RARE EARTH ELEMENT ABUNDANCES IN VAPOR DEPOSITED MINERALS IN IBITIRA VESICLES.

N. A. Heim[1], M. Wadhwa[2], and A. M. Davis[1,3]. [1]Department of Geophysical Sciences and [3]Enrico Fermi Institute, University of Chicago, Chicago, IL 60637; [2]Dept. of Geology, The Field Museum, Roosevelt Rd. at Lake Shore Dr., Chicago, IL 60605.

Introduction: Ibitira is a unique, unbrecciated, non-cumulate eucrite that contains vesicles comprising ~5-7 vol.% of the rock [1,2,3]. The relatively uniform sizes and spherical to ellipsoidal shapes of the vesicles suggest that they were formed by volatile exsolution from the parent magma, and not from shrinkage during cooling or other post-crystallization processes [2,3]. Previous studies have noted the presence of vapor deposited minerals in Ibitira vesicles, primarily through optical documentation and qualitative scanning electron microscope (SEM) and microprobe analysis [e.g., 3,4]. However, thus far no quantitative analyses have been reported for the compositions of these minerals. It is recognized that the chemical composition of these vapor deposited minerals (in particular, the abundances of minor and trace elements, including rare earth elements) can provide valuable constraints on their formation and shed light on the source and composition of the vapor phase that deposited them. Therefore, we have begun a systematic study of the compositions of vapor deposited minerals in Ibitira vesicles. Last year we reported the results of SEM characterization of a portion of a 9cm x 5cm x 1cm Ibitira slab [5]. We have since completed SEM documentation of the entire slab; additionally, we report here the abundances of rare earth elements measured in vapor deposited minerals in vesicles of Ibitira.

Experimental: We completed SEM characterization and documentation of minerals in ~1200 vesicles in both sawn surfaces of the Ibitira slab (area ~ 90 cm^2), by methods previously described by [5]. We also performed SEM documentation of five thin sections of Ibitira. Subsequently, we made ion microprobe measurements of rare earth element (REE) abundances in selected grains of vesicle phases, as well as minerals in the Ibitira matrix.

Results and Discussion: SEM documentation of the slab confirmed the findings initially reported in [5], which showed that the majority of the vesicles contained one or more of the following: (i) titanian chromite, (ii) ilmenite, (iii) whitlockite, and (iv) pure Fe^0. Additionally, we also noted the presence of vapor deposited plagioclase and pyroxene in some vesicles.

All of these minerals were noted to be present in vesicles in Ibitira thin sections as well. In the five sections studied by us, we documented the presence of 69 whitlockite grains, 1 apatite (which was found coexisting with a whitlockite), 23 chromites, 19 Ilmenites, 3 Fe^0 crystals, 3 plagioclase and 14 pyroxene grains in the vesicles (we note that observed abundances of these minerals may not be representative of actual abundances since some fraction was undoubtedly lost during the thin section making process). Of these, we made ion microprobe analyses of 8 whitlockite grains (one associated with apatite), 1 apatite, 1 plagioclase and 2 pyroxenes (one of which was included within a vapor deposited chromite crystal). For comparison, we also analyzed REE abundances in 4 whitlockite crystals (two co-existing with apatite), 2 apatites (both co-existing with whitlockite), 2 each of plagioclase and pyroxene, 1 chromite, 1 ilmenite and 1 silica grain in the Ibitira matrix. It is noted that pyroxene in Ibitira is predominantly pigeonite that has inverted to orthopyroxene and relatively fine (up to ~10μm thick) augite lamellae; we "averaged" over the orthopyroxene and augite lamellae to obtain bulk pigeonite compositions since our ion microprobe beam spot was ~50 μm diameter for pyroxene analysis.

The results of our ion microprobe analyses are shown in Fig. 1. REE abundances in matrix plagioclase and pyroxene appear to be uniform and are in agreement with those obtained by [6]. Additionally, the range of REE concentrations in the isolated whitlockite grains in the matrix (La~7400-8500xCI) is similar to that measured by [6]. However, REE abundances in whitlockites associated with apatites are considerably higher (La~13,500-19,000xCI). REE patterns of co-existing whitlockites and apatites are approximately parallel, although apatites have lower REE abundances (La~150-230xCI). Concentrations of REEs in opaque phases (ilmenite and chromite) and silica are negligible and are not shown in Fig. 1.

