

The nature and significance of sulphate-rich, aluminous efflorescences from the Te Kopia geothermal field, Taupo Volcanic Zone, New Zealand

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ABSTRACT

Alunogen and meta-alunogen are the dominant phases present in transient sulphate efflorescences that are the latest products of the alteration of ignimbrite country rocks in the long-lived Te Kopia geothermal field. Meta-alunogen pseudomorphs alunogen and both species occur as white, fibrous, tangled masses, as prismatic, parallel growths, and as thin, platy, crystals, 8–15 µm across, that coalesce in an open cellular network. Small (<2 mm diam.) spherical aggregates of radiating, acicular halotrichite ($\text{Fe}_{0.51}\text{Mg}_{0.49}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$), potash alum, mirabilite, melanterite and tschermigite are present locally. The cations needed to form these minerals derive from the host rocks with the exception of sulphur and ammonia that come from H_2S and NH_3 gases ascending with steam. The particular efflorescence assemblage reflects the prevailing conditions and ionic activities of a local micro-environment. Kaolinite formed by acid sulphate alteration is now being altered by steam to yield alunogen. In turn, alunogen can react with silica, or co-dissociate with silicic acid, to form kaolinite. The alternating dissolution and reprecipitation of kaolinite and alunogen moves aluminium in and through the surficial environment at Te Kopia.

KEYWORDS: alunogen, halotrichite, kaolinite, aluminium, geothermal, efflorescence, alteration.

Introduction

ALUNOGEN and tamarugite were reported as constituents of a transient efflorescence forming on previously hot water-altered ignimbrites that are now undergoing further alteration by steam condensate in the Te Kopia geothermal area (Mackenzie *et al.*, 1995). Minor constituents included potash alum, halotrichite-pickeringite, and, possibly, anhydrite, epsomite and hexahydrite. This study describes similar, water-soluble efflorescences formed 250 m southwest and discusses their implications for understanding processes of surface alteration and mass transfer at the surface of this geothermal system.

Setting

The Te Kopia geothermal field (Fig. 1) is located in the Taupo Volcanic Zone (TVZ) at latitude 38° 24' S, longitude 176° 13' E and straddles the active Paeroa Fault (Bignall and Browne, 1994). Patches of altered and steaming ground extend for over 2.5 km along the fault scarp and occur within 500 m of it. The country rocks consist of three Quaternary, gently east-dipping ignimbrite sheets. Where fresh, these contain phenocrysts of quartz and andesine plus minor rock fragments, pyroxene and hornblende with accessory iron-titanium oxides, set in a glassy matrix of rhyolitic composition.

The Te Kopia geothermal field has had a long (~120,000 years) history during which time episodic movements on the Paeroa Fault have affected its hydrology (Bignall and Browne, 1994). Some of the changes in hydrology are

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recorded by the hydrothermal alteration of its rocks. The ascending parent fluid was, and is, alkali chloride water of near neutral pH. This reacts within the reservoir with the ignimbrites so that they alter to an assemblage that includes mainly quartz, adularia, albite, chlorite, calcite and pyrite. Drillcores and down hole measurements show that these minerals are still stable within the Te Kopia reservoir at temperatures that reach 240°C (Bignall and Browne, 1994). However, on the upthrown block, exposed along the western footwall fault scarp, they are now unstable, as is illite that earlier replaced adularia.

The latest alteration event, now in progress, involves interaction of these previously altered rocks by steam, gases and steam condensate. At any instant the minerals forming reflect the then prevailing temperatures, fluid pHs and permeabilities. However, temporal changes are recorded by the textural relations of the hydrothermal minerals and the intensity of rock alteration.

