SILICA FROM STEAM CONDENSATE ALTERATION AT TIKITERE, NEW ZEALAND

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ABSTRACT

Silica residue is the main product of the alteration of a rhyolitic, tuff-rich, volcanic substrate by acid sulfate condensate formed, in a major steam field at Tikitere, near Rotorua. Here steam and accompanying H_2S discharge in an area characterized by large standing pools of acid water and mud pots. As in silica sinters, that precipitate from hot, near-neutral, alkali chloride waters, the first formed silica phase in the residue consists of non-crystalline opal-A that subsequently crystallizes to paracrystalline opal-CT. Residue and sinter can superficially resemble each other and there is a need to clearly differentiate both types of deposit in order to correctly interpret the hydrology or paleohydrology of a geothermal field. Both the opal-A_N and opal-CT in the Tikitere residues are more disordered than those in typical sinters. Tikitere residue also lacks mesoscopically-recognizable, biologically mediated textures, vascular plant remains, and unaltered tuffaceous clasts, commonly present in silica sinters. However, once crystallized to opal-CT lepispheres (1-3 μm across) and, subsequently, to quartz, both residue and sinter are less readily distinguished as earlier textures become overprinted.

INTRODUCTION

Tikitere is a hot water geothermal field in which a large amount of steam discharges. It is one of the most active thermal areas in New Zealand. It is remarkable in that alkali chloride waters are not known to have ever discharged at the surface in the most visibly active portion of the field. The surface alteration products are soley those resulting from acid-sulfate thermal activity, including the action of acidified steam condensate, gases and steam upon the formerly pristine country rock.

One of the distinctive effects of the acid-sulfate surface activity is the accumulation of silica residues that result from the surface and near-surface leaching of silicate rock by sulfuric acid, derived from oxidation of ascending H_2S (White *et al.,* 1956). Silica residues contrast with silica sinters deposited from near-neutral, alkali chloride waters and with which they have sometimes been confused. In both types of deposits the first-formed silica phase is opaline silica and Herdianita *et al.* (2000a) have stressed the importance of clearly differentiating residue from sinter if either is to be used to interpret hydrology or paleohydrology. Although a large body of literature exists as to the nature and origins of silica sinters, no systematic characterization of any residue deposit has been undertaken. The results presented here include a mineralogical and textural examination of three typical residue samples collected from the surface of the Tikitere field. They illustrate how alike both residue and sinter can be, and the need for caution in appraising any geothermal-derived silica deposit in the field.

SETTING

The Tikitere geothermal field is situated within the Rotorua Volcanic Centre of New Zealand's Taupo Volcanic Zone (TVZ), 18 km east of Rotorua City (Fig. 1). The country rock consists of late Pleistocene (~60,000 BP), largely rhyolitic, Rotoiti Breccia. Minor amounts of Holocene, basaltic Rotokawau Ash may be present. Thermal activity occurs over an area 3.2 x 2.4 km. Two adjacent zones at the southern extent of the field, due north of the Rotorua-Whakatane Road, comprise the Tikitere tourist area known as Hell's Gate. The output of H_2S from this southern part of the field was regarded by Grange (1937) as probably the highest in the Rotorua-Taupo area.

The confusion of alkali-chloride-derived sinter with silica residue is seen in Grange's 1937 description of the Tikitere field. He reported the presence of encrusting masses of white sinter throughout much of the field and cited their presence as evidence that alkali-chloride waters had once discharged at the surface there in the past. All such deposits within the main body of the field are now interpreted as silica residue, consistent with the presence of acid sulfate waters and the now-known absence of any discharge of alkali-chloride waters at the surface, both at present and in the past (Glover, 1974).

