Proceedings World Geothermal Congress 2000
Kyushu - Tohoku, Japan, May 28 - June 10, 2000

MIXED-LAYER CLAYS IN GEOTHERMAL SYSTEMS AND THEIR EFFECTIVENESS AS MINERAL GEOTHERMOMETERS

Colin Harvey[1] and Patrick Browne[2]
[1]GENZL Division of PB Power NZ Ltd., P.O. Box 3935, Auckland, New Zealand
[2]Geothermal Institute, University of Auckland, P.O. Box 92019, Auckland, New Zealand

Key Words: Clay minerals, alteration, geothermometers

ABSTRACT

Mixed-layer clay structures have proved useful mineral geothermometers in the study of many geothermal systems around the world. The earliest work was built on the dioctahedral smectite to illite transformation but it was subsequently extended to other transformations such as trioctahedral smectite to chlorite. More recently, numerous other mixed-layer structures which may have significance as sensitive indicators of changes in either temperature or chemical environment have been recognised.

In this paper, the development of mixed-layer clay geothermometry is followed from its first applications in sedimentary sequences, through its early applications at the Wairakei geothermal system and then its general application to mixed-layer studies of other geothermal systems. The technique is successful in many fields but less so in others. The possible reasons for these successes and failures almost always is directly associated with permeability, and the ability of a system to achieve equilibrium between fluid and rocks. However, the chemical environment and the sites of substitution within the smectites (octahedral versus tetrahedral) will also impact the transformation pathways for the smectite to illite transition.

1. HISTORICAL

1.1 Dioctahedral smectite to illite transformation

The temperature significance of the dioctahedral smectite to illite mixed-layer clay transformation was first proposed by Weaver (1956) and Burst (1958,1959), in early X-ray diffraction studies of clay minerals in Gulf Coast sediments of the US. The earliest published studies of this transformation in geothermal systems was made by Steiner (1968) who carried out very detailed and classic petrographic studies, and less detailed X-ray diffraction analyses of alteration mineral assemblages present in the Wairakei geothermal system in New Zealand. The earliest observations by these workers recognised the end members as low temperature smectite and high temperature illite and some evidence of mixed layer structures, in between.

By the early 1970's the dioctahedral smectite to illite transformation was receiving wider acceptance. This coincided with the move towards deep drilling for oil exploration in the Gulf of Mexico. It is interesting to note that the oil price hike of the early 1970's provided both the impetus for world-wide geothermal exploration and deep offshore oil exploration. Detailed studies by Perry and Hower (1970) of relatively uniform sedimentary sequences in a series of wells drilled to depths of 5,800 m (18,000 ft) in the Gulf Coast sediments provided evidence for the progressive nature of this transformation in terms of both increasing the proportion of illite, and increasing order with increasing temperature and depth of burial. Hower *et al.* (1976) noted randomly interstratified illite-smectite with 20% illite layers at shallow depths while between 3 and 4 km depth (formation temperature 100 ^{o}C) an ordered (regular) structure was present with 60% illite layers. Nadeau and Reynolds (1981) working in the Mancos Shale sequence of the Western US further advanced these studies by classifying the levels of ordering of the structures as R=0 random interstratification at less than 50% illite layers, R=1 allevardite or ISISIS type ordering (60-85% illite layers) to R>3 Kalkberg or IIIS type ordering at >85% illite layers.

1.2 Trioctahedral smectite to chlorite

Iijima and Utada (1971) recorded the diagenetic transformation of trioctahedral smectite to chlorite via a chlorite-smectite (corrensite) structure in tuffaceous sediments of the Niigata oilfield in Japan, stating that smectite disappeared and corrensite first appeared at temperatures of 85-95^{o}C. Chang *et al*. (1986) subsequently reported corrensite forming at 70^{o}C in the Cassipore Basin in Brazil. They showed chemically that the transformation from smectite to chlorite involved an increase in tetrahedral substitution (aluminium for silicon).

1.3 The Newmod Program

During this period Reynolds (1980) was working on the development of the Newmod computer program for calculating X-ray diffraction data for mixed-layer clay structures which proved to be a very useful tool for characterising both the X-ray diffraction patterns for the smectite to illite sequences, as well as the effects of ordering.

