Raman spectroscopy of volcanic lavas and inclusions of relevance to astrobiological exploration

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Volcanic eruptions and lava flows comprise one of the most highly stressed terrestrial environments for the survival of biological organisms; the destruction of botanical and biological colonies by molten lava, pyroclastic flows, lahars, poisonous gas emissions and the deposition of highly toxic materials from fumaroles is the normal expectation from such events. However, the role of lichens and cyanobacteria in the earlier colonization of volcanic lava outcrops has now been recognized. In this paper, we build upon earlier Raman spectroscopic studies on extremophilic colonies in old lava flows to assess the potential of finding evidence of biological colonization in more recent lava deposits that would inform, first, the new colonization of these rocks and also provide evidence for the relict presence of biological colonies that existed before the volcanism occurred and were engulfed by the lava. In this research, samples were collected from a recent expedition to the active volcano at Kilauea, Hawaii, which comprises very recent lava flows, active fumaroles and volcanic rocks that had broken through to the ocean and had engulfed a coral reef. The Raman spectra indicated that biological and geobiological signatures could be identified in the presence of geological matrices, which is encouraging for the planned exploration of Mars, where it is believed that there is evidence of an active volcanism that perhaps could have preserved traces of biological activity that once existed on the planet’s surface, especially in sites near the old Martian oceans.

Keywords: Raman spectroscopy; volcanic outcrops; lava flows; fumaroles; organic signatures

1. Introduction

The formation of molten rocks in the terrestrial geological record can be attributed to volcanic eruptions, meteorite bombardment and air-to-ground lightning strikes; whereas the former events produce much of the new basalts and glass currently, the latter phenomena, while still ongoing, have also been very important in the Earth’s history (Chen & El Goresy 2000; Crespo et al. 2009). Recent analytical studies of the impact breccia from meteorite craters

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(Dressler & Sharpton 1997; Edwards et al. 2005; Pullan et al. 2008) have demonstrated that the changes induced in the terrestrial geology resulting from these major catastrophic events have provided a source for the favourable recolonization by cyanobacterial organisms that have been able to adapt to the new conditions of the host geological matrix.

Similarly, the discovery of extremophilic cyanobacterial colonies living inside bubbles near the surface of old lava flows in the Arctic (Jorge Villar et al. 2006) has widened the prospect of finding new sites for these extreme scenarios on Earth. Glassy areas have been identified within meteorites, including the Shergotty–Nakhla–Chassigny group of Martian meteorites; these often contain morphological features that are of interest to astrobiologists who are attempting to understand the geological activity of early Mars (Poitrasson et al. 2004; Bonin & Bebien 2005).

Some recent work on fulgurites, a class of glassy geological materials that have been formed as a result of air-to-ground lightning strikes (which comprise some 30% of electric storm activity), have revealed that, despite the large thermal energy transfer in these processes which involves typically about 1 GJ, evidence has been found for gas bubbles inside the glass matrix that contain carbon dioxide and monoxide, and inclusions in these glass bubbles that contain polyaromatic hydrocarbons (Daly et al. 1993; Heymann et al. 2003) and other molecules of relevance to life-detection studies. Another example of glassy deposits that have arisen from extraterrestrial impact events is Libyan desert glass (Navarro-Gonzalez et al. 2007), which contains kilogram pieces of glassy material with inclusions. Although not containing residual organisms per se, such evidence clearly demonstrates that carbonaceous materials were undoubtedly present at or near the ground zone of the meteorite impact or lightning strike and that the biological signatures have been preserved in the geological record—this information informs evolutionary biologists about operational scenarios in an ever-widening area of extreme environments. It is also of relevance to astrobiological exploration since events on early planetary surfaces would have mirrored those that we now have recognized on Earth (Lammer et al. 2009).

