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**Poster Presentations**

## **GESPEA: WORKING GROUP ON VOLCANIC CAVES OF AZORES**

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In 1998, the Regional Government of the Azores established a working group (called GESPEA) to be in charge of studying volcanic caves of the archipelago. This was done because of the rich geological and biological resources and values of the volcanic caves of this region, and their uniqueness. This group is developing a data base and a classification system intended to gather all available information on these caves. It also intends to streamline management of Azorean caves and pits for tourism as well as scientific study.

The various volcanic caves the Azores jointly form a distinct entity. As a whole they provide a diversified geological, biological and aesthetic patrimony that must be publicized and protected in ways consistent with each of these factors. In addition to developing the data base and classification system, the GESPEA is working on policies for overall protection, and on specific legislation where special needs exist.

# **ANALYSIS OF IRON SPECIATION MICROSTRUCTURES IN LAVA SAMPLES FROM HAWAII BY POSITION SENSITIVE X-RAY ABSORPTION SPECTROSCOPY**

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As a result of rapid cooling and solidification of liquid lava after eruption, many volcanic rocks are fine-grained and homogeneous. However, many of them contain fragmented minerals which formed before the eruption and are evident as comparatively large particles within a fine matrix. Also the rock may contain numerous vesicles formed by gases expanding within the melt.

Iron is a common element in volcanic rocks. It may be present in different states of oxidation, depending on the time and speed of oxidation processes during and after cooling. Hematite is specifically noticeable in the form of a thin, shiny bluish-grey layer on surfaces of natural lava tunnels, which have been active for a long time. This shiny layer is commonly called “glaze”.

X-ray absorption fine structure spectrometry (XAFS) has become a powerful, widely-used method of speciation analysis. It allows direct, non-destructive determination of chemical bonding forms of selected elements, provided that they are present in sufficiently high concentration and suitable reference data are available. Analysis of the near-edge structure (XANES) of the absorption spectrum provides information about the valence state and coordination geometry. The valence determines the exact location of the absorption edge on the energy axis, called the edge energy (E<sub>0</sub>). The coordination influences the shape of the absorption edge.

The standard application of XAFS is bulk analysis of homogenized samples. If a sample contains several different species of the selected element, it may be possible to identify all components from the resulting absorption spectrum although without gaining any information on their spatial distribution. Spatial XAFS analyses of metal speciation in solid samples at the micrometer scale have been largely limited to spot analyses, using a microfocussed beam directed at a few pre-elected spots on the sample. The investigation of entire sample areas by this method is not practicable because a spot-by-spot collection of absorption spectra is extremely time-consuming. Only a few attempts have been made to perform XAFS imaging experiments by parallel detection (Kersten and Wroblewski, 1999, Mizusawa and Sakurai, 2004).

Lava glaze samples from Three Fingers Mauka Cave, Mackenzie State Park, Hawaii were analyzed. The rocks which form these lava tubes are known to contain different ratios of FeO / Fe<sub>2</sub>O<sub>3</sub>, depending on their location (Kempe, 2003). In thin sections, some particles up to 1 mm in diameter were visible within the fine matrix. Details of the analyses will be presented.

The micro XAFS experiments were conducted at HASYLAB Beamline G3. A spatially resolved image of the sample area penetrated by the monochromatic beam (approx. 10 mm wide and 5 mm high) was recorded directly on the X-ray sensitive CCD chip of the camera

(Hamamatsu C-4880, chip dimension 13 x 13 mm, pixel resolution 13  $\mu\text{m}$ , cooled down to -65 °C). The shutter was synchronized with the readout of the CCD and the ionization chambers (I0 in front of the sample, I1 behind it) so the exposure time could be optimized by normalizing it to the I1 reading. The energy range was from 7000 to 7400 eV with incremental steps of 1 eV, so each scan contained a sequence of 401 images along with the readings from the ionization chambers. The monochromator was stabilized electronically.

The image sequences were processed using specific IDL<sup>®</sup> routines and the remote sensing software ENVI<sup>®</sup>. After creating a stack of absorption coefficient images, the Minimum Noise Fraction (MNF) transformation was calculated for an energy range of 100 eV around the absorption edge. Thus the areas on the sample with the most evident differences in the image range around the absorption edge were found. Then classes of different XAFS spectra were identified by selecting specific features from a scatter plot created from two eigenimages. The according spectra were obtained by summarizing the absorption spectra of all pixels which were assigned to the same class. E0 was defined as “halfway up the absorption edge”.

The varying shape and height of the absorption edges reflect the inhomogeneous distribution of iron in the sample with a clear resemblance of the map to the visible structures. The E0 values obtained from the average of three scans are 7117.73 eV for class 1 and 7118.15 eV for class 2. These must be interpreted with some caution. A precise calibration of the monochromator was not possible, and since energy steps of 1 eV were used, the difference between the E0 of classes 1 and 2, which is less than 1 eV, may not be significant. However, each scan showed the same E0 with only negligible variation, and the same difference between classes 1 and 2: thus it is believed that the average can be trusted quite well. The edge energy of trivalent iron species is known to be approximately 2 eV above E0 of divalent species.

The results of the present study suggest that the samples contain an inhomogeneous mix of different iron species with slightly different valence states. Pyroxenes and/or olivines are the most likely components, and some hematite particles also may be present, although they could not be seen in the sample. Due to the lack of calibration and the small difference between the absorption edges, a more definite identification of species is not possible at this point. For this purpose, a better signal to noise ratio is needed so that the full EXAFS spectra can be analyzed, not just the XANES region.

With this setup, position sensitive x-ray absorption spectroscopy is possible at about 10 $\mu\text{m}$  spatial resolution. By detailed examination of the XANES spectra, information about differences in Fe concentration and oxidation state between areas was obtained. Future efforts will focus on samples with clearly visible hematite glazing while avoiding the presence of holes in the samples. With an improved setup, we will seek to make the full EXAFS range usable for analysis.

## REFERENCES

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## **NEW DATA ON THE PROBABLE MALHA GRANDE LAVA FLOW COMPLEX INCLUDING MALHA, BURACOS AND BALCÕES CAVES, TERCEIRA, AZORES**

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Located in the Malha Grande lava field, Gruta dos Balcões is the longest cave on Terceira island. The current length of its mapped passages is 4.421 km.

Recent field surveys have shown that two other nearby lava tube caves are probably isolated segments of the principal tube of Gruta dos Balcões: Gruta dos Buracos and Gruta da Malha Grande. This would make the total length of Gruta dos Balcões system about 5.021 km. Further, other lava tube caves north of Gruta dos Balcões (e.g. Terra Mole, Cascata, Principiantes, Opala Branca and Chocolate) are in the same flow field and probably also belong to the same complex. If this is true, the total length of the Gruta dos Balcões Complex is around 6 km. This would make Gruta dos Balcões the longest lava tube system in the Azores, surpassing the Gruta das Torres lava tube system on Pico island.

The Malha Grande lava tubes are believed to have been formed by the eruption of Pico do Fogo volcano 240 years ago. Its caves are occasionally visited by local people and need protection from vandalism above and below ground. Moreover, the presence of cattle is creating some disturbance in and around entrances to some of the caves. We recommend that this notable area of large and beautiful caves be specifically managed to protect and preserve its extraordinary underground resources.