THE MINERALOGY, TEXTURE *AND* SIGNIFICANCE OF SILICA RESIDUE FROM THE TE KOPIA GEOTHERMAL FIELD, TAUPO VOLCANIC ZONE

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SUMMARY - In the Te Kopia geothermal field, steam, accompanied by H_2S, rises through landslide debris at the foot of the Paeroa Fault. The resulting acid-sulfate fluids corrode the variably altered rhyolitic country rocks. Silica precipitates during this alteration process as rinds, botryoidal loaves, and recemented crusts. The initial silica is strongly disordered opal-A_N, commonly as transparent to translucent hyalite. Depending upon conditions, including humidity, pH, and aluminium activity, this opaline silica can (1) react with aluminous solutions to yield kaolinite, **(2)** crystallise to microcrystalline quartz plus moganite, or, **(3)** wholly dissolve in acidified rainwater, fogdrip or additional steam condensate - the ultimate stage in alteration of the country rock. No silica phase intermediate between opal-A and quartz **was** conclusively identified at Te Kopia, but the presence of small amounts of poorly ordered opal-CT are suspected from skewed x-ray diffraction traces.

1. INTRODUCTION

Silica accumulates at the surface of geothermal fields in two primary and discrete ways: by deposition as sinter from near-neutral pH, alkali chloride waters and as a product of surface and near-surface leaching of silicate country rock by sulfuric acid, derived from oxidation of ascending H_2S (White *et al.,* 1956). It is the latter precipitate that is referred to here as silica residue. In both sinter and residue deposition the first-formed silica phase is opaline silica, and Herdianita *et al.* (2000a) have stressed the importance of clearly differentiating the two types of deposits if either is to be used to interpret hydrology or paleohydrology. However, no systematic characterization of residue and its silica phase mineralogy has been undertaken beyond generalisations, in contrast to the large body of literature that exists concerning the nature and origins of sinter. This paper reports the results of a preliminary mineralogical and textural analysis of residue samples collected from a quadrat in the centre of the Te Kopia geothermal field described by Martin *et al.* (2000a), and discusses the intimate relationship the silica has with kaolin and other aluminous minerals presently forming in the field.

2. SETTING

The **Te** Kopia geothermal field (Fig. 1) is located in the Taupo Volcanic Zone (TVZ) where it 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, variably altered, Quaternary, ignimbrite sheets. The field has had a long (~120,000 years) history during which time movements on the Paeroa Fault have affected its hydrology episodically (Bignall and Browne, 1994). The ascending parent fluid was, and is, alkali chloride water of near neutral pH. This reacts with the ignimbrites within the reservoir to yield an assemblage that includes **quartz, adularia,** albite, chlorite, calcite and pyrite. However, on the

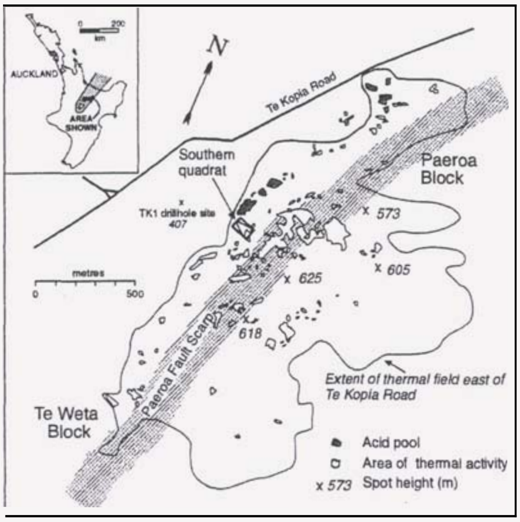

Figure 1. The Te Kopia thermal area, showing location of quadrat from which silica residue was collected for the present study.