In the current study, we have extended the investigation for the search for life signatures entrapped in glassy materials to basaltic rocks on Earth; recent studies have demonstrated that epilithic and chasmolithic lichens are able to colonize new volcanic rocks very rapidly (Coleman et al. 2005; Jorge Villar et al. 2006) and that endolithic species are able to accomplish subsurface colonies in a similar way. However, the purpose of the present work is to examine a scenario that would have been quite prevalent in early evolutionary history that is still ongoing, namely, that of a volcanic eruption in which the lava flows have entered the ocean; there could be evidence in the specimens taken from such sites of the entrapment of material, which is indicative of the organisms that may have populated and colonized the oceans. Such an opportunity has been afforded by a recent expedition to the active Kilauea volcano on Kona, Hawaii, where lava flows meet the Pacific Ocean and create new land forms. In such an area, there is evidence from previous eruptions that the older lava flows, often several feet in thickness, have entrapped material inside their structure, which would provide an interesting example to evaluate our hypothesis and extend our search patterns for terrestrial analogues relevant to the detection of life signatures in planetary exploration. In this experiment, Raman spectroscopy will be used...
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to look for the geomolecular and biomolecular spectral signatures that would indicate the presence of relict or extant life in volcanic rocks. With the adoption of a miniaturized Raman spectrometer for the forthcoming ExoMars mission as part of the Pasteur life-detection instrumentation suite (Escudero-Sanz et al. 2008; Jehlička & Edwards 2008; Jehlička et al. 2008). The results from this study will extend the existing database of extremophilic sites that should be investigated for possible life signatures in the geological record both for terrestrial Mars analogues and, especially, for the planned exploration of the surface and subsurface of Mars, and will inform the possible selection of suitable landing sites for possible astrobiological studies.

2. Experimental

Specimens were collected on an expedition to the Kilauea volcano, led by the University of Manoa, Hawaii, field geologists; three types of specimen were acquired from the volcanic rocks and outcrops of Kilauea—two were taken from the new lava flows of the current eruption, only a few days after the hot lava had cooled sufficiently to enable safe sampling to be undertaken. One sample was collected from the edge of a fumarole in the new lava, comprising mineralized deposits and the basaltic rock substrate. Other samples of mineral inclusions in the basalt from the same lava flow were also taken. Finally, samples were collected from a beach area where older lava flows had broken through a coral reef at the ocean fringe and had now totally covered the reef itself. These last samples have, perhaps, the most significance for early evolutionary studies since this scenario would have applied to a turbulent volcanically active planet and the emergence of life in the early oceans—the basic analytical scenario here would be the detection of the characteristic biological and biogeological spectral signatures of the coral reef organisms, which could have been preserved in the basaltic matrix of the rock that has destroyed the reef.

Raman spectra were obtained using a Renishaw InVia confocal Raman spectrometer coupled to a Leica DM LM microscope and operating at a laser wavelength of 785 nm; lens objectives of 20× and 50× magnification were used to provide a sample footprint of between 5 and 2 μm diameter at the specimen, and 50–70 accumulations at 10s exposure were made to achieve improved signal-to-noise ratios in the spectra. Wavenumbers recorded over the range 1800–100 cm\(^{-1}\) are accurate to ±1 cm\(^{-1}\) under the operating spectral resolution of 2 cm\(^{-1}\). Comparison of the spectral wavenumbers was effected with mineralogical, biogeological and biological databases (Jorge Villar & Edwards 2005a,b; Jorge Villar et al. 2005, 2006; Moody et al. 2005; Jehlička & Edwards 2008; Jehlička et al. 2008) in the literature to identify the presence and indicators of extinct or extant life in the geological matrices.

3. Results and discussion

(a) Volcanic rock samples

The specimens of old lava that had broken through a coral reef on meeting the ocean contained several aggregates whose Raman spectra gave signatures attributable to both calcite and aragonite, two polymorphs of calcium carbonate,
Figure 1. Raman spectrum of calcite and aragonite, both polymorphs of calcium carbonate, are easily distinguished by Raman spectroscopy owing to the band at 283 cm\(^{-1}\) characteristic for calcite, whereas aragonite shows a band at 203 cm\(^{-1}\).

Figure 2. Raman spectrum showing the presence of calcite and gypsum.

with bands at 1086, 712 and 283 cm\(^{-1}\) and 1086, 704 and 203 cm\(^{-1}\), respectively, as shown in figure 1. These minerals are compatible with those expected from incorporation of materials from the coral reef into the lava matrix. Further signatures in figure 2 at 1007, 671, 619, 493 and 413 cm\(^{-1}\) are assignable to gypsum, in admixture with calcite. The presence of gypsum could be explained owing to oceanic salts in the atmosphere.

Green coloured areas in the carbonate aggregates from the reef are visible with optical microscopy, and the Raman spectra from these regions show signatures at 1324, 1230 and 1200 cm\(^{-1}\) assignable to chlorophyll features in
the carbonate inclusions (figure 3) and at 1522 and 1159 cm$^{-1}$ characteristic of a carotenoid, probably zeaxanthin. Raman spectroscopy has confirmed that the incorporation of carbonates into the lava from volcanic activity at the shore of an ocean and resulting in the destruction of a reef has left signatures of biochemicals that indicate the presence of relict life; the astrobiological significance of this result is that evidence of extraterrestrial volcanic activity near an ancient ocean might be a suitable place to search for evidence of relict biomolecules in the planetary geological record that have been preserved in the volcanic matrix.

