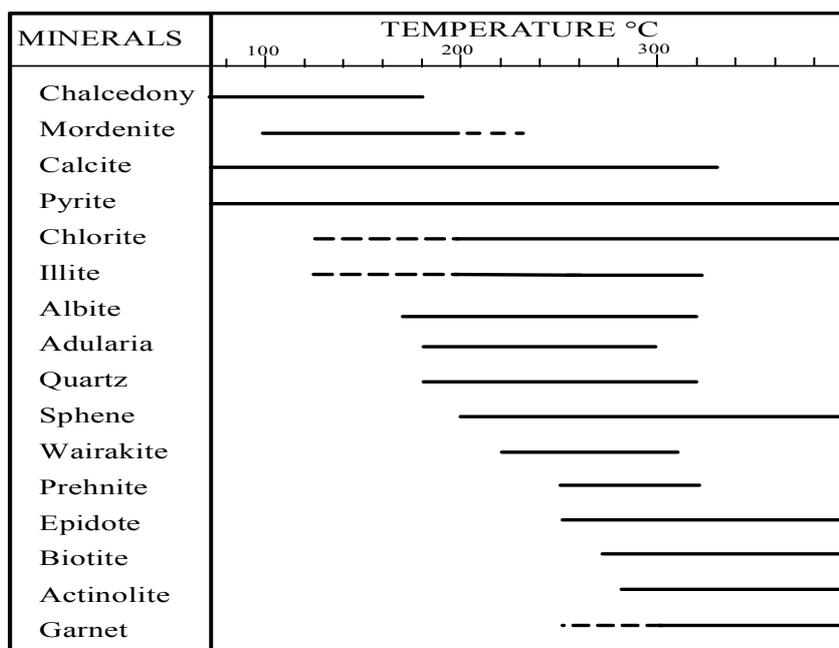


Figure 1: Common hydrothermal alteration minerals used as geothermometers and their temperature stability ranges. Dotted sections indicate mineral outside their usual stability ranges (modified from Reyes, 1990)

### 5.2 Permeability indicators

Indicators of high permeability in Olkaria geothermal system apart from high intensity alteration, bleaching of rocks, sheared or fractured rocks includes abundance of veins are quartz, illite adularia, abundant calcite and abundant pyrite. These minerals are commonly found in or adjacent to aquifers penetrated by wells and occur as alteration of the rock and in veins often as well formed crystals. Consequently indicators of low permeability apart from low alteration intensity and the absence of the above mentioned minerals are; prehnite, pyrhotite, abundant laumontite, abundant sphene instead of epidote occurring as rock alteration or tight veins.

### 5.3 Fluid chemistry

Acid alteration is accompanied by intense hydrogen metasomatism, base cation leaching and sulphate metasomatism. In general acid-altered rocks are composed of residual elements: aluminium, titanium, iron, silica, some potassium, and calcium, with most of the base cations in the original rock being leached away. Potassium is relatively immobile compared to other base cations; it occurs in alunite at low pH and high sulphate activity, and illite at higher temperatures, higher pH and high silica activity. In neutral pH suite, less hydrolysis occur and cations are less mobile. Alteration here largely involves the reshuffling of elements in the original rock into secondary minerals, and since replacement is often incomplete, primary chemical trends are usually retained.

### 5.4 Thermal history

The thermal history of a geothermal field can be obtained by studying the fluid inclusion homogenization temperatures ( $T_h$ ), which are reliable predictors of past to present subsurface temperatures. These temperatures are correlated with the measured stable formation temperatures and interpreted hydrothermal alteration temperatures. Interpreted alteration mineral temperatures and fluid homogenization temperatures ( $T_h$ ) that are above their stability and measured temperatures respectively indicate that the geothermal system has undergone some heating whereas those that are below indicate that geothermal system has undergone some cooling.

### **5.5 Setting the production casing**

The temperature ranges of minerals (especially clays and calc silicates) supported by fluid inclusion homogenisation temperatures and Standard Formation Temperature Tests (SFTT) are used to determine the depth that the production casing is set during drilling especially exploration wells. This ensures that the cold zones or the unwanted aquifers are cased off during drilling and hence no incursion of cold fluids into the well occurs.

### **5.6 Predicting scaling and corrosion tendencies of a well**

Acid fluids in wells form scales primarily composed of e.g. anhydrite, barite and pyrite corrode the well liners (Reyes, 1990). Acid-sulphate fluids may also attack the casing externally, reducing it largely to iron oxides and iron oxyhydroxides. The sulphides and the iron oxyhydroxides in the formation may be used to determine the corroding tendencies of fluids.

## **6. ALTERATION MINERALOGY (CASE EXAMPLE OLKARIA DOMES)**

### **6.1 Primary minerals**

The lithology of Olkaria domes is composed of unconsolidated pyroclastics that are dominant in the shallow levels overlying a volcanic sequence whose lithological composition is dominated by comenditic rhyolite, trachyte, basalt, tuff and some doleritic and syenitic dykes. The primary minerals found in the area are those normally contained in acid to basic rocks. Like elsewhere, primary minerals in Olkaria domes field are unstable and therefore tend to alter into those phases that are either stable or at least metastable in geothermal environments. The degree of primary textures is a function of formation permeability and the type, abundance, and grain size of primary minerals. Alteration of primary minerals occurs similarly in most geothermal fields, but some are specific to some fields. Shown below in Table 1 are the main primary minerals contained in Olkaria Domes rocks arranged according to decreasing susceptibility to hydrothermal fluids. Note that the susceptibility is the reverse or Bowen's reaction series where the earlier formed minerals are the last to alter whereas the later formed are the first to alter.

### **6.2 Alteration mineralogy**

In the Olkaria Domes geothermal field, hydrothermal alteration minerals appear both as replacement of the primary minerals, as well as fillings in vesicles, vugs and fractures. The distribution and abundance of the hydrothermal minerals were obtained from the petrographic and XRD studies of drill cuttings samples taken after every 2 m from the 3 exploration wells drilled in the area.

TABLE 1: Primary minerals, order of replacement and alteration products of Olkaria Domes volcanics

| Order of replacement  | Primary phases                   | Alteration products  |
|---|----------------------------------|--|
| <br>Increasing order | Volcanic glass                   | Zeolites, clays, quartz, calcite                           |
|   | Olivine                          | Chlorite, actinolite, hematite, clay minerals              |
|   | Pyroxenes, amphiboles            | Chlorite, illite, quartz, pyrite, calcite                  |
|   | Ca-plagioclase                   | Calcite, albite, adularia, quartz, illite, epidote, sphene |
|   | Sanidine, orthoclase, microcline | Adularia   |
|   | Magnetite                        | Pyrite, sphene, haematite                                  |
|   | Quartz                           | No alteration  |

The main hydrothermal minerals in Olkaria Domes field are albite, amphibole (actinolite), biotite, calcite, chlorite, chalcedony, epidote, fluorite, garnet, illite, K-feldspar (adularia), mordenite, secondary Fe-Ti oxides, sulfides (pyrite), titanite (sphene) and quartz. In addition, minor amounts of wairakite and prehnite are present. Mineral associations in vesicles are common and consist of two or more of the following minerals; chlorite, quartz, calcite, epidote and pyrite with the paragenetic sequence varying with depth and from one well to another.

### 6.3 Description and distribution of alteration minerals in Olkaria Domes

The distribution of hydrothermal minerals in wells OW-901, OW-902 and OW-903 are shown in Figures 2, 3 and 4 respectively. Below is a description of the hydrothermal alteration minerals encountered in the Olkaria Domes wells. The elevations of wells OW-901, OW-902 and OW-903 are 1890 m, 1957, and 2043 m respectively.

#### Adularia

Adularia occurs below 1238 m a.s.l in well OW-901; below 1197 m a.s.l in well OW-902 and below 1315 m a.s.l in well OW-903. The mineral forms minute anhedral to euhedral crystals that are pseudo-orthorhombic and are usually diamond shaped. It occurs as replacement of plagioclase or primary K-feldspars and is occasionally deposited in veins as well as forming incrustations in fissured rocks. Where it occurs as a replacement of plagioclase or K-feldspars, there is nearly an isochemical transformation to an optically and structurally different phase –adularia. In pseudomorphs after plagioclase phenocrysts, it produces a streaky extinction suggesting that the pseudomorphs are made up of numerous overlapping crystals of rhombic section. The mineral becomes rare until it disappears at 404 m a.s.l in well OW-901, 79 m a.s.l in well OW-902 and 441 m a.s.l in well OW-903.

