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THE DETECTION AND SIGNIFICANCE OF MOGANITE IN PLIOCENE SINTER AT PLUMDUFF, NORTHLAND

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SUMMARY - Raman spectral microsampling, from 100-600 cm^{-1}, of clean slabs of Pliocene breccias show moganite, monoclinic SiO_2, is disseminated through the Plumduff sinter, that otherwise consists predominantly of microcrystalline quartz. Moganite forms as a metastable phase during the recrystallisation of the sinter from opal-CT and opal-C to quartz and these are the oldest sinters in New Zealand in which moganite has been recognised. The distribution of moganite is uneven e.g. it is absent from recrystallised examples of palisade, tufted network, finely laminated, peloidal and plant-rich primary sinter textures but is present in both fenestral network and columnar types. Its distribution reflects heterogeneity of process that has affected the outcrop since development of the initial sinter apron e.g. hydrothermal activity and weathering. The rapidity of Raman analysis and its ability to microsample individual textural elements allow the twin paths of mineralogical and textural maturation of sinters to be mapped together.

1. INTRODUCTION

Moganite is a distinctive monoclinic polymorph of silica. Heaney and Post (1992) showed that it is "a fairly common mineral of the earth's crust" where it occurs as a frequent component of microcrystalline quartz-rich silicas including chalcedonies, cherts and flints. Rodgers and Cressey (2001) found it to form up to 13% of quartz-bearing sinters of New Zealand between 20,000 and 200,000 years old, derived from crystallisation of noncrystalline and paracrystalline opaline silicas. However, they noted moganite to be below the level of detection in New Zealand Tertiary sinters, all of which are predominantly microcrystalline. quartz, albeit derived from at least two silicification processes. The present account reports the first discovery of moganite in a New Zealand Tertiary sinter: the Mid to Late Pliocene occurrence at Plumduff, one of three southernmost sinter masses of the fossil Puhipuhi geothermal field. The identification was made using the latest generation of laser Raman microprobes, a Renishaw Raman 1000 system, that allows individual textural elements of the sinter to be recognised and their mineralogy identified, a considerable advance on the technology available to Rodgers and Cressey (2001). The opportunity is taken to document the determinative details and also to consider possible implications for the presence of moganite in geothermal systems.

2. THE PLUMDUFF SINTER AND ITS ROCKS

Today the Pliocene Plumduff sinter consists of little more than a mass of boulders littered across a steep sided (15°-20°), conical hillock in the south of the Puhipuhi fossil geothermal field that rises ~40 m above the Whenuaroa Stream (Fig. 1). The strewn field covers ~300 m^2 about a former hot spring that had a varied and long lived history. Epithermal deposits occur beneath the site.

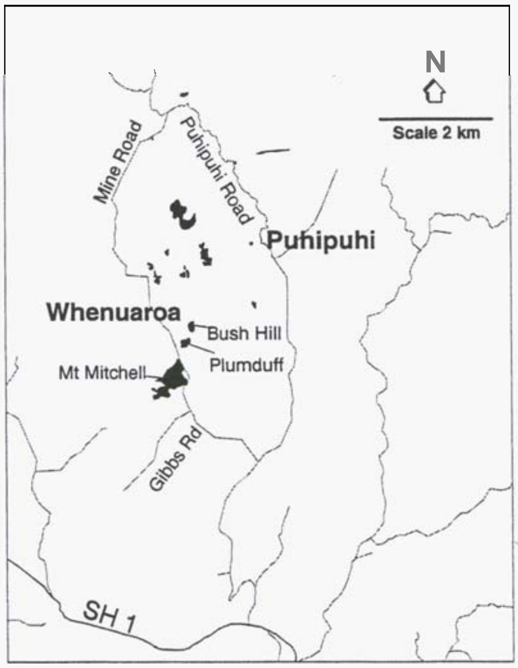

Figure 1. Location of Plumduff sinter within the Puhipuhi fossil geothermal field, Northland.