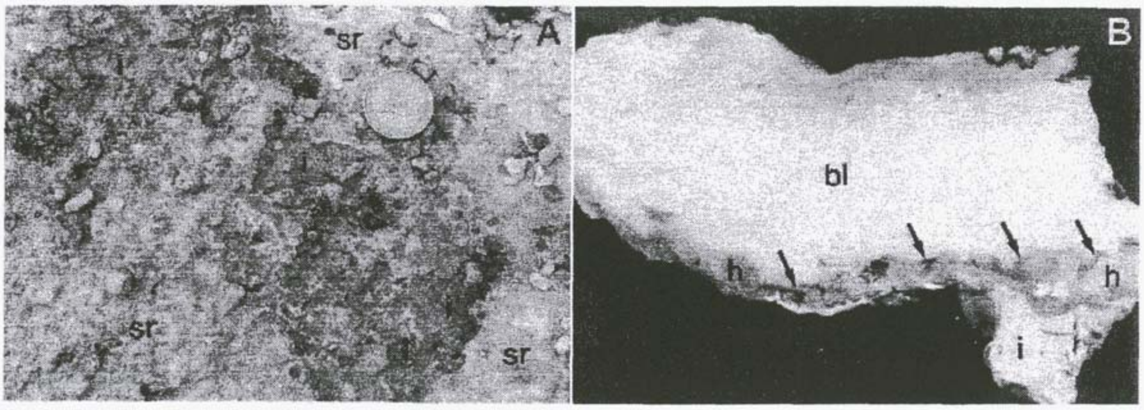

Figure 2. (a) Surface of terraced landslide debris, Te Kopia, showing typical accumulation of thin (<5 mm) *crustose* residue. Welded fragments and irregular surface of silica residue (sr) reflect repeated dissolution and precipitation of silica. Windows of subjacent, pink-stained, altered ignimbrite (i) are rimmed by white efflorescences of aluminium sulfates. Coin = 23 mm diameter. (b) Sawn section through *20* mm thick, quartz-rich, botryoidal (bl) loaf silica (AU49867) collected adjacent to weakly steaming fumarole. Convex-down, stalactitic botryoids form laminae <2 mm thick. Dark layer, pitted in places, at present ground surface is shown by arrows. Altered ignimbrite (i) remnant beneath dark layer. Glassy hyalite (opal-A) horizon (h) below ground surface and above remnant.

upthrown block, exposed along the western footwall fault scarp, both the primary and secondary minerals of the ignimbrites are now unstable, as is illite that locally replaced adularia.

Alkali-chloride waters discharged from hot pools and geysers as recently as 3000 years ago (Martin *et al.,* 2000b). Today surface thermal manifestations consist of boiling acid pools, small steam vents, mudpots, and steaming ground, all typical of acid-sulfate thermal activity. The latest surface alteration event, now in progress, involves interaction of all the previously altered rocks by steam, gases and steam condensate to yield an assemblage initially dominated by kaolinite±opal-A±alunite±alunogen (Martin *et al.,* 1999, 2000a). The silica residues described here represent the penultimate stage in this steam condensate alteration process. They were collected from a quadrat in the centre of the Te Kopia field (Fig. 1) sited upon crudely-terraced, warm (25-30 °C at 50 mm depth), ancient landslide debris at the foot of the Paeroa Fault (Martin *et al.,* 2000a).

3. SAMPLES

Eight samples were collected of three morphologies of residual silica. Each type of residue has a distinctive appearance but all grade one into the other. Sample numbers prefixed AU are those of the University of Auckland, Department of Geology, petrology collection. Nomenclature of the silica species follows Smith (1997, 1998).

Rind silica occurs typically as <3 mm thick, white coatings of glistening silica that coat exposed surfaces of variably altered ignimbrite boulders, subjected to steam condensate drip either in the past or today (AU49866). These coatings we common in elevated northeast sections of the quadrat. In places they thicken to form irregular masses of silica up to 15 mm thick (AU49871). Often they are discoloured by splotches of iron oxyhydroxides and biological coatings. The silica varies from milky white and crystalline, to transparent, water-clear hyalite with an irregular conchoidal fracture. Dissolution pits are common.