#### Actinolite

Actinolite is green to greyish green in colour, forms radiating fibers or acicular crystals and also massive to granular aggregates in the groundmass and has a moderate birefringence. The mineral is formed as a replacement of ferromagnesian minerals in association with epidote and chlorite. Actinolite appeared in the deeper hotter parts of wells OW-901 and OW-903 (below 150 m a.s.l in well OW-901 and below 143 m a.s.l in well OW-903) but was conspicuously absent in well OW-902.

### Well OW-901 Lithology and Drilling Data

Location: **Olkaria Domes, Kenya** Fig: **N370** Circulation fluid: **Mud and aerated water**  
 Well no.: **OW-903** Depth range: **0-2200 m** Logger (-s): **G. Muchemi, P. Omenda, J. Mungania and J. Lagat**

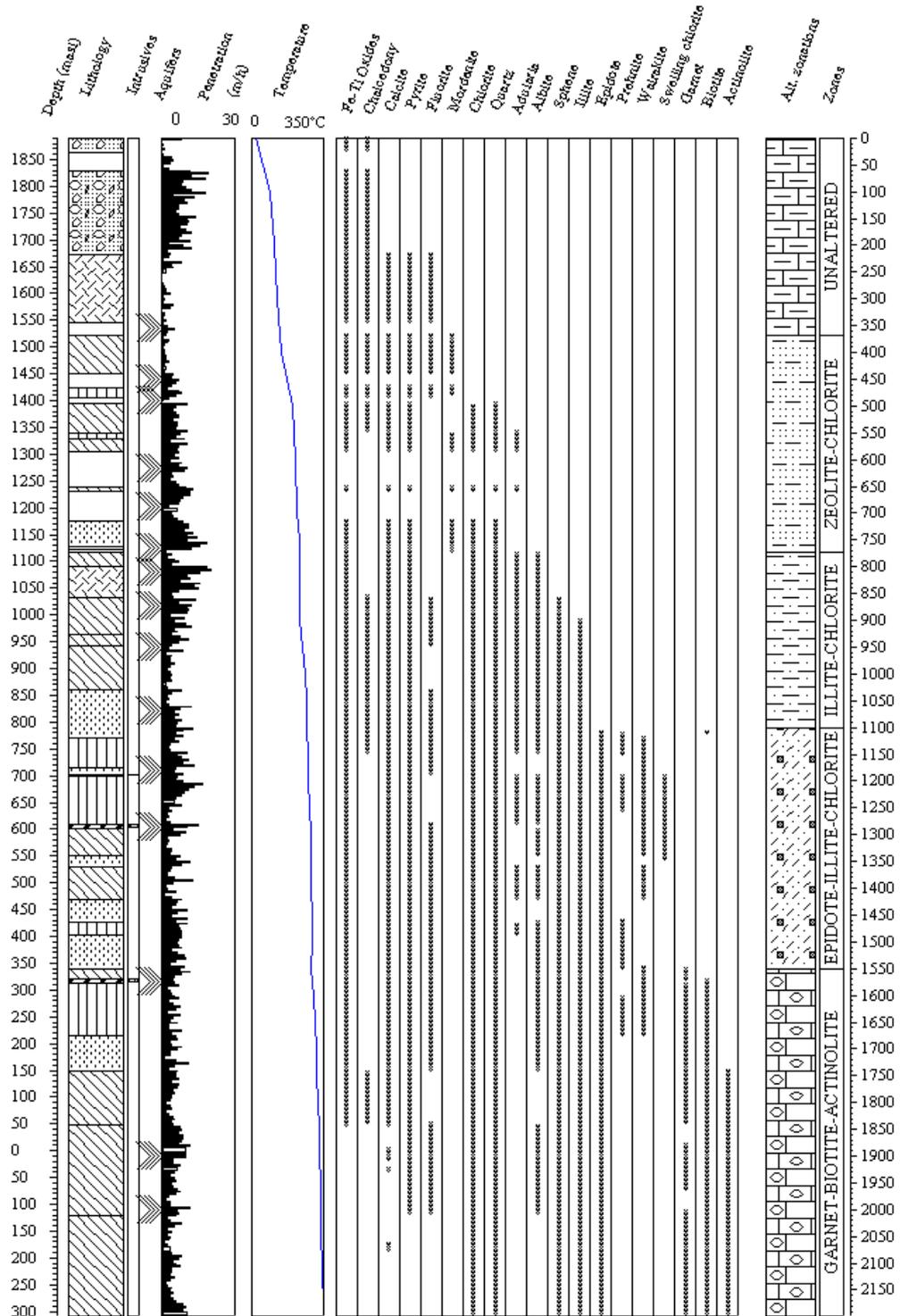


FIGURE 2: Lithology, distribution of hydrothermal alteration minerals and zonations in well OW-901

### Well OW-902 Lithology and Drilling Data

Location: **Olkaria Domes, Kenya** Fig: N 370 Circulation fluid: **Mud and aerated water**  
 Well no.: **OW-902** Depth range: **0-2199 m** Logger (-s): **G. Muchemi, P. Omenda, J. Mungania and J. Lagat**

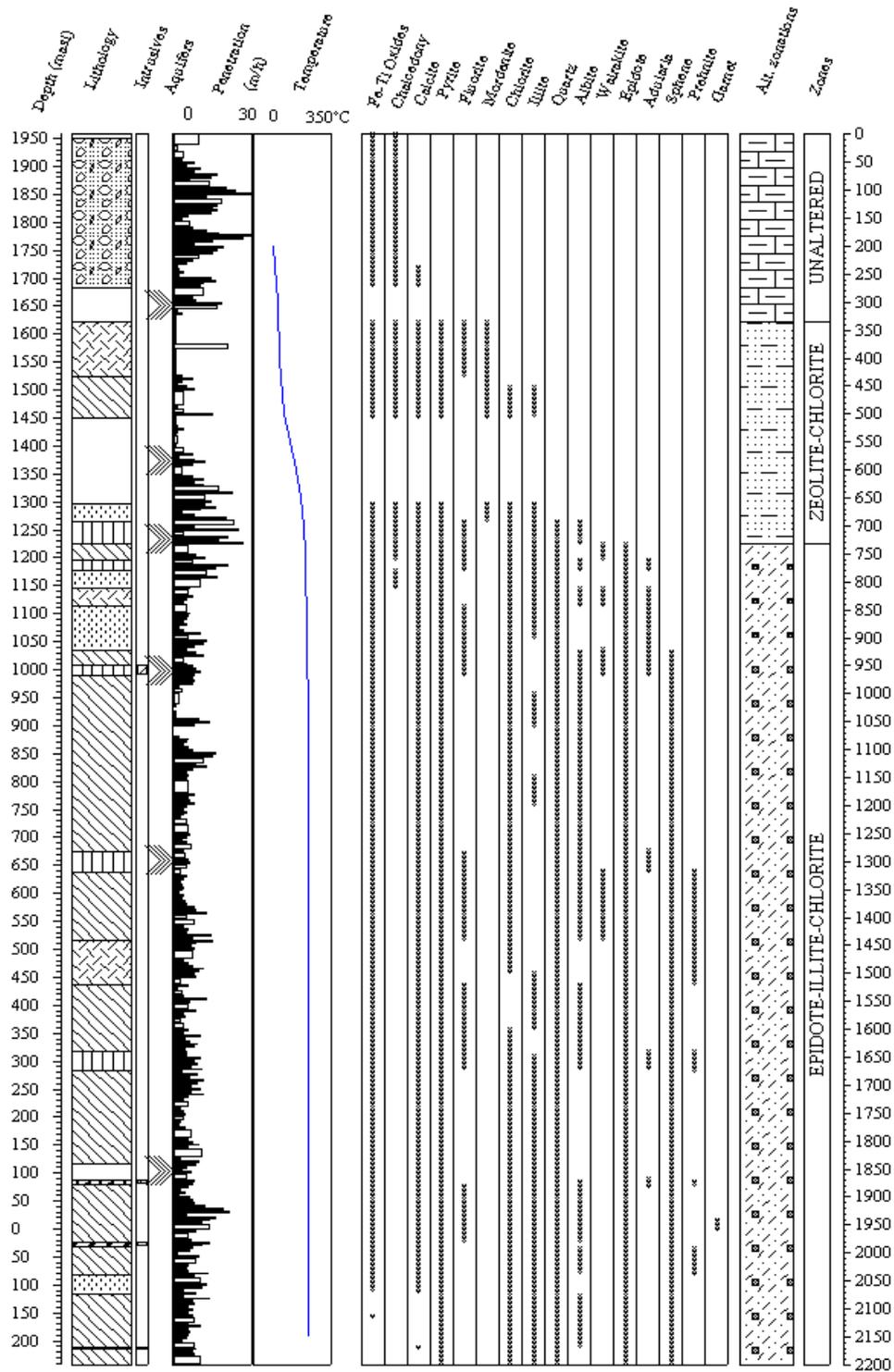


FIGURE 3: Lithology, distribution of hydrothermal alteration minerals and zonation in well OW-902. For lithology legend, see Appendix 3