Today, surface manifestations and alteration are dominated by steam discharges. Several small, shallow, steam-heated pools are contained within landslide debris along the foot of the scarp. These are filled with acid-sulphate waters that are mixtures of steam condensate and rainwater, with only a small amount of thermal water derived directly from the deep reservoir. The efflorescence described by Mackenzie *et al.* (1995) came from the eastern margin of a sub-circular depression within altered ground near the foot of the scarp (Fig. 1). The occurrences described here lie 250 m to the southwest, near the centre of the field and occupy crudely terraced, warm (25–30°C) ground south and east of the southernmost of a series of warm acid ponds (pH 2.5–3.0, 35–50°C). This area is dominated by the steaming face and sidescarps of a 3 m high landslide toe, some 15 m wide, and perched 13 m above the valley floor upon older landslide debris. The southern sidescarp is marked by a series of near- (and continuously-) boiling acid pools (pH 1.9–2.1, 89–102°C), and small fumaroles within an erosional channel alongside the sidescarp margin. Twenty to thirty metres north-east are a group of small bubbling acid pools (pH 2.4–2.8, 90–96°C), mudpots and fumaroles.

Throughout this entire area (Fig. 1) transient, water-soluble efflorescences of hydrous aluminosulphates and hydrous sulphates, commonly 2–5 mm thick, develop upon the substrate whenever and wherever conditions prove appro-

priate for their growth. This commonly occurs in sheltered areas, made hot and humid by steam and condensation, but also takes place upon residual siliceous crusts in open areas of bare, warm ground during extended periods of dry weather. Good examples occur near the erosional channel that bounds the northern sidescarp of the landslide. At the uppermost site sampled, location A hereafter, there is a spheroidally weathered boulder of ignimbrite, approximately 1.5 × 1.5 × 2 m alongside a steam vent. Its successive layers record some of the mineralogical changes that have occurred in the country rocks at Te Kopia. At its centre is a hard ($\rho = 2320 \text{ kg/m}^3$), silicified, but otherwise only slightly altered ignimbrite (AU 48150). Its outer surface is silica- and clay-rich (AU 48147) with $\rho = 2100 \text{ kg/m}^3$. Efflorescences develop on this surface upon the inner side of an overhang that not only protects them from rain but also provides appropriate micro-environmental conditions. The temperature 50 mm below the silica rich clay crust is 35–40°C.

Composition

Alunogen, $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$, and/or meta-alunogen, $\text{Al}_4(\text{SO}_4)_6 \cdot 27\text{H}_2\text{O}$, are the main components of all efflorescences studied. The two species are indistinguishable except by X-ray powder diffraction (XRPD). Both occur in three distinct morphologies with the meta-alunogen pseudomorphous after alunogen.

The commonest, but most ephemeral habit consists of fibrous tangled masses of white crystals. These grow typically from the edges of semi-circular siliceous scabs (<5 mm diam.) formed on patches of steaming ground. They are common in flat areas atop landslide debris and towards the base of the fault scarp, west of the southern acid pool (Fig. 1). They also occur where sulphur is depositing, as along the ridge crest atop the steaming face of the landslide debris pile. Smaller occurrences are scattered in most areas of warm (~30–50°C) ground.

The other two alunogen habits are confined to humid, sheltered, micro-environments. Here, white, elongate-prismatic, parallel crystal growths of alunogen ± meta-alunogen are common (Fig. 2a). A rounded, corroded appearance typifies many of these crystal groups and suggests they have partly dissolved. Thin, platy, clear crystals of alunogen ± meta-alunogen, 8–15 µm across, grow from the sides and tips