Four large acid-sulfate pools occupy the valley floor, in the southern portion of the Hell's Gate area (Fig.1). Small

deposits of both sulfur and pyrite have formed on different areas of the valley's surface and Grange (1937, p.87) noted that "white sinter to a small extent encrusts much of the area." The northern portion of Hell's Gate is dominated by three, large, acid, shallow pools with diameters that vary up to 100 m across, and about which Grange (1937, p.87) observed "some big blocks of white sinter." The overflow from these pools feeds Mariwai Creek. All springs discharging in the field today are fairly close to present groundwater level but the water supply is probably small.
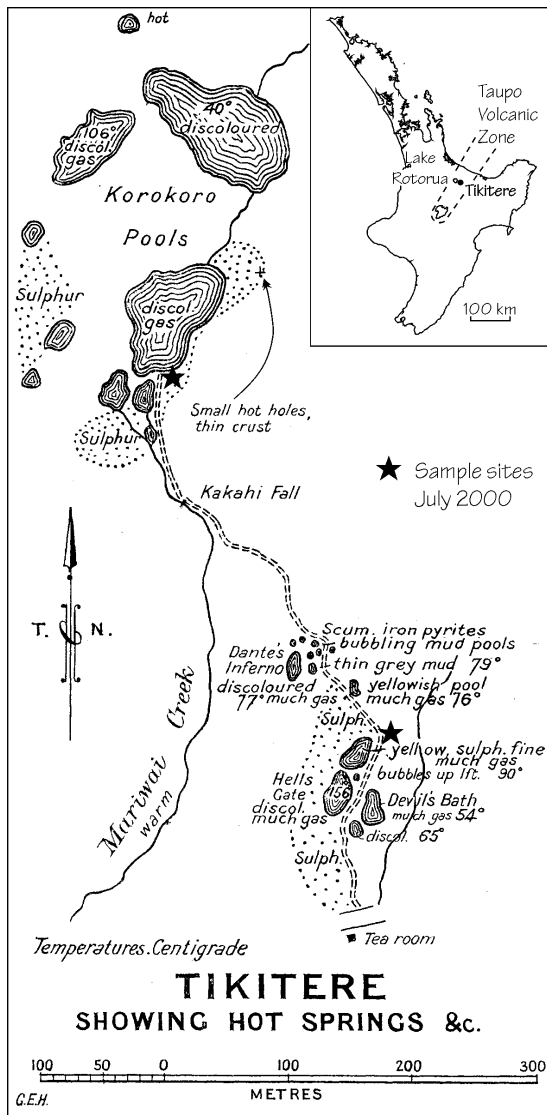

Fig. 1. Locality map, Tikitere steam field, modified slightly after Grange (1937, p.88), showing locations from which silica residue was collected for the present study. Insert: location of Tikitere within the Taupo Volcanic Zone (TVZ).

SAMPLES

Environmental concerns restricted sampling and only three specimens were collected. Each represented a different morphological and textural aspect of the upstanding silica blocks described by Grange (1937). All such masses proved to be sub-recent erosional remnants such that no examples of residue forming today were collected. Sample numbers prefixed AU are those of the University of Auckland, Department of Geology, petrology collection.

The block-like mounds of residue are typically 400-1200 mm across and from 250 to 750 mm high (Fig. 2a,b). In many instances they are sited in and around the edges of acid pools where they outcrop amongst moderately sorted, medium to coarse silica gravel. Elsewhere, they protrude above masses of white, kaolin-rich clay. In color, the residue mounds range from a bleached white, through a pale cream to light grey. Most surfaces are heavily corroded and/or abraded, but in protected nooks and crannies throughout the area, porous grey crusts and irregular lumps of weakly-cemented, friable, fine opaline sand encrust brown, clay-rich altered tuff (e.g. AU49877).