Therefore by the mid 80's the methodology was well established for oil basin studies. The importance of careful size separation, sample preparation, glycolation and careful X-ray scanning at low angles was also recognised. In addition, the Newmod program of Reynolds (1980) provided an excellent support tool for identification and possible quantification of the clay minerals.

2. SIGNIFICANCE OF SITES OF SUBSTITUTION IN SMECTITES AND PATHWAYS OF TRANSFORMATION

The wide variability in both the composition and substitution sites of smectites has long been recognised. Weaver (1956), Burst (1958,1959) and later Pollard (1971) attempted to address the significance of these different starting materials in mixed-layer clay transformations.

The basic smectite structures may be classified as:

Dioctahedral smectites where Al $^{3+}$ or Fe^{3+} are the dominant octahedral cations and the end members are:

Montmorillonite (Al^{3+} rich but no substitution in the tetrahedral layer)
Beidellite (Al^{3+} rich but significant Al substitution in tetrahedral layer)
Nontronite (Fe^{3+} rich and significant Al substitution in tetrahedral layer)

Trioctahedral smectites where Mg^{2+} and Fe^{2+} are the dominant octahedral cations and the end members are:

Saponite (aluminous trioctahedral smectite with substitution in both the octahedral layer (Al,Fe and Mg) and the tetrahedral layer (Al)
Stevensite (magnesium smectite)

Transforming dioctahedral smectites to illite requires that significant aluminium substitute in the tetrahedral sites. Obviously the starting structure of the smectite will play some role in determining the pathways for the transformations. For example, the Gulf Coast sediments are silicic and the smectite phase is mainly montmorillonite, The Salton Sea geothermal mixed-layer clay studies by Jennings and Thompson (1986) were in pelitic sediments and it is likely that montmorillonite was the dominant smectite.

In andesitic environments, which commonly host hydrothermal systems, this may not be the case. Indeed, Patrier et al. (1998) records predominantly beidellite as the dominant smectite in the andesitic-hosted Chipilapa (El Salvador) hydrothermal system. Since andesites are amongst the most common host rocks for volcanically-hosted hydrothermal systems on crustal plate margins perhaps beidellites are the more common starting phase in hydrothermal alteration. Not withstanding these assumptions, it can be concluded that the transformation of these different smectite structures to illite may follow different pathways.

3. TIME AND REACTION KINETICS

In Gulf Coast sequences the deeper sediments are Pliocene allowing up to 5 million years for reactions to occur. In the Salton Sea the fluviatile sedimentary basin is over 6 km deep and temperature gradients are much steeper. Jennings and Thompson (1986) concluded that below approximately 175^{o}C kinetics significantly affect the stabilities of the mixed-layer clays while above 175^{o}C temperature rather than time, governs the reactions.

4. PERMEABILITY

Some alteration mineral studies of geothermal systems in fractured-dominated reservoirs have identified higher temperature minerals growing in open fractures while lower temperature assemblages may be present in non-fractured rocks adjacent to these major flow paths. Mixed-layer clay studies have often shown analogous patterns. Well developed sequential mixed-layer clay sequences are best developed in low permeability sediments or tuffs (Jennings and Thompson, 1986, Harvey and Browne, 1991) where perhaps sediments and/or tuffs have sufficient volumes of pore fluids available for the transformation.

5. ROLE OF PORE FLUIDS AND SOURCE OF POTASSIUM

5.1 Sedimentary Rocks

In the Gulf Coast sediments, the availability of pore fluids within the sedimentary pile and their progressive removal under diagenesis have provided a suitable environment in which to record the progressive sequence of mixed layer clay transformations. In addition, detrital potassium feldspars provided a source of potassium for the illite formation. The sedimentary sequences of the Salton Sea also are pelitic. Within the sedimentary rocks at Wairakei, pore fluids also were present while the source of potassium was considered to be fragments of volcanic glass, washed into these lacustrine environments. Such environments therefore have both the fluid flows and chemical environments which under diagenesis and/or subsequent hydrothermal alteration can record the mixed-layer transformation.

