Spatial Correlation of Trace Elements with Zoning Patterns in Agates

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INTRODUCTION

Autonomous pattern formation is now recognized as a universal phenomenon common to many physical, chemical, and biological systems. Commonly patterns are observed over several different length scales. The key to understanding how systems self-organize to create patterns lies in detailed analysis of the mechanisms that operate over the different length scales. Banded agate has often been cited as an example of such pattern formation. Variation in size, orientation, defect density, and composition of chalcedony fibers have been associated with banding patterns, and many of these have been documented by studies.

Because chalcedony, a fibrous variety of quartz, typically contains only extremely low concentrations of impurity elements, few tests have been made to determine whether chemical variations exist within the fine-scale banding ranging typically from <10 to >100 μm and whether such variations may record periodic fluctuations in fluid chemistry.

EXPERIMENT AND PRELIMINARY RESULTS

As a preliminary study, we examined several thin slices (< 20 μm thick) of banded agate at beam line 10.3.2. The distribution of Al, Fe, Ca, Zn, and Si was mapped over several optically visible bands corresponding to variations in size and orientation of chalcedony fibers. This was done using an incident monochromatic beam of 10.5 keV and rastering the sample over the area of interest whilst collecting the fluorescent photons at specific energies corresponding to the elements of interest. Results are shown in the figures below. These clearly demonstrate that thin bands with larger fiber size are depleted in Fe and enriched in Al relative to the zones composed of smaller fibers. In addition there is an indication that Ca varies spatially with a zoning pattern that is commensurate with the others, but suggesting that the maxima in concentration do not coincide exactly with minima for Fe and Al. This is an intriguing new finding, and raises the question of whether significant changes in fluid composition accompany the pattern formation.

For iron, which was the most easily detectable element in the agate, it was also possible to measure the microXAFS to determine its oxidation state. This is shown in figure2 and, by comparison to standard iron compounds it appears that the oxidation state is 3+ both inside and outside of the bands.

These preliminary findings would not have been possible with electron-probe techniques, in which minimum detection limits are too high to allow quantitative mapping. Secondary ion mass spectroscopy has been used to document variations in Al, but heavier elements pose difficulties. Thus spectro-microscopy at a synchrotron source offers the best means of characterizing micro-scale chemical variations, and further provides the opportunity for determining the oxidation state of certain trace elements and possibly even information on local structure.

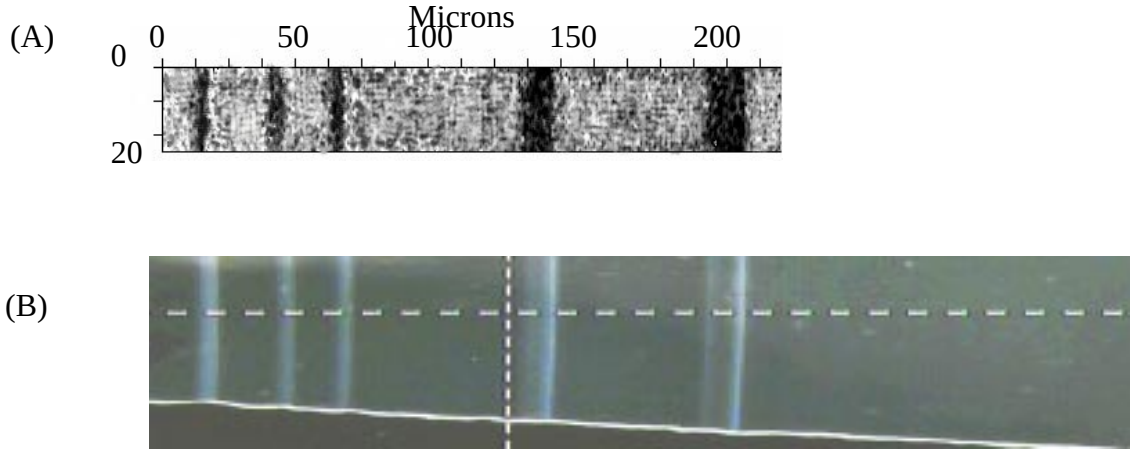

Figure 1: (A) Shows fluorescence map of Fe Kα radiation over the agate bands shown at corresponding distances in the optical micrograph shown in (B). The Fe concentration in the sample is a few tens of ppm: Within the bands about 20 ppm and outside about 35 ppm.

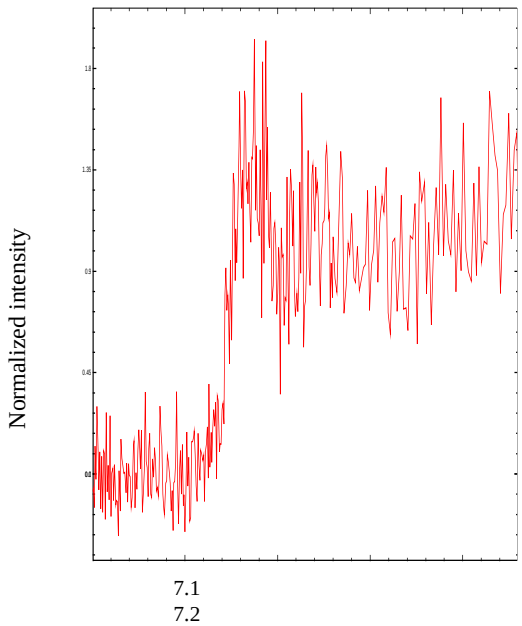

Figure 2: This near edge region of the Fe between the bands indicates that it is in the Fe 3+ oxidation state. The concentration here is about 35 ppm. Better statistics are required for a complete speciation determination.

The results of this work are of interest not only for understanding agate, but more generally for unraveling the mechanisms by which patterns form in mineral systems. Such zoning patterns exist in a wide variety of minerals, including those produced biogenically.

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