Minerals in the volcanic rock samples, exhibiting typical Raman spectra of crystalline materials, included olivine with Raman spectral signatures at 951, 915, 850, 819, 582, 535, 423, 295 and 211 cm$^{-1}$, a calcium plagioclase with bands at 555, 505, 482, 403 and 281 cm$^{-1}$ and a clinopyroxene (augite) with bands at 1008, 663, 389 and 323 cm$^{-1}$ (figure 4).

Magnetite features are observed at 662, 490 and 310 cm$^{-1}$; the broad bands at 962, 800 and 500 cm$^{-1}$ belong to the volcanic glass matrix, being $Q^0$–$Q^4$ components of chain, tetrahedral and tectosilicate structures (figure 4). It is to be noted that the observation of these host matrix features does not compromise the spectral recognition of the relict biomolecules in the biogeological aggregates.

(b) Fumarole sample

Raman bands from the mineral matrix of the fumarole specimen indicate calcite, with band signatures at 1086, 712 and 283 cm$^{-1}$, sulphur, with bands at 472, 438, 383, 246, 217, 197, 185 and 152 cm$^{-1}$, and haematite, with bands at 613, 500, 410, 293 and 226 cm$^{-1}$. Goethite, an iron (III) oxyhydroxide, is also noted with bands at 243, 314, 385 and 576 cm$^{-1}$. Gypsum is seen with bands at 1007 and 620 cm$^{-1}$ and baryte with features at 980, 677 and 405 cm$^{-1}$. A selection of spectra representing these features is shown in figure 5.
In several regions of the fumarole sample, bands at 1530, 1450, 1342, 1143, 1098, 834, 748, 680, 595, 438 and 257 cm$^{-1}$ have been detected. Although the signatures at 1530 and 1143 cm$^{-1}$ could be assigned to a carotenoid with a short C=C conjugated chain and the features at 1450, 1342, 834, 748, 680, 595, 438 and 257 cm$^{-1}$ could be assignable to chlorophyll, this spectrum is comparable with a previous one collected on a stromatolite from the North Pole Dome, Pilbara, Australia, which gave the spectrum shown in figure 6. It is, therefore, possible that, since the wavenumbers and relative intensities of the strongest bands in both spectra are very similar, this Raman spectrum could either reflect the signatures of one single compound or a combination of carotenoid and chlorophyll in the same proportions at the two sites.
**Secondary minerals**

These are observed as crumbly coloured deposits at or near the surface of the new lava specimens and are generally yellow, orange and white. Their presence is consistent with the rapid cooling of the hot lava (ca 1300°C) and gases in contact with the atmosphere. The signatures at 143, 288, 400, 509 and 632 cm$^{-1}$ provide an identification of anatase (figure 7), a polymorph of titanium (IV) oxide, whereas haematite can be assigned to the bands observed at 223, 290, 410, 500 and 610 cm$^{-1}$. The presence of augite in another region is recognized from its characteristic bands at 662 and 332 cm$^{-1}$, and this seems to provide the major
substratal mineral component with gypsum and goethite. Bands at 1004, 623 and 327 cm$^{-1}$ are assignable to a pyroxene with a composition approximating to enstatite, a magnesium orthopyroxene. Finally, in some spectra, bands at 950 and 160 cm$^{-1}$ are indicators of mullite, which contains aluminium oxide and silica in the ratio of two to three and are formed by fusion at high temperatures.

4. Conclusions

The recognition of spectral signatures of minerals, biogeological materials and key protective biochemicals of extant or extinct extremophilic life indicative of basaltic rock colonization is an important aspect of the search for terrestrial life in stressed environments and for the recognition of relic life extraterrestrially. The key function of remote planetary life-detection instrumentation is the ability to discriminate between the host geological matrix, which may harbour relic life signatures, and the niche areas, which contain the key spectral biogeological markers and biomarkers. This investigation has addressed the detection of key life markers in the Raman spectrum associated with a complex geological matrix, comprising new and old volcanic rocks containing a variety of minerals and biological material of relevance to the survival of extremophilic colonies on Earth and to the astrobiological quest for life on other planets and their satellites, some of which exhibit volcanic activity. The results of this present study show that it would be possible for Raman spectroscopic instrumentation on a remote planetary rover with access to volcanic lava sites to acquire molecular information about life residues if they were occupying niche areas.

References


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