Most boulders consist of breccia composed of silica-cemented sinter clasts, both in matrix and clast support. Clast size varies from >0.5 m across in rudrocks (very coarse breccias) (Fig. 2), through <1 m angular slabs of coarse breccia, to angular to sub-angular sinter fragments from <10 to 120 mm across of finer breccias. Clasts include layered and massive sinter blocks, as well as discrete fragments of microbial fabrics such as stromatolites. The matrix of these rocks is mainly massive, microcrystalline, white to brown quartz. Rocks in which clast size is <150 mm form a minor proportion of the Plumduff breccias. Some of these clasts consist of a distinctive blue translucent chalcedony. Sinter conglomerates containing sub-rounded, spherical to oblate clasts of chalcedony <5 mm in diameter occur at one locality on the eastern side of Plumduff.

Figure 2. (a) Typical very coarse sinter breccia (rudrock) boulder, Plumduff. Hammer lower centre for scale.

The quartz-rich microcrystalline character of the rocks indicates that the sinter has been modified, post-deposition, from its original opaline, non-crystalline nature. The sinter clasts of the breccias are cemented by later generations of microcrystalline silica derived, in its turn, from crystallisation and recrystallisation of late stage sinter i.e. the boulders consist of sinter intraclasts imbedded in later generation(s) of sinter, the whole mass having suffered transformation to microcrystalline silica. At least four episodes of deposition, fragmentation and recementation have been involved, along with at least one recrystallisation event as well as late stage deposition of quartz in voids.

Ten different types of sinter fabric have been identified at Plumduff: finely laminated, columnar, palisade, filamentous networks including fenestral, tufted, clotted, domed stromatolites, peloids/pisoids, and plant rich, with silicified filamentous networks being the dominant type. These fabrics are typical of those about modern opaline hot spring deposits of the Taupo Volcanic Zone (TVZ) and span the high to medium temperature range of Cady and Farmer (1996). The highest temperatures of >73°C are indicated by finely laminated sinter, columnar structures, peloids and associated pisoids. Temperatures of <59°C are implied by the presence of palisade fabric and plant material.

3. EXPERIMENTAL

Moganite has not been identified unequivocally in thin section. Heaney and Post (1992) speculate that the length-slow lutecite of Michel-Lévy and Munier-Chalmas (1892) is moganite as are other length-slow fibrous silicas, some of which have been identified as length-fast quartz. The optical properties of moganite are not known so conventional petrography can not be used to recognise it.

Certainly, the x-ray powder diffraction (XRPD) patterns of a-quartz and moganite are sufficiently distinct to allow the two phases to be distinguished by careful, albeit conventional powder diffraction methods. However, the patterns are also sufficiently similar that minor amounts of moganite (<20%) can be readily masked by quartz (Smith, 1998, p.9). Very slow scan speeds with step sizes of <0.05° 2θ, on a conventional powder diffraction scanning goniometer fitted with a graphite monochromator, are required to adequately determine moganite at the 20% level in the presence of quartz (Rodgers and Cressey, 2001).

This proportion is quite common in sinters and, consequently, conventional diffraction techniques e.g. 1°/min scans can result in minor amounts of moganite being overlooked. This, together with a lack of awareness of the possible presence of moganite, is likely to have been the principal cause of moganite failing to be identified in earlier sinter studies (*cf.* Smith, 1997, p.205). In order to confirm the presence of moganite in their microcrystalline quartz samples, Heaney and Post (1992) undertook Rietveld refinement of their diffraction data, after having counted for 1.4-7.2 hours per sample. Such a requirement is not conducive to routine analyses of sinter samples.

Kingma and Hemley (1994), Götze *et al.*, (1998), and Rodgers and Cressey (2001) have demonstrated that satisfactory analysis of microcrystalline silicas is readily achieved using laser Raman microspectroscopy. Quartz, α-cristobalite, a-tridymite and moganite all possess distinctive, intense, Raman-active. scattering bands in the region 350-550 cm^{-1} that allow each phase to be distinguished from the others.