About the edge of ponds in the northern end of the field, residue mounds of low relief have smooth, if somewhat irregular abraded surfaces (Fig. 2a). Higher-standing coralloidal-like mounds in both the northern and southern portions of the field typically display extremely rough, gnarled surfaces (Fig. 2b). In many respects this contorted appearance resembles that of sub-aerial coralline algal masses subject to differential solution and endolithic microbial attack on tropical atolls. Spiculose, knobby masses, 2-10 mm high and 2-5 mm across, protrude from the surface and coalesce to form irregular ridges and stony prominences. Broken knobs show crudely concentric structure. Elsewhere, undulose ridges, 2-5 mm high, wander erratically over the surface. The depressions between knobs and/or ridges are commonly lined with a porous layer of silica-cemented, well sorted, medium sand-sized clasts. Broken masses of residue commonly show a clasts of massive to finely laminated, pale incarnadine to sallow, opaline silica. Color differences highlight the laminae, that are generally <<1 mm thick and display small sedimentary structures consistent with a water-laid origin (Fig 2c). Typically these laminae truncate abruptly against the opaline matrix and indicate the clasts are derived from an earlier-formed deposit. Clusters of diatom skeletons are also common as are those of other aquatic microorganisms and confirm the residue originated in an environment that contained standing water.

The general impression in the field is that all blocks and silica masses have been, and continue to be, subject to cycles of silica deposition, erosion and cementation on
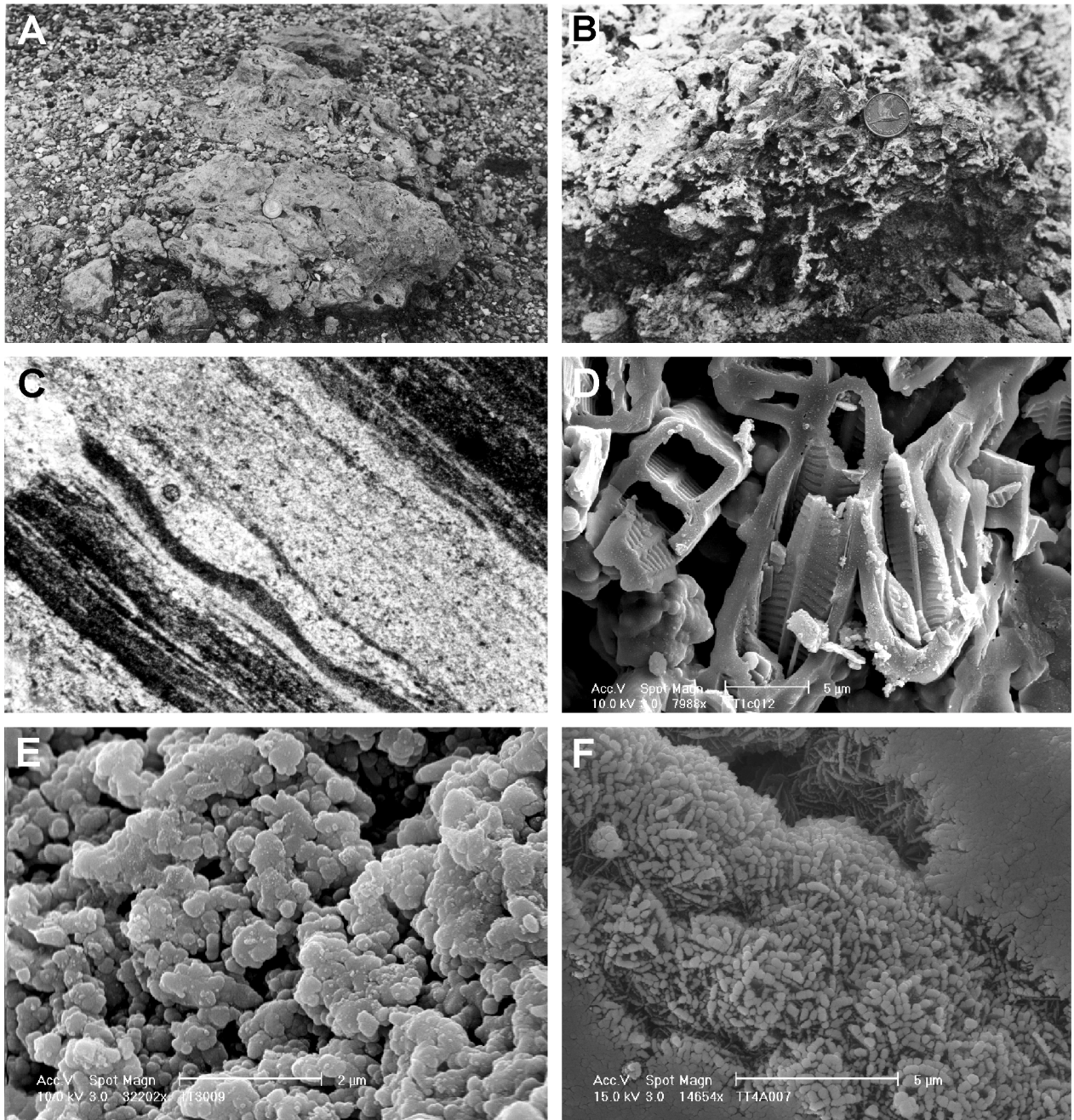
Figure 2. (a) Coralloidal silica residue mounds outcropping among silica gravel, southern rim of shallow acid pool, northern region of Tikitere steam area. Coin is 26 mm in diameter. (b) Irregular, gnarly, corroded surface of large residue mound, southern edge of shallow acid pool, northern region of Tikitere steam field. Coin is 26 mm in diameter. (c) Thin section photomicrograph of finely laminated opaline silica residue (AU49876). Note sedimentary structures consistent with water-laid sediment, and the abrupt truncation of the laminae at left. Plane polarised light. Base of photo is 3 mm. (d) Scanning electron microscope image of diatoms contributing to the gnarly residue mass (AU49875), and testifying to its origin within a source of standing water. (e) Scanning electron microscope image of clusters of opal-A microspheres that form the bulk of the weakly-cemented, encrusting opaline residue (AU49877). (f) Scanning electron microscope image of opal-CT lepispheres occupying a cavity in gnarly residue (AU49875). Blades of opal-CT grow out from and form the bulk of the enclosing matrix comprising the broken surfaces at top right and bottom left.