### Well OW-903 Lithology and Drilling Data

Location: **Olkaria Domes, Kenya**    Rig: **N370**    Circulation fluid: **Mud and aerated water**  
 Well no.: **OW-903**    Depth range: **0-2200 m**    Logger (-s): **G. Muchemi, P. Omenda, J. Mungania and J. Lagat**

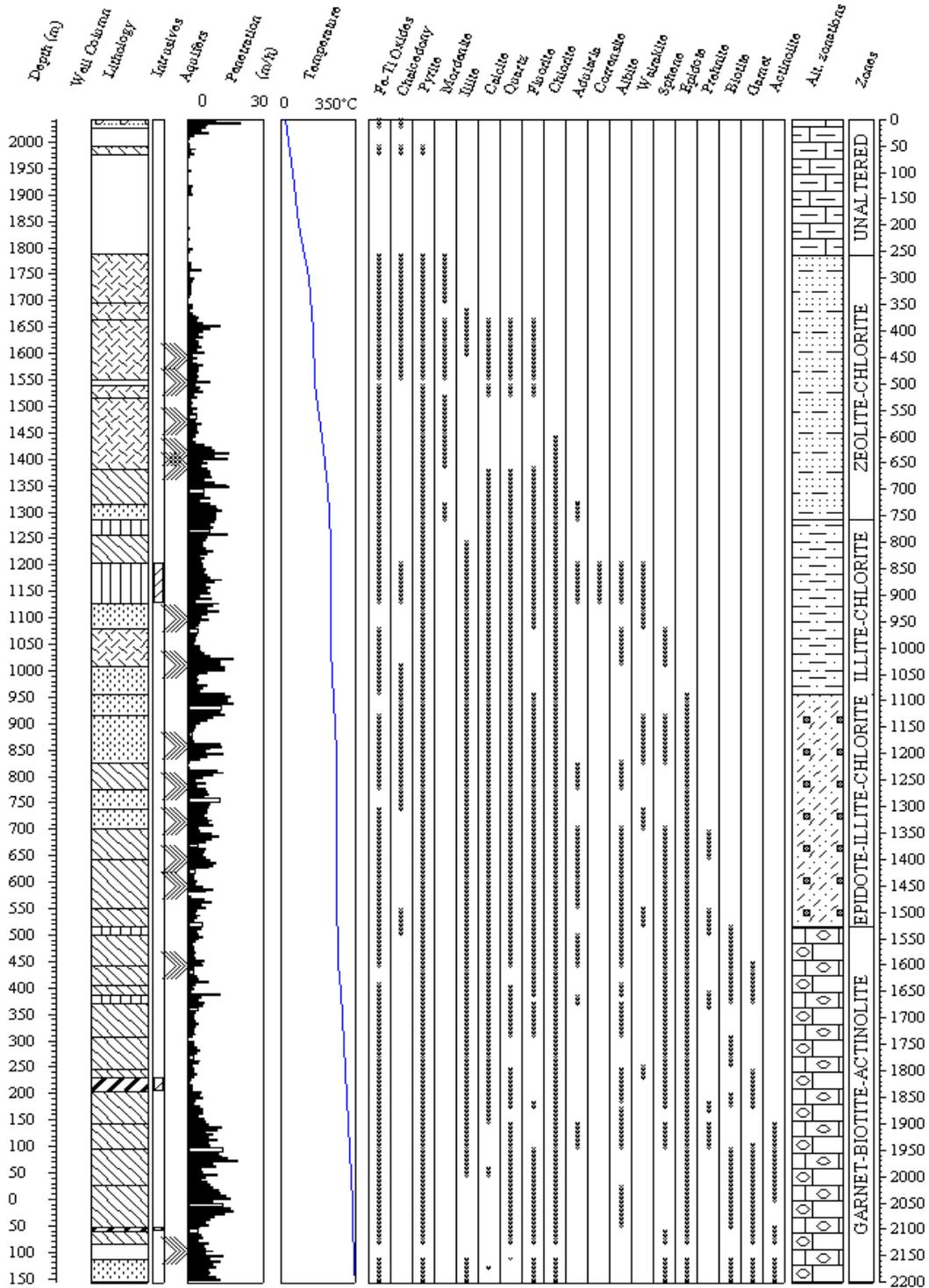


FIGURE 4: Lithology, distribution of hydrothermal alteration minerals and zonations in well OW-903

**Albite**

The term albitization here is referred to replacement of primary K-feldspar and plagioclase phenocrysts by hydrothermal albite. Albitization occurs below 1116 m a.s.l in well OW-901, below 1265 m a.s.l in well OW-902 and below 1203 m a.s.l in well OW-903. Albitized K-feldspar has a low refractive index and shows no zoning but typical chessboard like twinning is common.

**Biotite**

Authigenic biotite is occasionally present in several geothermal systems (Salton Sea, McDowell and Elders, 1980; Cerro Prieto, Schiffman, et al., 1984; Philippines, Reyes, 1990; Ngawha, Cox and Browne, 1998 and Aluto-Langano, Teklemariam, et al., 1996). Biotite at Olkaria Domes occurs sparingly at around 860 m a.s.l and continuously below 312 m a.s.l in well OW-901 and continuously below 517 m a.s.l in well OW-903. The mineral was, however, not encountered in well OW-902. Biotite forms weakly pleochroic, pale-green to brown-green crystals, which range from patchy aggregates of grains to sheet-like forms with sometimes-radial fan-shaped arrays. In association with garnet and actinolite, biotite is commonly used as an indicator of high temperatures of over 280°C (Bird et al., 1984).

**Calcite**

Calcite is a widely distributed alteration mineral occurring in all the three Olkaria Domes wells. Vesicles, fractures and veins contain white massive or colourless crystalline calcite deposits. Calcite replaces plagioclase phenocrysts, pyroxenes and volcanic glass. Crystal morphology of calcite is variable and ranges from individual thin-bladed crystals to equant or needle like crystals. Calcite crystals deposited in veins at 1578-1576 m a.s.l in well OW-901 were analysed qualitatively by X-ray diffraction (XRD) and the most intense peak ranged from about 3.02 to 3.05 Å, however, some of the calcite samples had their most intense X-ray reflection between 2.99 and 3.01 Å which indicate that the mineral contains significant manganese (Bargar and Beeson, 1984).

**Chalcedony**

In well OW-901 chalcedony occurs from the surface (1890 m a.s.l) to 1340 m a.s.l, at 1032-740 m a.s.l and at the deeper parts of the well at 150-48 m a.s.l where it is seen to be partly transformed into quartz. In well OW-902, it occurs from the surface (1957 m a.s.l) to 1145 m a.s.l except for basaltic formation at 1197-1177 m a.s.l where it was absent. In well OW-903, it occurs from the surface of the well (2043 m a.s.l) to 1539 m a.s.l, at 1203-1127 m a.s.l and from 1009-737 m a.s.l. Colourless, white, or bluish-grey cryptocrystalline chalcedony lines vesicles and coat fractures and veins. The open space cryptocrystalline silica deposits generally have massive, banded, or botryoidal texture. At greater depths where temperatures are high, chalcedony in vesicles is seen transforming or is completely transformed into quartz but the chalcedonic outline is still preserved.

**Chlorite**

Chlorite occurs below 1390 m a.s.l in well OW-901, below 1507 m a.s.l in well OW-902 and below 1234 m a.s.l in well OW-903 down to the bottom of the three wells. Chlorite shows a wide distribution and a big variability in colours, forms and textures. It varies in colour from light-to-dark green, has low birefringence and occasionally shows anomalously blue, brown or purple interference colours and presents two different forms. In the upper levels of the volcanic sequences, chlorite appears in small intergranular patches whereas at the deepest levels, chlorite is idiomorphic, forming radial aggregates in veinlets and vugs in association with quartz, calcite, epidote, amphibole and pyrite. Within veins, chlorite occurs as microspherules enclosed within epidote, but it may also replace primary pyroxene, and the matrix. XRD analyses of chlorite show conspicuous peaks at 7.0-7.2 Å and 14.0-14.5 Å in the untreated, glycolated and oven heated samples.

**Epidote**

The first appearance of epidote is from 780 m a.s.l in well OW-901, from 1225 m a.s.l in well OW-902 and from 955 m a.s.l in well OW-903 to the bottom of all the three wells. Epidote shows a systematic textural development with increasing depth. First crystals are anhedral and form fine-

grained aggregates and in deeper zones they are idiomorphic, tabular, radiated or fibrous. Epidote is found filling fractures, vesicles, and replacing primary plagioclase and pyroxene and in most cases forms mineral associations with mainly quartz, chlorite and sometimes calcite, wairakite and pyrite. Microprobe analyses of epidote from well OW-901 at 288 m a.s.l shown in Table 2 indicate that the mineral is a solid solution between epidote and clinozoisite.