Broken portions of, and slabs sawn fiom the main textural types at Plumduff were examined by a Renishaw Raman 1000 system laser Raman microprobe with deep depletion CCD and dual 1200 and 2400 line/mm gratings. Experimental procedures differed from those used by Kingma and Hemley (1994), Herdianita et *al.* (2000) and Rodgers and Cressey (2001) with the Raman spectra of each sample collected from c. 100-600 cm^{-1}, with a slit of 100 µm and an integration time of 10 s under high gain. Spectral bandpass was –2.0 cm^{-1}. The intensity of the moganite scattering bands made it desirable to collect and coadd five spectral runs from each sampled area. Both a SpectraPhysics Model 163 air cooled Argon 488 nm 25mW (blue) laser and Renishaw model 780 solid state 785 nm 25mW (red) laser were employed using laser power reduction filters of 25% and 100%. Raman range was 100-4000 cm^{-1} using 488nm laser and 200-2500 cm^{-1} using 785nm laser; resolution is –2 cm^{-1}. In the event, while the red laser proved less sensitive to fluorescence, the cut off at c. 200 cm^{-1} made it desirable, where possible to employ the blue laser with a 25% reduction filter.

Microsampling was undertaken with an uncoated x20 or x50 objective of the customized Leica DM LM microscope, fitted with an XYZ motorised stage, the conventional arrangement of stage and lens giving a 180° scattering geometry. One of the advantages of the Renishaw 1000 system is to allow CCD imaging of the precise area of each specimen, and hence the specific textural element to be determined (Fig. 3). Image resolution is –1 µm using the x20 objective.

Except as indicated below, no preparation of the specimens was undertaken beyond breaking or sawing a fresh surface and ensuring it was clean and dry. Prism faces of quartz were microsampled where these were developed, as among crystals occurring in cavities, but elsewhere both the size of the microcrystals and the massive nature of the matrix aggregates precluded the possibility of rigorous orientation procedures such as are used in band assignment studies. A consequence of this approach is reflected in variations in relative intensities and/or absence of some Raman bands in some spectra depending on differing orientations of the individual microsampled quartz crystal with respect to the polarisation direction of the laser.

As with the powder diffraction signatures of quartz and moganite, the many shared structural elements of the two minerals result in their possessing similar vibrational spectra (Kingma and Hemley, 1994; Götze et *al.,* 1998). The most intense band in quartz lies at 464 cm^{-1} and that of moganite is at 501 cm^{-1} (Fig. 4). However, moganite also possesses a moderately intense scattering band at 463 cm^{-1} and the presence (or absence) of other quartz modes, such as the sharp A, vibration at 355 cm^{-1}, is used to monitor the presence (or absence) of quartz in a sample (Kingma and Hemley, 1994; Rodgers and Cressey, 2001).

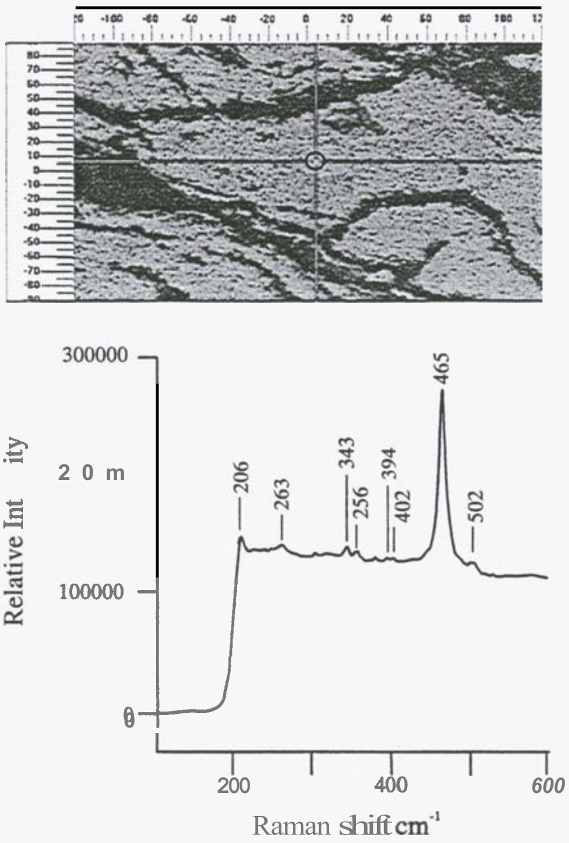

Figure 3. Example of CCD image and Raman spectra of the sampled area of specimen PD097 permitted by the Renishaw 1000 system (red laser) with the cross hairs of laser beam shown. Circle represents approximate size of sampled area. Image is of a blue breccia clast composed of patches of blue (dark) and beige. Base of image is 240 µm across, scale divisions are 5 µm.

