Characterization of carbon compounds on a pyroxene surface from a gabbro xenolith in basalt by time-of-flight secondary ion mass spectrometry

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ABSTRACT

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) yields mass spectra of the upper several monolayers of an analytical surface. The applicability of TOF-SIMS to the characterization of C compounds on crack surfaces in rocks is demonstrated. A pyroxene grain recovered from the interior of a gabbro xenolith from the 1801 flow of Hualalai volcano, Hawaii, was chosen for this initial study because well-developed carbonaceous films are known to exist on many of the crack surfaces in these rocks. In addition to the anticipated major elements (Si, Al, Fe, Mg, Ca), several minor and trace elements (B, Li, Na, Ti, Mn, Co, Ni, Cu) were identified in the positive ion mass spectra. The unsputtered surface is covered with a hydrocarbon-rich layer, as indicated by the presence of numerous light CxH y fragments as well as several masses of several hundred atomic mass units (amu). This layer is much better developed than the ubiquitous atmosphere-derived hydrocarbon layer observed on nominally clean, unsputtered surfaces and therefore must be indigenous. High concentrations of Ni and Cu are associated with the C-rich layer and may exist as organo-metallic compounds. Several C-N fragments, possibly indicative of biogenic compounds, were also identified in negative ion spectra. Imaging reveals the presence of localized islands enriched in oxides of Si, Al, Na, and Ca beneath the carbonaceous layer. This study demonstrates that TOF-SIMS can be used to provide unique and geochemically useful information on crack surfaces in rocks.

INTRODUCTION

Analysis of crystalline rocks using surface-sensitive spectroscopies reveals that C is ubiquitous as a thin film on microcrack surfaces (e.g., Tingle et al. 1991). The origin of the carbonaceous films is not obvious; one hypothesis, proposed for peridotite xenoliths in basalts, is that they form rapidly by reaction of the fresh mineral surface with whatever fluid or gas penetrates the crack initially (Mathez 1987). Such carbonaceous films could well be relegated to the status of mere curiosities except that they may influence electrical conductivity of rocks (Shankland et al. 1997), participate in trace element partitioning and redox reactions, and represent evidence of, or provide sustenance for, a subsurface biological community.

A major obstacle to deducing how carbonaceous films form is the few means available for chemical and spatial characterization. Electron microprobe techniques have proven useful for determining the distribution of C-bearing microcracks but provide little information about composition; analysis by Auger spectroscopy (AES) is hampered by problems associated with working with insulators and does not provide chemical information; and X-ray photoelectron spectroscopy (XPS) has been used to detect hydrocarbons on crack surfaces and infer information on the chemical state of C (Mathez 1987), but identification of specific molecular species is beyond the capability of this technique.

The purpose of this communication is to report on the applicability of time-of-flight secondary ion mass spectrometry (TOF-SIMS) to the characterization of C in rocks. In our development of the methodology, it has become clear that TOF-SIMS holds great promise for determining the composition and distribution of C compounds, including organics, and more generally for studies that require detection and identification of contaminants in microcracks in rocks.

ANALYSIS

Description of technique

TOF-SIMS is a surface-sensitive technique capable of providing high-resolution mass spectra (0.0001 amu) over a mass range of 1 to 10,000 amu, and maps of the distribution of individual masses with submicron spatial resolution. Such analysis obviously entails minimal damage of the analytical surface by the incident ion beam. This is in contrast to the more routinely used dynamic SIMS (ion probe), in which elemental sensitivity is maximized by dissociating ions from within a volume of the sample by sputtering. Detailed descriptions of TOF-SIMS may