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Complex Redox and Magmatic Histories of Lava from East Africa and Martian Basalt Revealed by Synchrotron MicroXANES Spectroscopy Quantification of Micrometer-scale, Ferric/ferrous Zoning

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Beamline(s) X26A

Clinopyroxene crystals (cpx) in lavas from the East African volcano Satiman (adjacent to hominid locality, Olduvai Gorge, Tanzania) have dramatic oscillatory zoning. Backscattered electron imaging reveals at least 30 bands 1-150 um wide, indicating compositional oscillations in the mantles of these grains (Figure 1). The East African volcanoes provide some of the most complex igneous rocks seen at the Earth's surface. Strong compositional variations occur within the core (~15%area of grain) and mantle (~75%area.) of this grain that constrain the complex magmatic history of this lava flow.

The solid solutions in these grains must be expressed in terms of at least five compositional end members: enstatite(Mg), ferrosilite(Fe^{2+}), wollastonite (Ca), jadeite (NaAl) and acmite ($NaFe^{3+}$). The core has moderate variation, $En_{18-20}Fs_{25}Wo_{42}$ with Acm_8Jd_3 while the mantle varies dramatically, $En_{8-10}Fs_{35}Wo_{42}$ with $Jd_{3-5}Acm_{5-7}$. An obvious break in zoning pattern occurs between core and mantle. A 10-30 um discontinuous rim (~10% area) surrounds the crystal. Electron probe results suggest that the core has constant Fs_{25} but increasing acmite (Acm_{8-14}) toward the interface with the mantle where a 10% rise in Fs and a 8% drop in Acm component occurs. *In situ* Synchrotron microXANES determination of ferric/ferrous on 15-20 um areas in the core, mantle and rim indicate values of Fe^{3+}/TotalFe: 30-35% in the core increasing to 45% at the core-mantle interface and a drop to 25-30% in the mantle. The rim is 60% ferric. Orientation effects contribute no scatter to SmX results as all analyses are made at constant orientation.

Fe oxidation state changes within crystals cannot be reconciled with progressive oxidation as the magma evolved. The growth of ferric-rich cpx inhibited formation of oxides so conventional oxybarometry is not usable. Other than the rim, the highest ferric is in the outer core of the cpx and indicate that the magma become oxidized during early growth. A major change in crystallization conditions is represented by the onset of very fine scale oscillations in the mantles that perhaps reflect many small-scale changes in a closed magma chamber (convective cycling?). Redox conditions were constant throughout this phase but oxidizing conditions became important again at the end of cpx growth, perhaps during the eruptive phase. The subdued oxidation state changes in the mantle despite the prominent compositional changes perhaps reflect constant oxygen content during magma evolution in a closed chamber, despite the clear decrease of fO_2 between the core and mantle growth stages of cpx. Fine fO_2 variations in a Satiman magma chamber can be extracted from the ferric/ferrous measurements.

Pyroxene in Martian basalt QUE94201 appears much simpler (Figure 2). Progressive enrichment of Fe relative to Mg from center to edge of pyroxene grains is superficially consistent with classical models of magma differentiation and crystal growth. However, combined compositional measurements by electron probe and in situ synchrotron microXANES determinations of Fe oxidation state taken at beamline X26A again reveal a complex magmatic history. The cores of the pyroxene grains have variations in Mg, Mn and Fe that cannot be produced under isobaric conditions (of constant oxygen pressure). The data suggest that the growth of the pyroxene cores was accompanied by a pattern of Fe enrichment, consistent with increasingly oxidizing conditions. Using synchrotron microXANES results, the mantles and rims of these same grains however show decreasing Fe^{3+}/Fe^{2+} relative to the cores and imply late stage reduction of the crystallizing magma. This pattern is not compatible with many classical models of magma crystallization but may require a system closed to oxygen activity changes.

RESULTS The combination of synchrotron microXANES results with more conventional electron microprobe data provides unique insight into the magmatic histories of lavas from both Earth and Mars, and demonstrates that magma formation and volcanism on Mars can be as complex as some of the most complex patterns seen on Earth. Despite size differences between Earth and Mars and different inferred water-oxygen budgets on their surfaces, complexities seen in terrestrial volcanic rocks provide an analogue for Martian systems that must be evaluated as our knowledge of Mars improves.