4. RESULTS

Representative spectra of the Plumduff sinters are shown in Fig. 4. The full data set shows moganite is present at Plumduff but is disseminated unevenly through all portions of the outcrop that otherwise consists predominantly of microcrystalline quartz. In general, the ratio of the moganite 501 cm^{-1} scattering band to the composite band at –465 cm^{-1} was less than that illustrated by Rodgers and Cressey (2001) from Quaternary quartz-rich sinters of Umukuri and Otamakokore suggesting the proportion of moganite is lower at Plumduff.

No moganite was found in samples of finely laminated, peloidal, tufted network, palisade, or plant-rich primary sinter textures. It was, however, detected in portions of clasts of both fenestral network and columnar types but was not uniformly distributed in these. For example, in fenestral network PD077 it was discerned in a solid band of silica but not in the matrix surrounding this band. Similarly, it was found in one vitreous white clot in columnar sinter PD038 but absent in a seemingly identical clot alongside.

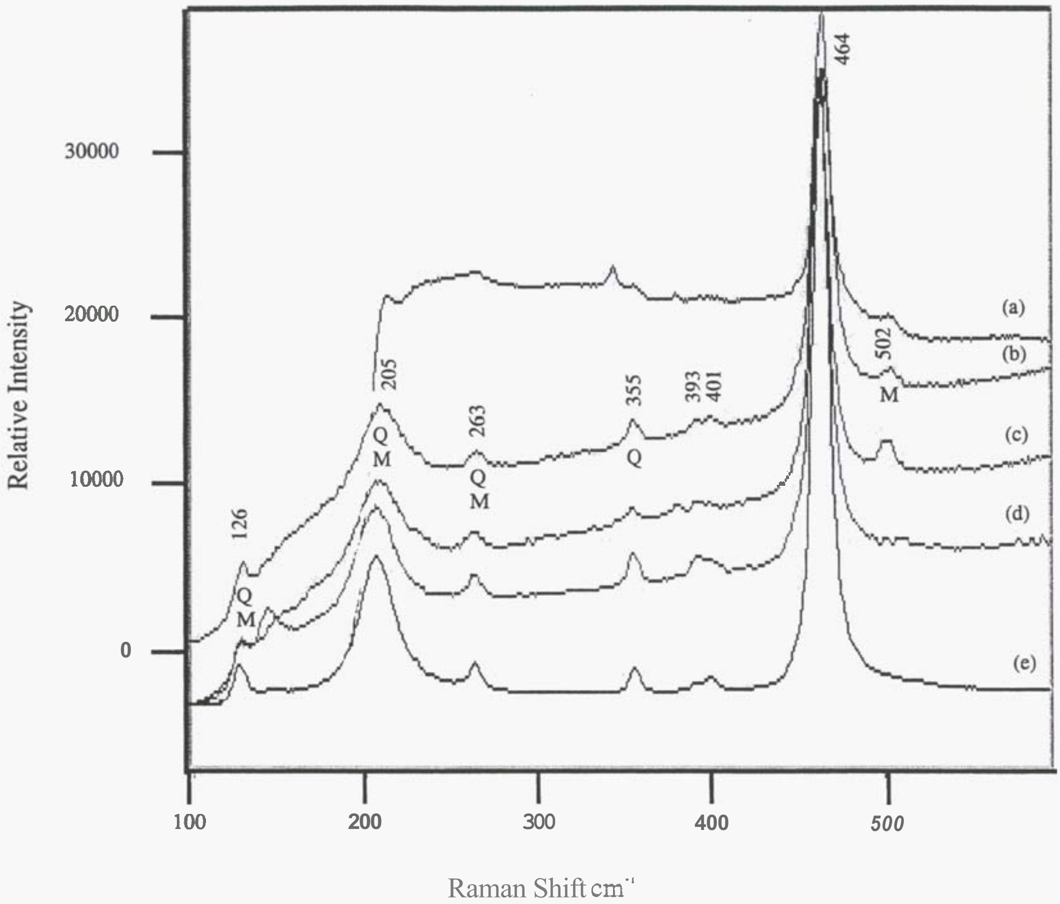

Figure 4. Laser Raman spectra of Plumduff silica sinter textural types. (a) microcrystal <10 µm in cavity of blue clast breccia (PD097) with red laser, (b) solid band in irregular fenestral fabric (PD077), (c) microcrystalline blue portion of blue clast breccia (PD091), (d) microcrystalline beige matrix of blue breccia (PD091), (e) microcrystal (>20 µm) lining cavity of white clast breccia (PD094), (b)-(e) with blue laser.

Moganite is present among some individual quartz crystals but not others. In general, as observed by Rodgers and Cressey (2001) in Umukuri and Otamakokore Quaternary moganite tends to be present among the smaller crystals and particularly those formed by recrystallisation of the opaline sinter. It is believed to be absent from late stage quartz that grew perpendicular to cavity walls. For example, it was detected in a 20 µm crystal in PD091 and a <10 µm crystal in PD097, but was absent in a 180 x 120 µm crystal in PD031 and a >10 µm crystal in PD099 e.g. Fig. 4. Varicoloured, translucent, vitreous, chalcedonic clasts in the breccia proved to be both moganite-bearing and moganite-free as, indeed, did the matrix of the breccia itself.

5. DISCUSSION

A principal advantage of the Raman microprobe as a determinative tool lies in its ability to microsample individual textural elements. Coupled with the high rate of spectral acquisition available from the latest generation of instruments, and the limited sample preparation, the technique allows the twin paths of mineralogical and textural maturation of sinters to be mapped together, at least in their later stages, both in outcrop and hand specimen. This contrasts with techniques such as