

THE ROLE OF MICROCHEMICAL ENVIRONMENTS IN THE ALTERATION OF WARK-LOVERING RIMS ON ALLENDE MELILITE-RICH CALCIUM-ALUMINUM-RICH INCLUSIONS. S. Che and A. J. Brearley, Department of Earth and Planetary Sciences, MSC03-2040, 1University of New Mexico, Albuquerque, NM 87131, USA. (E-mail: shaofanche@unm.edu; brearley@unm.edu).

Introduction: Many CAIs are surrounded by Wark-Lovering (WL) rims, which are refractory multilayered rim sequences that may have formed contemporaneously with, or after the formation of the host CAIs. Different mechanisms have been proposed for their formation [e.g., 1-3]. The WL rims and their host CAIs often have different mineralogy and structures. Therefore, differences in their responses to secondary alteration should be expected. This is particularly true for Allende melilite-rich CAIs where a layered alteration sequence of grossular-feldspar-feldspathoid is ubiquitous in the host CAIs, but rare in the rims. Many of these CAIs are surrounded by two- or three-layered WL rims with complex textures, such as symplectic intergrowths of two phases. We conducted a systematic investigation of WL rims on Allende melilite-rich CAIs to better understand their behavior during secondary alteration.

Methodology: Backscattered electron (BSE) images were obtained using a FEI Quanta 3D FEG-SEM/FIB instrument. Several FIB sections were characterized using a JEOL 2010F FASTEM field emission gun scanning TEM (STEM/TEM).

Results: The WL rims on Allende melilite-rich CAIs have a complex alteration texture. For example, the WL rim on a fluffy Type A CAI (ALNH-06) is composed of four layers: (1) a spinel-rich innermost layer; (2) a feldspathoid (nepheline + sodalite) layer; (3) an Fe-rich olivine layer; and (4) an outermost diopside layer. The Fe-rich olivine forms a layer 1-5 μm thick between the feldspathoid and the diopside layers, and is devoid of pores. The interface of olivine with feldspathoids is sharp and smooth. On the other hand, diopside has been replaced by Fe-rich olivine along the inner boundary of layer (4), forming a mesh texture (Fig. 1) similar to that observed in terrestrial olivine-rich rocks that are partially serpentinized. Porosity is well-developed in the diopside layer, in contrast to the pore-free olivine layer. Ilmenite grains $<2 \mu\text{m}$ in size are present in the diopside layer, and they tend to fill pores. The interface between diopside and the matrix is smooth, and forsteritic olivine grains, which are part of the WL rim overgrow the diopside. Diopside in contact with the matrix is less altered than on the inner edge of the diopside layer. In less-altered regions, the diopside layer shows compositional zoning, with decreasing Al_2O_3 and TiO_2 towards the matrix, as demonstrated by EDS X-ray mapping.

A FIB section was taken from the WL rim surrounding a Type B1 CAI (ALNA3-01) from Allende. It

samples a layer sequence of spinel-nepheline-olivine-diopside-Ca-pyroxene (Fig. 2). The innermost spinel-rich layer contains several rounded perovskite grains ($\sim 300 \text{ nm}$) that have been partially altered to ilmenite. All the primary melilite and anorthite has been completely altered to nepheline. The olivine layer is composed of Fe-bearing olivine (Fa_{20-25}) that is typically $\sim 200 \text{ nm}$ in size. Abundant ilmenite grains ($\sim 150 \text{ nm}$) are present between olivine grains. The olivine layer extends into the diopside layer, and diopside grains adjacent to the interface between the two layers show a dissolution structure. Individual diopside grains are compositionally homogeneous, but many grains show Fe-enrichment on their edges. Porosity is well-developed on the Fe-rich diopside rims and along grain boundaries. Some diopside grains are porous, and often intergrown with Fe-rich olivine. The diopside layer is overgrown by a Ca-rich pyroxene layer in the matrix. Pyroxene in this layer shows variations in composition, and represents a solid solution between diopside and hedenbergite ($\text{Di}_{5-70}\text{Hed}_{30-95}$). Porosity is poorly developed in this layer. Other major phases in this layer include lath-shaped Fe-rich olivine (Fa_{35-40}), feldspathoids, and sulfides.

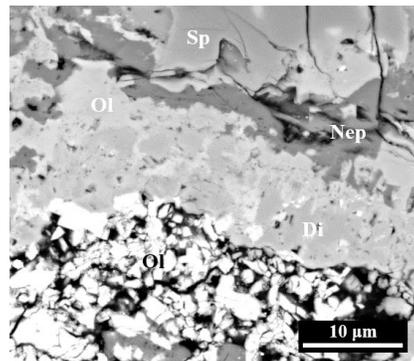


Fig. 1. BSE image of the WL rim on ALNH-06 showing the mesh-like texture of the diopside layer. Olivine in the WL rim is less Fe-rich than that in the matrix.