REE distributions in the matrix minerals may be used to constrain the equilibration history of Ibitira. Fig. 2 shows mineral-mineral REE partition coefficients obtained from our data and compares them with literature values for these partition coefficients at magmatic temperatures (red lines) and at sub-solidus temperatures (blue lines); note that the partitioning values obtained from our data and those taken from the literature for magmatic temperatures match reasonably well. This suggests that Ibitira underwent thorough and extended equilibration at near-magmatic temperatures (above ~950°C [7]), during which pigeonite inverted to orthopyroxene and augite lamellae; subsequently the rock underwent fast cooling through the low temperature range. It is also apparent from Fig. 2 that the higher REE abundances in whitlockite co-existing with apatite are due to equilibration between these two minerals (in contrast to the isolated whitlockites that equilibrated with the silicates).

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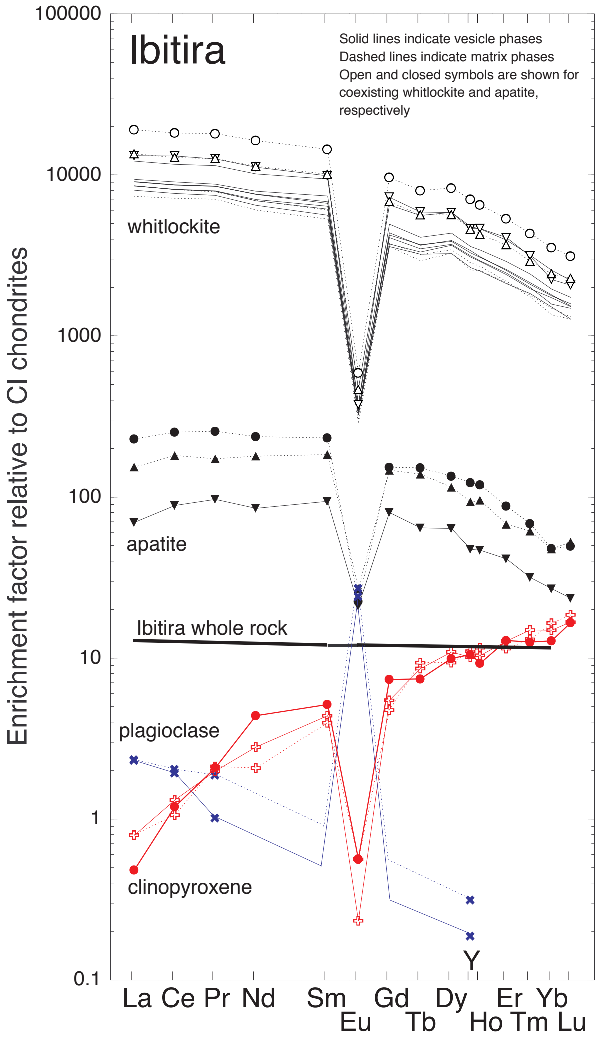

Fig. 1. REE abundances in minerals in vesicles and the matrix of Ibitira. The matrix plagioclase and pyroxene data shown in the figure are averages of the two analyses that were made for each mineral; the pyroxene occurring within the vapor deposited chromite is shown by red closed circles. Error bars are not shown for the sake of clarity of the figure. 1σ errors are $<$2-3% for whitlockites; for apatites, error bars are typically smaller than the symbols. For pyroxenes, 1σ errors are ±15% for LREEs and ±10% for HREEs; for plagioclase, ±10% for La and Ce, ±40% for Pr and ±20% for Y. Whole rock data are from [8].