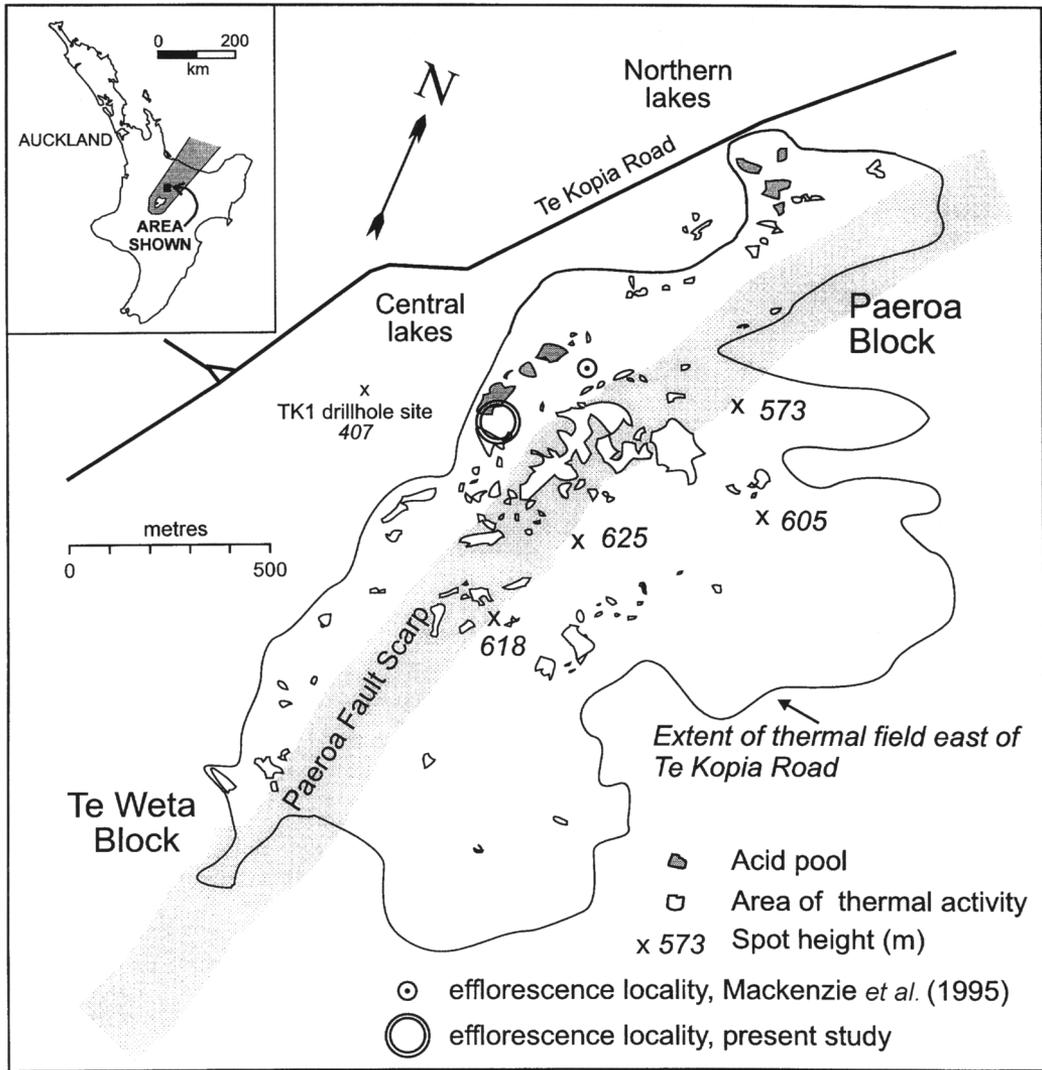


FIG. 1. Locality map, Te Kopia thermal area, showing location of efflorescence described by Mackenzie *et al.* (1995) and occurrences discussed here.

of the prisms and eventually coalesce to form a cellular network (Fig. 2*b*). Small (<2 mm diam.) radiating spherical aggregates of acicular crystals of magnesian halotrichite grow upon samples of both modes of occurrence (Fig. 3).

Semi-quantitative EDAX analysis of halotrichite from the boulder surface at location A shows its composition is mid-range in the halotrichite-pickeringite series, i.e. $\sim\text{Fe}_{0.51}\text{Mg}_{0.49}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$. The XRPD analysis of a hand

picked sample of the fibres confirmed the mineral's identity but not its place in the isomorphous series (cf. Cody and Grammer, 1979).

Potash alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, is a minor, but common phase in a number of Te Kopia efflorescences (cf. Mackenzie *et al.*, 1995), including one from location A and several from the lower portions of the landslide ridge crest. A semi-quantitative EDAX analysis of yellow-