powder diffraction that allow for identification of only bulk, albeit small (–400 mg), samples that are not always clearly related to specific microtextural components. However, Rodgers and Cressey (2001) have shown that where contaminants are present, such as organic debris and iron oxides, Raman does not allow the full range of silica phases present in sinter samples to be identified unambiguously nor for their degree of lattice order and disorder to be evaluated.

The sinter analysed from Plumduff is a terrestrial rock. It has not experienced any significant burial. Moganite developed as a metastable intermediate phase during the maturation processes that affected the original opaline silica and caused it to crystallise to achieve thermodynamic equilibrium with ambient conditions. It formed when opal-CT and opal-C transformed to quartz (Campbell et *al.,* 2001). Heaney and Post (1992) noted that little or no moganite was present in six of their samples that had been exposed either to weathering or to hydrothermal fluids. This perhaps accounts for the uneven distribution of moganite among the different textural types analysed from Plumduff.

Much of this deposit has been subject to protracted hydrothermal activity and weathering following development of the initial sinter apron. If subsequent reheating of earlier generations of sinter was not particularly uniform, then the moganite distribution would be expected to reflect this heterogeneity of process. It could contribute to the presence of moganite in some recrystallised matrices and in some cavity-lining quartz crystals but the mineral's absence in adjacent portions of the same samples.

Importantly, Heaney and Post **(1992)** argued that moganite readily recrystallises to quartz in the presence of water, while Gislason *et al.* **(1997)** have demonstrated that moganite is thermodynamically less stable than quartz. Consequently, the moganite → quartz transformation does not require permeation of hydrothermal fluids through the sinter outcrop, but the water expelled from opaline silica is sufficient to facilitate the recrystallisation process (*cf.* Herdianita *et al.*, 2000).

Although moganite at Plumduff has formed from opal, its presence in a geothermal system sounds a note of caution for geothermal workers, notably geochemists. The conditions under which moganite forms are not known but irrespective of any theoretical considerations, like many metastable phases it may well be capable of crystallising outside its ideal stability field. Gislason *et al.* **(1997)** have shown moganite to be more soluble than quartz so that, should it occur in a geothermal reservoir, this could affect the status of the silica geothermometer.

5. ACKNOWLEDGEMENTS

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