both macroscopic and microscopic chemical scales; presently destructional processes exceed constructional among the upstanding residue masses.

MINERALOGY

Determinative techniques used were those of Herdianita *et al.* (2000b) so that direct comparison could be made of the residue results with those obtained from sinters (e.g. Herdianita *et al.,* 2000a, Sannazzaro *et al.,* 2001).

The x-ray powder diffraction patterns of three silica phases were found in the three samples analyzed (Fig. 3): opal-A, opal-CT and quartz. Other diffraction lines present were those of a feldspar and possibly alunogen. Opal-A was the principal phase in the grey, porous friable
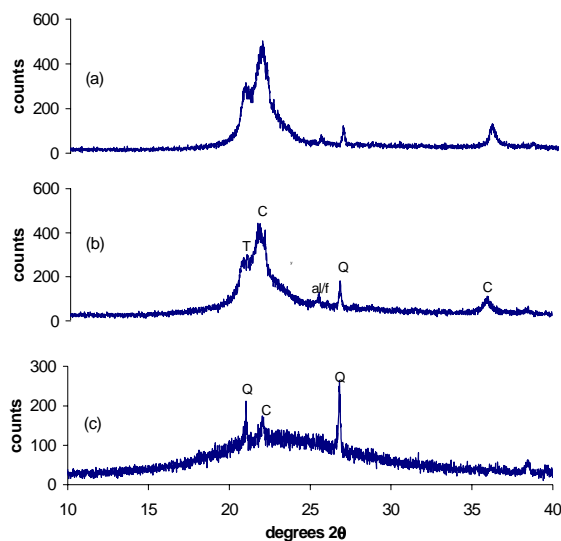

Fig. 3. Typical x-ray powder diffraction and scattering traces of silica residue, Tikitere, showing variation in silica species and other minerals. Broad scattering band with intense fine structure and maximum at ~4 Å arises from opal A_N. Q = quartz; CT = opal-CT; al = alunogen: (a) finely-laminated, massive opaline residue, AU49876; (b) pale-grey, gnarly residue, AU49875; (c) weakly-cemented, friable, fine opaline sand, AU49877.

opaline crust (AU49877). Superimposed upon the opal-A x-ray scattering broadband were the weakly developed principal diffraction lines of quartz, and ill-defined broad diffraction lines of opal-CT at ~4.07 and ~2.5 Å, respectively.