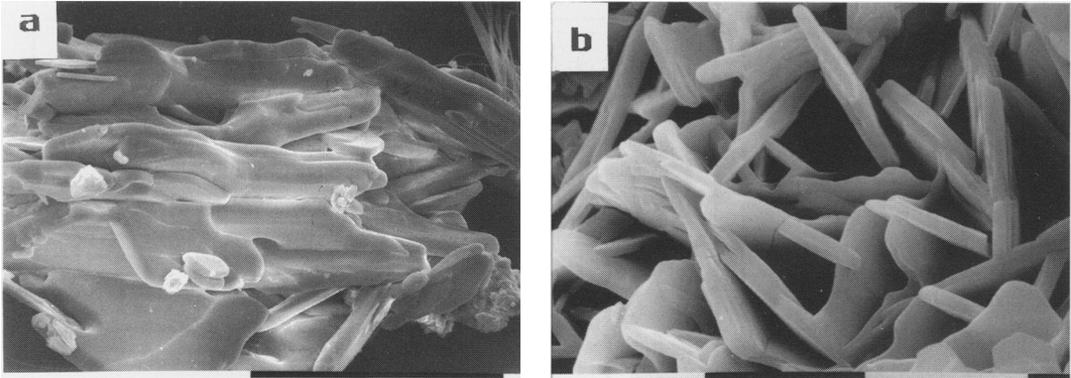


FIG. 2. Scanning electron micrographs of: (a) partially resorbed, prismatic, parallel crystal growths of alunogen \pm meta-alunogen (scale bars 0.1 mm); (b) thin, platy crystals of alunogen \pm meta-alunogen coalescing to form a cellular network (scale bars 10 μm).

stained crystals of potash alum from location A showed slight substitution of Na for K. Traces of tschermigite, $\text{NH}_4\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, were identified by XRPD, associated with alunogen and potash alum at a location low on the northern sidescarp.

Mirabilite, $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$, and melanterite, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, were found in one sample from location A that otherwise is predominantly alunogen.

In none of the samples examined was any tamarugite found.

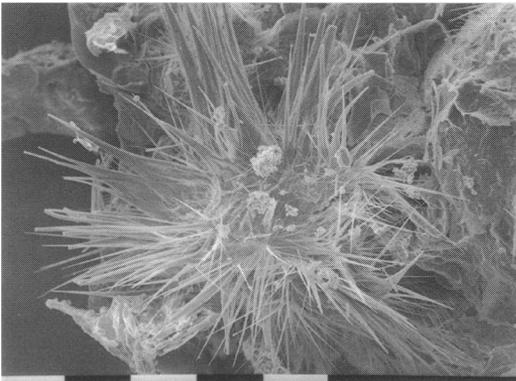


FIG. 3. Scanning electron micrograph of radiating acicular spray of halotrichite growing upon prismatic alunogen. Scale bar 0.1 mm.

Discussion

The efflorescences represent the latest in a temporal sequence of alteration stages of the host ignimbrites that are a result of the long and complex evolution of the Te Kopia geothermal field. In the first recorded phase, alkali chloride fluids reacted with the ignimbrites to yield a quartz-adularia dominant assemblage. This has been altered locally by hot, but slightly acidic waters to produce illite. Later, some of these already twice-altered rocks were converted to kaolinite-alunite-silica \pm hematite \pm jarosite \pm leucocene by more acidic sulphate waters (Bignall and Browne, 1994). A blend of all assemblages, as typified by boulder A, now forms the country rocks currently undergoing further alteration by steam condensate and/or weathering.

A plot of some major elements in four samples (AU 48147–48150) from the surface to the core of an ignimbrite boulder at location A show variations that are most marked near the boulder surface (Fig. 4). There is a progressive depletion of Na as a result of incremental breakdown of plagioclase. Silica, Al, Fe and K are partly incorporated into secondary minerals (kaolinite, silica, alunite, hematite) during alteration but this process is largely isochemical. Aluminium, Fe and K are released in significant amounts only in the last stage, whereas silica shows an apparent increase. The relative abundance of Mg does not change throughout the alteration sequence but Ca is present in proportions that are too low for its