***Crustose** silica* **Rough,** scab-like, grey to off-white opaline crusts, usually <5 mm thick, are common upon warm, variably altered ignimbritic debris surfaces throughout much of the terraced area. They are particularly abundant about active and extinct fumaroles (Fig. 2a). The crusts resemble autobreccias in that they are composed predominantly of silica-welded fragments of former scabious generations (AU49863). In places they are crudely-layered and occasionally display transparent, microcrystalline euhedral quartz between layers (AU49870). Dissolution features are common and include fine, irregular, dark, vein-like, minute ridges that anastomose across the upper surfaces of the crusts. In sheltered, humid locations and also on open, bare, warm ground, the crusts are intimately associated with transient, water-soluble efflorescences of hydrous alumina-sulfates and hydrous sulfates (Fig. 2a; Martin *et al.,* 1999, 2000a).

Loaf ***silica*** Small masses, typically 100x50 mm, of dense, laminated, botryoidal, white, translucent silica up to 20 mm thick occur among the crustose residue, particularly adjacent to weakly steaming or extinct fumarole vents. In AU48967, the curved botryoidal growth surface is directed convexdown i.e. each botryoid is stalactitic (Fig. 2b). The lowermost (= youngest) of the white, translucent layers is succeeded downward by a thin (<0.5 mm), brown horizon that coincides with present ground level (arrows in Fig. 2b). This horizon is coated by a 1-2 mm thick layer of transparent, botryoidal hyalite, just below ground level (h in Fig. 2b) and immediately above clay-rich, hematite-stained ignimbrite (i in Fig 2b). Dissolution features on the air-exposed, quartzose surface of this sample are similar to those on other residue morphotypes and include pits and dark-veined ridges.

4. MINERALOGY

Determinative techniques used were those of Herdianita et *al.* (2000b). This procedure enabled direct comparison of the residue results with those obtained from sinters (e.g. Herdianita et *al.,* 2000a; Holland, 2000; **Pastars,** 2000; Teece, 2000).

Well defined, x-ray scattering bands of non-crystalline opal-A are present in all samples of crustose silica, two of the rind silicas and the hyalite base of the loaf silica (Fig. 3a-e). The width at half maximum intensity (FWHM) of these bands shows a range of 1.34-1.58 ΔÅ (7.6-8.50° $\Delta 2\theta$), with their **maxima** occurring from 4.11 to 3.85 **Å**. These values correspond with a limited degree of two-dimensional lattice ordering (*cf.* Smith, 1998) and are comparable to those reported for silicas deposited from highly acid waters at Rotokawa (ΔÅ = 1.29-1.50, $\Delta 2\theta$ = 7.40-8.90°). FWHM values of low temperature (sinter apron), alkali chloride-sourced sinters are typically lower ($\Delta 2\theta$ = 5.0-7.0); values similar to those of the residues occur among only very young sinters from the Wairakei discharge drain ($\Delta 2\theta$ = 7.20-7.80), the high temperature facies sinter of the Crow's Nest geyser vent ($\Delta 2\theta$ = 7-10), and surface samples of porous and friable sinters that have been subjected to weathering ($\Delta 2\theta$ = 7.00-8.20).

If FWHM is taken to indicate the degree of disorder within the opal-A structure then, presumably, the larger A28 values indicate that the level of disorder in opal-A deposited from acid fluid, is greater than that in silica deposited from the near neutral waters at temperatures <60°C. Further, the fine structure of the residue scattering bands closely resembles that of opal-A$_N$ rather than opal-A$_G$, the phase present in sinters formed at low temperatures (*cf.* Florke et *al.,* 1991; Smith, 1998). All **XRPD** traces, with the exception of AU49871, show the characteristic diffraction lines of quartz (Fig. 3b-f). In the hyalite sample from the loaf silica, AU49867, only a weak quartz pattern is superimposed on the opal-A scattering band (Fig. 3b). By way of contrast, the main mass of this proved to be principally quartz (Fig. **3f),** as did the massive rind silica, AU49868. Raman microprobe analysis of these quartz-rich samples showed moganite to be intimately associated with the quartz (*cf.* Rodgers and Cressey, *in* press) with up to 15% present in the loaf silica.