The width at half maximum intensity (FWHM) of the opal-A scattering band is 1.52 Å Δd (9.30° $\Delta 2\theta$). Such a value is exceptional among opal-A silicas. It is found only at the higher end of the range reported by Teece

(2000) from silicas deposited from highly acid waters at Rotokawa, Δd = 1.29-1.52 Å ($\Delta 2\theta$ = 7.40-9.30°). FWHM values among low temperature (sinter apron), alkali chloride-sourced sinters are typically lower: Δd = 0.95-1.25 Å ($\Delta 2\theta$ = 5.0-7.0°). Higher values have been found 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°) (Herdianita, 1996; Holland, 2000; Pastars, 2000). The fine structure of the Tikitere scattering band closely resembles that of opal-A_N, rather than opal-A_G, the latter of which is the typical, first-deposited phase of low to moderate temperature alkali-chloride sinters (*cf.* Flörke *et al.,* 1991; Smith, 1998).

In both the gnarly residue (AU49875) and the finely laminated, massive opaline residue (AU49876), paracrystalline opal-CT is the dominant silica phase. Weak quartz lines are present in the diffraction scans of both deposits, and in AU49875 a subdued scattering broadband, with an FWHM of ~1.35 Å Δd (~8.00° $\Delta 2\theta$), similar to that in the porous crust (AU49877) underlies the opal-CT pattern. The maxima of the principal opal-CT line ranges from 4.04 to 4.08 Å and its FWHM from 0.33 to 0.42 Å Δd (1.70-2.25° $\Delta 2\theta$). The FWHM values are considerably larger than those found among cristobalitic-opals reported by Sannazzaro *et al.* (2001) from recrystallized, Late Quaternary, low-temperature facies sinter from Umukuri. In samples in which opal-CT was dominant, these authors reported FWHM values of between 0.54 and 0.69° $\Delta 2\theta$. The marked differences between Tikitere and Umukuri result, in large part, from the ill-defined nature of the principal opal-CT diffraction line in the Tikitere samples. This line is a composite. It consists of a main reflection at ~4 Å, arising from small, coherently-scattering domains that mimic the arrangement of atoms in cristobalite (Smith, 1998), and a prominent satellite at ~4.3, that arises from tridymite interlayers within the structure. The ratio of the relative intensities of the cristobalitic and tridymitic components of this composite line in the Tikitere residues (tridymite/cristobalite ~0.6) is considerably greater than that of Umukuri opal-CT (~0.3). Presumably, the difference in this ratio implies a greater proportion of the tridymitic lattice component in the Tikitere opal-CT samples. However, it also means that measurement of FWHM in the Tikitere samples occurs in that part of the band that is broadened by overlap of the tridymite and cristobalite diffraction responses (Fig. 3). In the Umukuri sinter the measurement is made within that part of the composite line ascribed to diffraction from cristobalitic stacking alone. Hence the two sets of measurements are not directly comparable. Nonetheless the general structure, shape and line width of the Tikitere samples

strongly suggest that acid-deposited silicas display a lower sensitivity diffraction response, and hence have a reduced level of ordering than occurs in recrystallized sinter samples, such as Umukuri.

MICROTEXTURES

Imperfectly formed opal-A microspheres, typically 0.1-0.5 μm in diameter, dominate the weakly-cemented, friable, fine opaline sand (AU49877). These form irregular clusters up to 5 μm across and coalesce in ill-defined microbotryoidal gel-like masses that line pores and coat clast surfaces including diatoms and other microfossils (Fig. 2e). Pockets of similarly-sized opal-A microspheres are common in the coralloidal-like residue (AU49875) but the principal silica phase in this rock, consists of lepispheres of opal-CT up to 2 μm across. In places, these lepispheres occur as subspherical masses in which the blades that characterise typical opal-CT (e.g. Sannazzaro *et al.* 2001) are reduced to little more than raised surface lumps. Amalgamated masses of these incipient lepispheres swarm across surfaces and line pores and their textural expression can be traced into the matrix of the surrounding residue. Elsewhere, clusters of opal-CT lining cavities show a more typical bladed habit but, unlike that common in sinters, the termination of the blades are modified by uneven silica microclumps (Fig. 2f). The texture of these residue-derived bladed lepispheres also can be traced into the surrounding matrix. However, the diatoms that abound in this sample show little sign of replacement or coating by opal-CT (Fig. 2d). Dissolution features are common on the external surface of all opaline residues under the scanning electron microscope. These include remnant veiniform ridges and knobs, and solution micropits.