REE abundances in plagioclase and pyroxene in vesicles and in the matrix are, within errors, identical (Fig. 1). Range of REE concentrations in isolated whitlockites in vesicles falls within that of isolated matrix whitlockites. Further, REE systematics in co-existing whitlockite and apatite in a vesicle are similar to those in the Ibitira matrix (i.e., higher REE abundances in the whitlockite co-exiting with apatite relative to the isolated ones). An exception is an apparently isolated vesicle whitlockite which has REE abundances similar to those in the whitlockite co-existing with apatite (La~13,000xCI); it is likely that this whitlockite also has an associated apatite, but not in the plane of the thin section.

The similarity of REE abundances in minerals in vesicles and the matrix shows that the vapor phase that deposited the vesicle minerals was in equilibrium with the matrix minerals. This in turn indicates that the process of vapor formation and deposition of vesicle minerals was not a fast, kinetically driven one, but one that allowed equilibrium conditions to be established.

Conclusions: It has been suggested that Ibitira vesicles resulted from volatile exsolution from the parent magma [2,3]. Our data show that the subsequent post-crystallization history of Ibitira was complex and involved prolonged equilibration at near-magmatic temperatures, followed by fast cooling. Moreover, the vapor phase that deposited minerals in the vesicles was likely produced during a later event of thermal metamorphism (as suggested previously [4,5]), but at temperatures and timescales that allowed complete equilibrium between the vapor and the matrix minerals; however, this event did not disturb the REE microdistributions in Ibitira matrix minerals that were established during the high temperature equilibration event.

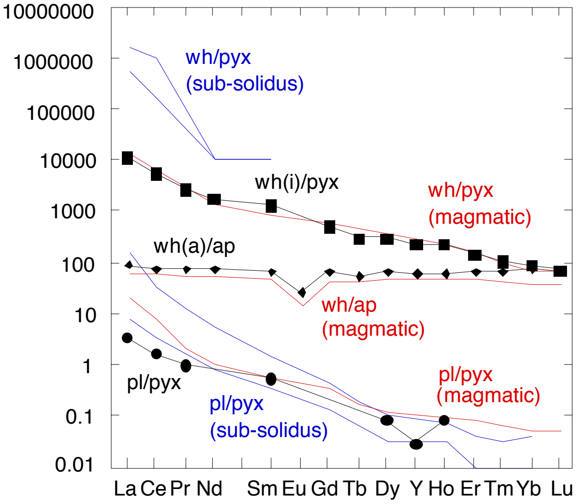

Fig. 2. Mineral-mineral partition coefficients for REE. Our data from Ibitira matrix minerals are shown by closed black symbols; squares are whitlockite/pyroxene partition coefficients obtained using the REE composition of an isolated whitlockite grain (wh(i)/pyx), diamonds are whitlockite/apatite values obtained from a co-existing whitlockite-apatite pair (wh(a)/pyx), and circles are plagioclase/pyroxene values obtained using average REE concentrations in plagioclase and pyroxene (pl/pyx). For comparison mineral-mineral partition coefficients at magmatic temperatures (red lines) are shown for whitlockite/pigeonite (wh/pyx) [9], plagioclase/pigeonite (pl/pyx) [9], and whitlockite/apatite (wh/ap) (from lunar sample 14161,7044; [10]); those at sub-solidus temperatures (blue lines) are shown for whitlockite/low-Ca pyroxene (wh/pyx) [9] and plagioclase/low-Ca pyroxene (pl/pyx) [9].

References: [1] Wänke H. *et al.* (1972) *PLPSC 3rd*, 1251. [2] Wilkening L. L. and Anders E. (1974) *GCA 39,* 1205. [3] Gomes C. B. and Keil K. (1980) in *Brazilian stone meteorites*, UNM Press, pp. 65–74. [4] Steele I. M. and Smith J. V. (1976) *EPSL 33,* 67. [5] Wadhwa M. and Davis A. M. (1998) *LPS XXIX,* #1931. [6] Hsu W. and Crozaz G. (1996) *GCA 60,* 4571. [7] Ishii et al. (1976) *LPS VII,* 408. [8] Wänke *et al.* (1974) *PLPSC* 5^{th}, 1307. [9] Treiman A. H. (1996) *GCA 60,* 147, and references therein. [10] Jolliff *et al.* (1993) *GCA 57,* 4069.

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