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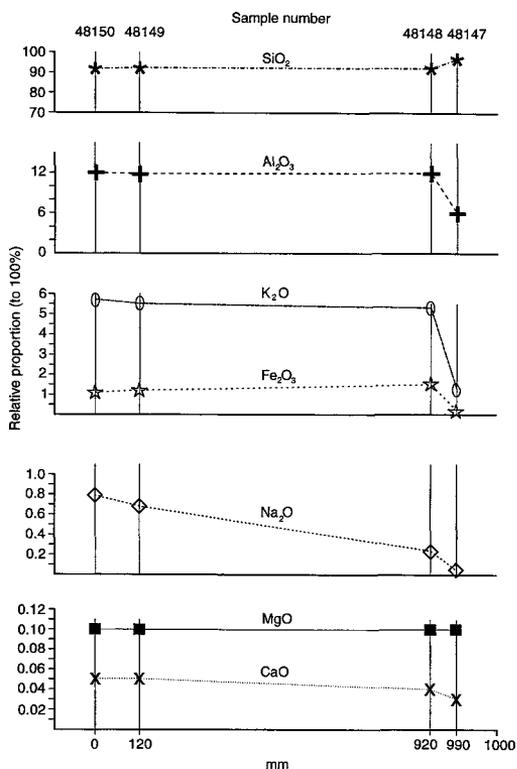


FIG. 4. Variations in major elements, determined by X-ray fluorescence analysis, normalized to TiO_2 and adjusted for density changes, for the core-to-surface alteration suite from the ignimbrite boulder at location A.

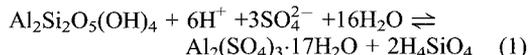
behaviour to be deduced. Liberated ions migrate in solution by capillary action towards the surface where they form ephemeral efflorescences (alunogen, halotrichite, potash alum, mirabilite) or else are removed directly in solution. A similar sequence of progressive alteration was described from basaltic andesites at Steamboat Springs in Nevada by Schoen *et al.* (1974).

The suite of minerals that make up an efflorescence at Te Kopia is controlled partly by the activity of the ions available and partly by the physical conditions at a particular environment. Under highly acid conditions that result in oxidation of H_2S when steam condenses, alunogen is the principal stable Al sulphate phase (cf. Nordstrom, 1982) and, given the ready supply of Al and sulphate, forms wherever efflorescences develop. In contrast, species such as halotrichite, tschermigite and melanterite

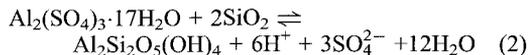
require either more specific conditions and/or favourable ionic activities that occur only locally. For example, both halotrichite and melanterite are more soluble than alunogen and demand a more sheltered environment such as that provided by the boulder surface to survive. They were not found on the exposed flats during the summer and autumn months of 1997 which were wetter than usual. An essential component of tschermigite is ammonia, indicating that it is being discharged from gas vents in the vicinity. The formation of tamarugite reported by Mackenzie *et al.* (1995) may imply both a suitably high local activity of Na coupled with the dry summer that prevailed in 1993/94 when the specimen was collected.

Regardless of the precise species present, all are rich in sulphate and the majority are aluminous. Their continued formation gives clear evidence of a persistent flux of Al in and at the surface in the now dominantly acid-sulphate environment at Te Kopia.

Nordstrom (1982) demonstrated that kaolinite may decompose in acid sulphate fluids, under appropriate conditions, to yield alunogen:

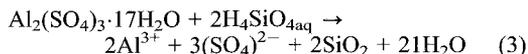


It is this process that forms alunogen on areas of warm, bare ground at Te Kopia. Note that the process is reversible and alunogen exposed to fluids less acid than that from which it formed, and in the presence of non-crystalline silica, will itself dissolve to yield kaolinite:



Generally, at Te Kopia, pH varies temporally from 2–3 to >4, depending upon the degree of mixing between thermal and rain waters. There is likely to be considerable variation in the pH of surficial waters due to the dilution of the steam condensate with rain and fog drip.

Thus, an increase in the amount of moisture present at a microenvironment where alunogen has grown may cause it to dissolve. Apart from rain and steam condensation, water may also derive from the disassociation of silicic acid with consequential deposition of silica:



At Te Kopia, silica-rich, alumina-depleted crusts are common in areas where aluminous efflorescences develop and testify to the impor-

tance of reaction (3). (As a corollary, the distance any Al released travels is determined by the activity of the SiO_4^{4-} ion.)