TABLE 2: Epidote solid solution chemical formulae and mole fraction

| Well    | Chemical Formulae  | Ca   | Fe   | Al   | Si   | X <sub>epi</sub> | X <sub>czo</sub> |
|---------|--|------|------|------|------|------------------|------------------|
| OW-05   | Ca <sub>1.94</sub> Fe <sub>1.07</sub> Al <sub>1.93</sub> Si <sub>3.01</sub> O <sub>12</sub> (OH) | 1.94 | 1.07 | 1.93 | 3.01 | 0.36             | 0.64             |
| OW-19   | Ca <sub>1.99</sub> Fe <sub>1.11</sub> Al <sub>1.92</sub> Si <sub>2.98</sub> O <sub>12</sub> (OH) | 1.99 | 1.11 | 1.92 | 2.98 | 0.37             | 0.63             |
| OW-28   | Ca <sub>2.01</sub> Fe <sub>0.79</sub> Al <sub>2.34</sub> Si <sub>2.90</sub> O <sub>12</sub> (OH) | 2.01 | 0.79 | 2.34 | 2.90 | 0.25             | 0.75             |
| OW-33   | Ca <sub>1.96</sub> Fe <sub>0.92</sub> Al <sub>2.16</sub> Si <sub>2.95</sub> O <sub>12</sub> (OH) | 1.96 | 0.92 | 2.16 | 2.95 | 0.30             | 0.70             |
| OW-34   | Ca <sub>1.92</sub> Fe <sub>0.81</sub> Al <sub>2.26</sub> Si <sub>2.94</sub> O <sub>12</sub> (OH) | 1.92 | 0.81 | 2.26 | 2.94 | 0.26             | 0.74             |
| OW-901  | Ca <sub>2.05</sub> Fe <sub>0.88</sub> Al <sub>2.09</sub> Si <sub>2.97</sub> O <sub>12</sub> (OH) | 2.05 | 0.88 | 2.09 | 2.97 | 0.30             | 0.70             |
| Average |  | 1.98 | 0.93 | 2.12 | 2.96 | 0.31             | 0.69             |

### Fluorite

In all the three wells fluorite occurs intermittently, to the bottom of the wells from 1675 m a.s.l , 1621 m a.s.l and 1663 m a.s.l in wells OW-901, OW-902 and OW-903 respectively. Fluorite is dark brown, pink to reddish orange in colour and occurs in veins in association with calcite and quartz. It forms a typical cubic and to a lesser extent the octahedron as well as combinations of these two and other rarer isometric habits. A vein filling analyzed for mineral identification qualitatively using the XRD in well OW-901 at 1578-1576 m a.s.l consisted of both calcite and fluorite. Fluorite crystals picked in well OW-903 at 1221-1219 m a.s.l were analyzed qualitatively using the XRD and the diffractogram showed strong peaks at 3.16 Å and 1.93 Å.

### Garnet

Garnet occurs as clusters of anhedral to subhedral crystals in association with epidote, biotite, amphibole and chlorite in veins in rocks below 1550 m a.s.l in well OW-901 and below 405 m a.s.l in well OW-903. Microscopic studies failed to identify garnet in OW-902, but it was detected by the electron microprobe at 9-3 m a.s.l. The exact depth of its first occurrence and distribution is not therefore certain. Garnet has a moderately high relief, exhibits no cleavage and is isotropic. Table 3 shows the electron microprobe analyses of garnet from 288-286 m a.s.l in well OW-901, 9-3 m a.s.l in well OW-902 and 27-25 m a.s.l in well OW-903 by Karingithi (2002). The results indicate garnet to be a solid solution between andradite and grossular. Presence of garnet normally indicates temperatures of over 300°C (Bird et al., 1984).

TABLE 3: Garnet solid solution chemical formulae and mole fraction

| Well   | Chemical Formulae   | Ca   | Fe   | Al   | Si   | X <sub>and</sub> | X <sub>gro</sub> |
|--------|---|------|------|------|------|------------------|------------------|
| OW-05  | Ca <sub>2.95</sub> Fe <sub>1.29</sub> Al <sub>0.73</sub> Si <sub>2.94</sub> O <sub>12</sub> | 2.95 | 1.29 | 0.73 | 2.94 | 0.64             | 0.36             |
| OW-19  | Ca <sub>2.97</sub> Fe <sub>1.16</sub> Al <sub>0.82</sub> Si <sub>2.99</sub> O <sub>12</sub> | 2.97 | 1.16 | 0.82 | 2.99 | 0.58             | 0.42             |
| OW-28  | Ca <sub>3.09</sub> Fe <sub>1.25</sub> Al <sub>0.79</sub> Si <sub>2.88</sub> O <sub>12</sub> | 3.09 | 1.25 | 0.79 | 2.88 | 0.61             | 0.39             |
| OW-33  | Ca <sub>3.03</sub> Fe <sub>1.01</sub> Al <sub>1.06</sub> Si <sub>2.89</sub> O <sub>12</sub> | 3.03 | 1.01 | 1.06 | 2.89 | 0.49             | 0.51             |
| OW-34  | Ca <sub>2.96</sub> Fe <sub>1.13</sub> Al <sub>0.97</sub> Si <sub>2.89</sub> O <sub>12</sub> | 2.96 | 1.13 | 0.97 | 2.89 | 0.54             | 0.46             |
| OW-901 | Ca <sub>2.98</sub> Fe <sub>1.20</sub> Al <sub>0.84</sub> Si <sub>2.91</sub> O <sub>12</sub> | 2.98 | 1.20 | 0.84 | 2.91 | 0.59             | 0.41             |
| OW-902 | Ca <sub>3.01</sub> Fe <sub>1.20</sub> Al <sub>1.07</sub> Si <sub>2.84</sub> O <sub>12</sub> | 3.01 | 1.20 | 1.07 | 2.84 | 0.53             | 0.47             |
| OW-903 | Ca <sub>2.88</sub> Fe <sub>1.30</sub> Al <sub>0.88</sub> Si <sub>2.66</sub> O <sub>12</sub> | 2.88 | 1.30 | 0.88 | 2.66 | 0.60             | 0.40             |

**Illite**

Illite is detected below 990 m a.s.l in well OW-901, below 1557 m a.s.l in well OW-902 and below 1243 m a.s.l in well OW-903. The mineral is light green to white in colour, replaces K-feldspar and occurs as a vein and vesicle-filling mineral. XRD analyses of illite show no change at the 10 Å XRD in the untreated, glycolated and oven-heated samples (Grim, 1968).

**Mordenite**

White fibrous radiating hemispherical crystals of acicular mordenite are deposited in vesicles of lavas, open spaces between breccia fragments and perlitic cracks of partly altered glass in the upper few hundred meters of the three wells. Qualitative XRD analysis of the mineral showed strong peaks at 9.08 Å and 3.35 Å. In Icelandic geothermal systems, mordenite forms over a temperature range of about 75°C to around 230°C (Kristmannsdóttir and Tómasson, 1978). The measured temperature range at the depths where mordenite occurs in Olkaria Domes is in the range 100-220°C which is comparable to that of Icelandic systems.

**Oxides**

Oxidation is simply the formation of any type of oxide mineral. The most common ones to form are mainly iron oxides, but many different types can form, depending on the metal cations present. Sulfide minerals often weather easily because they are susceptible to oxidation and replacement by iron oxides. Oxides form readily in the surface or near surface environment, where oxygen from the atmosphere is more readily available and at the baked contact between the cold and the hot rock. Oxidation was noted in all the three wells from the surface to near the bottom of the wells where it becomes rare to none at all.

**Prehnite**

Prehnite is a rare mineral in Olkaria Domes wells and occurs intermittently below 770 m a.s.l in well OW-901, below 639 m a.s.l in well OW-902 and below 701 m a.s.l in well OW-903. The mineral becomes rare disappearing completely below 214 m a.s.l in well OW-901, below -81 m a.s.l in well OW-902 and below 95 m a.s.l in well OW-903. It occurs as a vein-filling mineral mainly in association with albite, epidote, chlorite, calcite and quartz. It is recognized in thin section by its sheaf like 'bow-tie' structure, good cleavage in one direction and strong birefringence. Three analyses of prehnite in well OW-901 at 288-286 m a.s.l indicate an average composition of  $\text{Ca}_{2.4}\text{Fe}_{0.8}\text{Al}_{1.2}\text{Si}_{3.3}\text{O}_{10}(\text{OH})_2$ . The few analyses may not be representative, but they may indicate substantial concentration of iron (Fe) in the prehnite.