DISCUSSION

At Tikitere the considerable volume of rising steam condenses both above and below ground level. Accompanying H_2S oxidizes to sulfur or sulfate, or remains as sulfide, depending on local Eh. Where conditions permit sulfuric acid to form, the country rock is attacked. Dissolution of the country rock is a progressive, step-wise process. The particular assemblage of remnant primary and new secondary minerals present at any one moment at Tikitere reflects the prevailing conditions and ionic activities of a particular environment.

The mineral assemblage is, in the first instance, dependent on a sufficient supply of moisture both to host the various reactions and also supply and remove the various reacting species. In the Tikitere steam field, a continuous supply of moisture is not everywhere uniformly available nor even present. Moisture varies with weather, ground and air temperature, steam throughput and condensation, and groundwater supply. The most obvious expression is seen in the presence, absence, and fluctuations, of the standing pools where conditions are relatively constant, or change only slowly with time. Reactions also occur on a microchemical scale upon exposed surfaces wherever fluid films are present and conditions can vary rapidly, millimeter by millimeter across a rock surface.

Of the different conditions prevailing in the surface, pH is of paramount importance. Oxidation of available H_2S may afford a primary supply of protons but this also is controlled by the rate at which the dissolution of primary minerals in the substrate consumes them, by the precipitation rate of secondary hydroxyl-bearing minerals, and by dilution from rain, fog drip, or continuing steam condensation. Local variations in proton supply alone can provide the opportunity for alternation of episodes of residue precipitation and dissolution (White *et al.* 1956). Only some generalizations as to the processes involved are given here.

Numerous mechanisms are available to produce (and dissolve) silica at the surface in acid conditions. For example, a principal component that results from the attack on the country rock by the acidified steam condensate is silicic acid. In appropriate conditions this will dissociate and silica precipitate. The simplest scenario is given by:

$$H_4SiO_4 \rightarrow SiO_2 + 2H_2O$$

However, intermediate species occur, including those of unknown stoichiometry and denoted here by $(*)^{\ddagger}$ (Dove and Rimstidt, 1994). For example,

$$H_4SiO_4 \rightarrow (*)^{\ddagger} \rightarrow SiO_2 + 2H_2O$$

and $\quad H_4SiO_4 \rightarrow (SiO_2.2H_2O)^{\ddagger}$
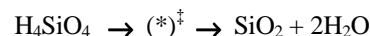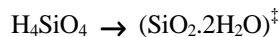
Silica also can result from dissolution of the transitory hydrous aluminous sulfates that abound in acid conditions (Martin *et al.* 2000). For example, alunogen can dissolve in the moisture supplied by the dissociation of silicic acid and yield silica as a result:

$$Al_2(SO_4)_3.17H_2O + 2H_4SiO_4 \rightarrow$$
$$2Al^{3+} + 3(SO_4)^{2-} + 2SiO_2 + 21H_2O$$
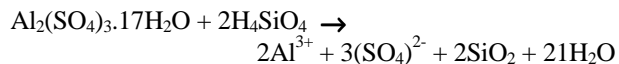
The importance of this reaction arises from the intimate relationship that exists in an acid environment among clays, silica and aluminous sulfates; e.g. acid sulfate fluids react with kaolinite to yield alunogen (Nordstrom, 1982):