5.2 Low Permeability Volcanic or Plutonic Rocks

In such low primary permeability rocks there may be only limited water-rock interaction, and mixed-layer clay sequences may not be well developed. Conduit flow may lead to direct precipitation of high temperature alteration minerals which may not be in equilibrium with alteration minerals within the adjacent low permeability environments.

6. GENERAL APPLICABILITY TO GEOTHERMAL SYSTEMS

Steiner (1968) at Wairakei was the first to recognise the progressive transformation of dioctahedral smectite to illite in geothermal systems. However, he included clay minerals within a host of alteration mineral studies, and reported a predominance of smectite-like spacings at between 11 and 14 A at shallow depths and the dominance of 10 to 11 A above 150 ^{o}C. Steiner however, focussed not only on the clays but his studies included recognising many zeolites as useful mineral geothermometers including wairakite.

Possibly the most detailed study of mixed-layer clay geothermometry in geothermal was by Jennings and Thompson (1986) who applied the detailed clay mineralogical techniques developed in oil basin studies, to a systematic study of Pliocene-Pleistocene sediments in the Salton Trough (southern California). Figure 1 after Jennings and Thompson (1986) illustrates clearly the successive sequence of increasing illitisation and ordering in this geothermal system.

A similarly detailed study of cuttings from the Wairakei geothermal system was undertaken by Harvey and Browne (1991). This built upon the much earlier work of Steiner (1968). The Wairakei system is hosted in both volcanic and sedimentary rocks and one objective was compare the effectiveness of the technique in the different host rocks. Within the sedimentary rocks at Wairakei, Harvey and Browne (1991) showed a progressive change from smectite to illite through the mixed-layer clay sequence (see Figure 1). In low primary permeability volcanic rock units where conduit flow predominated, the clay mineral assemblages and many other non-clay mineral geothermometers were not in equilibrium with the prevailing thermal regime.

Clay minerals are typically amongst the most abundant alteration minerals in samples recovered from holes drilled in both low and high temperature fields in Iceland Kristmanssdottir, 1977).

The technique has been applied elsewhere in geothermal investigations and Table 1 summarises the general effectiveness of the technique from a selection of fields.

6. SUMMARY

6.1 Limitations

At the present time many geothermal workers adopt the temperature stability ranges of mixed-layer clay minerals established by the oil patch and yet there are fundamental differences that need to be appreciated. These are:

(i) The starting smectite compositions in volcanically-hosted geothermal systems may be different from those of Gulf Coast sediments and the flowpath of alteration from smectite to illite may be less systematic.

(ii) In fracture-dominated geothermal reservoirs incomplete water-rock interaction away from major flow paths may invalidate the use of mixed-layer clays as mineral geothermometers

(iii) The kinetics of clay mineral transformations in currently active geothermal systems may not be directly comparable to the transformations that have taken place over several million years old Gulf Coast sediments.

(iv) The fluid compositions and potassium ion availability in active geothermal systems may be different from the water-rock environment of the Gulf Coast. This also may significantly impact on the mixed-layer clay transformations.

6.2 Applicability

Despite these constraints it is apparent from the summary in Table 1 that mixed-layer clay studies have proved to be very useful in modelling the temperature regimes in many exploited geothermal systems world-wide. They have proved most effective in sediments or tuff sequences but frequently they are reported within a cocktail of other methods which include other alteration mineral studies and perhaps fluid inclusion geothermometry.

REFERENCES

Akaku, K., Reed, M.H., Yagi, M., Kai, K. and Yasuda, Y.(1991) . Geochemical Journal v.25, 315-333.

Burst, J.F. Jnr. (1958) Glauconite pellets: their mineral nature and applications for stratigraphic interpretation: Amer. Assoc. of Petrol. Geol. Bull. V. 42, 310-327.

Burst, J.F. Jnr. (1959) Post diagenetic clay mineral environmental relationships in the Gulf Coast Eocene: in Clays and Clay Minerals. Proc. 6th nat. Conf. Berkeley, Calif. 1957. Ada Swineford, ed., Pergammon Press, N.Y.pp 327-341.