**Pyrite**

Pyrite crystals are present in well OW-901 from 1675 m a.s.l, becoming rare until it disappears below -120. In well OW-902 it occurs from 1621 m a.s.l to the bottom of the well and in well OW-903 it occurs from 1991 m a.s.l to the bottom of the well. It occurs as euhedral cubic crystals with brassy yellow luster in reflected light. Tiny cubic pyrite crystals were deposited in fractures, vesicles and veins and as disseminations in the groundmass. XRD analysis of pyrite indicate strong peaks at 3.13 Å, 2.71 Å, 2.42 Å, 2.21 Å and 1.91 Å

**Quartz**

Quartz is colourless to white in colour and occurs in euhedral to subhedral crystals. It is identified both as open space (vesicle) fillings and vein filling mineral. In well OW-901, quartz occurs from 1395 m a.s.l to the bottom of the well, in well OW-902, it occurs from 1265 m a.s.l to the bottom of the well and in well OW-903 it occurs from 1663 m a.s.l to the bottom of the well. Euhedral open space quartz crystals up to 2 mm long were deposited later than chalcedony in basaltic formation at 1203-1127 m a.s.l in well OW-903. Most of these quartz deposits consist of tiny euhedral to subhedral crystals that formed on top of botryoidal chalcedony in vesicles, veins and fractures. The same rock unit also consists of thin veins of quartz or tiny colourless crystals that formed in open spaces without earlier chalcedony deposits.

**Sphene**

In well OW-901, sphene was encountered from 1032 m a.s.l to the bottom of the well, in well OW-902, it occurs from 1035 m a.s.l to the bottom of the well and in well OW-903, it occurs sporadically from 1079 m a.s.l to the bottom of the well. Sphene occurs mainly as irregular grains and rarely as clear euhedral crystals having acute rhombic sections. The mineral occurs mainly as a result of alteration of ferromagnesian minerals in association with chlorite, quartz and calcite.

**Swelling chlorite and corrensite**

Swelling chlorite was encountered in a basaltic formation at 686-588 m a.s.l in well OW-901. XRD analysis of the clay showed peaks for the untreated run at 14.28 Å, the glycolated run swells to 16.74 Å and the oven heated run collapses to 14.16 Å. Corrensite was also identified in a basaltic formation in well OW-903 at 1143-1137 m a.s.l. The untreated sample peak is at 29.30 Å, the glycolated peak swell to 31.30 Å and the oven heated run collapses completely.

**Wairakite**

Wairakite occurs rarely and intermittently below 770 m a.s.l in well OW-901, below 1225 m a.s.l in well OW-902 and below 103 m a.s.l in well OW-903, disappearing at depth in all the three wells. The mineral is found as open space filling in association with quartz and calcite. XRD analysis indicated strong peaks at 3.39 Å and 5.56 Å.

**6.4 Fluid inclusion geothermometry**

The homogenization temperatures ( $T_h$ ) of fluid inclusions in Olkaria Domes field samples were measured to determine the formation temperatures during their entrapment. These inclusions are all hosted by calcite and quartz, which occurs widely in the geothermal system. The  $T_h$  values at 240 m a.s.l in well OW-901 ranged from 238-272°C in quartz veins and from 280-320°C in calcite veins. The formation temperature at this depth is 314°C. The lowest  $T_h$  value (238°C) in quartz veins from this well is 76°C below the measured formation temperature and the highest value (272°C) is 42°C below to the measured formation temperature (314°C). The average value for the inclusions in quartz veins is 256 °C and is 58 °C below the measured formation temperature. In the calcite veins the lowest  $T_h$  value of 280°C is 34°C below the measured formation temperature and the highest  $T_h$  value (320°C) is 6°C above the measured formation temperatures (314°C). The average value for the inclusions in the calcite vein is 301°C and is 13°C below the measured formation temperature. These measurements indicate the inclusions in calcite vein represent close to the current formation temperatures whereas the quartz veins indicate past cooler conditions. If this interpretation is valid, it implies that the silica in quartz precipitated from hotter fluids is mostly derived from the primary feldspars of the rock and not of the earlier quartz precipitated under cooler conditions.

In well OW-902 at 689 m a.s.l  $T_h$  values in inclusions hosted in quartz veins ranged from 210-256°C with an average of 237°C, whereas the formation temperature at this depth is 247°C. In well OW-902, the highest value from the  $T_h$  value (256°C) is equivalent to the boiling point curve value (256°C) and 8°C above the measured formation temperature of 247°C. The lowest  $T_h$  value (210°C) is 37°C lower than the maximum measured formation temperature. The average  $T_h$  value of 237°C in this well corresponds fairly well with the present day conditions. The  $T_h$  values of inclusions in quartz veins at 517 m a.s.l in well OW-903 varied widely between 178-275°C with an average of 219°C whereas the formation temperature at this depth is 265°C. The lowest  $T_h$  value of 178°C is 87°C lower than the measured formation temperature suggesting that the fluids were trapped when temperatures were lower than the present day values. The highest  $T_h$  measurement of 275°C is 10°C higher than the measured formation temperature indicating that the fluids in these inclusions were trapped at nearly the same temperatures as current measured formation temperatures. The fluid compositions could not be determined because the inclusions were very tiny and was difficult to measure the melting temperature ( $T_m$ )

### 6.5 Measured, hydrothermal alteration and fluid inclusion temperatures

In any geothermal system, there is always some uncertainty whether observed minerals distribution and zonations reflect current formation temperatures or are related to some previous thermal events or regimes. In the Greater Olkaria geothermal area as in other geothermal fields throughout the world, hydrothermal alteration minerals are important indicators of subsurface thermal changes. A correlation between measured, hydrothermal alteration and fluid inclusion temperatures indicate how a particular geothermal system has evolved with time. Figure 5 shows the correlation between measured, interpreted hydrothermal alteration and fluid inclusion temperatures in well OW-901.

Geothermometry of alteration minerals and fluid inclusions in well OW-901 indicate that there has been some heating. However, calcite veins with homogenization temperatures averaging 301°C closely reflect current conditions in the reservoir. High temperature hydrothermal alteration minerals e.g. epidote, biotite, actinolite and garnet seem to be in equilibrium with the present geothermal system in well OW-901, with all the minerals occurring within their temperature stability ranges. The correlation between measured, interpreted hydrothermal alteration and fluid inclusion temperatures in well OW-902 shown in Figure 6 indicate probable cooling with hydrothermal minerals occurring below their stability temperature ranges. Here garnet occurs where the measured formation temperature is below its temperature stability range indicating it is relict.

Fluid inclusion temperatures, however, seem to reflect current conditions with the average homogenization temperature of 237°C being close to the measured formation temperatures of 247°C. Well OW-903 (Figure 7) had average fluid inclusion temperatures in quartz veins way below the measured formation temperatures with an average of 219°C while the measured formation temperature at that depth is 265°C. This indicates that there has been heating in the system since the inclusions were trapped. The interpreted hydrothermal alteration temperatures indicate that the alteration minerals are in equilibrium with the geothermal system with illite, epidote, biotite, garnet and actinolite all occurring within their temperature stability ranges.

Index minerals used to construct isograds across wells OW-901, OW-903 and OW-903 in Olkaria Domes field include actinolite, chlorite, epidote, garnet and illite. Isograds give a general picture of the temperature distribution in a geothermal system. Strictly speaking, however, a definite isograd (e.g. the epidote isograd) does not necessarily represent a definite temperature. The distribution of hydrothermal minerals isograds is not distinctly parallel to the isothermal contours (Figure 8) indicating that hydrothermal alteration is not a function of subsurface temperature only but the rock composition also influences the kinetics of the hydrothermal alteration minerals formation. The isograds clearly indicate high and shallow temperatures towards well OW-901 and low temperatures towards well OW-902. In well OW-902, below 1000 m a.s.l, the temperature becomes more or less isothermal, with very little or no change with depth. Biotite and actinolite were not encountered in the well, but garnet was encountered at temperatures well below its stability temperature range.