$$Al_2Si_2O_5(OH)_4 + 6H^+ + 3SO_4^{2-} + 16H_2O \rightarrow$$
$$Al_2(SO_4)_3.17H_2O + 2H_4SiO_4$$
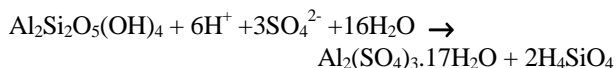
Consequently, as microchemical conditions vary across a debris mound, kaolinite can dissolve and silica precipitate wherever areas are sufficiently acidic. However, when the fluid obtains a pH higher than that which dissolved the kaolinite, as where protons are removed during rock dissolution, kaolinite can reprecipitate and earlier-formed silica accumulations dissolve (Martin *et al.* 1999). The penultimate result of these reactions is to produce leached, aluminum-poor, siliceous rocks at the surface, underlain by kaolinite deposited at or near the water table such as is found at Tikitere, at Yellowstone (Ramahashay, 1968) and Steamboat Springs (Schoen, *et al.* 1974). Where large silica residue masses accumulated, it is likely that a continuous supply of fluid, of more or less constant high acidity, was available throughout the rock dissolution. Such an environment could be afforded by a standing acid pool. At Tikitere the present pools were once more extensive due to a previous higher water table. These conditions could produce the finely laminated, water-laid silica sediment. Subsequent disruption of the system by hydrothermal activity could have brecciated the cemented sediment and led to its mixing with altered tuff, which in turn became cemented by continued precipitation of silica produced from further condensate. Changes within the water table, or in steam patterns within the field, could have exhumed the exposed silica mounds that are now undergoing dissolution as a result of these changed conditions.

In its initial state an accumulation of residue bares only superficial resemblance to silica sinter. In the present residue samples, the original opal-A appears to have a markedly greater FWHM for its scattering band than that formed from alkali chloride waters. Importantly, the initial textures of the two deposit types are markedly different. The residue lacks any of the microbially mediated textures commonly present in sinters, which are readily seen both at a mesoscopic and at an ultrastructural level. In general, evidence of microbial activity in residues is markedly less than in sinters, although its nature and extent has not been defined in formation of these deposits. Where such textural evidence is absent and where the FWHM of opal-A is >7.2° Δ2θ, it is likely

that the silica is of residue, or at least acid water origin.

Other differences that set silica residue apart from TVZ sinters include corrosion of associated tuffs and the absence of vascular plant material. Sinter-related tuffs occur on discreet horizons (Sannazzaro *et al.* 2001) or as water-worn clasts (Holland, 2000). Diatoms, however, are a common feature in both sinter and residue deposits.

Based on limited evidence from the Tikitere specimens, it is apparent that care needs to be exercised in distinguishing the two types of siliceous deposits following their crystallization to opal-CT, and subsequent chemical and/or physical weathering. Erosional residuals, such as commonly occur in thermal settings, can be misidentified as sinter as proved to be the case with Grange (1937), an otherwise careful and thorough field worker. However, hand lens examination should reveal the presence or absence of modified primary features typically associated with sinters. These generally survive at least the initial stages of mineralogical transformation and include biologically mediated textures, plant remains and unaltered clasts (e.g. Holland, 2000; Pastars 2000; Sannazzaro *et al.* 2001). Certainly, the presence of any country rock residuals that have undergone substantial alteration should suggest that a siliceous deposit has a probable residue origin. Strongly disordered phases, as seen in XRPD traces, also appear to be indicative of residue-derived silicas and the chemistry of the two types of deposits could well prove to be different, although evidence is slight at this stage. Grange (1937) reported the absence of gold and silver and the presence of ~0.5 wt% TiO_2 in the Tikitere silica. Both features contrast with the relatively high levels of precious metals and the markedly lower titania found in typical TVZ sinters (e.g. Nicholson and Parker, 1990).

The difficulties in distinguishing sinter or residue in the field become enhanced as recrystallization of these deposits to quartz advances. Densities increase and porosities decrease in both cases. Earlier-formed textures become overprinted or are obliterated (e.g. Sannazzaro *et al.,* 2001). There is a convergence in overall appearance and macroscopic features. However, whether textural features of the Tikitere deposits are characteristic of all residue-derived silica has yet to be determined.

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