Cox, M.E. and Browne, P.R.L. (1998) Hydrothermal alteration mineralogy as an indicator of hydrology at the Ngawha Geothermal Filed, New Zealand. V. 27, 259-270.

Harvey, C.C. and Browne, P.R.L. (1991) Mixed-layer clay geothermometry in the Wairakei geothermal field, New Zealand, Clay and Clay Minerals, v. 39, 614-621.

Jennings, S. and Thompson, G.R. (1986) Diagenesis of Plio-Pleistocene sediments of the Colorado River Delta, southern California: J. Sediment. Petrol.v 56, 89-98.

Kristmannsdottir, H. (1977) Types of clay minerals in hydrothermally altered basaltic rocks, Reykjanes, Iceland. Jokull, v. 26, 3-39.

Leach, T.M.L., Wood, C.P. and Reyes, A. (1983) Geology and hydrothermal alteration of the Tongonan Geothermal Field, Leyte, Republic of the Philippines, 4th Symposium on Water Rock interaction, Misasa, Japan. Extended abstracts, 275-278.

Nadeau, P.H. and Reynolds, C.R. (1981) Burial and contact metamorphism in the Mancos Shale: Clays and Clay Minerals, 29, 249-259.

Patrier, P., Traineau, H., Papanagiotou, P. Turgne, E. and Beaufort, D. (1998) I-S series in geothermal fields: Comparison with diagenetic I-S series. Proc. 9th WRI Conf.eds Arehart, G.B. and J.R. Hulston, pub. A.A. Balkema, Rotterdam 1998 pp 683-686.

Perry, E. and Hower, J. (1970) Burial diagenesis in Gulf Coast pelitic sediments: Clay and Clay Minerals, 18, 165-177.

Reyes, A.G. (1990) Petrology of Philippine geothermal systems and the application of alteration mineralogy to their assessment. Jour. Volc. and Geothermal Research. v.43, 279-309.

Reynolds, R.C. (1980) Interstratified clay minerals: in Crystal Structures of Clay Minerals and their X-ray Identification. G.W. Brindley and G. Brown, eds., Mineralogical Society of London, 249-303.

Seki, Y. (1991) The physical and chemical structure of the Oku-aizu geothermal system, Japan. Geochemical Journal v.25, 245-265.

Simmons, S.F. and Browne, P.R.L. (1998) Illite, illite-smectite and smectite occurrences in the Broadlands-Ohaaki geothermal system and their implications for clay mineral geothermometry. Proc. 9th WRI Conf. eds G.B. Arehart, and J.R. Hulston, pub. A.A. Balkema, Rotterdam 1998 pp 691-694.

Steiner, A. (1968) Clay minerals in hydrothermally altered rocks at Wairakei, New Zealand: Clays and Clay Minerals 18, 165-177.

Taguchi, S. and Nakamura, M. (1991) Subsurface thermal structure of the Hatchobaru geothermal system, Japan, determined by fluid inclusion study. Geochemical Journal v.25, 301-314.

Takenaka, T. and Furuya, S. (1991) Geochemical model of the Takigami geothermal system, Northeast Kyushu, Japan. Geochemical Journal v.25, 267-281.

Utami, P., and Browne, P.R.L. (1999) Subsurface hydrothermal alteration in the Kamojang geothermal field, West Java, Indonesia: Proc. 24th Workshop Geothermal Reservoir Engineering. Stanford, 383-390.

Weaver, C.E. (1956) The distribution and identification of mixed-layer clays in sedimentary rocks: Am. Mineral. 41, 202-221.