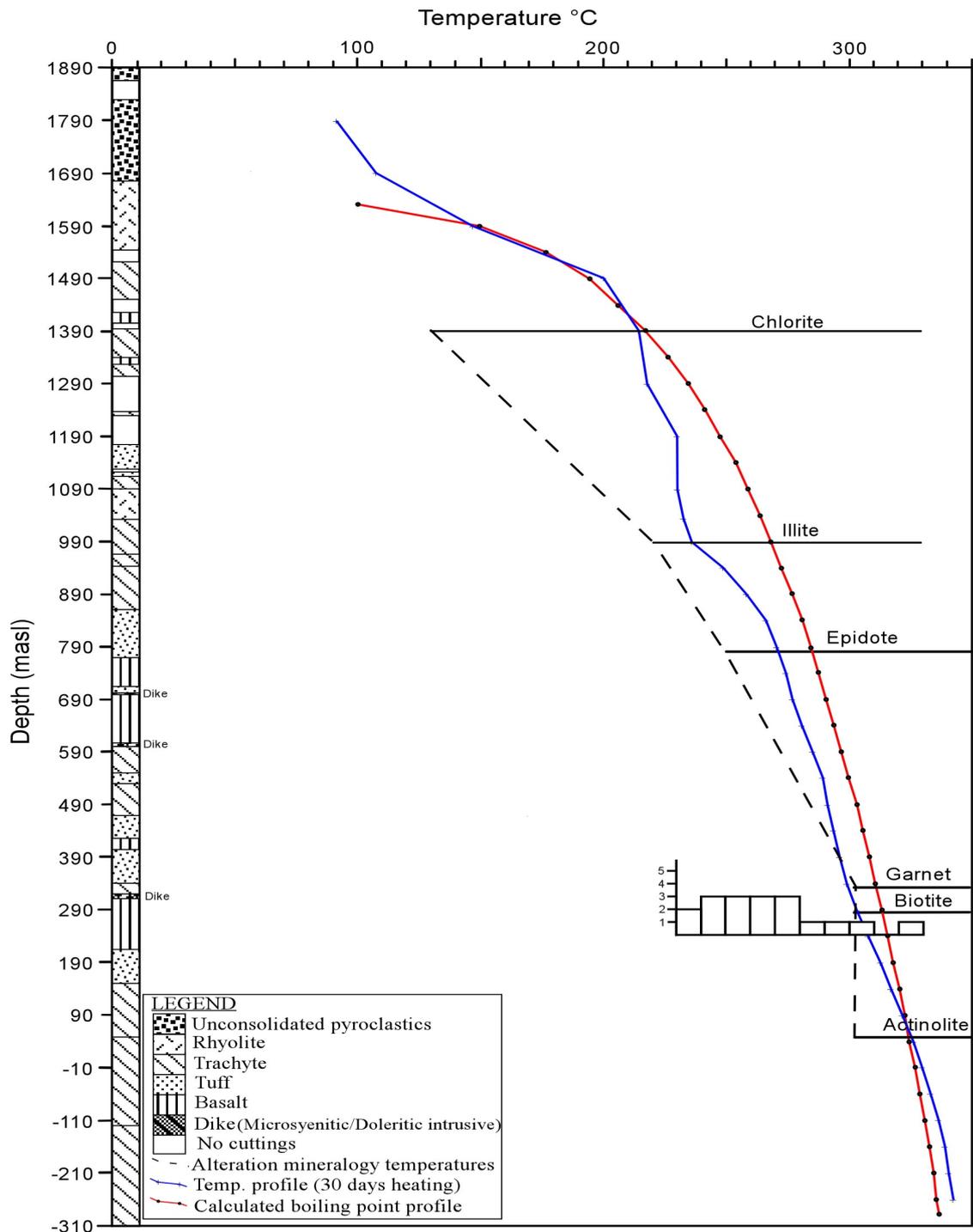


FIGURE 5: Plot of lithology and correlation between measured, interpreted hydrothermal alteration minerals and fluid inclusion temperatures with depth of well OW-901

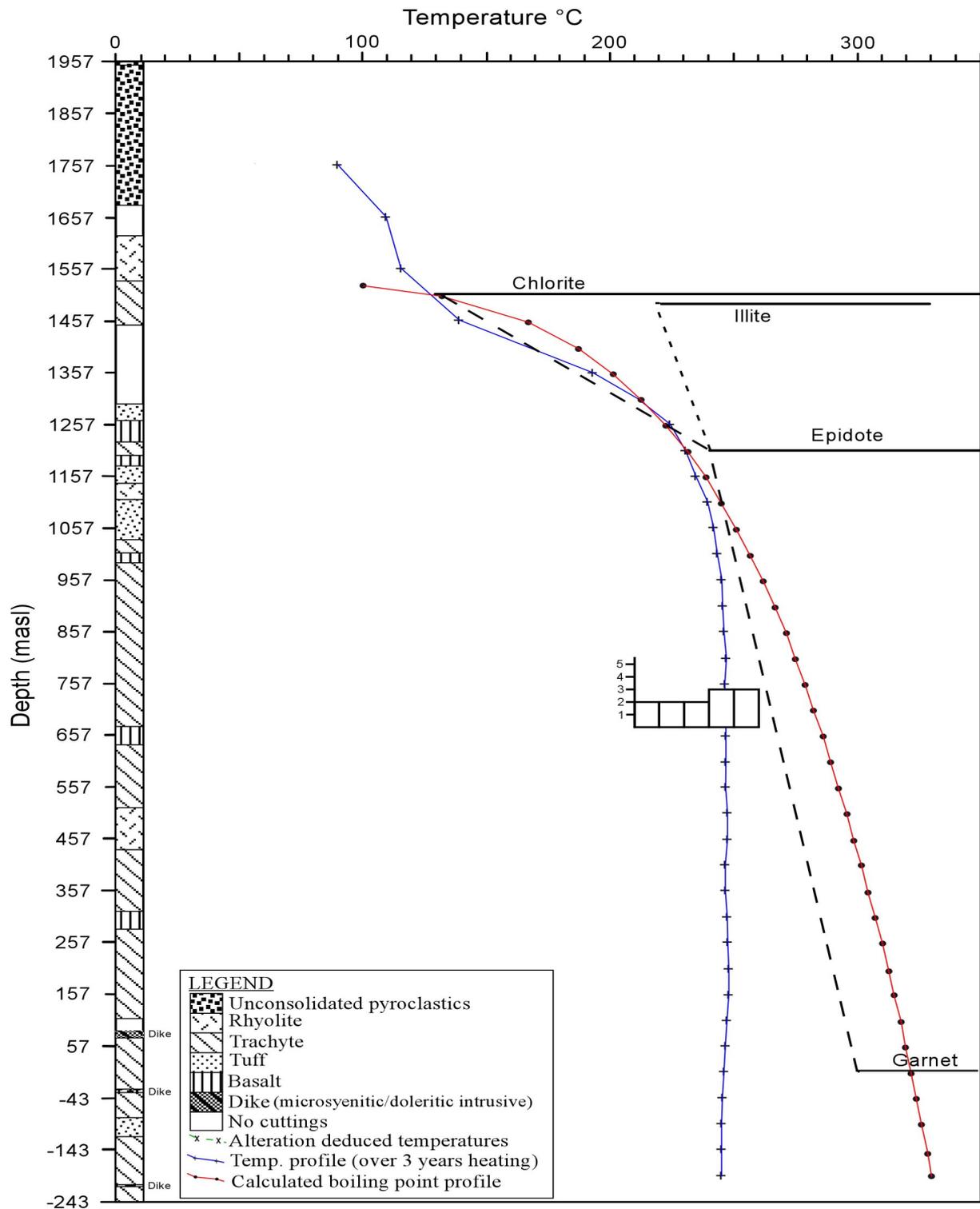


FIGURE 6: Plot of lithology and correlation between measured, interpreted hydrothermal alteration minerals and fluid inclusion temperatures with depth of well OW-902