The diffraction patterns of kaolinite (rare), feldspar (rare), alunite, alunogen and possible nontronite are superimposed upon the opal-A scattering bands in the crustose silica (e.g. Fig. 3e). Kaolinite also is present with rind silicas. Further, the opal-A scattering bands of a number of crustose and rind silicas were oddly skewed about 21-24" 28 in a manner that can not be accounted for by the presence of any of these mineral phases (e.g. Fig. 3e). This skewed appearance is, however, consistent with the presence of small amounts of very poorly ordered paracrystalline opal-CT.

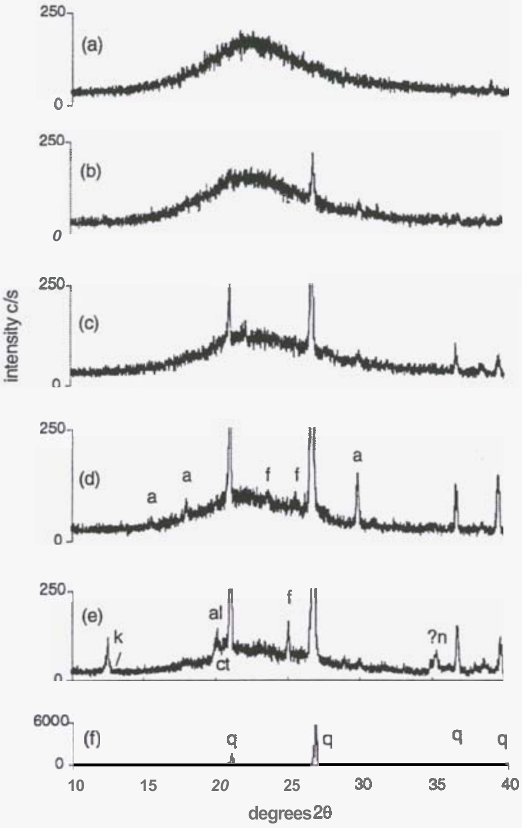

Figure 3 Typical x-ray powder diffraction traces of silica residue, Te Kopia, showing variation in silica species and other minerals. Broad scattering band with intense fine structure and a maximum at –4 Å (~26.5° 2θ) arises from opal A$_N$; q = quartz; k = kaolinite; f = feldspar; a = alunite; al = alunogen; n = nontronite; ct = opal-CT. (a) rind silica mass AU49871; (b) hyalite, base of loaf silica AU49867; (c) crustose silica AU49863; (d) crustose silica AU49870; (e) rind silica AU49866; *(f)* layered **milky** quartz, loaf silica AU49867.

5. MICROTEXTURES

The quartz-rich areas of the botryoidal loaf silica, AU49867, contain both well-defined, prismatic,