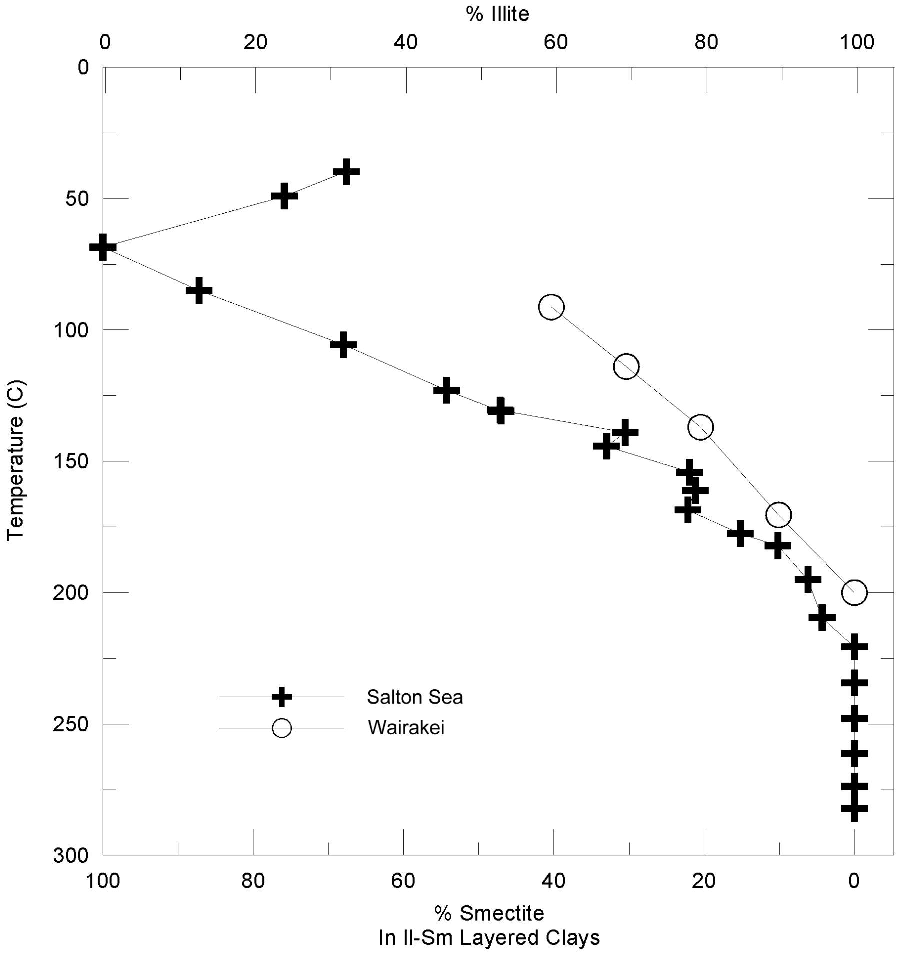

Figure 1. Observed proportions of illite and smectite in mixed-layer clays with respect to reservoir temperature in the Salton Sea (modified after Jennings and Thompson, 1986) and Wairakei (Harvey and Browne, 1991).

Table 1: Summary of the general effectiveness of the technique from a selection of fields

System	**Effectiveness of the technique**	**Reference**
Chipilapa (El Salvador)	Effective in low permeability rocks but not in permeable rocks.	Patrier et al. (1998)
Fushime (Kyushu, Japan)	Sea water system and chlorite-smectite sequence	Akaku et al.(1991)
Hatchobaru, Kyushu, Japan	Apparently successful	Taguchi and Nakamura (1991)
Kamojang, Indonesia	Effective in andesitic volcanic rocks in combination with calc-silicates	Utami and Browne, (1999)
Ngawha, New Zealand	Moderately successful in marine sediments	Cox and Browne (1998)
Ohaaki (New Zealand)	Effective in sediments Not effective in fracture-dominated permeability	Simmons and Browne (1998)
Oku-aizu Honshu, Japan	Close agreement with measured temperatures	Seki (1991)
Salton Sea (USA)	Very effective in sediments	Jennings and Thompson (1986)
Takigami, Kyushu, Japan	Close agreement with measured temperatures	Takenaka and Furuya (1991)
Tongonan (Philippines)	Effective in the central zone of the system within interbedded flow, tuffs breccias and some sediments	Leach et al. (1983)
Philippines fields	Often effective in combination with other alteration mineral studies	Reyes (1990)
Wairakei (New Zealand)	Effective in lacustrine sediments. Not effective in fractured volcanic rocks	Harvey and Browne (1991)