Episodic kaolinite dissolution and precipitation have been proposed by Nordstrom (1982) as a mechanism affecting the distribution of this mineral in some soils. Where kaolinite dissolves, reaction (2) moves to the left and both alunogen and silica are deposited. Kaolinite forms when reaction (2) moves to the right and silica and alunogen are eliminated. Where the processes is repeated many times, and coupled with direct dissolution of aluminous sulphates e.g. reaction (3), Al is episodically released into the groundwater and can be transported downslope and/or to deeper horizons. The end product will be a leached, kaolinite-impooverished, siliceous surface residue such as that now accumulating in steam-heated areas at Te Kopia, similar to

those at Steamboat Springs (Schoen *et al.*, 1974).

If such processes move Al at or near the surface at Te Kopia (Fig. 5), then a surficial silica residue might be expected to accumulate in the east with kaolinite in the west, given the direction of groundwater flow and surface runoff. This is generally true. Silica residue (Browne, 1978) coats surfaces in elevated sections to the north-east. However, its main habit is that of a smooth to hummocky coating, often with ripple or swirl textures and occasional inclusions of hematite. By contrast, secondary silica formed and dissolved together with alunogen efflorescences on flat areas occurs usually as scabs with numerous inclusions.

About 3000 years prior to the development of the surficial, acid-dominated conditions now prevailing at the Te Kopia study site, Al was already moving. Elevated sections of many

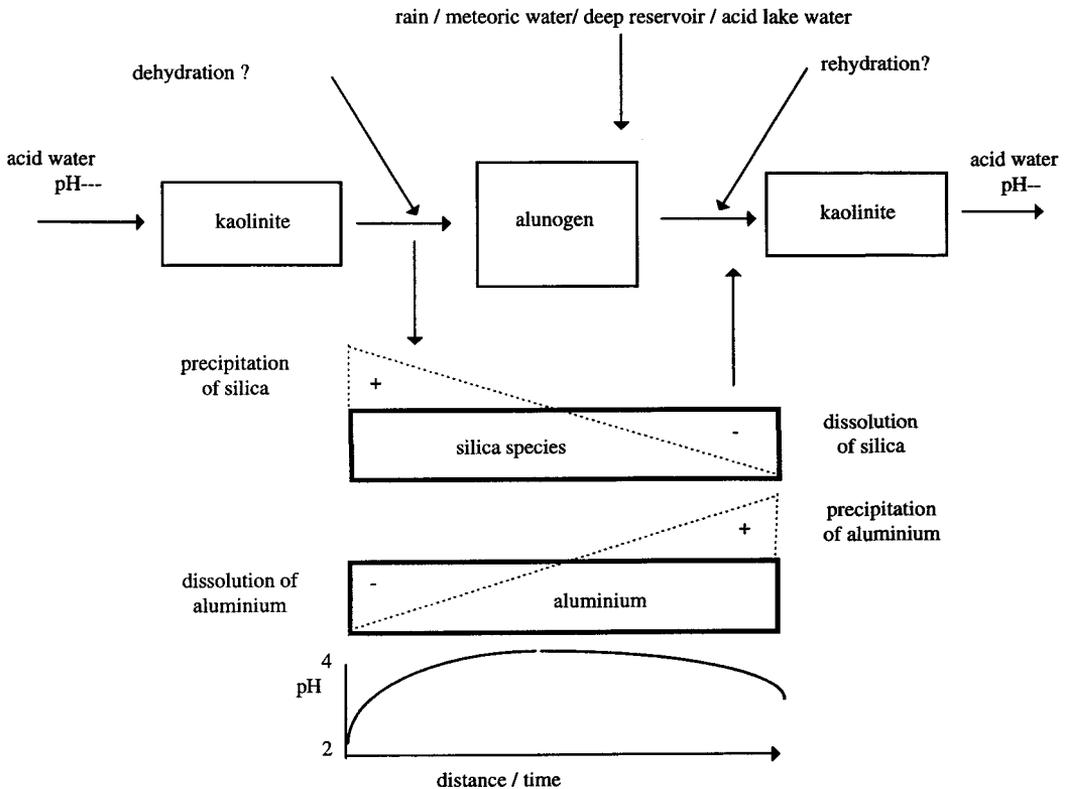


FIG. 5. Schematic representation of the movement of Al in the surface at Te Kopia as a result of alternating, episodic dissolution and reprecipitation of kaolinite and alunogen.