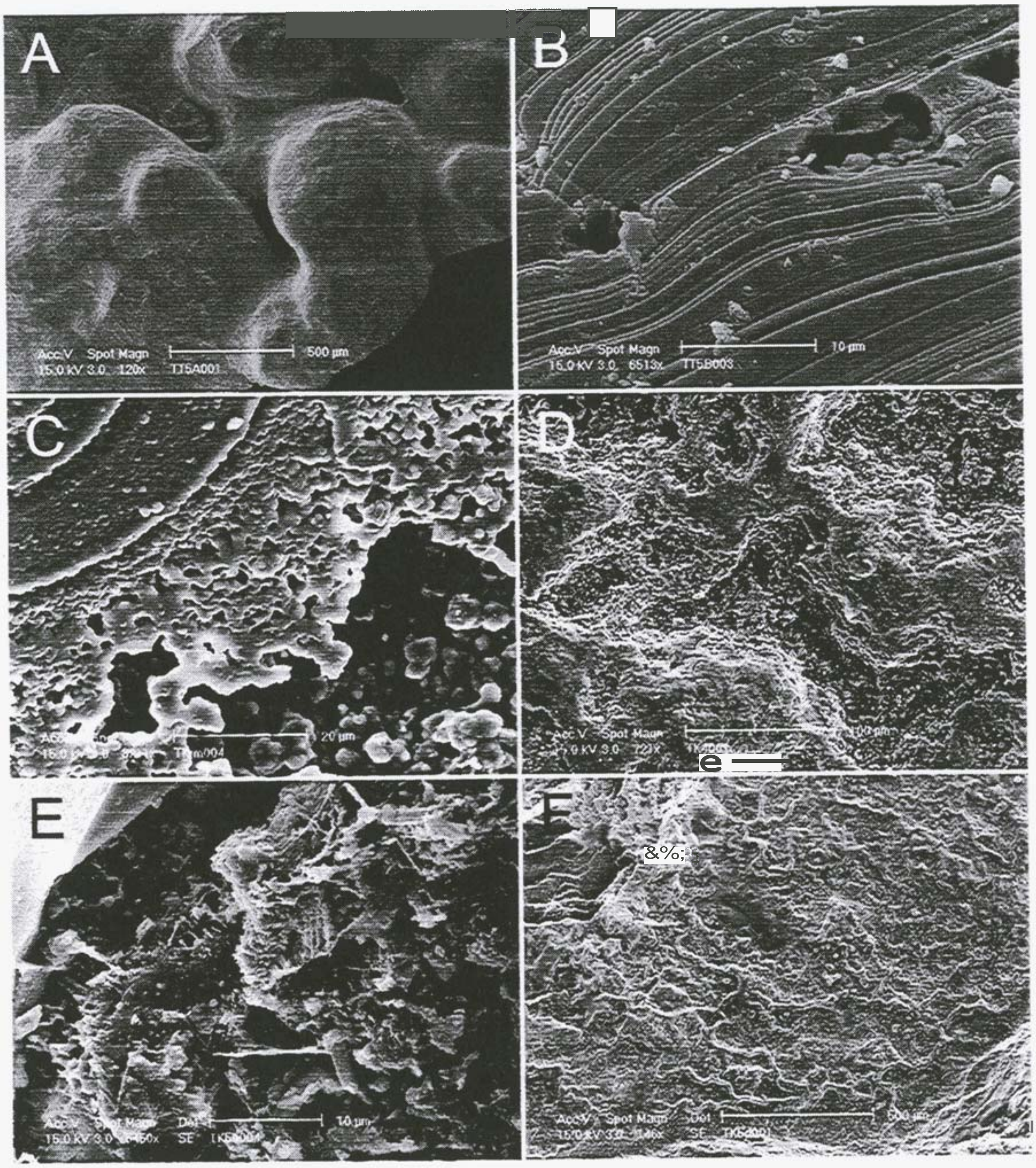

Figure 4. Examples of scanning electron microscope images of silica residue textures, Te Kopia: (a) Botryoidal surface of hyalite at base of silica loaf and abutting altered ignimbrite, i.e. this is a downward-facing growth surface. (b) Laminae of opaline silica in transverse section through hyalite botryoid. Note agglomerations of silica spheres imbedded in laminae. (c) Longitudinal section across opaline botryoid. Laminae consist of agglomerated opal-A spheres 300-600 nm in diameter. Larger spheres have coalesced in porous regions. (d) Dissolution surface of crustose silica showing crude layering. Irregular coalesced opaline spheres crowd depressions. (e) Altered and corroded mineral particles, coated with and partially replaced by opaline silica, from subjacent ignimbrite immediately beneath lower hyalite horizon of loaf silica. (e) Dissolution ridges on quartz. Air-exposed surface of loaf silica AU49867.