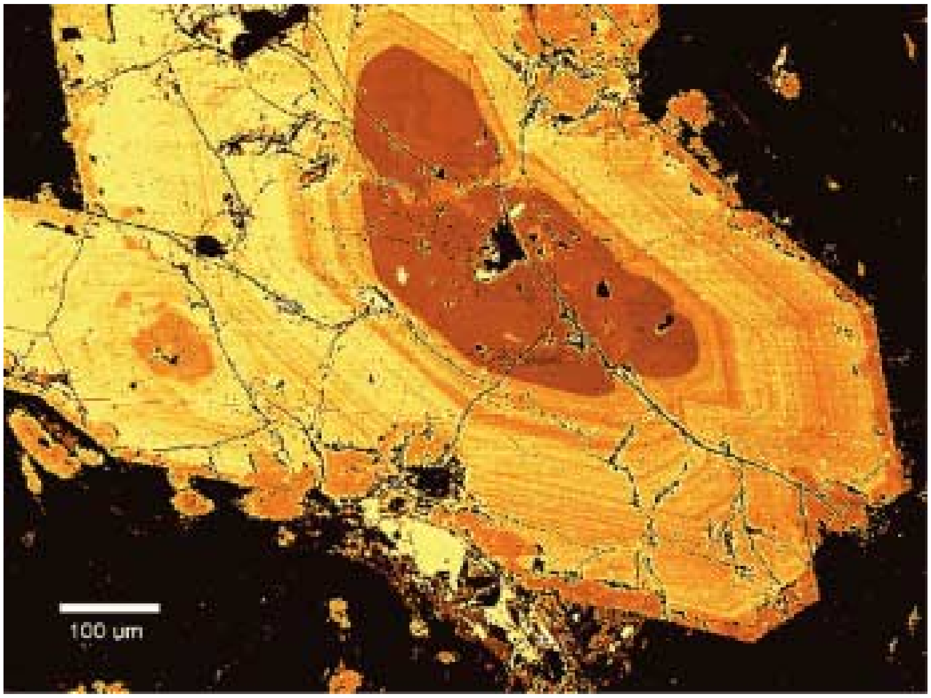

Figure 1: Backscattered electron image of Complex oscillatory zoning in pyroxene from Satiman volcano, East Africa. Dark Mantle is Mg Fe^{3+} rich while fine rings in mantle have decreasing Fe^{3+}/Fe^{2+}

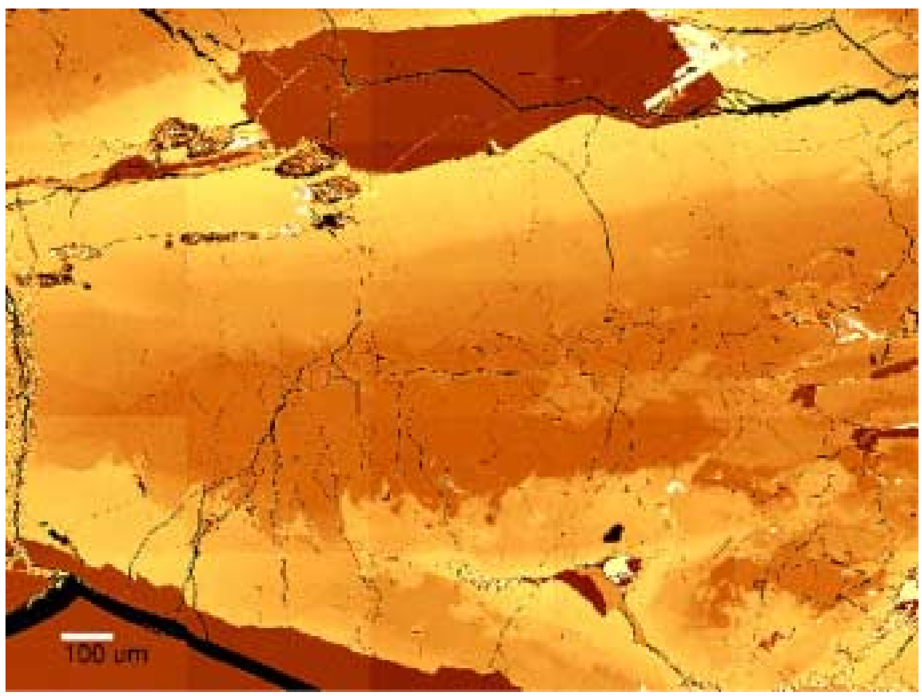

Figure 2: Backscattered electron image of zoning of MARTIAN basalt QUE94201 with Mg-Fe^{3+}-rich core and decreasing Fe^{3+}/Fe^{2+} toward rim.