thermal areas are steam dominated (i.e. acidic) but near neutral pH chloride waters occur below. The earlier signature of the alkali-chloride fluid was an important precursor to the production of kaolinite, as it altered primary andesine to adularia, and locally to illite, thereby moving Al. Later, as kaolinitic assemblages formed in a silica over-saturated acidic environment, the adularia and other phases became unstable, and Al moved for the third or fourth time (Chesworth, 1975).

Conclusions

At present, different assemblages of hydrothermal minerals are being produced in different parts of the Te Kopia geothermal field. For example, adularia, quartz, calcite, chlorite, wairakite and other minerals are undoubtedly still forming from waters of near-neutral pH within the reservoir where temperatures reach 240°C (Bignall and Browne, 1994).

Within a few metres of, and at the ground surface, however, the markedly different physical and chemical conditions that prevail, produce a suite of dissimilar minerals by fluid/rock interactions. Thus where acid sulphate waters occur, the typical assemblage produced is kaolinite, alunite and silica residue. The peculiar circumstances of the Te Kopia geothermal field, lying as it does astride the active Paeroa Fault, means that its upthrown footwall block contains rocks that are now undergoing alteration for the second or third or even fourth time, by fluids of quite different compositions from those that affected them earlier. This is evident from their overprint textures and secondary mineralogy.

A feature of the present surficial alteration is the occurrence of widespread silica residue and kaolin plus ephemeral occurrences of metastable sulphate-rich aluminous efflorescences. The sulphate component of the efflorescences derives mostly from ascending H₂S that oxidizes to H₂SO₄, but some may also come from oxidation of earlier deposited pyrite. The Fe, Mg, Na, K and Al contributions must come from the rocks themselves since none of these elements move with the steam phase. They must be leached, via capillary action, from within the host rocks in response to the prevailing chemical gradients. At the surface, these constituents combine with sulphate and water to form the efflorescences; the identities of the phases in them depend upon the local physicochemical conditions. Water,

whether steam condensate, rain, or fog drip, is both the creator and destroyer of efflorescences so that they survive longest only in the most sheltered (but not dry) areas. The proportions of acid condensate and rain water mixing at a particular location vary temporally. At times the former will be 100% so very acid conditions prevail and alunogen dominates; when heavy rain falls, the acid sulphate water is diluted so that the resultant water affects the surficial salts by either dissolving the more soluble of them or by increasing the pH of the water so that phases such as alunogen become unstable whereas others, like kaolinite, stabilize.

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References

- Bignall, G. and Browne, P.R.L. (1994) Surface hydrothermal alteration and evolution of the Te Kopia thermal area, New Zealand. *Geothermics*, **26**, 645–58.
- Browne, P.R.L. (1978) Hydrothermal alteration in active geothermal fields. *Ann. Rev., Earth Planet. Sci.*, 229–50.
- Chesworth, W. (1975) Soil minerals in the system Al₂O₃-SiO₂-H₂O: Phase equilibrium model. *Clays Clay Miner.*, **23**, 55–60.
- Cody, A.D. and Grammer, T.R. (1979) Magnesian halotrichite from White Island. *N.Z. J. Geol. Geophys.*, **22**(4), 495–8.
- Mackenzie, K.M., Rodgers, K.A. and Browne, P.R.L. (1995) Tamarugite, NaAl(SO₄)₂.6H₂O, from Te Kopia, New Zealand. *Mineral. Mag.*, **59**, 754–7.
- Nordstrom, D.K. (1982) The effect of sulfate on aluminium concentrations in natural waters: some stability relations in the system Al₂O₃-SO₃-H₂O at 298 K. *Geochim. Cosmochim. Acta*, **46**, 681–92.
- Schoen, R., White, D.E. and Hemley, J.J. (1974) Argillization by descending acid at Steamboat Springs, Nevada. *Clays Clay Miner.*, **22**, 1–22.

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