microcrystalline quartz and chalcedonic spheroids of length-fast fibrous quartz commonly 0.5-2 mm across. At ground level, at the base of the quartz, small (<1 mm) pockets of framboidal pyrite cluster above the thin horizon of isotropic, murky-brown hyalite. The subsurface hyalite has a faint globular texture (1-2 mm diameter) resembling frog-spawn. Scanning electron microscope observation reveals the underlying, laminated, character of the microbotryoidal hyalite layers (Figs 4a-c). Each subsurface hyalite layer is formed of agglomerations of imperfectly defined spheres of opal-A, 300-600 nm across (Fig. 4b,c). Spaces between the individual botryoids are progressively infilled by porous accumulations of larger coalesced spheres, up to 2 µm diameter (Fig. 4c). This basic structure also is apparent on opaline surfaces undergoing dissolution. Layers are exposed along the length of remnant ridges with irregular clusters of spheres lining the depressions between (Fig. 4d). At the junction between the hyalite and the underlying country rock, corroded remnants of primary and secondary minerals occur, both overgrown and in the process of being replaced by opaline silica (Fig. 4e).

The intimate relationship between both quartz and opaline silica is emphasised in a rather compact, layered crust (AU49870). A well-crystallised mosaic of roughly equidimensional quartz, with remnant primary quartz and feldspar crystals, nestles cheek-by-jowl with ill-defined, near-isotropic globules of hyalite; the contact between the two horizons marks a temporal hiatus (=disconformity) between the two generations of silica. Numerous euhedral crystals of quartz occupy pore space and have developed, perpendicular to the layers. The euhedral crystals commonly show overgrowths of quartz which, in turn, may or may not be invested in opal.

Dissolution features are readily seen among both the opaline and quartzose residues under the scanning electron microscope. These are particularly evident where internal structures are exposed as a result of the corrosion. For example, the remnant veiniform ridges, common to both exposed, flat-lying opal and quartz surfaces, show crude layering along their length (Figs 4d,f).

6. DISCUSSION

At Te Kopia silica residue develops on and near the surface of landslide debris that mantles the outcrop of the Paeroa Fault. Steam ascends through this mass until it starts to condense when the ambient temperature drops to <100 °C. The height below ground level at which this occurs varies in the chaotic, altered mass and much steam escapes and condenses above the ground. Oxidation of the accompanying H_2S occurs both above and below ground level since, like temperature, Eh varies throughout the tumbled mass. Sulfur crystals ($S = 0$) grow beneath ignimbrite boulders in the steaming landslide. Pyrite ($S = -2$) grew immediately below ground level at the base of the loaf silica. Sulfuric acid, ($S = +6$) forms at and below the surface where it converts the already altered country rocks to kaolinite-alunite/alunogen-opal-A±hematite±jarosite±leucoxene (Bignall and Browne, 1994).

In addition to silica precipitating directly from silica-saturated condensate, Martin *et al.* (1999) demonstrated that on areas of bare warm ground at Te Kopia an intimate relationship exists between clays, silica, and aluminous sulfates. Acid sulfate fluids react with kaolinite to yield alunogen (*cf.* Nordstrom, 1982):

$$\mathrm{Al_2Si_2O_5(OH)_4 + 6H^+ + 3SO_4^{2-} + 16H_2O \rightarrow}$$
$$\mathrm{Al_2(SO_4)_3.17H_2O + 2H_4SiO_4}$$

This process is reversible. When alunogen is exposed to fluids less acid than those from which it formed, and in the presence of poorly crystalline silica, it dissolves to yield kaolinite. Alternatively, where silicic acid dissociates in the presence of alunogen, silica deposits:

$$\mathrm{Al_2(SO_4)_3.17H_2O + 2H_4SiO_4 \rightarrow 2Al^{3+} + 3(SO_4)^{2-}}$$
$$\mathrm{+ 2SiO_2 + 21H_2O}$$