Discussion: The well-developed porosity in the diopside layer is indicative of fluid alteration. The response of the diopside layer to alteration is counterintuitive, since it was the outer boundary of the diopside layer that was first in contact with the fluid. It would be expected that the fluid should have begun to alter diopside from the outer margin, and progressively consumed it inwards. Heterogeneous alteration effects have been widely reported in chondritic meteorites [e.g., 4-5]. One

plausible explanation for these phenomena is that the fluid chemistry is heterogeneous on a localized scale, which can be partly attributed to the different responses of primary phases to alteration. Based on petrographic observations and hydrothermal alteration experiments [e.g., 6-7], diopside is among the phases most resistant to secondary alteration, whereas anorthite and melilite are the first phases to be altered. In addition, grain size plays an important role in controlling the alteration rate. In general, a finer grain size (a larger surface area) corresponds to a faster alteration rate. For the alteration of silicate phases, the hydrolysis reactions increase the local pH conditions due to interactions between protons in the fluid and metal-oxygen bonds in silicates [e.g., 4, 8]. Consequently, silicate phases that contain a low metal cation content and a high number of Si-O-Si bonds would produce a smaller increase in pH. This effect, combined with the effects of grain size, are capable of producing different microchemical environments on a very local scale. The generation of these microchemical environments over small length scales may be promoted if the amount of fluid is limited, as is the case for CV3 chondrites [e.g., 9]. The existence of these environments implies that dissolution of silicates in chondritic components is kinetically more rapid than diffusion of dissolved species in the fluid.

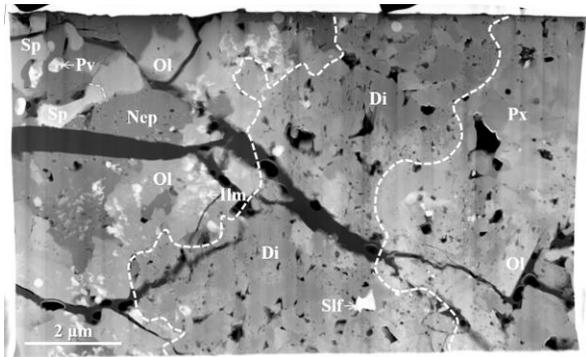


Fig. 2. DF-STEM image of the WL rim on ALNA3-01. The diopside layer is outlined by white dashed lines.

This microchemical environment mechanism can be applied to the alteration of WL rims on the melilite-rich CAIs we have studied. The dissolution rate of diopside is pH-dependent [e.g., 10-11]: the dissolution rate decreases with increasing pH. An early, low-pH, possibly HCl-rich fluid was likely to be present on chondrite parent bodies [e.g., 12]. The precursor matrix materials outside the diopside WL rim layer would have been finer-grained than anorthite in the rim, and therefore they were altered preferentially. In Allende, the matrix was probably modified extensively before significant alteration of the rim occurred. Consequently, the fluid in the matrix may have had a higher pH during the alteration

of the WL rim. This resulted in a faster alteration rate of the inner boundary of the diopside layer during the earliest stages of WL rim alteration. A similar mechanism was proposed for alteration of some CM chondrules [4].

The formation of ilmenite in the altered WL rims may record a late-stage event when the fluid became alkaline enough to stabilize ilmenite. Thermodynamic studies of phase stability in the Ti-Fe-H₂O system show that ilmenite tends to dissolve into an acidic fluid, producing pseudorutile (Fe³⁺₂Ti₃O₉) or rutile depending on the redox condition [e.g., 13-14], but is stabilized in more alkaline solutions. The presence of ilmenite therefore further supports our hypothesis that the fluid pH increased progressively during alteration due to hydrolysis reactions. The source of Ti for ilmenite may be perovskite in the WL rims, with dissolution of perovskite releasing Ca and Ti ions, which diffused outward in the fluid. The precipitation location of ilmenite was likely to be controlled by the least mobile aqueous species of Ti, which in this case, is TiO₂⁺ [e.g., 13-14]. However, the mobility of Ti has been demonstrated to be very limited in terrestrial metamorphic systems, compared to other elements [e.g., 15]. Therefore, an alternative scenario is that ilmenite is a product of diopside alteration. The diopside layer commonly has a compositional zoning, with a decreasing TiO₂ contents outwards. Therefore, the Ti to form ilmenite may come from dissolved Ti-bearing diopside grains that have been replaced extensively by olivine.

Conclusions: The alteration behavior of the diopside WL rim layer can be explained by different pH conditions on its inner and outer edges. The dissolution of diopside probably occurred at the early stage of fluid alteration on the Allende parent body, when the fluid pH was at its lowest value.

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