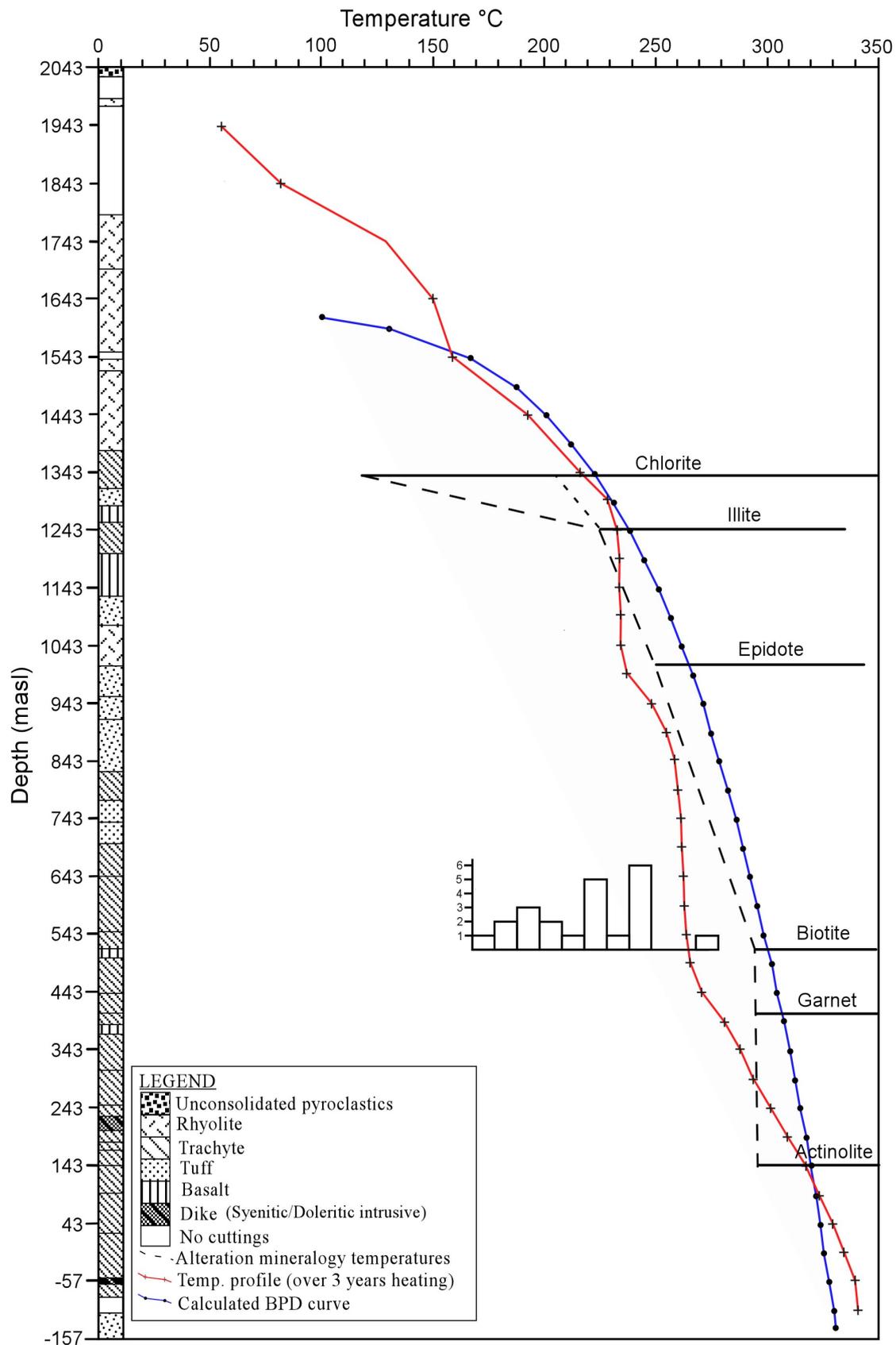


FIGURE 7: Plot of lithology and correlation between measured, interpreted hydrothermal alteration minerals and fluid inclusion temperatures with depth of well OW-903

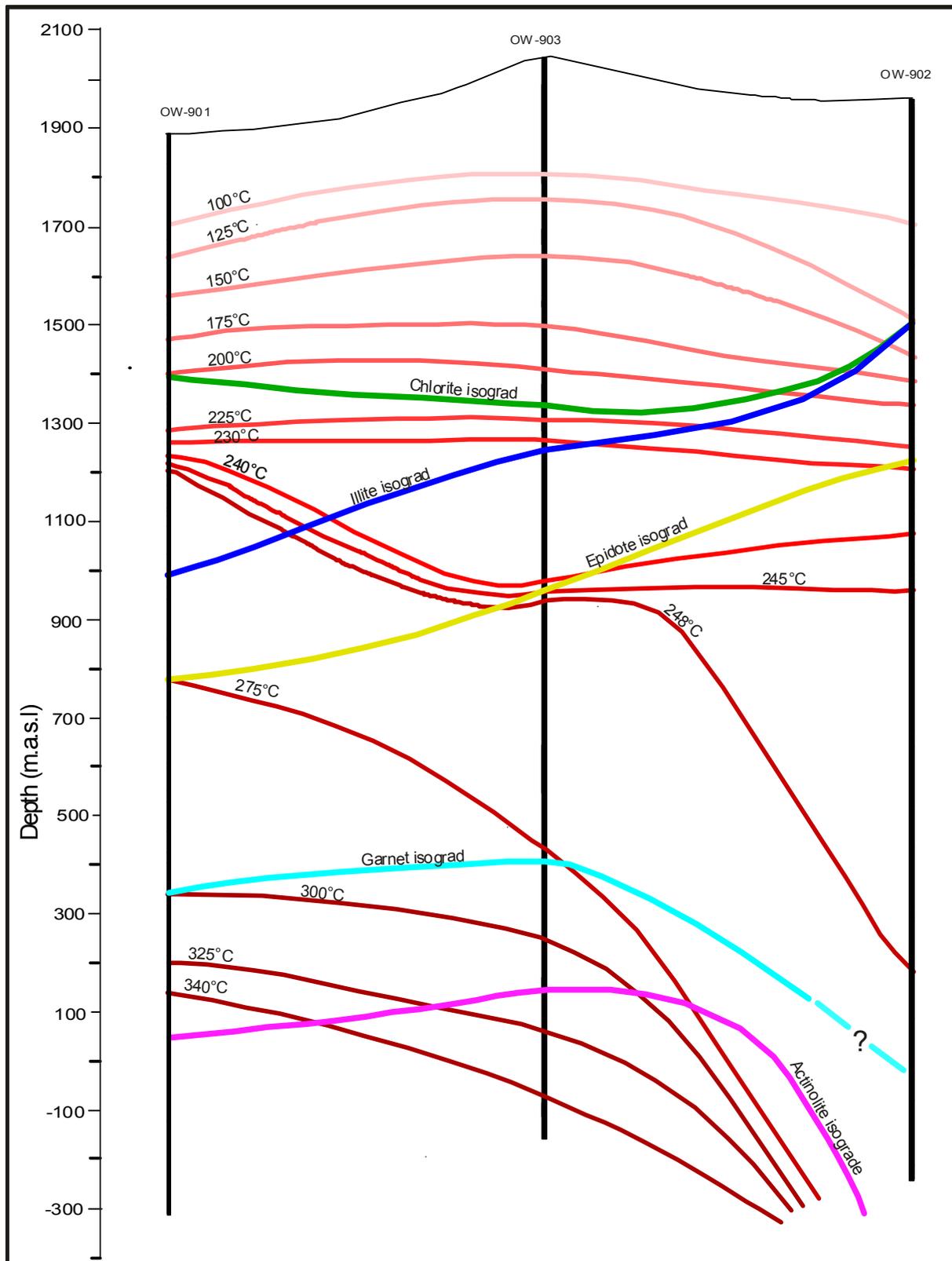


FIGURE 8: Plot of epidote, illite, chlorite, actinolite and garnet isograds and measured temperature isotherms across wells OW-901, OW-903 and OW-902

## 7. ALTERATION TYPES

There are as many alteration types as there minerals. The following types are the most commonly described types:

**Propylitic:** (Chlorite, epidote, actinolite and tremolite) Propylitic alteration turns rocks green, because the new minerals formed are green. These minerals include chlorite, actinolite and epidote. They usually form from the decomposition of Fe-Mg-bearing minerals, such as biotite, amphibole or pyroxene, although they can also replace feldspar. Propylitic alteration occurs at high temperatures. Propylitic alteration will generally form in a distal setting relative to other alteration types. Presence of chlorite and epidote indicate temperatures of 220-340°C and appearance of actinolite-tremolite occurs at 280-350°C.

**Sericitic:** (Sericite) Sericitic alteration alters the rock to the mineral sericite, which is a very fine-grained white mica. It typically forms by the decomposition of feldspars, so it replaces feldspar. In the field, its presence in a rock can be detected by the softness of the rock, as it is easily scratchable. It also has a rather greasy feel (when present in abundance), and its color is white, yellowish, golden brown or greenish. Sericitic alteration implies low pH (acidic) conditions. Alteration consisting of sericite + quartz is called “phyllic” alteration. Phyllic alteration associated with porphyry copper deposits may contain appreciable quantities of fine-grained, disseminated pyrite which is directly associated with the alteration event.

**Potassic:** (Biotite, k-feldspar, adularia) Potassic alteration is a relatively high temperature type of alteration, which results from potassium enrichment. This style of alteration can form before complete crystallization of magma, as evidenced by the typically sinuous, and rather discontinuous vein patterns. Potassic alteration can occur in deeper plutonic environments, where orthoclase will be formed, or in shallow, volcanic environments where adularia is formed.

**Albitic:** (Albite) Albitic alteration forms albite, or sodic plagioclase. Its presence is usually an indication of Na enrichment. This type of alteration is also a relatively high temperature type of alteration. The white mica paragonite (Na-rich) is also formed sometimes. Albite is precipitated in vugs and fractures at >280°C.