Martin *et al.* (1999) claim this latter process explains the common association of silica-rich, alumina-depleted residue crusts with aluminous efflorescences at Te Kopia. Further, they argued that where episodic dissolution and precipitation of kaolinite occurs (*cf.* Nordstrom, 1982), the cumulative effect will be production of a leached, kaolinite-impoverished, siliceous surface residue such as that now accumulating in steam-heated areas at Te Kopia and similar to those described from Steamboat Springs (Schoen *et al.*, 1974).

Nonetheless, the layered nature of the residues, their many dissolution features, and the textural juxtaposition of opaline silica and quartz, in both loaf and crustose silicas, provides clear evidence that accretion and corrosion of silica residue, and hence kaolinite dissolution and reprecipitation, has not happened continuously and uniformly throughout the Te Kopia substrate. Rather, the process has occurred episodically. For example, the first formed residue silica is opal-A (White *et al.* 1956; 1988). Quartz forms by crystallisation of the earlier precipitated opal-A. Whether this occurs at Te Kopia via an intermediate opal-CT or opal-C phase, as described for silica sinters (White *et al.* 1988; Herdianita *et al.* 2000a) and deep sea sediments (e.g. Kano 1983), is uncertain. Regardless, in both the loaf (AU49867) and the crustose (AU49870) residues, a hiatus occurred between deposition of the original opal-A, now crystallized to quartz, and the subsequent resumption of opal-A accretion today. Such an interruption could result fiom a simple change in the steam flow pattern within the substrate, and hence restrict supply **of** acid sulfate-enriched steam condensate. It was during this hiatus that crystallisation of the original opal-A could have occurred.

Given that alkali chloride waters have discharged adjacent to the southern quadrat within the past 3000 years (Martin *et al.* 2000b), the silica residues in the quadrat are young, post-dating this event. Hence, maturation of the opal-A to quartz has occupied considerably less time than proposed by Herdianita *et al.* (2000a) for aging silica sinters - *c.*40,000 years. Perhaps highly disordered opal-A_N **is** more susceptible to crystallisation than the metastable opal-A_G of silica sinters. Possibly the sustained supply of heat and moisture facilitated the process. However, these conditions have not been of sufficient intensity or duration to eliminate moganite **as** a transitory phase in the maturation process *(cf.* Rodgers and Cressey, ***in press).*** Heaney and Post (1992) point out that moganite is more soluble than quartz and will not long endure contact with hot fluids. Perhaps it is the presence of **this** more soluble phase that facilitates dissolution, even of quartz-rich residue, under surface conditions at Te Kopia.

In **summary:** silica residue forms at and near the surface of Te Kopia, **as** a result of dissolution of the country rock by dilute sulfuric acid. Subsequently, silica residue can react with aluminous solutions to yield kaolinite, or crystallise to microcrystalline **quartz** plus moganite, or completely dissolve in acidified rainwater, fogdrip or further steam condensate - the terminal stage in alteration of the country rock *(cf.* White *et al.* 1956). The precise pathway followed depends upon the prevailing surface conditions, including humidity, pH, and aluminium activity.

Finally is should be noted, that "silica residue" **is** not a resistate *sensu strictu*. The name is a misnomer, insofar **as** silica residue is a chemical precipitate, comparable in this regard to silica sinter. Not only is silica continuously depositing, but it also is undergoing continuous dissolution in the surface at Te Kopia today. It enjoys reaction relationships with both kaolinite and alunogen. Silica residue is itself but a metastable, transitory phase that represents the penultimate product of a succession of alteration events at Te Kopia. The ultimate stage of steam condensate alteration is ***tabula rasa.***

7. ACKNOWLEDGEMENTS

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