**Silicification:** (Quartz) Silicification is the addition of secondary silica (SiO<sub>2</sub>). Silicification is one of the most common types of alteration, and it occurs in many different styles. One of the most common styles is called “silica flooding”, which results from replacement of the rock with microcrystalline quartz (chalcedony). Greater porosity of a rock will facilitate this process. Another common style of silicification is the formation of close-spaced fractures in a network, or “stockworks”, which are filled with quartz. Silica flooding and/or stockworks are sometimes present in the wall rock along the margins of quartz veins. Silicification can occur over a wide range of temperatures.

**Silication:** (Silicate minerals+/-quartz) Silication is a general term for the addition of silica by forming any type of silicate mineral. These are commonly formed in association with quartz. Examples include the formation of biotite or garnet or tourmaline. Silication can occur over a wide range of temperatures. The classic example is the replacement of limestone (calcium carbonate) by silicate minerals forming a “skarn”, which usually form at the contact of igneous intrusions. A special subset of silication is a style of alteration called “greisenization”. This is the formation of a type of rock called “greisen”, which is a rock containing parallel veins of quartz + muscovite + other minerals (often tourmaline). The parallel veins are formed in the roof zone of a pluton and/or in the adjacent country rocks (if fractures are open). With intense veining, some wallrocks can become completely replaced by new minerals similar to the ones forming the veins.

**Carbonatization:** (Carbonate minerals) Carbonitization is a general term for the addition of any type of carbonate mineral. The most common are calcite, ankerite and dolomite. Carbonatization is also

usually associated with the addition of other minerals, some of which include talc, chlorite, sericite and albite. Carbonate alteration can form zonal patterns around ore deposits with more iron-rich types occurring proximal to the deposit.

**Alunitic:** (Alunite) Alunitic alteration is closely associated with certain hot springs environments. Alunite is a potassium aluminum sulfate mineral, which tends to form massive ledges in some areas. The presence of alunite suggests high SO<sub>4</sub> gas contents were present, which is thought to result from the oxidation of sulfide minerals.

**Argillic:** (Clay minerals) Argillic alteration is that which introduces any one of a wide variety of clay minerals, including kaolinite, smectite and illite. Argillic alteration is generally a low temperature event, and some may occur in atmospheric conditions. The earliest signs of argillic alteration include the bleaching out of feldspars. A special subcategory of argillic alteration is “advanced argillic”. This consists of kaolinite + quartz + hematite + limonite, feldspars leached and altered to sericite. The presence of this assemblage suggests low pH (highly acidic) conditions and temperatures of <220°C. At higher temperatures, the mineral pyrophyllite (white mica) forms in place of kaolinite.

**Zeolitic:** (Zeolite minerals) Zeolitic alteration is often associated with volcanic environments, but it can occur at considerable distances from these. In volcanic environments, the zeolite minerals replace the glass matrix. Zeolite minerals are low temperature minerals, so they are generally formed during the waning stages of volcanic activity, in near-surface environments. Zeolitization occurs at over <220°C.

**Serpentinization and Talc Alteration:** (Serpentine, Talc) Serpentinization forms serpentine, which recognized softness, waxy, greenish appearance, and often massive habit. This type of alteration is only common when the host rocks are mafic to ultramafic in composition. These types of rocks have relatively higher iron and magnesium contents. Serpentine is a relatively low temperature mineral. Talc is very similar to the mineral serpentine, but its appearance is slightly different (pale to white). Talc alteration indicates a higher concentration of magnesium was available during crystallization.

**Oxidation:** (Oxide minerals) Oxidation is simply the formation of any type of oxide mineral. The most common ones to form are haematite and limonite (iron oxides), but many different types can form, depending on the metals, which are present. Sulfide minerals often weather easily because they are susceptible to oxidation and replacement by iron oxides. Oxides form most easily in the surface or near surface environment, where oxygen from the atmosphere is more readily available. The temperature range for oxidation is variable. It can occur at surface or atmospheric conditions, or it can occur as a result of having low to moderate fluid temperatures.

## 8. FACTORS AFFECTING HYDROTHERMAL ALTERATION

Factors that influence the distribution and kind of mineral assemblages present in hydrothermal systems include permeability, rock and water composition, temperature, pressure and duration of hydrothermal alteration (Browne and Ellis, 1970). These factors are largely independent, but the effects of one or more of the factors can exert a dominant influence in the location and extent of hydrothermal alteration.

**Permeability:** Permeability of the rocks controls the access of thermal fluids, which cause hydrothermal alteration of the rocks and precipitation of secondary minerals in open spaces. Rocks, which have very restricted permeability or are completely impervious to fluid, will be only slightly altered. Crystallinity of the host rock is of importance because glass is more easily altered than crystalline rock.

**Chemical composition:** The chemical composition of the host rock determines the availability of components to form alteration minerals as well as possible fugitive components from the presumed magmatic heat source.

**Temperature:** Temperature is the most significant factor in hydrothermal alteration because most of the chemical reactions require elevated temperatures and also minerals are thermodynamically stable at high temperatures.

**Pressures:** Pressures at the depths penetrated by drill holes in geothermal fields in the world are not sufficient to greatly affect hydrothermal alteration minerals transformation (Browne and Ellis, 1970). The main effect of pressure on hydrothermal alteration is an indirect one in that it controls the depth at which boiling occurs.

**Duration of the hydrothermal alteration:** A geothermal system has a beginning and it should have an end. The earth is naturally cooling and for old systems where there is no renewed activity, we have extinct geothermal systems. In plate boundaries where there is continuously activity, the geothermal systems are continually being kept alive by renewed heat sources.

## 9. CONCLUSIONS

The study of hydrothermal mineralogy is important in exploration and development in geothermal fields all over the world. These studies coupled with geophysical logging techniques, fluid inclusion geothermometry, completion tests, standard formation temperature tests (SFTT), discharge fluid chemistry, stratigraphy and structural geology will always give an understanding and the nature of a geothermal system. Below are some of the problems that can be solved by the above-mentioned methods:

1. Setting the production casing during drilling especially in exploration wells.
2. Understanding the reservoir by modelling the inflow, upflow and the outflow zones of the geothermal system/field.
3. Understand the nature of the reservoir and know whether temporal changes in have occurred in the past.
4. Understand the fluids chemistry so as to predict future problems in the wells/fields such as casing corrosion, acid inflow, cold-water incursion and scaling tendencies.
5. Exploring new geothermal fields and siting next appraisal or production wells.

**APPENDIX 1: PREPARATION OF SAMPLES FOR CLAY MINERAL ANALYSIS**

- Into a clean test tube place approximately two spoonfuls of drill cuttings. Wash the cuttings to remove the dust with distilled water and fill the tube to approximately two-third full with distilled water. Place the tubes in a mechanical shaker for 4-6 hours depending on the intensity of alteration of the cuttings.
- Allow the particles to settle for 1-2 hours, until those particles less than approximately 4 Å are left in suspension. Pipette a few milliliters from each tube and place approximately 10 drops on a labeled glass plate, not making the film thick. Make a duplicate of each sample and let them dry at room temperature overnight.
- Place one sample at the desiccator containing glycol (C<sub>2</sub>H<sub>6</sub>O<sub>2</sub>) solution and the other in a set of desiccator containing hydrated calcium chloride (CaCl<sub>2</sub>.H<sub>2</sub>O). Store it at room temperature for at least 24 hours. Thicker samples need more time at least 48 hours.
- Run both sets of samples in the range 2-14° at intervals of 0.02°, 2θ for a time of 1 second on the XRD machine.
- Place one set of samples (usually the glycolated one) on an asbestos plate and insert in a preheated oven. Heat the samples at 500-550°C for one hour making sure the oven temperatures does not exceed 600°C. When the samples have cooled, run them in the range 2-14° on the XRD machine.

**APPENDIX 2: PREPARATION OF SAMPLES FOR XRD QUALITATIVE MINERAL ANALYSIS**

- Handpick grain fillings from vein fillings or vesicles under the binocular microscope and put them in an agate bowl.
- Crush the samples to a grain size of 5-10 Å. Acetone is usually added to prevent loss of sample while powdering.
- Smear the sample on quartz plate and let the acetone dry.
- Run the sample from 5°-56° at intervals of 0.04°, 2θ for a time of 1 second on the XRD machine.

**APPENDIX 3: LEGEND OF THE ROCKS ENCOUNTERED IN OLKARIA DOMES USED IN FIGURES 2, 3 AND 4**

|   |              |
|---|--------------|
|  | Pyroclastics |
|  | Tuff         |
|  | Rhyolite     |
|  | Trachyte     |
|  | Basalt       |
|  | Total Loss   |

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